Phosphorus recycling in sediments of the Central Baltic Sea

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Abstract

Benthic fluxes of dissolved inorganic phosphorus (DIP) were measured in situ in the Eastern Gotland Basin (EGB), Central Baltic Sea, using benthic landers. A total of 40 flux measurements on 13 stations at water depths ranging from 30–210 m and under different oxygen regimes were carried out on three cruises during three consecutive years (2008–2010) in August–September. Our study is the first to report in situ DIP fluxes in the Baltic Proper, and it provides the most comprehensive data set of benthic DIP fluxes in the Baltic Proper existing to date. DIP fluxes increased with increasing water depth and with decreasing bottom water oxygen concentration. Average fluxes were calculated for oxic bottom water conditions (−0.003 ± 0.040 mmol m\(^{-2}\) d\(^{-1}\)), hypoxic conditions (0.027 ± 0.067 mmol m\(^{-2}\) d\(^{-1}\)) and anoxic conditions (0.376 ± 0.214 mmol m\(^{-2}\) d\(^{-1}\)). The mean flux on anoxic bottoms was ca. 5–10 times higher than previous estimates based on ex situ measurements, but agreed well with previous flux estimations from changes in the basin water DIP pool. The DIP flux was positively correlated with the organic carbon inventory of sediment and the benthic flux of dissolved inorganic carbon (DIC) on anoxic stations, but these variables were uncorrelated on oxic stations. The positive correlation between DIP and DIC fluxes suggests that the benthic DIP flux on anoxic bottoms in the Baltic Proper is mainly controlled by rates of deposition and degradation of organic matter. The flux from anoxic sediment was very P rich in relation to both C and N, and the average C : P ratio in fluxes on anoxic accumulation bottoms was 69 ± 15, which is well below the Redfield C : P ratio of 106 : 1. On oxic stations, however, the C : P flux ratio was much higher than the Redfield ratio, consistent with well-known P retention mechanisms associated with iron and bacteria in oxidized sediment. Using a benthic mass balance approach, a burial efficiency of 4 % was calculated for the anoxic part of the EGB, which suggests that anoxic Baltic sediments are very efficient in recycling deposited P. Based on the measured fluxes and recent estimates of the areal extent of anoxic and hypoxic bottoms, an internal load of 146 kton yr\(^{-1}\) was calculated. This is 7–12 times higher than
recent estimates of the external load and clearly highlights the dominance of anoxic sediments as a P source in the Baltic Sea.

1 Introduction

Phosphorus (P) is a major and vital component of the biosphere. The biogeochemical cycling of this element has therefore attracted massive scientific study for almost a century. It has been long known that primary production is often rate-limited by the amount of bioavailable P in aquatic environments, especially in fresh water lakes (Schindler, 1977). Phosphorus limitation also occurs in coastal marine and oceanic systems (Granéli et al., 1990; Krom et al., 1991; Wu et al., 2000). One example is the Baltic Sea, a brackish semi-enclosed eutrophicated sea area in Northern Europe constituting a total area of about 377 000 km$^2$ (Elmgren, 2001). Nutrient limitation in the southernmost and largest water body of the Baltic Sea, the Baltic Proper, generally shifts seasonally; after the N-limited spring bloom has settled out, the system becomes limited by P as diazotrophic cyanobacteria begin to dominate the phytoplankton community (Granéli et al., 1990; Hagström et al., 2001; Nausch et al., 2008).

The frequency at which massive cyanobacterial blooms develop is reported to have increased over the last 50 yr in the Baltic Sea (Finni et al., 2001; Poutanen and Nikkilä, 2001). This is most likely an effect of the sharp increase of the winter water dissolved inorganic phosphorus (DIP) concentration that occurred between 1965 to 1985 in the Eastern Gotland, Arkona and Bornholm Basins (Finni et al., 2001; Nausch et al., 2008; Eilola et al., 2009). Cyanobacterial N-fixation adds new nitrogen to the system in roughly equal amounts to the total riverine input, or the anthropogenic supply (Larsson et al., 2001). Hence, diazotrophic cyanobacteria are not only a sign of, but also conducive to, eutrophication of the Baltic Sea (Voss et al., 2011). A similar statement is valid for the expansion of bottom water oxygen deficiency, which has occurred in the Baltic Sea since the mid 20th century (Jonsson et al., 1990). Low bottom water oxygen conditions have been shown to lower the sedimentary retention capacity of P in many
marine environments (Sundby et al., 1986; Faganeli and Ogrinc, 2009), including the Baltic Sea (Balzer, 1983; Koop et al., 1990; Gunnars and Blomqvist, 1997; Ekeroth et al., 2012; Viktorsson et al., 2012). Thus, a positive feedback mechanism has been proposed where surface water nutrient enrichments result in increased sedimentation of organic matter, bottom water oxygen depletion and increased sedimentary P release back to the water column (Emeis et al., 2000; Vahtera et al., 2007).

