THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

PHOSPHORUS RECYCLING IN BRACKISH AND MARINE ENVIRONMENTS

– SEDIMENT INVESTIGATIONS IN SITU IN THE BALTIC SEA AND THE BY FJORD

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DOCTORAL THESIS A 144
UNIVERSITY OF GOTHENBURG
DEPARTMENT OF EARTH SCIENCES
GOTHENBURG, SWEDEN 2012

ISBN 978-91-628-8604-2
ISSN 1400-3813

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A-144
ISBN 978-91-628-8604-2
ISSN 1400-3813
Internet-ID: http://hdl.handle.net/2077/31246
Printed at Ale Tryckteam, Bohus

Distribution: Department of Earth Sciences, University of Gothenburg

Abstract

The phosphorus load to the oceans from land started to increase since around 1950 when man started to mine phosphorus-mineral from phosphorus-rich soils and bedrock. The increased use of phosphorus fertilizers in agriculture together with the growth of coastal cities increased the load of phosphorus to the coastal ocean where plankton production flourished. In the Baltic Sea the increase in plankton production resulted in an increased frequency of harmful cyanobacterial blooms and in expanding areas of anoxic bottoms due to the restricted water exchange with the North Sea. Introduction of sewage treatment plants in major cities in the 1960's and further improvements of these in the 70's and 80's decreased the phosphorus and later nitrogen loads to the waters. Despite the decreased loads to the Baltic Sea the water quality did not improve. Recently, this led researchers to focus more on internal feedback mechanisms instead of external sources to understand the eutrophication of the Baltic Sea.

From a combination of in situ measurements of the phosphorus flux from sediment to water and a budget model for the Baltic Sea, the importance of the sediments as a source of phosphorus have been investigated. In situ measurements were performed in two basins of the Baltic Sea (the Eastern Gotland Basin and the Gulf of Finland) and in a small fjord on the Swedish west coast (the By Fjord). These measurements showed that the flux of dissolved inorganic phosphorus (DIP) was higher at anoxic bottoms than at oxic in all three areas. Furthermore the flux at anoxic bottoms was enriched in phosphorus compared to carbon (and nitrogen). At oxic bottoms, on the other hand, the flux was lower and at times also showed an uptake of DIP from the water to the sediment. The fluxes at oxic bottoms in the Baltic Sea did not show any correlation with the degradation rate of organic carbon while the fluxes from anoxic bottoms in the Baltic Sea and at all bottoms in the By Fjord showed a positive correlation with the degradation rate of organic carbon. This indicated that at the oxic bottoms in By Fjord the DIP flux was primarily controlled by the degradation rate. On the contrary, the fluxes at oxic bottoms in the Baltic Sea were controlled by secondary mechanisms like adsorption to iron-oxides or storage of poly-phosphates in bacteria.

The flux measurements indicate that phosphorus is preferentially remineralised under anoxic conditions and the budget model shows that anoxic sediment act as a source of phosphorus in the Baltic Sea. This calls for further investigations of phosphorus remineralisation under anoxic conditions and highlights the importance of the anoxic bottoms for the on-going eutrophication of the Baltic Sea.

Populärvetenskaplig sammanfattning

Fosfor är en ändlig resurs på jorden som behövs för både växters och djurs tillväxt. Sedan mitten på 1900-talet har fosfor genom brytning från mineralrika jordarter använts för att öka tillväxten på våra åkrar. Detta tillsammans med växande befolkning har lett till att allt större mängder fosfor når våra vattendrag. Den ökade tillförseln av fosfor till Östersjön antas vara en av orsakerna till ökningen av planktonblomningar och minskade koncentrationer av syre i detta innanhav. Trots att tillförseln av fosfor till Östersjön har minskat från 1980-talet, framförallt genom utbyggnaden av reningsverk, märktes ingen minskning av planktonblomningarna. Eftersom den minskade tillförseln av fosfor från land inte minskade mängden fosfor i Östersjön har forskare börjat söka andra källor till fosfor än tillförsel från land.

Den här avhandlingen undersöker sedimentens (bottnarnas) betydelse som en intern källa till fosfor. För att uppskatta utbytet av fosfor mellan sediment och vattenmassa har två metoder använts. Den första metoden går ut på att mäta flödet in situ, det vill säga direkt på botten. Det görs genom att sända ner en så kallad landare som inkuberar sediment och överliggande vatten. Denna metod har använts för att beräkna fosforflödet från sedimenten i två bassänger i Östersjön, Finska viken och Östra Gotlandsbassängen samt i Byfjorden på svenska västkusten. Dessa mätningar visade att fosforflödet från botten är betydligt högre då bottenvattnet och sedimenten var syrefria än när de var syresatta. På de syrefria bottnarna styrs flödet av den hastighet med vilken organiskt material bryts ned, vilket också var förväntat. Däremot är fosforflödet betydligt högre i förhållande till nedbrytningshastigheten än vad som var förväntat. Detta tyder på att de syrefria bottnarna är en stor källa till fosfor i Östersjön under senare år, till och med större än tillförseln av fosfor från land. På syresatta bottnar styrs tvärtom inte flödet av nedbrytningshastigheten av organiskt material. Istället är det andra processer som styr hur mycket fosfor som släpps ut, dessa processer gör att fosfor som produceras i sedimenten kan hållas kvar i dem så länge det finns syre i sedimenten.

Den här studien visar att den fosforkälla som de syrefria bottnarna utgör har en stor påverkan på fosforinnehållet i Östersjön och att denna källa inte kan kompenseras av det fosfor som hålls fast i de syresatta sedimenten. Eftersom källan till fosfor från de syrefria bottnarna är numera större än källan från land är det sannolikt att den snabbaste vägen till en minskning av fosforinnehållet i Östersjön går via syresättning av de bottnar som är syrefria.

List of publications

I. Viktorsson, L., Almroth-Rosell, E., Tengberg, Vankevich, R., A., Neelov, I., Isaev, A., Kravtsov, V., and Hall P.O.J. (2012) Benthic Phosphorus dynamics in the Gulf of Finland, Baltic Sea. Aquatic Geochemistry, doi: 10.1007/s10498-011-9155-y

Viktorsson had a leading role in writing the text, performed most of the data analysis and prepared most of the figures.

