

**Sedimentary deposition
and reflux of phosphorus
(P) in the Eastern
Gotland Basin and
their coupling with P
concentrations in the
water column***

OCEANOLOGIA, 47 (4), 2005.
pp. 663–679.

© 2005, by Institute of
Oceanology PAS.

KEYWORDS

Baltic Sea
Gotland Basin
Sediment
Phosphorus
Deposition
Reflux

SVEN HILLE
GÜNTHER NAUSCH
THOMAS LEIPE

Leibniz Institute for Baltic Sea Research Warnemünde (IOW),
Seestrasse 15, D-18119 Warnemünde, Germany;

e-mail: sven.hille@io-warnemuende.de

Received 31 May 2005, revised 27 September 2005, accepted 3 October 2005.

Abstract

In order to describe the role of sedimentary processes for the phosphorus (P) cycle in the open Baltic Proper, P deposition and reflux were quantified for the predominately anoxic sediments of the Eastern Gotland Basin. The study is based on investigations of 53 surface sediment samples and pore water samples from 8 sediment cores. The average P deposition rate was estimated at $0.20 \text{ g} \pm 0.18 \text{ g m}^{-2} \text{ yr}^{-1}$, the fluctuation being due to variable bulk sediment deposition rates. P refluxes were estimated by applying Fick's First Law of Diffusion. A fairly good positive correlation between sedimentary P deposition and P release was obtained. P release from sediments by diffusion exceeds net P deposition by a factor of 2. This suggests that 2/3 of the deposited gross P is recycled in the sediments and released back into the water column; only 1/3 remains in the sediment permanently. A budget calculation demonstrates that the released dissolved inorganic phosphorus (DIP) accounts for the observed increase in DIP concentrations in the deep water during periods of stagnation, which is noticeable even at the surface P concentrations. Under such conditions and with the present

* This publication is basically a condensed version of doctoral research by the first author supported by the Leibniz Institute for Baltic Sea Research Warnemünde.

remediation conditions it is not possible to freely manage P concentrations in the water column on short time scales.

1. Introduction

The ventilation of the deep basins in the Baltic Proper is closely connected with the inflow of saltwater and is governed mainly by meteorological conditions, sea level and salinity distributions (Schinke & Matthäus 1998). The amount of saltwater entering the Baltic Sea varies in time and it too is governed largely by weather conditions, sea level and salinity distributions (Schinke & Matthäus 1998). Matthäus & Franck (1992) define inflows of large volumes of high-salinity water ($\text{PSU} \geq 17$) as 'major Baltic inflows' (MBIs). The time spans between inflows are regarded as periods of stagnation. When such periods are long, hypoxic to anoxic conditions are established in the deep parts of the basins (Unverzagt 2001, Conley et al. 2002a). Oxygen depletion at the seafloor has large-scale consequences for benthic organisms. Extinctions of benthic flora and fauna have been reported from many coastal areas (Andersin et al. 1990, Rheinheimer 1998, Conley et al. 2002b, Ærtebjerg et al. 2003) and from deep basins (Laine et al. 1997). Bottom water oxygen deficiency also influences the biogeochemical processes controlling nutrient concentrations in the water column (Mortimer 1941, Nehring 1987). The period between the mid-1970s and 2003 was characterised by a low inflow activity with only 4 major events recorded. The last MBI occurred in spring 2003, 10 years after the previous one (Feistel et al. 2003). The 2003 inflow led to a deep-water renewal, a steep fall in deep water temperatures and an increase in the salinity of this water (Nausch et al. 2003a). The change in the redox conditions affected the nutrient distribution in the water column to a considerable extent. Stagnation periods (anoxia) are characterised by the enrichment of phosphate and ammonium and the absence of nitrate. The ventilation of the Gotland Basin resulted in an abrupt fall in phosphate from 7 to $2 \mu\text{mol dm}^{-3}$, the nitrification of ammonium and subsequently the formation of nitrate in the deep water (Nausch et al. 2003b). All these facts thus highlight the importance of the state of ventilation for the biogeochemical processes controlling nutrient concentrations in the water column (Nehring 1987). Studies by Matthiesen (1998) and Emeis et al. (2000) have suggested that increasing P-stocks in the water column during a stagnation period in the Gotland Basin are related to sedimentary processes. However, their results were based on a small number of sediment cores originating from the deepest part of the Gotland Basin, where the highest sediment deposition rates occur (Hille 2005) and led to overestimations. Hence, in this study we have used data not only from P-stock monitoring in the water column

during the last stagnation period but also from a large-scale sediment study in order to evaluate the impact of sedimentary processes on the stock of dissolved P in the water column.

2. Material and methods

2.1. Study area and sampling

The present study is based on investigations of 53 short sediment cores from the deepest part (< 150 m) of the Eastern Gotland Basin. Sediment sampling took place during a research cruise on the r/v 'Prof. A. Penck' from 4th to 19th June 2003 (Fig. 1). Sediment cores were collected by a multiple corer device (MUC) as described by Barnett et al. (1984), but additionally equipped with core catchers. The MUC was equipped with eight 60 cm long acrylic tubes with an inner diameter of 10 cm. At all stations the topmost surface sediments (0 to 2 cm) were sub-sampled by extrusion with a plunger device. Based on the sediment classification of Emelyanov et al. (1994), all the sediments examined could be classified as pelitic mud, i.e. fine-grained sediments dominated by silt particles ($\leq 63 \mu\text{m}$) with