Rising P concentrations in the benthic efflux at the onset of bottom water hypoxia/anoxia is often related to the biogeochemical reduction and dissolution of P-rich Fe oxyhydroxide particles (Fe-P) in the sediment (Gunnars and Blomqvist, 1997; McManus et al., 1997). Also, when the oxygen regime is oscillating, bacterial phosphate assimilation is high during oxic periods, and the stored polyphosphate is hydrolysed and released as phosphate during anoxia, when it is utilized in the anaerobic energy metabolism, or following the death and degradation of the bacteria themselves (Gächter and Meyer, 1993). Relative to carbon (C), the burial efficiency of P is generally also very low in permanently anoxic sediments in which the pool of Fe-P has long been depleted (Ingall et al., 1993, 2005; Ingall and Jahnke, 1997; Emeis et al., 2000; Mort et al., 2010). The mechanism(s) responsible for the preferential or enhanced regeneration of P under such conditions remain enigmatic. Recent evidence suggests, however, that microbial phosphatases are an important part of the explanation (Steenbergh et al., 2011). Phosphatases, enzymes which cleave off phosphate groups from organic matter, are used by C-limited bacteria to increase the bioavailability of the organic matter C moiety (Steenbergh et al., 2011, and references therein). Under anoxic conditions, the phosphate diffuse out into the bottom water to a much larger degree than in oxic sediments where a substantial proportion is trapped in surficial oxidized sediment layers (Steenbergh et al., 2011) through bacterial phosphate assimilation and Fe scavenging.

The amount of P annually supplied from land to the Baltic Proper ranged from about 12–20 kton total P yr\(^{-1}\) in years 1994–2008 and was closely coupled to variations in water flow between years (HELCOM, 2011). Present estimates of the “internal” load (i.e.
flux from the sediment) to the water column of the Baltic Proper are within the same range. The nutrient budget by Savchuk (2005) for the years 1991–1999 gives a net release of 17.7 kton P yr\(^{-1}\). Emeis et al. (2000) based their calculation of 14 kton P yr\(^{-1}\) released to the Baltic Proper bottom water between 1970–1994 on solid phase C : P ratios in \(^{210}\)Pb dated sediment cores from the Eastern Gotland Basin (EGB). As the total P inventory in the water column of the Baltic Sea shows remarkable annual changes in size of up to 112 kton, which can only be explained by concurrent changes of bottom water oxygen conditions (Conley et al., 2002), estimates of such low temporal resolution may not, however, fully depict to what extent the sediments regulate productivity in the Baltic Sea.

One aim of this paper was to quantify the difference in benthic P flux between different oxygen conditions and bottom types, and improve the understanding of which processes control the P flux under different Baltic Proper environmental conditions. We worked on stations transecting the EGB (Central Baltic Proper) from shallow oxygenated transport bottoms on the western side via anoxic/sulfidic deep accumulation bottoms to shallow oxygenated sandy bottoms on the eastern side of the EGB. We measured fluxes in situ with autonomous benthic landers, pore water profiles, sediment distributions, and estimated burial rates. Furthermore, we provide a new estimate of the integrated benthic P flux (the internal load) on a basin-wide (Baltic Proper) scale based on our direct flux measurements under different oxygen regimes. This paper is the first to report in situ measured benthic P fluxes in the open Baltic Proper.

2 Materials and methods

2.1 Study site

The largest basin of the Baltic Sea is the Baltic Proper, which consists of a number of sub-basins, namely, the Western Gotland, Eastern Gotland, Gdansk, Bornholm and Arkona basins. A permanent halocline is present in the Baltic Proper at 60–80 m depth
(Stigebrandt, 2001). The sub-halocline water mass, which is hypoxic-anoxic (hypoxic is here defined as $O_2 \leq 91.4 \mu M$), constitutes about 30% of the total volume and it is only rarely replaced by oxygenated saltier water by inflows from the Kattegat (Stigebrandt and Wulff, 1987). The catchment area of the Baltic Proper is 575 000 km$^2$ and comprises 12 countries (HELCOM, 2004).