II. Viktorsson, L., Ekeroth, N., Nilsson, M., Kononets, M. and Hall, P.O.J. (2012) Phosphorus recycling in the sediments of the Baltic Sea. Biogeosciences Discussions, vol. 9(11), doi: 10.5194/bgd-9-15459-2012, www.biogeosciences-discuss.net/9/15459/2012/

Viktorsson had a leading role in writing the text, performed all the data analysis and prepared all figures.

III. Stigebrandt, A., Rahm, L., Viktorsson, L., Hall, P.O.J. and Liljebladh B. (2012) A new phosphorus paradigm for the Baltic proper. Submitted to PNAS Plus, but according to PNAS formatting.

Viktorsson contributed with discussion on content, comments on the text and ideas

IV. Viktorsson, L., Kononets, M., Roos, P., and Hall, P.O.J. (2012) Recycling and burial of phosphorus in sediments of an anoxic fjord - the By fjord, western Sweden. Submitted to Journal of Marine Research

Viktorsson had a leading role in writing the text, performed all the data analysis, and prepared all figures.

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Part I

Summary

1 Introduction

1.1 Phosphorus

Phosphorus (P) is found in mineral form in bedrock, mostly as apatite. The mineral P is not bio-available and has to be dissolved to orthophosphate through weathering, after which plants can assimilate it. Orthophosphate is the major part of dissolved inorganic phosphorus (DIP) in water. DIP from weathering is transported with rivers to the ocean. On a global scale this is the main source of P to the ocean (Benitez-Nelson 2000). For the areas studied here the river run off comprise about half of the load of P from land, the other half is discharge from sewage treatment plants (HELCOM 2004, Viktorsson 2007). Phosphorus is also transported to the ocean through the atmosphere via dusts and aerosols, of which only a third is soluble in sea water (Graham and Duce 1982). Atmospheric transport of P can be a large source in some areas but in the areas that we focus on here the atmospheric deposition is negligible in relation to the land P source (Gustafsson et al. 2012).

In the ocean, DIP is assimilated by phytoplankton in the process of photosynthesis, together with other constituents of organic matter such as carbon (C) and nitrogen (N). Thus, there are principally three forms of P found in the ocean, dissolved inorganic P (DIP), P bound in organic matter and mineral P. As the organic matter is degraded, or remineralised, nutrients are recycled to the water. This means that the cycling of P is coupled to the other nutrients via the formation and degradation of organic matter. The proportion of C:N:P in fresh marine organic matter has been shown to be on average 106:16:1 (Redfield, 1963), deviations from this ratio indicates excess or shortage of one of the nutrients.

1.2 Increased nutrient supply to the marine environment

A coastal sea has mainly two sources of P, land transport and inflowing water from adjacent seas. In an enclosed coastal sea nutrients are recycled many times in the water column and the sediment, before they leave the system, either via burial in the sediment or through the water exchange to the sea outside. Figure 1 presents an overview of the internal cycling and sources and sinks in an enclosed coastal sea. The internal cycling of P is illustrated with grey arrows and the sources and sinks to the system are shown as black arrows. If the system is in steady state the sinks balance the sources. When the system is perturbed, for example by increased external sources of nutrients, the sinks and sources can become unbalanced. The dashed line represents the halocline, which limits exchange between the basin water and the surface water. This restriction in water exchange renders the deep basin water sensitive to increased input of organic matter which cause increased consumption of oxygen and thus can lead to anoxic water conditions.

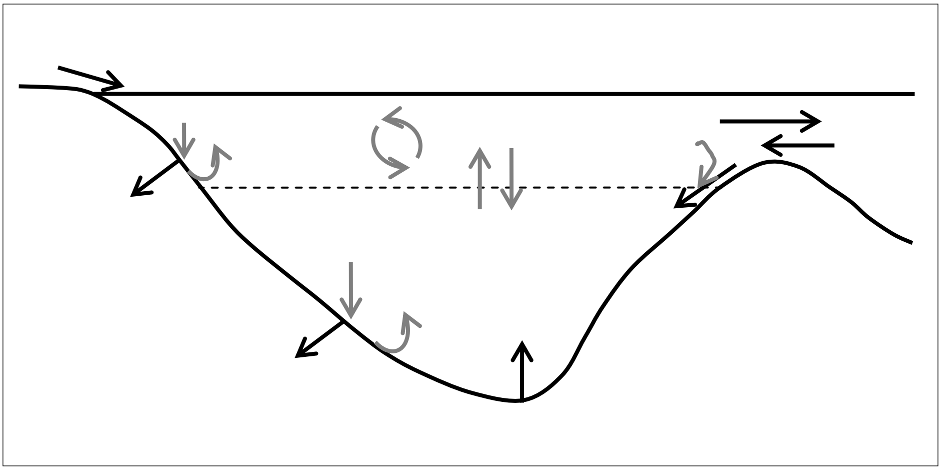

Figure 1. Schematic figure showing sources and sinks of P to a coastal water basin as black arrows and the internal cycling of P as grey arrows. The dashed line represents the halocline, which limits exchange between the basin water and the surface water. The land runoff is shown with the black arrow at the top left and the exchange with the adjacent seas with the black arrows over the sill to the right.