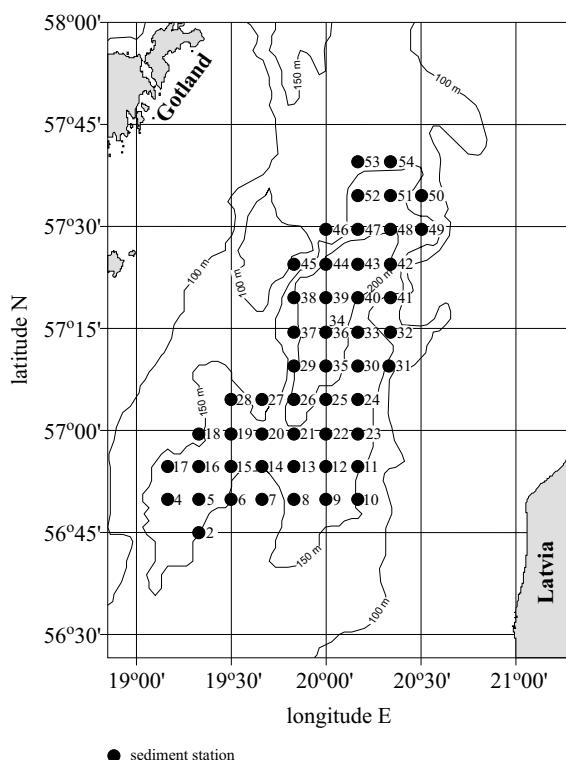


Fig. 1. Distribution of sediment sampling stations in the Eastern Gotland Basin with IOW station numbers and bathymetry of the study area (according to Seifert et al. 2001)

a significant contribution of clay ($\leq 2 \mu\text{m}$). Surface sediments from four to six cores per station were pooled, stored in polyethylene Petri dishes, and kept frozen until retrieval to onshore laboratories. Upon return to the shore, the sediment samples were desalted, lyophilised and homogenised for later geochemical investigations.

At eight stations (3, 13, 21, 23, 29, 34, 40, 49) sediment cores were used for pore water extraction. For this purpose the cores were sub-sampled in a glove box in an argon atmosphere immediately after retrieval. The top 5 cm of the sediment cores were cut up into 1 cm slices, the remainder of the cores into 2 cm slices. The pore water was extracted from the sediment slices inside the box using a pressure squeezing device equipped with a $0.45 \mu\text{m}$ Sartorius cellulose acetate filter. The pressure was produced by compressed argon flow (2 to 4 bar).

2.2. Geochemical methods

The contents of total sediment phosphorus (TP) and iron (TFe) were measured by the ICP-AES technique as described by Neumann et al. (1996). Briefly, sediment samples were completely dissolved using a cocktail of HF/HCl and $\text{HClO}_4/\text{HNO}_3$ acids in pressure bombs at 180°C for 3 h. The digested elements were measured with ICP-AES equipment (Liberty 200, Varian). The digestion method was validated using commercial reference material (MESS-2). Titrisol standards (1000 mg dm^{-3}) from Merck were used for calibration purposes.

Dissolved inorganic phosphorus in pore water samples (DIP) was measured spectrophotometrically according to the protocol of Koroleff (1983) on an Evolution III autoanalyser (Alliance Instruments). Dissolved iron (DFe) in pore water was measured using the Analyst 800 graphite furnace atomic absorption spectrometer with Zeeman correction (Perkin-Elmer). Before measurement the samples were diluted (1:100).

Dissolved oxygen in bottom water (above intact sediment cores) was measured with a Clark-type oxygen microsensor (Ox 11, Unisense, Århus, Denmark) mounted on a micromanipulator as described by Revsbech & Jørgensen (1986) and Revsbech (1989). A two-point linear calibration for the oxygen sensor (Revsbech 1989) was obtained by reading the signal in well-aerated overlying water and anoxic sediment. Since 1993 the laboratories at the Leibniz Institute for Baltic Sea Research Warnemünde have successfully participated in the international QUASIMEME quality assurance program (Cofino & Wells 1994).

2.3. P fluxes across the sediment water interface (SWI)

Fluxes of DIP across the SWI were estimated by applying Fick's First Law of Diffusion as described by Lavery et al. (2001):

$$F = \Phi D_s dC/dz,$$

where

F – flux [$\mu\text{mol m}^{-2} \text{s}^{-1}$],

D_s – diffusion coefficient [$\text{m}^2 \text{s}^{-1}$],

dC/dz – concentration gradient across the SWI [$\mu\text{mol m}^{-3} \text{m}^{-1}$].

The diffusion coefficient D_s depends mainly on the ions of interest, temperature, and sediment porosity (Berner 1980, Boudreau 1997). The constants used in this study were taken from Boudreau (1997). All constants were corrected with respect to *in situ* temperatures and porosities.

3. Results

3.1. Sedimentary P deposition rates

The sedimentary deposition rates for total phosphorus (TP_{DR}) were calculated on the basis of estimated bulk sediment deposition rates of the study area as described by Hille (2005) and on the measured TP contents. The average TP_{DR} is $0.20 \pm 0.18 \text{ g TP m}^{-2} \text{ yr}^{-1}$. TP_{DR} represents values for the uppermost 2 cm of the sediments – its spatial distribution is shown in Fig. 2. Evidently, the highest TP depositions occur in the NE part of the study area. Most of the stations are characterised by low rates $< 0.2 \text{ g TP m}^{-2} \text{ yr}^{-1}$ and only a few stations in the NE exceed $0.5 \text{ g TP m}^{-2} \text{ yr}^{-1}$. Altogether, the mean TP_{DR} is dominated by very low rates in the southern and western part of the study area. On comparing the distribution pattern of TP deposition and bulk sediment deposition (Hille 2005), it becomes clear that the TP_{DR} values mirror the bulk sediment deposition rates very well.