This study was carried out in the major basin of the Baltic Proper, the EGB with a maximum depth of 249 m (the Gotland deep). The EGB is surrounded by the island of Gotland in the west, Latvia and Lithuania in the east, Estonia in the north-east and Poland in the south. The eastern part of the EGB is strongly influenced by winds, wave action and bottom stress. The sediments are therefore strongly reworked making them sandy, and they are often classified as erosion or transport bottoms (E or T bottoms). Sediments of the central and western part of the basin close to the island of Gotland is less reworked due to its more wind and wave protected location, making more particles settle even on shallower depths and sediments here therefore consist of clayey/silty material. Accumulation bottoms (A bottoms) are more frequent in this area. According to Carman and Cederwall (2001), 38 % of the Baltic Proper consists of A-bottoms, 38 % of T-bottoms and 24 % are E-bottoms.

Three expeditions were conducted; in September 2008, September 2009 and August 2010. In total, data was collected from 13 stations in the EGB of which five were visited on two different expeditions, and several stations were visited more than once on each expedition. A description of the stations is presented in Table 1. The stations were located in an east-west transect across the EGB, including stations with both oxic and anoxic bottom water (Fig. 1). Station bottom depths ranged from 30 m (station J) to 210 m (station F). Stations D, E, F, Y and Z were located at greater depths (>124 m), and considered to be long-term anoxic. Stations A, J, H and U were located shallower, above the halocline and they were permanently oxic. Stations B, C, V and X were located in a depth range (75–90 m) with shifting (or oscillating) bottom water oxygen conditions. At these stations the bottom water oxygen concentration ranged from 3 to 36 $\mu M$ with the exception of station B in 2008 when it was 125 $\mu M$ (Table 1).
2.2 Sediment sampling

Sediment cores were collected with a Multiple Corer, MUC (Barnett et al., 1984). The MUC was equipped with 55 cm long Plexiglas tubes with an inner diameter of 9.9 cm. Only cores with minimal sampling disturbance were used, indicated by clear overlying water, appearance of a fluffy layer or bacterial mats (Beggiatoa spp.) at the sediment-water interface and/or undisturbed laminas in anoxic sediments. Cores were sliced in 0.5, 1 and 2 cm thick intervals down to a sediment depth of 20 cm with the highest vertical resolution in the upper part of the core. Cores were sliced instantly after recovery to minimize contact with atmospheric oxygen and other recovery artifacts. Cores that were used for pore-water sampling were handled under anoxic conditions using a “glove bag” (Aldrich Atmosbag, Sigma Aldrich) filled with and under continuous flow of nitrogen gas. Different samples were taken from each core and were saved for later treatment and analysis; see methods below. Parameters determined in the solid phase were organic carbon (Corg), total phosphorus (TP) and water content (WC).

Pore water was extracted by means of centrifugation at 2500–3000 rpm (about 670 G) for 30 min. The pore water was filtered (0.45 µm nominal pore size cellulose acetate filters, pre-cleaned in MQ water) and saved for later analysis of dissolved inorganic phosphorus (DIP), dissolved iron (DFe) and dissolved manganese (DMn).

2.3 In situ chamber incubations with the Göteborg benthic landers

Two landers were used during this study, the big and small Göteborg landers. The big Göteborg benthic lander is a fully autonomous instrument that can operate on the seafloor down to 6000 m depth without any contact with the ship or the surface (Ståhl et al., 2004; Almroth et al., 2009). The big lander is equipped with four incubation chamber modules. The small Göteborg lander is a simplified version of the big lander. The small lander must be deployed with a rope for recovery, using a surface buoy, or by dredging. The small lander has two incubation chamber modules, identical to those installed on the big. For incubation, each chamber encloses a 400 cm² area.
of the sediment surface together with overlying bottom water. The incubated water is stirred by a horizontal paddle wheel placed centrally inside the chamber to prevent the development of concentration gradients in the chamber (Tengberg et al., 2004). Each chamber carries ten syringes for injection or water sampling. Nine syringes were used for sampling chamber water at pre-set times making it possible to measure fluxes (concentration changes over time) of solutes across the sediment-water interface. The tenth syringe was used to inject a small and known volume of MQ water (about 60 ml, corresponding to less than 0.5% of total chamber volume). Based on the following salinity change, measured by a conductivity sensor, the chamber volume could then be calculated, as described by Nilsson (2008).

During the chamber incubations, oxygen concentrations were measured in each chamber with 1-min intervals using oxygen optodes, model 3830 (the big lander) or 3835 (the small lander) from Aanderaa Data Instruments, Norway (Tengberg et al., 2006). Measurements of conductivity for chamber volume control and leakage detection were made with conductivity sensors model 3919A (Aanderaa Data Instruments, Norway). Conductivity was measured in each chamber at 1-min interval.