Around 1950 extensive mining of P from P-rich soils and rocks started. The industrial P-fertilizer production has since then been an important prerequisite in the greatly increased productivity on agricultural fields and thus the increased efficiency in food production. The industrial mining of mineral P can be thought of as increased weathering leading to an increased source of P to the oceans. This has resulted in eutrophication of many coastal seas and an increase in the number of sites and areas with poor oxygen conditions (Conley et al. 2011; Diaz and Rosenberg 2008). One of the areas that have been reported to suffer from eutrophication due to increased nutrient loads from land is the Baltic Sea. In about 30 years, from the 1950's to the 1980's the amount of P reaching the Baltic Sea from land tripled (Gustafsson et al. 2012). This led to an increase in the frequency of cyanobacterial blooms (Finni et al. 2001) and spreading bottom water anoxia (Conley et al. 2009, 2011). Anoxia (no oxygen) by itself is a threat to the ecosystem causing death of higher life, on top of this, anoxia has also been shown to increase the flux of DIP from the sediment to the water (e.g. Balzer et al. 1983; Ingall and Jahnke 1997; Sundby et al. 1986). This fuels primary production and results in higher sedimentation rates of organic matter, which in turn sustains the anoxia and a continuously enhanced P flux (Howarth et al. 2011; Slomp and Van Cappellen 2007; Vahtera et al. 2007). The effect of bottom water oxygen conditions on the benthic P recycling is the main focus of this thesis. In this context the word hypoxic is often used, which means that the oxygen concentrations are low but not zero. The exact definition of hypoxic varies between 63.0 µM and 91.4 µM oxygen (Rabalais et al., 2010).

1.3 Phosphorus in marine sediments

Phosphorus reaches the sediment through sedimentation in either organic or inorganic form. Inorganic mineral P (for example apatite) that reaches the sediment is buried and does not contribute to the reflux of P from the sediment to the water. Reactive inorganic P, e.g. iron bound P, that reaches the sediment can in some environments comprise a large part of the sediment P reflux. Of the organic P that reaches the sediment much is remineralised to dissolved inorganic P (DIP) and contributes to the reflux of P to the water column. Some of the organic P escapes degradation in the sediment and becomes permanently buried (as refractory organic P). The amount of P in sediments is variable and the range of the TP content in the sediments of the Eastern Gotland Basin was 0.05-0.14% of sediment dry weight (Paper II). The fractions of TP in sediment are almost always determined indirectly by sequential extraction, where stronger and stronger extractants are used to extract the different forms of P (Ruttenberg 1992). Due to the methodological difficulties in determining different P species, for the general case only rough numbers can be given. In the Baltic Sea organic P is the largest fraction of TP and comprises ≥50% of TP dry weight (Mort et al., 2010). At oxic bottoms, the fraction of iron bound P can be as large as the organic P fraction in the top 1-2 cm of the sediment (Mort et al., 2010). Apatite P is constant with sediment depth and comprises a minor part of TP or ≤0.01% of total sediment dry weight (Mort et al., 2010). In the open ocean only about 1-5% of the P that reaches the sediment is permanently buried (Benitez-Nelson 2000, Follmi 1996). Here we will focus on the difference in the recycling of P from sediments overlain by anoxic water (reducing sediment surface) and those overlain by oxic water (oxidizing sediment surface).

1.4 Sediment-water fluxes of Phosphorus

When organic P in the sediment is degraded a concentration gradient of DIP builds up between the pore water and the over lying water. This will cause a net flux of DIP along the concentration gradient, driven by diffusion. This is a general description of the fate of any solute produced in the sediment that is released to the pore water and then does not react further in the sediments. This means that the remineralisation rate should be equal to the flux out of the sediment. However, it has been shown that secondary processes can affect the DIP concentration in pore water. This means that the DIP flux from the sediment does not necessarily reflect the remineralisation rate of DIP in the sediment. There are mainly two processes that have been shown to retain DIP in the sediment, adsorption to Fe(III) and bacterial storage of poly-phosphates (poly-P).

Phosphate has been shown to adsorb to iron-oxy-hydroxides (Gunnars et al. 2002; Hyacinthe and Van Cappellen 2004) and DIP cycling in sediments can be, as a consequence of this, intimately linked with iron cycling. Iron oxides are found in particulate form in sediments and function as an electron acceptor for the oxidation of organic carbon. When organic carbon is oxidized by Fe(III) the iron oxide particle adsorbing phosphate undergoes reductive dissolution, whereby Fe(II) and phosphate are released into the pore water. This couples the pore water concentrations of Fe(II) and phosphate to each other. When Fe(II) again meets oxic conditions it is oxidized to Fe(III) and precipitates as an iron oxide particle, again trapping phosphate from the pore water around it. This retention mechanism of DIP in the sediment can cause DIP fluxes from sediments to be significantly lower than expected from the degradation rate of organic carbon (e.g. Ingall et al. 2005; McManus et al. 1997). The coupling of Fe and P cycles was described already in 1936 by Einsele and has since been documented by others, e.g. Mortimer (1941) Froelich et al. (1982), Jensen et al. (1995) and Sundby et al. (1992). The connection of Fe and P cycling was first documented in fresh water systems and the effect of Fe adsorption on P cycling has less impact in marine systems (e.g. Jensen et al., 1995, McManus et al., 1997). The reason that the effect of iron adsorption is lower in salt waters is a shortage of iron oxides in marine sediment due to the higher sulphate concentrations in the salt water, favouring bacterial sulphate reduction and sulphide production (Caraco et al., 1990). Fe(II) can precipitate as ironsulphides in sulphidic environments, and iron sulphides are stable compounds which act as a sink for iron in the sediment. Less Fe(III) is thus become available to scavenge DIP, and DIP immobilization in oxic sediments can therefore be weaker in marine environments compared to fresh water and brackish environments (Blomqvist et al. 2004, Caraco et al. 1990).

It has also been proposed that phosphate adsorption is not always the reason for the apparent coupling between Fe-cycling and phosphate, but that other redox sensitive mechanisms might cause the simultaneous changes in Fe(II) and phosphate concentrations (Davelaar 1993; Gachter and Muller 2003). The proposed mechanism for this is bacterial storage of poly-P under oxic conditions and the subsequent release of DIP under anoxic conditions. Bacterial assimilation of DIP and formation of poly-P is well-documented in freshwaters (Hupfer et al., 2007, and references therein) and it is used in sewage treatment plants to increase the P removal. The poly-P storage is an adaptation of micro-organisms to environments with oscillating redox conditions, since they can use the poly-P stored under oxic conditions as an energy source under anoxic conditions (Hupfer et al. 2007). Poly-P has not been extensively studied in marine sediments, but it has been found to comprise 8% of the total P in the upper most 1-2 cm of the sediment under oxic conditions while no poly-P was found on the anoxic site or below 2 cm sediment depth on the oxic site (Sannigrahi and Ingall 2005). These authors estimated the potential DIP flux from poly-P in anoxic sediments to comprise 12% of their measured P efflux.