3.2. DIP pore water profiles and fluxes

Pore water samples were taken to approximately 24 cm below the sediment surface from eight sediment cores. All stations were located in hypoxic ($< 2 \text{ ml O}_2 \text{ dm}^{-3}$; according to Tyson & Pearson 1991) or anoxic areas. The vertical distribution of DIP is shown in Fig. 3. The measured DIP concentrations ranged from 4.6 to $146 \mu\text{mol dm}^{-3}$. On average, bottom water from about 0.5 cm above the sediment surface contained $4.1 \pm 1.1 \mu\text{mol dm}^{-3}$, and the small standard deviation indicates a small variability with respect to DIP concentrations in the near-bottom water layer within the study area. On average, the topmost pore water samples (taken

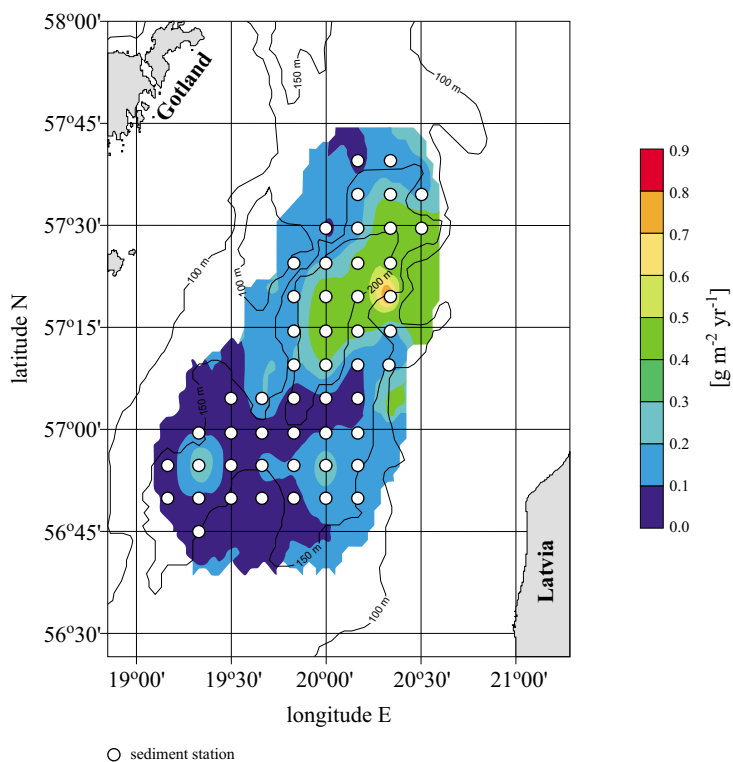


Fig. 2. Distribution of total sedimentary phosphorus deposition rates (TP_{DR})

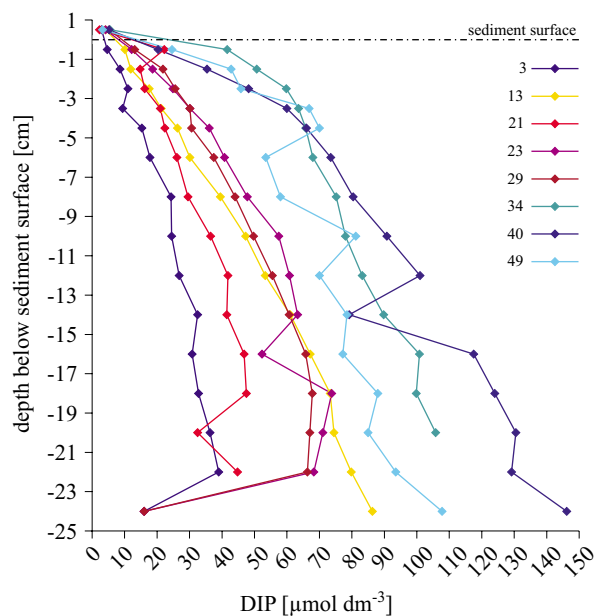


Fig. 3. Distribution of dissolved inorganic phosphorus in pore water from 8 sediment cores. The dashed line represents the sediment surface; the uppermost points represent bottom water samples

0.5 cm below the sediment surface) contained $18.6 \pm 10.7 \mu\text{mol DIP dm}^{-3}$ and the variability of the standard deviation is greater than that of the bottom water samples. Application of the T-Test showed that these mean DIP values differ significantly ($T = -3.695$, $df = 7$, $p = 0.008$). The less variable DIP concentrations in the bottom water may be explained by hydrodynamic processes in the deep water that result in homogenisation of the DIP concentrations. The flux of the solute (DIP) is proportional to the concentration gradient across the SWI and assumes steady state conditions. Hence, the DIP gradient between bottom water samples and the topmost pore water samples were calculated and then used to calculate DIP fluxes across the SWI by means of Fick's First Law of Diffusion (see Table 1). All profiles show gradually decreasing DIP concentrations towards the SWI, which indicates an upward transport of DIP. However, the profiles differ a lot with respect to their individual slopes. It is worth noting that on average the DIP concentrations in pore water exceed those of dissolved iron (DFe) by a factor of 26 ± 18 on a molar basis. The respective average factor for bottom water DFe is 58 ± 78 . However, the high standard deviations display a high variability.

Table 1. Parameters used for calculating fluxes of dissolved inorganic phosphorus (DIP) and respective flux estimates

| Station ¹ | DIP-gradient [$\mu\text{mol m}^{-3} \text{ m}^{-1}$] | Porosity | Diffusion coefficient ² [$\text{m}^2 \text{ s}^{-1}$] | DIP flux ³ [$\mu\text{mol m}^{-2} \text{ h}^{-1}$] |
|----------------------|---|----------|---|--|
| 3 ^a | -1.73 | 0.95 | 3.76E-06 | -0.21 |
| 13 ^a | -6.00 | 0.96 | 3.83E-06 | -0.76 |
| 21 ^a | -6.29 | 0.94 | 3.69E-06 | -0.74 |
| 23 ^h | -8.07 | 0.97 | 3.91E-06 | -1.07 |
| 29 | -7.85 | 0.99 | 4.06E-06 | -1.13 |
| 34 ^h | -36.1 | 0.97 | 3.91E-06 | -4.78 |
| 40 ^h | -15.1 | 0.95 | 3.76E-06 | -1.84 |
| 49 ^a | -21.4 | 0.93 | 3.62E-06 | -2.41 |

^{1a}anoxic bottom water, ^{1h}hypoxic bottom water; ²taken from Boudreau (1997) and adapted to *in situ* temperatures (5°C) and porosities; ³converted from $\mu\text{mol m}^{-2} \text{ s}^{-1}$.