Immediately after the landers were recovered water samples were taken from each of the nine syringes in each chamber. The water was filtered through pre-cleaned 0.45 µm pore size cellulose acetate filter and saved for later analysis of DIP.

2.4 Analytical methods

2.4.1 DIP, DFe and DMn

All DIP samples were stored dark and cool and after each expedition sent for analysis according to standard method using Segmented Flow Analysis (SFA), modified after Koroleff (1983). The analytical precision was ±1 µg P L⁻¹ for low concentrations (0.5–25 µg P L⁻¹) and ±3 % for concentrations over 25 µg P L⁻¹.

Dissolved iron (DFe) and manganese (DMn) in pore water were determined photometrically using ferrozine and formaldoxyme procedures, respectively (Peshkova and
Ovsyannikova, 1937; Grasshoff et al., 1999; Kononets et al., 2002; Pakhomova, 2005). The limit of detection was 0.07 and 0.03 µM for Mn and Fe, respectively, using a 5-cm cell.

2.4.2 Sediment physical properties

The sediment WC (mass percent in the top centimetre) was used to determine the bottom type (A, T or E type) at each station. According to Håkanson and Jansson (2002) sediment with WC < 50% represent erosion bottoms while WC > 75% define accumulation bottoms. Transport bottoms are the intermediates. The sediment WC was obtained from the weight loss after drying at 78°C until constant weight, usually about 2–3 days.

2.4.3 Sediment geochemical properties

Determination of Corg in sediment was carried out by gas chromatography. The sediment was first freeze-dried until constant mass, ground and treated with fumes of HCl (37% for at least 48 h) to remove inorganic carbon. A small fraction of known weight (10–20 mg) was then analyzed in a Carlo ERBA N1500g gas chromatograph. The instrument and method are described in detail by Verardo et al. (1990). The precision for Corg was ±1%.

From the same freeze-dried and carefully grinded sediment sample, a small portion was used for TP determination. Sediment samples were then pre-burned at 500°C and further oxidized with acidic potassium peroxymonosulfate to get phosphate-P, which was detected with SFA. The precision was ±5%.

2.4.4 Calculation of benthic DIP fluxes

A linear regression of the DIP concentration against time in each chamber was made from the nine syringe samples. The slope, from the linear regression, times the chamber height (water column height) gives the net increase or decrease in the chamber DIP
content, per time and area. This is the benthic DIP flux which is given in mmol m$^{-2}$ d$^{-1}$ in this paper. Fluxes were approved to be significant if the $p$-value of the linear regression was $\leq 0.05$. However, since very low or zero fluxes are difficult to measure, a second condition was needed to avoid biasing towards high fluxes. If the flux was not significant according to the first condition ($p \leq 0.05$), the absolute concentration change was compared to the analytical precision. If the absolute concentration change was less than the analytical precision (given in analytical methods section above), the flux was set to zero; otherwise it was considered non-significant and rejected.

3 Results

3.1 Sediment total phosphorus

Total phosphorus was analyzed in sediment samples from stations A-08, B-08, C-08, E-08 and F-08 (see Table 1 for description of stations). The TP inventory in the upper 0–3 cm of the sediment generally increased with water depth (Fig. 2), as did Corg and total nitrogen (TN) inventories (Nilsson et al., 2012). The TP inventory was higher on the deep anoxic accumulation bottom than on the shallower bottoms (which most often were transport or erosion bottoms), and this is reflected in the upper part of the profiles. Below a depth of ca 5 cm, the sediment TP concentration was similar at all stations. TP in the profiles from the deep anoxic stations (E-08 and F-08) decreased with sediment depth down to 5 cm from where TP was constant with depth. On the shallow stations A-08, B-08 and C-08, the TP concentration decreased sharply in the first few cm to reach a minimum at 1.5–2 cm sediment depth. Below this zone, the TP content again increased to a stable value of ca 30 µmol g$^{-1}$ (Fig. 2).
3.2 Pore water DIP, DFe and DMn

Dissolved inorganic phosphorus in the pore water was measured at stations with water depths ranging from 60 m to 210 m. Pore water DIP concentrations from the deepest stations (130–210 m) all increased with sediment depth from near surface values of ca 5 µmol l⁻¹. The near-surface DIP concentrations were generally lower on the shallower stations (30–90 m) than on the deep stations (Fig. 3). Consistent with the organic carbon profiles (Nilsson et al., 2012), the pore water DIP concentrations on the shallow stations were generally very low below 8–10 cm sediment depth where the postglacial clay was reached. Stations C-08 and X-09, located at ca 90 m water depth, on the western and eastern side of the basin, were very different due to differences in sediment properties. The DIP profile from station X-09, with organic rich clayey sediment, much resembled the profiles from the deeper stations. The DIP profile from station C-08, with sandy sediment that also had gravel and larger stones in it, was similar to the shallower stations.