2 Aim

The aim of the work with this thesis has been to better understand the differences in the sediment recycling and removal of P under oxic and anoxic conditions (and thereby improve the understanding of plausible risks and possibilities with man-made oxygenation). This thesis is mainly based on in situ measurements of sediment-water P fluxes in the Baltic Sea and the By Fjord on the Swedish west coast. The direct measurements are supported by a budget model of the Baltic Sea and flux estimations from DIP water column changes in the Bornholm basin. Measurements were made both at permanently oxic and anoxic bottoms. From these data I hope to shed light on the controls of P flux from sediments. The studies were made in direct connection with a project to investigate the possibilities of man-made oxygenation of anoxic bottoms through increased mixing and the effect of this on P cycling (the BOX project, www.marsys.se).

3 Measuring sediment-water P fluxes

The flux of DIP between sediment and water can be estimated both from ex situ and in situ methods. Most commonly ex situ methods are used, since they require less expensive and technologically advanced equipment. Ex situ measured fluxes are determined either from incubation of a sediment core and overlying bottom water in the laboratory (e.g. Lehtoranta and Heiskanen 2003) or calculated from the concentration gradient in the pore water from Fick's first law of diffusion (e.g. Sundby et al 1992). The long-term flux can also be determined ex situ by calculating the difference between estimated P burial and the depositional flux of P (e.g. Rydin et al. 2011). In situ measured fluxes are based on incubations, performed on the sea floor (i.e. in situ) with a benthic chamber lander (Figure 2). For the in situ incubations the big and small autonomous Göteborg benthic chamber landers were used. From 2010 and onwards the smaller version of the original big lander was used in parallel with the big lander. The functioning of the small lander is the same as for the big lander, except the small version lacks the outer frame and cannot be deployed in fully autonomous mode. Furthermore, it carries only two chambers instead of four.

Fluxes can also be determined from oceanographic data, by calculating the change of P in the water column from time series of P measurements. This requires that the vertical turbulent diffusion is estimated from for example salinity data. The method is described in Paper III and is in essence analogous to the in situ chamber incubations (e.g. Schneider et al. 2002, Paper III). Although, in this case the chamber is an entire basin and the incubations time is several months or years instead of less than one day.

3.1 The Gothenburg autonomous lander

The Göteborg big lander consists of an inner frame with four chamber modules, and an outer frame which carries buoyancy and a Niskin bottle for bottom water sampling (Figure 2). The outer frame is used only when deployed in fully autonomous mode. Each chamber is equipped with a horizontal paddle wheel that stirs the water inside the chamber to mimic the turbulence of the surrounding water (Tengberg et al., 2004). To measure concentration changes of solutes other than oxygen each chamber was equipped with nine water sampling syringes and one injection syringe. The injection syringe is filled with a known volume of milli-Q water and by measuring the small salinity decrease after injection the chamber water volume can be back-calculated (Nilsson 2008). The nine sampling syringes were triggered at pre-programmed times during the incubation. After the last syringe has been triggered an acoustic signal is sent to the big lander which then releases the ballast weights and allows the lander to ascent to the surface where it is located by the ship and brought back on deck. The small lander has to be collected by dredging when the incubation has ended, since it is not equipped with buoyancy and ballast weights.

When the big lander is deployed in autonomous mode it descents by gravity at a rate of *ca.* 40 m min^{-1}, due to the weight of the ballast (two *ca.* 2 m long, 150 kg heavy railway tracks). When the ballast weight reaches the sea floor the inner frame of the lander hangs above the sea floor for 1-2 h, after which the chambers are gently inserted into the sediment with lids open. When the big or small lander is deployed in non-autonomous mode the inner frame is slowly lowered towards the bottom and the chambers penetrate the sediment immediately with their lids open. This method was used on all deployments in By Fjord. After the chambers have penetrated the sediment they are left with open lids for 3-4 h. When the lids close the incubation of the sediment and the overlying water starts (for detailed description see Tengberg et al 1995 and Ståhl et al., 2004). The incubations were 12-30 hours long, depending on the reactivity of the sediment. Salinity, temperature and oxygen were measured continuously in each chamber as well as in the ambient bottom water using sensors.

3.2 Calculation of fluxes from chamber incubations

The fluxes of DIP were determined from the slope of the line from a linear regression between the measured concentrations and time. The slope times the chamber height gives the flux in mass per unit of area and time; here all fluxes are given in mmol m^{-2} d^{-1} (if not differently stated). All slopes with a p-value <0.05 have been considered to represent a significant flux.

With this method it is not possible to detect a zero flux and very low fluxes (close to zero) are difficult to measure due to the analytical precision. There are two reasons that low or zero fluxes are difficult to measure. First, low DIP fluxes are often found at harder sediments with coarse grains, which increase the risk of leakage due to a too small penetration of the chambers into the sediment and water leakage into/out of the chamber caused by permeable sediment. Also, there is an analytical difficulty to determine low fluxes, because when the concentration change over time is small even a small error in each point can render a linear regression with a p-value >0.05.

To avoid bias towards high fluxes due to these difficulties in detecting low or zero fluxes a second evaluation criterion was used. There have been different approaches to set this criterion, the first being to just relax the p-value restrictions for the lowest fluxes (described in Almroth et al., 2009 and Paper I). This criterion was used for fluxes measured in the Gulf of Finland and in the By Fjord. The original criterion for low fluxes was found difficult to explain and not to rely on the analytical uncertainty. Because of this, a new formulation of the criterion for low fluxes was used for the fluxes measured in the Eastern Gotland Basin. This criterion uses the analytical precision to determine when fluxes should be set to zero and is described in Paper II. The difference in which fluxes were actually set to zero between the two criteria was small, but the criterion relying on the analytical precision is easier to explain and better describes the cause behind the problem.