Table 1 summarises all the parameters used for this calculation as well as estimates for DIP fluxes. The negative signs indicate that solute transport runs in the opposite direction to the concentration gradient: from high concentrations in the deeper part of the sediment cores to lower concentrations at the surface, which is indicative of DIP transport to the water column. At all stations the DIP fluxes derived from Fick's First Law of Diffusion indicate a transport across the SWI towards the water column:

this is indicated by the negative signs in Table 1. The calculated DIP release rates range from 0.21 to 4.78 $\mu\text{mol m}^{-2} \text{h}^{-1}$ and thus display a high variability that is visible in the high standard deviation of the mean flux rate of $-1.62 \pm 1.36 \mu\text{mol m}^{-2} \text{h}^{-1}$.

4. Discussion

4.1. Sedimentation of P

Nutrients which have entered the Baltic Sea will finally end up in the sediments or be laterally exported to the North Sea in the form of solutes or particles. The model results of Wulff et al. (2001) suggest that lateral export to the North Sea is only of minor importance as regards P removal – only 17% of the total external P load leaves the ecosystem by that route. The balance should thus end up in the Baltic Sea ecosystem by accumulation in particulate form in the sediments or in dissolved form in the water. Only a few studies have so far addressed the quantification of sedimentary P deposition for Baltic Sea sediments (e.g. Larsen & Brüggemann 1992, Carman et al. 1996, Emeis et al. 2000, Emelyanov 2001, Emelyanov ed. 2002). In most cases, these studies were based on a limited number of stations, so their validity for larger areas is questionable. The present study was therefore initiated in order to characterise the role of sediments in accumulation basins as sinks and sources for nutrients on a larger scale. The obtained TP_{DR} do not represent permanent burial rates of P because in the uppermost 2 cm diagenetic processes are still altering the composition of the sedimentary organic matter to some extent.

Maps of P distribution in the surface sediments of the Gotland and Gdańsk Basins have been compiled by Emelyanov (2001, Emelyanov ed. 2002). However, these data are not suitable for comparison because inadequate sampling techniques were used which cannot recover surface layers. This is clearly documented by the low contents of organic carbon (TOC): an average TOC content of 3.19 % was reported by Emelyanov (2001) for the surface sediments of the Gotland Basin, which is only 1/3 of the TOC content for the surface sediments used in this study (Hille 2005). Larsen & Brüggemann (1992) studied P deposition in different Baltic Sea basins and obtained a range from 0.31 to 1.19 with an average TP_{DR} of 0.61 $\text{g m}^{-2} \text{yr}^{-1}$. In their study a TP_{DR} of 0.58 $\text{g m}^{-2} \text{yr}^{-1}$ was obtained for the Gotland Deep. This is three times higher than the value reported for the Eastern Gotland Basin in this study. The insufficient spatial coverage of stations used by Larsen & Brüggemann (1992) may account for these discrepancies. In general, the occurrence of long-lasting oxygen depletion in the deep water of the Eastern Gotland Basin and, subsequently, the lowered

ability of anoxic sediments to retain P also help to explain the observed difference (Emeis et al. 2000). The latter study was performed in the deepest part of the Eastern Gotland Basin, and the average TP deposition of $0.51 \pm 0.03 \text{ g TP m}^{-2} \text{ yr}^{-1}$ was estimated on the basis of 3 sediment cores from the period 1970–94. These rates accord very well with the TP_{DR} estimated for the NE part of the study area in the present investigation. The impact of the redox stage on the sediment deposition of P is well described by Emeis et al. (2000). In their study the TOC:TP ratios from Gotland Basin sediments (predominantly anoxic) were on average 206, in contrast to the muddy sediments studied in the deepest parts of the Arkona (predominantly oxic), Bornholm and Gdańsk Basins (both frequently oxic), which were on average around 100. This indicates the better ability of oxic than anoxic sediments to retain P. This is in agreement with the results of Carman et al. (1996), who noted a TOC:TP ratio of 100 based on 26 sediment cores for the mostly oxic Gulf of Riga sediments. These authors calculated a mean TP_{DR} of $0.21 \text{ g m}^{-2} \text{ yr}^{-1}$. This is the same order of magnitude as the values obtained in the Eastern Gotland Basin. However, recorded TOC:TP ratios indicate that oxic sediments retain P more efficiently in relation to carbon than do anoxic sediments.

This observation is explainable by the linked cycles of P and Fe, first described for lakes (Einsele 1936, Mortimer 1941) and later also for the sea (e.g. Sundby et al. 1992, Gunnars & Blomqvist 1997). An important sink for P is the formation of Fe(III) oxide, which can precipitate at the SWI under oxic conditions. This Fe(III) oxide acts as an effective trap for upwards diffusing phosphate (Sundby et al. 1992, Gunnars & Blomqvist 1997) originating from the decomposition of organic matter. Jensen et al. (1992) found a molar ratio < 0.13 for TP:TFe, which efficiently traps phosphate under oxic conditions. However, this process is reversible and phosphate is reliberated if the system becomes anoxic. This explains the differences in sedimentary P removal between oxic and anoxic sediments.