In 2008, total dissolved Fe and Mn (DFe and DMn) concentrations in pore water were also measured (Fig. 4). On the shallow stations (A-08 and B-08), vertical changes in the DMn and/or DFe concentrations appeared to co-vary with the DIP concentrations. Furthermore and in all sediments, the DIP and TP concentrations were anti-correlated (Fig. 4). At the shallow oxic stations where the redox conditions significantly varied with sediment depth, DFe and DMn varied in a similar way down the cores, although Mn had higher concentrations at all stations. Both DFe and DMn had very low (close to zero) concentrations in the oxidized surface layer after which the concentrations increased to a maximum at about 2 cm sediment depth at stations A-08 and B-08. On station C-08, situated at a depth with oscillating oxygen conditions, the profiles were different, with only minor redox associated variations of DFe and DMn, and lower concentrations. On the deep anoxic stations DFe concentrations were low and decreased down the core. DMn concentrations, on the other hand, were as high on the anoxic stations as on the oxic stations, but on the deep anoxic stations DMn either did not change much in the
profile (D-08 and E-08, 130 and 170 m) or steadily increased down the sediment core (F-08, 210 m).

3.3 Benthic DIP flux

There were a larger number of significant fluxes from the in situ incubations on anoxic bottoms than oxic bottoms. This was due to the higher flux rates, higher absolute concentrations of DIP and the finer sediment on the anoxic bottoms. On shallow oxic stations, incubations were often more difficult for several reasons; (i) the coarser sediment (often with shells in it) increased the risk of water leakage into the chamber from the surrounding bottom water, (ii) the stiffness of the sediment can hinder the chambers to penetrate sufficiently deep into the sediment, and (iii) the determination of low DIP concentrations have larger relative (%) analytical errors. This resulted in higher relative uncertainty of the low fluxes on the oxic bottoms and also fewer successful flux measurements on these stations. For this reason, when evaluating fluxes, we used protocols avoiding biasing towards high DIP fluxes (see Sect. 2.4.4). Examples of DIP data from chamber incubations on oxic shallow transport/erosion bottoms and anoxic deep accumulation bottoms are presented in Figs. 5 and 6, respectively. DIP fluxes in general increased with bottom depth and decreased with increasing bottom water oxygen concentration (Fig. 7). Station C-08, where there was an uptake of DIP despite low bottom water oxygen, is an exception to this general pattern. The complete set of DIP flux data is given in the Supplement.

4 Discussion

4.1 Relations between pore water distributions of DIP, DFe, DMn and sediment TP

The pore water concentration peaks of DIP, DFe and DMn often coincided, and did this within a narrow TP-minimum zone in the sediment at the oxic stations (Fig. 4).
This suggests that the diagenetic release of DIP from the sediment solid phase to the pore water was coupled to Fe and/or Mn reduction in these sediments. Increase in DIP and decrease in TP were well correlated (Fig. 4), which strongly suggests that a large fraction (up to ca 50%) of the TP in surficial sediment on the oxic stations was P associated with Fe and/or Mn, which is mobile under anoxic conditions. Also on the anoxic stations, pore water DIP and sediment TP were anti-correlated (Fig. 4), which indicates that the diagenetic production of DIP in the pore water was coupled to remineralization of organic P at these stations. The DIP mobilization peak agreed better with mobilization of dissolved Mn than with dissolved Fe in some of the profiles (Fig. 4). These results indicate that Mn reduction may be as involved in DIP mobilization as Fe reduction in these sediments. In contrast, on deeper anoxic stations TP distributions in sediment were unrelated to the minor changes in dissolved metal concentrations. This was expected, as oxidized forms of these metals are unstable in the sediment under such conditions.