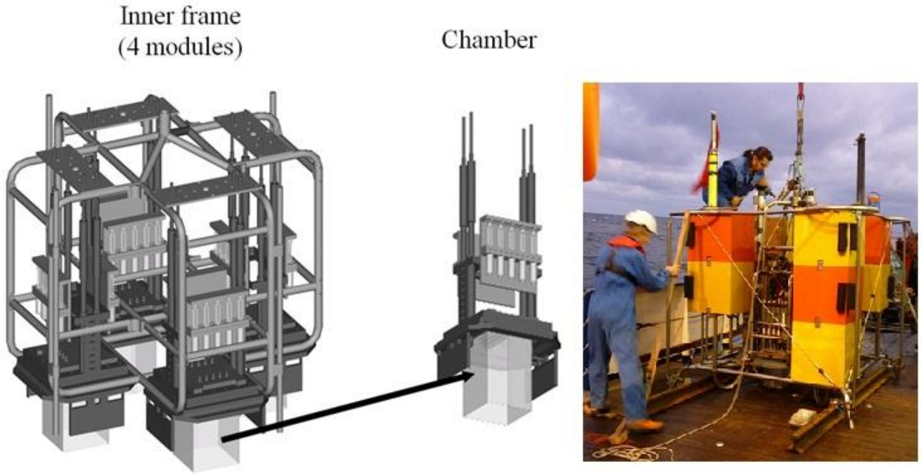

Figure 2. Left, drawing of the Göteborg big lander inner frame and a detail of one chamber module. Each chamber module carries two syringe racks with five syringes each. The syringes are programmed to take water samples evenly spread over the length of the incubation. Right, photograph of the lander on deck, just before deployment. One chamber and the outer syringe rack are visible between the orange/yellow buoyancy packages.

3.3 Calculation of fluxes from oceanographic data

For a basin were the water is stagnant below a certain depth the change in P content can be calculated from time-series of P measurements in the water column. This change is then a measure of the sediment DIP flux which is assumed to be the only source for DIP in the basin water. To estimate a flux from the sediment with this method all other sources and sinks have to be known or assumed to be zero, hence this method is easiest to apply to a basin were the water exchange is limited and the basin water is stagnant, such as the deep basin of a fjord or the deep water of the Baltic Sea. There the only source/sink is through diffusive exchange through the pycnocline and can be estimated from the vertical diffusivity. The vertical diffusivity is calculated from the change of salinity over time and the vertical salinity gradient (Gustafsson and Stigebrandt 2007). This approach was used to calculate the P flux in the Bornholm Basin for each decade from the 1960's to the 2000's (Paper III).

In an enclosed coastal system a budget model can be used to determine if the system has a net internal sink or source. This is done by setting up a budget model for the system, including the external sources and sinks and known internal processes, as illustrated in Figure 1. For the two layered Baltic Sea the budget equations include; mixing between the two layers; net production; entrainment at deep water inflows;

DIP change over time; water exchange with the sea outside and land load. When the budget equations for the two layers are added, the known internal processes (mixing between the two layers; net production; entrainment at deep water inflows) cancel out and the concentration change over the entire water column can be expressed as in the following equation

$$V\frac{d\bar{c}}{dt} = Extsource - Extsink - Intsink + Intsource$$

Here V is the volume of the Baltic Sea, $\bar{c}$ is the spatial mean concentrations, $Extsink$ is the loss to the water in the adjacent sea and $Extsource$ is the load from land. Thus, the only unknowns are the two last terms, $Intsink$ and $Intsource$. By entering numbers for the known terms the model will reveal if the system has a net internal source or sink, which was done in Paper III for the Baltic Sea.

4 Findings and Discussion

4.1 Phosphorus recycling

Phosphorus recycling was investigated in situ with the autonomous Göteborg benthic landers in the Baltic Sea and the By Fjord (Paper I, II and IV) and with a source-sink model in the Baltic Sea (Paper III). The in situ measurements showed that at each studied area the DIP fluxes were higher at anoxic bottom water conditions than at oxic (Figure 3). This is supported by water column changes of DIP in the Bornholm basin (Paper III) (0.07-0.15 mmol m^{-2} d^{-1} at oxic bottoms and 0.27-0.76 mmol m^{-2} d^{-1} at anoxic bottoms). The analysis of changes in water column DIP content in the Bornholm basin also shows that the DIP efflux has increased at both oxic and anoxic bottoms from the 1960s to the 2000s, and this was associated with an increasing length of the anoxic periods in the Bornholm basin. A comparison between in situ measured fluxes and ex situ measured fluxes show that fluxes measured ex situ under anoxic conditions are generally lower than fluxes measured in situ under anoxic conditions. At oxic conditions, however, ex situ and in situ methods agree well (Table 4 in Paper I). Reasons for this are discussed in Papers I and II.

The measured higher fluxes at anoxic bottoms compared to oxic bottoms in the same area (Figure 3) is in line with previous research, showing higher recycling rates and less efficient burial of P at anoxic bottoms (Sundby et al. 1992; Ingall and Jahnke 1997; Slomp et al. 1996). Still, the fluxes and bottom water oxygen conditions by themselves do not reveal whether the recycling rate was higher at the anoxic bottoms because of lack of oxygen or due to higher degradation rates of the bulk organic matter. Also, the DIP flux at oxic bottoms did not show any relation to the bottom water oxygen condition. This indicates that the DIP flux is not so much sensitive to the degree of oxygenation, as to the complete depletion of oxygen in the sediment. The DIP flux is therefore compared to the DIC flux (Figure 4). DIC flux is used as a measure of the remineralisation rate of organic carbon in the sediments, which should be proportional to the remineralisation rate of organic P.

The DIP flux showed a positive correlation with DIC flux at anoxic bottoms at all three studied areas (Figure 4). It is also clear that the flux at anoxic bottoms, in almost all measurements, was enriched in P compared to the Redfield C:P ratio, as indicated by the dashed line in Figure 4. In contrast, at oxic bottoms the flux was P poor in relation to C, and showed less correlation with organic carbon degradation rates (Figure 4).