4.2. Recycling and reflux of P

For this study, the fluxes of P across the SWI were estimated by applying Fick's First Law on detected P gradients in pore water and bottom water samples. This method is quick and was preferred to more time consuming ones (e.g. incubation experiments) because a comparatively large number of stations could thus be investigated during the cruise with the ensuing dense spatial coverage of the study area. The application of Fick's First Law for predicting pore water fluxes assumes that diffusive processes determine the transport of solutes across the sediment-water interface. Hence it is restricted to environments where bioturbation and

resuspension are not significant (Lavery et al. 2001). These authors noted the good agreement for hypoxic to anoxic conditions between P fluxes based on pore water studies and other results derived from incubation experiments. All these requirements were fulfilled in the study area and thus permitted the application of Fick's First Law for predicting nutrient fluxes. Evidently, the redox conditions had no marked affect on the DIP refluxes obtained because the highest fluxes were observed at stations where small amounts of oxygen were present (Table 1). This seems to be in contrast to the classical models described by Einsele (1936) and Mortimer (1941), which suggest that the highest fluxes occur under anoxic conditions.

However, the fluxes obtained are in accordance with other studies performed in the Baltic Sea (Conley et al. 1997, Matthiesen 1998), who also noted significant DIP release under oxic to hypoxic conditions. The high variability of flux rates can be accounted for by the large geographical extent of the study area covering different physicochemical environments. The present data for the Eastern Gotland Basin fall in the range reported by other authors for the Baltic Sea, even if they tend to be on the low side

Table 2. Comparison of DIP sediment-water-fluxes from different regions and derived with different methods. All negative fluxes rates are directed towards the water column (= reflux)

| Area | DIP flux [$\mu\text{mol m}^{-2} \text{ h}^{-1}$] | | Mean | Redox stage | Method | Remark |
|-------------------------------------|---|-------|---------------|---------------|-------------------------------|---------------|
| | Min | Max | | | | |
| Gotland Basin ¹ | -0.21 | -4.78 | -1.62 | oxic – anoxic | pore water | |
| Gotland Basin ² | -4.13 | -13.8 | not available | hypoxic | pore water | ⁸ |
| northern Baltic Proper ³ | -2.10 | -37.0 | -15.7 | anoxic | incubation | ⁹ |
| western Baltic ⁴ | -0.80 | -37.2 | -31.0 | oxic – anoxic | <i>in situ</i> enclosure exp. | |
| Gulf of Finland ⁵ | -4.20 | -41.7 | -17.6 | oxic – anoxic | incubation | ¹⁰ |
| Gulf of Finland ⁶ | -1.59 | -28.5 | -15.7 | oxic | incubation | |
| southern Baltic Proper ⁷ | +0.04 | -2.96 | -0.83 | oxic – anoxic | pore water | ¹¹ |

Source: ¹this study, ²Matthiesen (1998), ³Koop et al. (1990), ⁴Balzer (1984), ⁵Lehtoranta (2003), ⁶Conley et al. (1997), ⁷Bolalek (1992), ⁸fluxes recalculated applying diffusion coefficients from Boudreau (1997), ⁹all cores represented oxic bottom water conditions, ¹⁰only reduced sediments included, ¹¹only fluxes measured during the winter months were used.

(Table 2). The DIP fluxes obtained appear too high in comparison with the low total solid sedimentary TP:TFe molar ratios (0.08; mean of the topmost 1 cm of eight investigated 'pore water' cores). According to Jensen et al. (1992) this would suggest an efficient trapping of phosphate under oxic conditions. However, bearing in mind that the bulk of Fe is incorporated into stable FeS minerals and also the observation of Thamdrup et al. (1994) that Fe is to a large extent bound to sheet silicates, the TFe content does not reflect the pool of reactive Fe. Thus, the DIP refluxes obtained seem to be reasonable in spite of the observed low TP:TFe molar ratios. This is also confirmed by the detected pore water DFe:DIP molar ratio of 0.10 (data not shown; mean of the topmost 1 cm of eight investigated 'pore water' cores). Gunnars & Blomqvist (1997) and Gunnars et al. (2002) suggested a general good sediment retention ability when pore water molar DFe:DIP ratios exceed 2.0. The much lower ratios in the present study thus most likely indicate the formation of FeS (Rozaan et al. 2002). All in all, despite the hypoxic conditions at a few stations, DIP release seems to be unaffected by the trapping of DIP as Fe(III) oxides.

The significance of DIP refluxes for the net TP sediment deposition rate is expressed in Fig. 4. It is obvious that the DIP refluxes exceed the net deposition of P into sediments by a factor of nearly two. In conclusion, it shows that only 35% of the gross P that settles annually on the sediment surface is buried in the sediments, while 65% returns to the water column. This is in agreement with studies in the Kiel Bight, where 66% of the annually accumulated organic P was released back into the water (Balzer

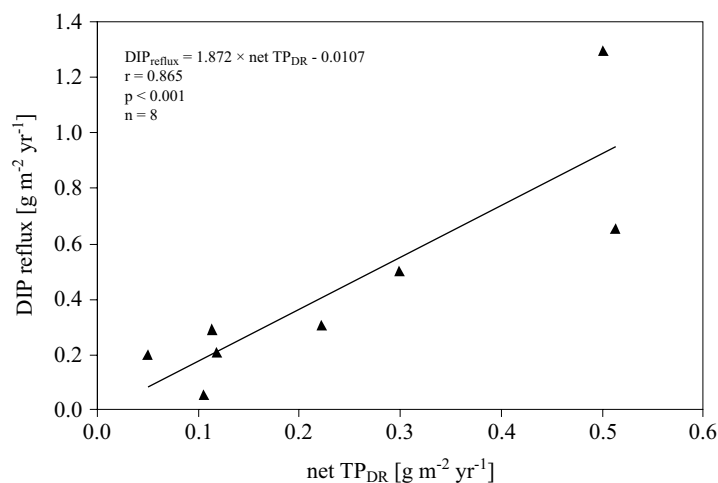


Fig. 4. Refluxes of dissolved inorganic phosphorus vs. net phosphorus deposition rates and summary of regression analyses