Fe-P particles formed by co-precipitation upon oxidation of Fe(II) have a molar ratio of Fe : P ≥ 2 (Gunnars and Blomqvist, 1997; Gunnars et al., 2002). Therefore, the pore water Fe : DIP ratio during bottom water anoxia may be used as an indicator for the capacity of newly formed Fe oxyhydroxides to scavenge DIP upon (re)oxygenation. The average molar Fe : DIP ratio in the upper 3 cm of the sediment on the deep anoxic stations D, E, F (2008) varied between 0.09 and 0.22. Thus, ca 5–10% of the pore water DIP could be scavenged by Fe(III) upon oxygenation of the bottom water at these sites. However this is probably an underestimate of the immobilization of DIP which would occur upon oxygenation, since there are also other mechanisms responsible for retention of P in oxidized sediment such as bacterial accumulation of poly-phosphate (Gächter and Meyer, 1993; Sannigrahi and Ingall, 2005).

4.2 Benthic P fluxes in the Baltic Proper

To categorize the measured DIP fluxes with regard to oxygen condition and water depth, they were divided into three groups (modified after Mort et al. 2010); group
1 include fluxes from permanently oxic bottoms in the depth range of 33–70 m; group 2 include fluxes from bottoms where oxygen conditions can oscillate between oxic, hypoxic and anoxic conditions in the depth range 75 m–90 m; and group 3 include fluxes from permanently anoxic bottoms (i.e. anoxic since latest Baltic Sea water exchange) in the depth range 124 m–210 m. Mean DIP fluxes for the three groups are presented in Table 2.

The large standard deviation of our fluxes within group 1 is probably due to the low fluxes measured on shallow oxic bottoms and the heterogeneity of these bottoms. The relatively large standard deviation of our fluxes within group 2 may partly be due to the low number of successful incubations on these sites ($n = 4$, stations B-10 and C-08). Deep, long-term anoxic (group 3) sediments had the highest average DIP flux and the lowest relative variability among fluxes. Partly, this may be due to the large number of successful flux incubations ($n = 26$) on the anoxic stations. There is patchiness on all bottoms, but our results suggest that the anoxic bottoms had less spatial variability than group 1 and 2 sediments.

One general finding of this study is that the DIP flux in the EGB increased with increasing water depth and with decreasing bottom water oxygen concentration or with increasingly reducing conditions (Figs. 7 and 8). This is consistent with studies in open sea and coastal areas of the Gulf of Finland (Pitkanen et al., 2001; Lehtoranta and Heiskanen, 2003; Viktorsson et al., 2012), and with the relation between hypoxic/anoxic area and the Baltic P pool size, reported by Conley et al. (2002). However, it is in contrast to the relation between water depth and DIP flux reported by Jilbert et al. (2011) and Mort et al. (2010). The latter discrepancy may be explained in several ways: the number of stations may have been too few to observe this relation, the depth range of stations may have been too limited, and the stations were spread over too many different basins including the Kattegat where environmental conditions are different from those in the Baltic Proper. An additional reason for the discrepancy may be related to how the fluxes were estimated as discussed below.
There are, to our knowledge, no previous in situ measurements of benthic DIP fluxes made in the Baltic Proper with which we can compare our results. However, fluxes estimated from pore water gradients in anoxic sediments in the open Baltic are in the ranges ca 0.1–0.3 mmol m\(^{-2}\) d\(^{-1}\) (Mort et al., 2010), 0.01–0.06 mmol m\(^{-2}\) d\(^{-1}\) (Hille et al., 2005), and ca 0.01–0.8 mmol m\(^{-2}\) d\(^{-1}\) (Jilbert et al., 2011). These fluxes are often lower than the in situ measured fluxes from anoxic sediments presented in this study. Diffusive fluxes based on pore water gradients have often been found to be lower than those based on incubations, and especially than those based on in situ incubations (see recent discussion in Viktorsson et al., 2012). There are several reasons for this: the vertical resolution of the pore water profile may be too coarse, thereby underestimating the steepness of the gradient (Sundby et al., 1986). Also, it is very difficult to avoid oxidation artifacts when bringing anoxic sediment cores through the water column, up on deck and into the laboratory. This oxidation may cause immobilization of DIP in the sediment, less steep concentration gradients, and hence too low flux estimates based on Fickian diffusion methodology. Incubations of anoxic sediment cores in the laboratory also tend to provide lower DIP flux estimates than incubations made in situ, since it is very difficult to maintain strictly anoxic conditions in the laboratory. Incubations made in situ, on the other hand, are always made under ambient oxygen conditions. We thus suggest that previous ex situ estimates of anoxic benthic DIP fluxes in the open Baltic Proper often are underestimates.