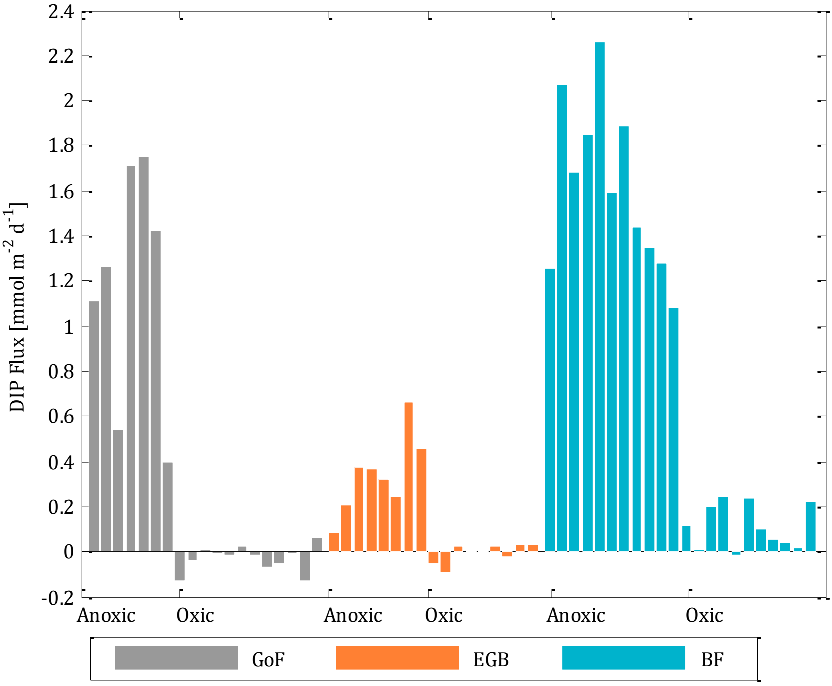

Figure 3. The flux of DIP at all three locations. Fluxes shown are averages from separate deployments and includes 1-4 chamber incubations. Colours represent the different areas; grey Gulf of Finland (GoF), orange, Eastern Gotland Basin (EGB), and blue By Fjord (BF). The DIP fluxes at each location are sorted from anoxic to oxic bottom water conditions, those that are oxic are sorted from the lowest to the highest bottom water oxygen concentration (at each location).

One explanation for the different C:P flux ratios at oxic and anoxic bottoms could be that the C:P ratio in the sediment also differed. Because we have no data on organic P in the sediment it is not possible to present an exact number on the organic C:P ratio in the surficial sediment. Despite that, it is possible to draw some conclusions for the sediment C:P organic ratio from other data. In the By Fjord the C:N ratio of the sediment was similar on oxic and anoxic stations, while the TC:TP ratio was lower at the oxic than at the anoxic bottoms (Paper IV). This indicates that the organic matter C:N:P composition is likely similar at both anoxic and oxic bottoms and the low TC:TP ratio at the oxic bottoms is likely an indication of increased P retention capacity of the oxic surficial sediments. Data from sediment traps in the Eastern Gotland Basin from the late 1990's showed that the sedimenting particles on average have a C:P ratio around 100 (Emeis et al. 2000). Therefore the low DIC:DIP ratio of the fluxes at anoxic bottoms can be attributed to processes in the sediment.

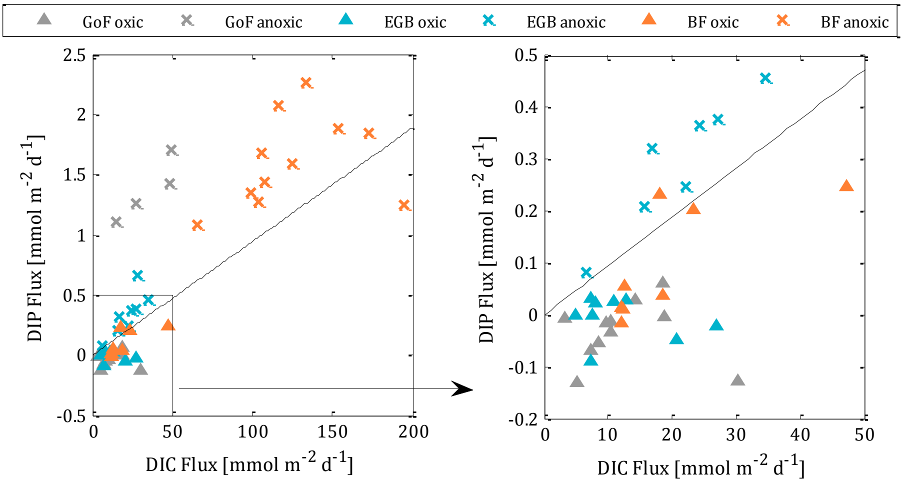

Figure 4. The flux of DIP versus the DIC flux. The data shown are averages from separate deployments including 1-4 chamber incubations. The left panel shows all measurements and the right panel is a blow-up of the lowest fluxes in the left panel (indicated by the small box). The black line indicates the Redfield C:P ratio of 106:1. Oxic bottom waters are marked with a triangle and anoxic/hypoxic with a cross, colors represent the different areas; grey Gulf of Finland (GoF), orange, Eastern Gotland Basin (EGB), and blue By Fjord (BF).

For the Gulf of Finland (GoF) and the Eastern Gotland Basin (EGB) it was shown that the DIP flux did not correlate with the organic carbon remineralisation rate at oxic bottoms, this was explained by the higher P retention capacity (Papers I and II). In contrast, at the marine site, By Fjord, the DIP flux shows a positive correlation to the DIC flux also at oxic bottoms, implying that salinity plays a key role in the DIP immobilization in oxic sediments. The high DIC:DIP flux ratio and the large variation of this ratio at oxic bottoms in By Fjord still shows that the immobilization of DIP was higher in the oxic than in the anoxic sediments in the marine environment.