1984). Investigations by Jensen et al. (1995) conducted in Århus Bay revealed that approximately 40% of the annual gross sedimentation of P is released back into the water and this can be used for corroborating the results for the Eastern Gotland Basin as well. This is specific not only to the Baltic Sea, but is also the case in other temperate regions, for example, the Gulf of St. Lawrence (Sundby et al. 1992). This author concluded that approximately half the annual sedimentation flux of particulate P is released back into the water column. All these different sediment studies suggest the importance of the contribution of sedimentary processes to the nutrient load in the water column. The regression equation obtained was used to estimate DIP release rates for all 53 stations in the study area where net P deposition rates are available (Fig. 2). An average P release of 0.37 ± 0.34 g DIP m^{-2} yr^{-1} was estimated.

4.3. DIP in the water column

The temporal development of the deep water P stock of the Eastern Gotland Basin during a stagnation period was investigated by Nausch et al. (2003b). From 1995 to 2002 the P pool below the redoxcline (around 140 m water depth) increased from 11 000 to 29 000 t. This accounts for a rate of 2150 t P yr^{-1} , which is very close to the estimated release of P from the area studied here ($4800 \text{ km}^2 = 1920 \text{ t P yr}^{-1}$). This suggests the large-scale significance of bottom-water oxygen deficiency as a trigger for biogeochemical processes that lead to a large scale relocation of P from the sedimentary environment to the water column.

A long-term data series on DIP concentrations in the mixed surface layer of the Eastern Gotland Basin in winter (Fig. 5) suggests that the concentrations are clearly influenced by the P pool stored in the deep water whereby the P pool between the halocline and the redoxcline is much more important than the one below the redoxcline. The significant drop in the DIP concentration after 1993 can be attributed to the major Baltic inflow of oxygen-rich water which caused a decrease in the deep-water DIP pool (Nausch et al. 2003b). From 1995 onwards there is good temporal agreement between the DIP concentrations in winter water and those observed in deep water. This hypothesis is substantiated by a P load compilation by Conley et al. (2002a), who noted that the P loads were remarkably constant during the 1990s (23 000 to 30 000 t). Thus, it is unlikely that the comparatively small changes in the external P load account for the observed variability in the DIP concentrations. However, it is still unknown which transport processes account for the upward transport of DIP, so this calls for further research. Transport mediated mainly by

diffusion is unlikely because of the small exchange rates across the halocline, as observed by Schneider et al. (2002). However, new results by Hagen & Feistel (2001, 2004) suggest that turbulent mixing and upwelling may account for the suspected upward transport of solutes. Also, the intensity of deep-reaching vertical mixing during winter driven by meteorological conditions can influence the surface layer significantly (Jansen et al. 2003). However, these processes still need to be quantified.

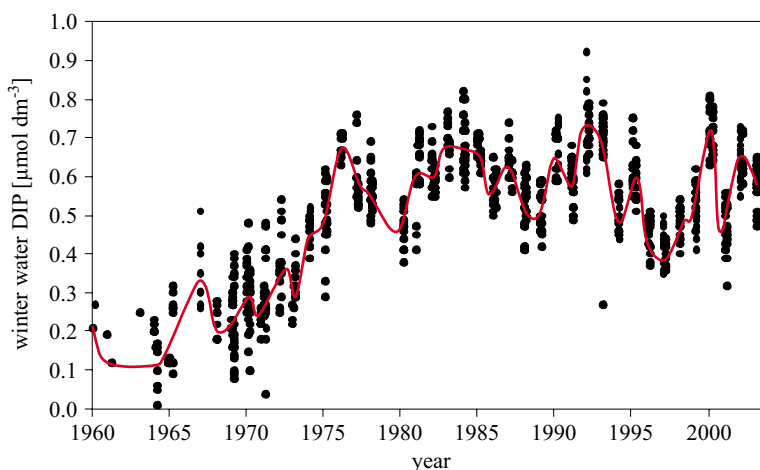


Fig. 5. Long-term development of phosphate concentrations in the mixed surface layer of the Eastern Gotland Basin in winter (January to April). Modified after Nausch et al. (2004). The red line represents the development of the mean annual winter water DIP

Altogether the results discussed here suggest that the changes in the DIP stocks in the water body of the Baltic Proper that have occurred in recent decades are triggered mainly by the changing oxygen situation in the deep water. Oxygenation of the deep water is strongly dependent on the frequency and intensity of major saltwater inflows from the North Sea (Matthäus & Franck 1992, Schinke & Matthäus 1998, Nausch et al. 2003a). Consequently, changes in the DIP pool on shorter time scales are triggered by climatic forcing beyond human control. This restricts the human ability to control P concentration in the open sea in the short term and should be taken into account when evaluating the success of measures undertaken to reduce nutrient input from the catchment area. Over a longer perspective, however, the increasing DIP concentrations, as observed during the late 1960s and 1970s (Fig. 5), have to be attributed to human impact. Considering also the large amounts of P which are stored in the sediments as a result of human activities that could be released under hypoxic or anoxic

conditions, the very substantial reduction of the P load entering the Baltic Sea could have a significant impact on its eutrophication status over longer time scales.

Acknowledgements

We wish to thank Mrs. A. Welz, D. Benesch and S. Klein for their excellent technical support with the analysis. This paper has been improved by the comments of two anonymous reviewers. The captain and crew of r/v Prof. A. Penck deserve our gratitude for providing excellent working conditions onboard and assistance during sediment sampling.