In contrast to the fluxes measured from pore water gradients, estimates from changes in the water column DIP pool agree with the fluxes reported in this study (0.18–0.44 mmol m\(^{-2}\) d\(^{-1}\), Conley et al., 2002, and 0.118 mmol m\(^{-2}\) d\(^{-1}\), Schneider et al., 2002). The fluxes presented by Conley et al. (2002) and Schneider et al. (2002) include both hypoxic and anoxic bottoms, and thus represent bottom conditions that we defined as group 2 and group 3. To our knowledge, no previous flux estimates, based on incubations or pore water gradients, have been made in the Baltic Proper in the depth range 75–90 m.
Benthic DIP fluxes have previously been measured during laboratory incubations of sediment cores from sites with oxic bottom water in the open Baltic Proper (Koop et al., 1990). These authors reported fluxes in the range $-0.02$ to $0.03\text{mmol m}^{-2}\text{d}^{-1}$. This is similar to fluxes measured in situ on oxic sites in the Gulf of Finland ($-0.01 \pm 0.08\text{m}^{-2}\text{d}^{-1}$, Viktorsson et al., 2012), and to the flux range obtained on shallow oxic stations in this study (Table 2). The similarity between fluxes on Baltic oxic bottoms reported by Koop et al. (1990) and this study is consistent with previous findings that DIP fluxes on such bottoms can be reliably measured by in situ as well as by ex situ incubations (Viktorsson et al., 2012).

4.3 Dependence of benthic P recycling on deposition and degradation of organic matter

The benthic DIP flux of this study was found to progressively increase along a gradient of increasing water depth and decreasing bottom water oxygen concentrations (Figs. 7 and 8). We also found that there was a positive correlation between the DIP flux and the organic carbon inventory of sediment on anoxic bottoms (Fig. 9). Since bottom water oxygen concentration decreased and sediment organic carbon inventory increased (Nilsson et al., 2012) with increasing water depth, we cannot from these correlations determine what caused the DIP flux to increase with increasing water depth. The benthic flux of dissolved inorganic carbon (DIC) was therefore correlated with the DIP flux. (The measurements of DIC fluxes will be fully presented in Nilsson et al., 2012). The DIC flux (in sediments where CaCO$_3$ dissolution is negligible like in the Baltic) is a measure of organic carbon oxidation in sediment (Anderson et al., 1986), which is proportional to organic matter input to sediment (Henrichs, 1992). Relating DIP fluxes with DIC fluxes will thus help understand what controls the benthic DIP flux in aquatic systems, but has nevertheless only been made in a few previous studies (Ingall and Jahnke, 1997; McManus et al., 1997; Ingall et al., 2005; Kiirikki et al., 2006; Viktorsson et al., 2012). We found that the DIP and the DIC fluxes correlated well on anoxic stations ($R^2 = 0.65$ and $p$-value $= 0.016$), but that they correlated poorly on oxic
stations ($R^2 = 0.05$ and $p$-value $= 0.6$; Fig. 10). Our results thus suggest that the DIP flux from anoxic Baltic sediments was controlled by the deposition and degradation rate of organic matter in the sediment. A similar conclusion was made for anoxic bottoms in the Gulf of Finland (Viktorsson et al., 2012). For oxic sediments our results confirm the classical paradigm of adsorption onto/coprecipitation with Fe(III) (Mortimer, 1942), but also bacterial accumulation of poly-phosphate (Gächter et al., 1988) may have contributed to the removal of DIP from the pore water making the DIP flux small or even directed into the sediment on oxic stations (Fig. 8). This means that the benthic DIP flux was proportional to the diagenetic production of DIP in the pore water, as a result of remineralization of organic P in anoxic bottoms. On oxic bottoms, however, it was not because of the abovementioned retention mechanisms. Our results cannot be used, and our aim was not, to elucidate if both or one of these “secondary” processes enhanced DIP retention in these shallow oxic Baltic Proper sediments. The difference in DIP flux between oxic and anoxic bottoms cannot be explained simply by the generally lower rate of organic carbon oxidation (and organic P remineralization) in the shallow oxic sediments, as the DIP flux was low even at moderately high organic carbon oxidation rates (Fig. 10). Thus, as long as there was enough oxygen in the bottom water, the DIP which was liberated to the pore water during remineralization of organic P was not released to the bottom water in proportion to the organic P remineralization rate.