It is likely that the effect of Fe(III) on DIP immobilization is weakened in the saltier and more sulphate rich environment (Caraco et al., 1990, Blomqvist et al., 2004). Instead bacterial accumulation of poly-P plays may play a relatively larger role in the By Fjord compared to the Baltic Sea, where both iron scavenging and bacterial poly-P accumulation are likely present.

In contrast to the oxic bottoms, at anoxic bottoms the DIC:DIP flux ratio does not show a dependence of salinity. The DIC:DIP flux ratio at anoxic bottoms in the By Fjord lies in between that of the GoF and the EGB. This implies that the cause for the P enrichment of the fluxes is not the same as the process/mechanism that cause the P immobilization in oxic sediment.

The DIP flux at anoxic bottoms in the GoF was at least two times higher than the flux in the EGB. But because the DIC flux was not higher in the GoF compared to the EGB the flux was more P enriched in the GoF than in the EGB (C:P flux ratio 29 in the GoF compared to 69 in the EGB). One reason for the higher and more P rich fluxes could be that the temporal variability in redox conditions was higher in the GoF than in the EGB. The anoxic bottoms of this study in the EGB were all situated at depths greater than 124 m, a depth at which the bottoms have been anoxic for several years. The anoxic bottoms in the GoF were located more shallow than this (<90 m) and the redox conditions are oscillating on a timescale <1 yr. The high temporal variability in oxygen concentration in the GoF is shown in Figure 3 in Paper I. This means that the flux measured at anoxic bottoms in the GoF was likely a combination of release from iron oxides, poly-P breakdown and remineralisation of organic P. In contrast, the only source for the DIP flux at the anoxic bottoms in the EGB and the By Fjord was the remineralisation of organic P.

In situ measurements of fluxes may be used to draw conclusions about the processes behind the fluxes and is a good way to improve the description of the sediment processes controlling P recycling from sediments. Nevertheless, this approach limits the possibility to draw conclusions on a system scale. It is possible to extrapolate the fluxes measured at different bottoms to a basin wide scale, but due to the spatial and temporal variations in fluxes the uncertainty of such estimates are generally quite large (Papers I and II).

Taking a system approach, a simple source-sink model of the Baltic Sea was applied in Paper III. This type of modelling is a straight forward way of investigating what the net effect of all processes in a system is. The model does not specify the internal sources and sinks but shows whether the system has an internal net source or sink. The model used in Paper III shows that to explain the changes in the DIP pool, in the Baltic Sea, there must be an internal net source of P. It also shows that the net source was larger in 2005 than in 1980. The model does not specify where the internal sources and sinks are located. Assuming the internal source is located at anoxic bottoms and the sink is distributed over the whole Baltic Sea it gave a flux from the anoxic sediments of 0.20 mmol m^{-2} d^{-1} (2.3 g m^{-2} yr^{-1}) and a total internal source of 91 500 ton yr^{-1} in 2005 and 45 750 ton yr^{-1} in 1980. These estimations agree well with the internal load from anoxic bottoms estimated from the in situ flux measurements in Paper II (132 000 ton yr^{-1} for the period 1999-2011 and 43 900 ton yr^{-1} for the period 1960-1998).

4.2 Importance of sediments as a source and sink

Much of the research on P recycling has been focused on the retention mechanisms at oxic bottoms. The common understanding is that the difference in P recycling between oxic and anoxic bottoms is mainly due to the lack of the P retention mechanisms at anoxic bottoms (e.g. Conley et al 2002). Accordingly, the flux at oxic bottoms is depleted in P, in relation to both C and N. If this would be the only difference between oxic and anoxic bottoms, the C:P ratio of the flux at anoxic bottoms should mirror the C:P ratio of the organic matter content, likely close to the Redfield ratio of 106. Yet, the C:P ratio of the flux at anoxic bottoms show that the flux is highly enriched with P, in relation to both C and N (Paper I and II).

The P rich fluxes at anoxic bottoms suggest that organic P is preferentially remineralised in relation to organic C. This was implied already by Ingall et al. (1993) as one reason for the high organic C:P ratios found in laminated shales. Steenbergh et al. (2012) hypothesized that extra-cellular phosphatase enzymes are used to remove P from organic matter when bacteria are C-limited. They also showed that in Baltic Sea sediments there was phosphatase activity in anoxic sediments and that this process was active at both anoxic bottoms and oxic bottoms below the oxygen penetration depth. Steenbergh et al. (2012) explain the lower fluxes measured at oxic bottoms with the higher P retention in the oxidized sediments. These results together with the constantly low C:P ratios in fluxes at anoxic bottoms (Ingall and Jahnke 1997, Ingall et al., 2005, Papers I and II) and high C:P ratios in anoxic sediment (Slomp et al. 2002, Mort el al., 2010, Emeis et al. 2000, Teodoru et al. 2007) strongly suggest that organic P is preferentially remineralised from the organic matter under anoxic conditions.

Assuming preferential P remineralisation is ongoing also in anoxic sediments at oxic bottoms implies that at oxic bottoms excess DIP is produced in the underlying anoxic sediment. This excess DIP should thus be retained in the oxic zone. The amount of P retained in the oxic zone should thus increase with time to store the continuous production of P from the preferential P remineralisation in the underlying anoxic sediment.

Increasing P retention with time could result from for example accumulation of Fe(III) at the zone in the sediment where Fe(II) diffusing upward from deeper sediment layers becomes re-oxidised. This may result in extremely iron rich sediments that could immobilize a large fraction of the diagenetically produced DIP. Both iron rich and manganese rich sediments are found in the Skagerrak (Canfield et al. 1993) and similarly manganese concretions have been found in the open GoF (J. Lehtoranta, personal communication). Hence, iron scavenging of DIP could be efficient enough in some areas to immobilize the excess DIP produced in underlying anoxic sediments, and manganese may help keeping the iron in oxidized form. It has been shown that to efficiently scavenge all DIP an Fe:P ratio ≥2 is needed (Gunnars et al. 2002). At oxic bottoms in the EGB the DIP and dissolved iron concentrations peak at almost equal concentrations in the pore water, implying that the Fe:P ratio is ≈1 (Paper II), which means oxic sediments in the Baltic proper are unlikely to retain all DIP produced in the sediment.