References

- Ærtebjerg G., Andersen J.H., Hansen S.O. (eds.), 2003, *Nutrients and eutrophication in Danish marine waters. A challenge for science and management*, Danish EPA & Natl. Environ. Res. Inst., Roskilde, 126 pp.
- Andersin A. B., Cederwall H., Gosseleck F., Josefson A., Järvekulg A., Gunnars A., Nörrevang J., Rumohr H., 1990, *Sediments and zoobenthos*, *Ambio*, 7, 11–12.
- Balzer W., 1984, *Organic matter degradation and biogenic element cycling in a nearshore sediment (Kiel Bight)*, *Limnol. Oceanogr.*, 29 (6), 1231–1246.
- Barnett P. R. O., Watson J., Connelly D., 1984, *A multiple corer for taking virtually undisturbed samples from shelf, bathyal and abyssal sediments*, *Oceanol. Acta*, 7 (4), 399–408.
- Berner R. A., 1980, *Early diagenesis: a theoretical approach*, Princeton Univ. Press, Princeton, 241 pp.
- Bolalek J., 1992, *Phosphate at the water-sediment interface in Puck Bay*, *Oceanologia*, 33, 159–182.
- Boudreau B.P., 1997, *Diagenetic models and their implementation: modelling transport and reactions in aquatic sediments*, Springer-Verl., Berlin, 414 pp.
- Carman R., Aigars J., Larsen B., 1996, *Carbon and nutrient geochemistry of the surface sediments of the Gulf of Riga, Baltic Sea*, *Mar. Geol.*, 134 (1)–(2), 57–76.
- Cofino W. P., Wells D. E., 1994, *Design and evaluation of the QUASIMEME inter-laboratory performance studies: a test case for robust statistics*, *Mar. Pollut. Bull.*, 29 (4)–(5), 149–158.
- Conley D. J., Humborg C., Rahm L., Savchuk O. P., Wulff F., 2002a, *Hypoxia in the Baltic Sea and basin-scale changes in phosphorus biogeochemistry*, *Environ. Sci. Technol.*, 36 (24), 5315–5320.
- Conley D. J., Markager S., Andersen J., Ellermann T., Svendsen L. M., 2002b, *Coastal eutrophication and the Danish National Aquatic Monitoring and Assessment Program*, *Estuaries*, 25 (4B), 848–861.

- Conley D. J., Stockenberg A., Carman R., Johnstone R. W., Rahm L., Wulff F., 1997, *Sediment-water nutrient fluxes in the Gulf of Finland, Baltic Sea*, Estuar. Coast. Shelf Sci., 45 (5), 591–598.
- Einsele W., 1936, *Über chemische und kolloidchemische Vorgänge in Eisen-Phosphat-Systemen unter limnochemischen und limnogeologischen Gesichtspunkten*, Arch. Hydrobiol., 33, 361–387.
- Emeis K.-C., Struck U., Leipe T., Pollehne F., Kunzendorf H., Christiansen C., 2000, *Changes in the burial rates and C:N:P ratios in the Baltic Sea sediments over the last 150 years*, Mar. Geol., 167 (1)–(2), 43–59.
- Emelyanov E. M., 2001, *Biogenic components and elements in sediments of the central Baltic and their redistribution*, Mar. Geol., 172 (1), 23–41.
- Emelyanov E. M. (ed.), 2002, *Geology of the Gdańsk Basin, Baltic Sea*, Yantarny Skaz, Kaliningrad, 494 pp.
- Emelyanov E. M., Neumann G., Lemke W., Kramarska R., Uscinowicz S., 1994, *Bottom sediments of the western Baltic 1:500 000*, Head Dept. Navigation and Oceanogr., Russian Fed. Min. Defense, St. Petersburg.
- Feistel R., Nausch G., Matthäus W., Hagen E., 2003, *Temporal and spatial evolution of the Baltic deep water renewal in spring 2003*, Oceanologia, 45 (4), 623–642.
- Gunnars A., Blomqvist S., 1997, *Phosphate exchange across the sediment-water interface when shifting from anoxic to oxic conditions – an experimental comparison of freshwater and brackish-marine systems*, Biogeochemistry, 37 (3), 203–226.
- Gunnars A., Blomqvist S., Johansson P., Andersson C., 2002, *Formation of Fe(III) oxyhydroxide colloids in freshwater and brackish seawater, with incorporation of phosphate and calcium*, Geochim. Cosmochim. Acta, 66 (5), 745–758.
- Hagen E., Feistel R., 2001, *Spreading of Baltic deep water: a case study for the winter 1997–1998*, Meereswiss. Ber., 45, 99–133.
- Hagen E., Feistel R., 2004, *Observations of low-frequency current fluctuations in deep water of the Eastern Gotland Basin/Baltic Sea*, J. Geophys. Res., 109 (C03044), 1–15.
- Hille S., 2005, *New aspects of sediment accumulation and reflux of nutrients in the Eastern Gotland Basin and its impact on nutrient cycling*, Institute of Biology, Rostock Univ., 119 pp.
- Jansen D. L., Lundqvist D. P., Christiansen Ch., Lund-Hansen L. C., Balstrøm T., Leipe T., 2003, *Deposition of organic matter and particulate nitrogen and phosphorus at the North Sea – Baltic Sea transition – a GIS study*, Oceanologia, 45 (2), 283–303.
- Jensen H. S., Kristensen P., Jeppesen E., Skytthe A., 1992, *Iron: phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes*, Hydrobiologia, 235/236, 731–743.
- Jensen H. S., Mortensen P. B., Andersen F. Ø., Rasmussen E., Jensen A., 1995, *Phosphorus cycling in a coastal marine sediment, Århus Bay, Denmark*, Limnol. Oceanogr., 40 (5), 908–917.