If the oxic sediments do not retain the excess DIP it must either diffuse through the oxic layer or become temporarily immobilized in the oxic sediment and through diagenesis undergo a sink-switch to a non-redox sensitive form which is permanently buried. It has been shown that at high concentrations of pore water DIP in anoxic sediments authigenic apatite formation can be mediated by sulphate bacteria (Schulz and Schulz 2005). However, the pore water DIP concentration in the study of Schulz and Schulz (2005) peaked at ca 300 µM, whereas the pore water DIP concentration peaked at ca 100 µM and ca 40 µM in the By Fjord and the Baltic Sea, respectively. Hence, apatite formation in the Baltic Sea and the By Fjord is unlikely, because DIP pore water concentrations are too low. It has also been shown that apatite precipitation is inhibited in the modern ocean due to high concentrations of magnesium and low calcium to magnesium ratios in seawater (Gunnars et al., 2004).

In the Baltic Sea it has been shown that most P is buried as organic P at both oxic and anoxic bottoms and the contribution of apatite P to the burial flux is small (Mort et al. 2010). Thus, P retained as inorganic P at oxic bottoms should contribute only to a small part of the permanent P burial. DIP accumulated by bacteria and retained as poly-P is potentially a part of the organic P that is buried. Then again, the study of Sannigrahi and Ingall (2005) found no poly-P in the below two centimetres sediment depth at oxic bottoms. This indicates that permanent burial via the P retention mechanisms at oxic bottoms is probably small.

C:P ratios in fluxes and sediments point at preferential P remineralisation under anoxic conditions and a mechanism for this has been suggested (Steenbergh et al. 2012). Jilbert et al. (2011) concluded that P is preferentially remineralised in anoxic waters and sediments, but to a lesser extent in oxic. They also showed that the preferential P remineralisation outweighed the retention of P at oxic bottoms as the area of hypoxic and anoxic bottoms decreased. This indicates that the preferential P remineralisation at anoxic bottoms is very important for the positive feed-back between eutrophication and increasing bottom water anoxia, regardless if oxic bottoms act as sinks or not. This was also shown in the model results in Paper III; the anoxic sediments in the Baltic Sea are a net source of P under the present conditions. Therefore attention should be focused on the preferential P remineralisation at anoxic conditions which seems to greatly affect the DIP content of the Baltic Sea (Conley et al., 2002, Paper I-III), rather than the temporary retention mechanisms on oxic bottoms.

5 Conclusions and future perspectives

The main conclusion from the large set of in situ measured fluxes is that DIP is preferentially remineralised in anoxic sediments in both brackish and marine environments. Preferential remineralisation of P is supported by previous studies in the Baltic Sea (Jilbert et al. 2011 and Steenbergh et al 2012). The mechanism for the preferential remineralisation cannot be concluded from the flux data alone, because measured fluxes only show the net effect of the processes in the sediment. This preferential P remineralisation suggests that the high DIP release under anoxic conditions is not only the result of decreased DIP retention, but that it is caused by the anoxic conditions *per se*. Hence, further research on the microbial processes behind anoxic preferential remineralisation is needed. Furthermore, the extent to which DIP can be permanently retained and eventually buried at oxic bottoms is unclear. For the Baltic Sea it appears that the most important factor for the positive relation between area of anoxic bottoms and water column DIP concentration is the preferential remineralisation at anoxic bottoms and not the lost sink of P at oxic bottoms.

In paper III a budget model of the Baltic Sea showed that there is a net source of DIP in the Baltic Sea and that this source gave a flux of the same magnitude as the fluxes measured in situ at anoxic bottoms. This means that more P is released from the anoxic bottoms than what is put in. It also suggests that organic P which sedimented when the sediments were oxic is now being degraded and contributing to the high recycling rate of DIP from anoxic sediment. This highlights the need of bottom water oxygenation to decrease the internal load of P to the Baltic Sea. Through oxygenation the increased release of DIP from sediments under anoxic conditions and increasing primary production (e.g. Vahtera et al. 2007, Van Capellen 1994) could be shut off, as long as bottom waters are kept oxic.

One aspect of P recycling from sediments that was not discussed in this work is the contribution of dissolved organic P efflux from sediments and effects of bioturbation on P recycling in oxic environments (Ekeroth et al. 2012). A few un-published measurements of dissolved organic P flux from anoxic and oxic bottoms, from the studies in the EGB and the By Fjord, indicate that this P flux could be of importance, especially at oxic bottoms. As the effects of faunal colonization are different depending on the species (due to animal functional type), this offers a complex area of further research. For future research other forms of DIP in the sediment P recycling should be addressed and in situ flux measurements should also be combined with detailed studies of sediment P speciation. For this purpose the Gothenburg autonomous big lander is being rebuilt to better recover the incubated sediment. In addition to further measurements, the findings of preferential P remineralisation in anoxic sediments should be incorporated and tested in biogeochemical models of various complexities.

6 Acknowledgements

This work would not have been possible without funding from the Swedish Environmental Protection Agency to the BOX project, led by my supervisor Anders Stigebrandt, and the Tellus research Platform at the University of Gothenburg initiated by Anders Stigebrandt.

The field measurement in this study were all financed through, initiated and led by my supervisor Per Hall who has been an always present and endless source of knowledge on sediment biogeochemistry, throughout my work with this thesis.

Thank you to Olof Pfannkuche and Stefan Sommer at GEOMAR in Kiel, Germany for inviting us to participate on the R/V Poseidon cruise in August 2007 and R/V Alkor cruise in September 2009. All the other field measurement from the Eastern Gotland basin and the By fjord in this thesis were performed on the the R/V Skagerak owned by the University of Gothenburg. A very special thank you to the crew on this vessel, who has made the field campaigns run smoothly and added an extra joy to the cruises.

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Part II

Papers I – IV