- Koop K., Boynton W. R., Wulff F., Carman R., 1990, *Sediment-water oxygen and nutrient exchanges along a depth gradient in the Baltic Sea*, Mar. Ecol. Prog. Ser., 63, 65–77.
- Koroleff F., 1983, *Determination of phosphorus*, [in:] *Methods of seawater analysis*, K. Grasshoff, M. Ehrhardt & K. Kremling (eds.), Verl. Chem., Weinheim, 125–131.
- Laine A. O., Sandler H., Andersin A.-B., Stigzelius J., 1997, *Long-term changes of macrozoobenthos in the Eastern Gotland Basin and the Gulf of Finland (Baltic Sea) in relation to the hydrographical regime*, J. Sea Res., 38, 135–159.
- Larsen B., Brüggemann L., 1992, *Phosphorus accumulation in the sediments of the Baltic Sea*, ICES Rep. No 180, 109–121.
- Lavery P.S., Oldham C.E., Ghisalberti M., 2001, *The use of Fick's First Law for predicting porewater nutrient fluxes under diffusive conditions*, Hydrol. Process., 15 (13), 2435–2451.
- Lehtoranta J., 2003, *Dynamics of sediment phosphorus in the brackish Gulf of Finland*, Monogr. Boreal Environ. Res., 24, 1–58.
- Matthäus W., Franck H., 1992, *Characteristics of major Baltic inflows – a statistical analysis*, Cont. Shelf Res., 12 (12), 1375–1400.
- Matthiesen H., 1998, *Phosphate release from marine sediments: by diffusion, advection and resuspension*, Ph.D. thesis, Faculty of Natural Sciences, Århus Univ., Århus, 153 pp.
- Mortimer C.H.J., 1941, *The exchange of dissolved substances between mud and water in lakes: I and II*, J. Ecol., 29, 280–329.
- Nausch G., Feistel R., Lass H.U., Nagel K., Siegel H., 2003a, *Hydrographisch-chemische Zustandseinschätzung der Ostsee 2002*, Meereswiss. Ber., 55, 1–71.
- Nausch G., Matthäus W., Feistel R., 2003b, *Hydrographic and hydrochemical conditions in the Gotland Deep area between 1992 and 2003*, Oceanologia, 45 (4), 557–569.
- Nausch M., Nausch G., Wasmund N., 2004, *Phosphorus dynamics during the transition from nitrogen to phosphate limitation in the central Baltic Sea*, Mar. Ecol. Prog. Ser., 266, 15–25.
- Nehring D., 1987, *Temporal variations of phosphate and inorganic nitrogen compounds in central Baltic deep waters*, Limnol. Oceanogr., 32 (2), 494–499.
- Neumann T., Leipe T., Brand T., Shimmiel G., 1996, *Accumulation of heavy metals in the Oder estuary and its off-shore basins*, Chem. Erde, 56, 207–222.
- Revsbech N.P., 1989, *An oxygen microsensor with a guard cathode*, Limnol. Oceanogr., 34 (2), 474–478.
- Revsbech N.P., Jørgensen B.B., 1986, *Microelectrodes: their use in microbial ecology*, Adv. Microb. Ecol., 9, 293–352.
- Rheinheimer G., 1998, *Pollution in the Baltic Sea*, Naturwissenschaften, 85 (7), 318–329.

- Rozan T. F., Taillefert M., Trouwborst R. E., Glazer B. T., Ma S. F., Herszage J., Valdes L. M., Price K.S., Luther G. W., 2002, *Iron-sulfur-phosphorous cycling in the sediments of a shallow coastal bay: implications for sediment nutrient release and benthic macroalgal blooms*, *Limnol. Oceanogr.*, 47 (5), 1346–1354.
- Schinke H., Matthäus W., 1998, *On the causes of major Baltic inflows – an analysis of long time-series*, *Cont. Shelf Res.*, 18 (1), 67–97.
- Schneider B., Nausch G., Kubsch H., Peterson I., 2002, *Accumulation of total CO₂ during stagnation in the Baltic Sea deep water and its relationship to nutrient and oxygen concentrations*, *Mar. Chem.*, 77, 277–291.
- Seifert T., Tauber F., Kayser B., 2001, *A high resolution spherical grid topography of the Baltic Sea*, 2nd edn., *Baltic Sea Sci. Congr.*, 25–29 November, Stockholm.
- Sundby B., Gobeil Ch., Silverberg C.G., Silverberg N., Mucci A., 1992, *The phosphorus cycle in coastal marine sediments*, *Limnol. Oceanogr.*, 37 (6), 1129–1145.
- Thamdrup B., Fossing H., Jørgensen B.B., 1994, *Manganese, iron, and sulfur cycling in a coastal marine sediment, Århus Bay, Denmark*, *Geochim. Cosmochim. Acta*, 58, 5115–5129.
- Tyson R. V., Pearson T.H., 1991, *Modern and ancient continental shelf anoxia: an overview*, [in:] *Modern and ancient continental shelf anoxia*, R. V. Tyson & T. H. Pearson (eds.), *Geol. Soc. Spec. Publ. No 58*, London, 1–24.
- Unverzagt S., 2001, *Räumliche und zeitliche Veränderungen der Gebiete mit Schwefelwasserstoff im Tiefenwasser der Ostsee*, Ph.D. thesis, Institute for Geography, Greifswald Univ., Greifswald, 123 pp.
- Wulff F., Rahm L., Hallin A.-K., Sandberg J., 2001, *A nutrient budget model of the Baltic Sea*, [in:] *A systems analysis of the Baltic Sea*, F. Wulff, L. Rahm & P. Larsson (eds.), Springer, Berlin, 353–372.