The simultaneous measurements of benthic DIP and DIC fluxes in the same chambers allowed us to investigate C : P ratios in the fluxes. The average C : P ratio in fluxes on anoxic accumulation bottoms was $69 \pm 15$ (mean $\pm 1\sigma$), which is well below the Redfield C : P ratio of 106 : 1 (Fig. 10). The average N:P ratio in fluxes ($3.8 \pm 2$, mean $\pm 1\sigma$) on anoxic bottoms (unpublished results) was also well below the Redfield N : P ratio of 16 : 1. This shows that the anoxic flux in the EGB was P rich in relation to both C and N. These results confirm previous observations (Ingall and Jahnke, 1997; Ingall et al., 2005; Kiirikki et al., 2006; Jilbert et al., 2011; Viktorsson et al., 2012) of low C : P ratios, well below that of fresh organic matter, in effluxes from permanently (or long-term) anoxic sediments. The previous C : P flux ratios found were 30 (Ingall and
Jahnke, 1997), 39 (Ingall et al., 2005), and 29 (Viktorsson et al., 2012). The low C : P ratios in fluxes cannot be explained by disintegration of the abovementioned P sinks, as they should since long have been depleted in long-term anoxic bottoms. One mechanistic explanation which has been proposed is that phosphatases, enzymes which cleave off phosphate groups from organic matter, are used by C-limited bacteria to increase the bioavailability of the organic matter C moiety (Steenbergh et al., 2011). The phenomenon of P rich fluxes has been called enhanced (in relation to carbon) P regeneration, and was first discussed for anoxic systems (Ingall and Jahnke, 1997; Ingall et al., 2005). Recently, it has been suggested that the enhanced P regeneration also occurs in sediment overlain by oxic water (Jilbert et al., 2011; Steenbergh et al., 2011) although to a larger extent in anoxic than in oxic sediment (Jilbert et al., 2011).

There was no correlation between the DIP and DIC flux on the oxic stations and it was not possible to give a value of the average C : P flux ratio since half of the DIP fluxes measured were negative (uptake of DIP and thus a C : P ratio → ∞). However, the C : P ratio using only the positive DIP fluxes was 361 ± 90 (mean ± 1σ). This is much higher than the ratios on the anoxic stations and than the Redfield ratio (Fig. 10). The obvious explanation for this is Fe(III) scavenging and bacterial assimilation as explained above. It is beyond the scope of this study to determine if the flux was P rich on anoxic bottoms due to anoxia per se or if the enhanced P regeneration occurred also in oxic sediments, but did not show up in the flux due to the high capacity of oxic sediments to retain DIP produced in the pore water during organic matter degradation (Steenbergh et al., 2011).

### 4.4 Internal P load in the Baltic Sea

The water column of the Baltic Sea has two main sources of P, supply from land (the so called external load) and input from sediments (the internal load). This study made it possible to make a new estimate of the magnitude of the internal load (or the integrated benthic P flux) in the Baltic Proper based on our direct flux measurements. Using the average benthic DIP fluxes, presented in Table 2, for the group 1, 2 and 3 bottoms,
respectively, an areal extrapolation of the internal P load to the water column of the entire Baltic Proper was made. Estimates of oxic, hypoxic and anoxic areas used for this calculation were the average estimated areas for the period 1999–2011, and were taken from the latest available report from the Swedish Meteorological and Hydrological Institute (Hansson et al., 2011). The resulting total internal load for the period 1999–2011 was 146 kton yr\(^{-1}\) (Table 3). This is 7–24 times higher than previous estimates for the EGB (Matthiesen, 1998; Emeis et al., 2000) and budget calculations for the Baltic Proper (Savchuk, 2005). The internal P load from anoxic bottoms was estimated by Matthiesen (1998) to range from 6 to 20 kton yr\(^{-1}\) using diffusive fluxes calculated from pore water gradients and an anoxic area of the EGB of 20 000 km\(^2\). Emeis et al. (2000) calculated a load of 14 tons yr\(^{-1}\) since the 1970s based on the change in sedimentary C : P ratios and sediment accumulation rate, and this estimate was also based only on the contribution from the EGB. Savchuk (2005), using a model approach, found that for the years 1991–1999 an internal load of 18 kton P yr\(^{-1}\) was needed to balance the P budget of the Baltic Proper. Our estimate of the internal load should be more reliable than previous estimates of several reasons: (i) some previous estimates were based on a smaller area (the EGB instead of the Baltic Proper), (ii) direct flux measurements should provide a more realistic number than model and budget estimates in which the internal load can be estimated “by difference” or are based on too few or less reliable flux data, and (iii) the in situ measured fluxes in this study were roughly 5–10 times higher than fluxes used for previous estimates. As discussed above, in situ measurements are likely to be more reliable than ex situ measurements (see review by Tengberg et al., 1995), and our fluxes agree well with estimates from changes in the Baltic water column DIP pool (Conley et al., 2002; Schneider et al., 2002). Thus, previous estimates of the internal P load in the Baltic Proper are likely underestimates.

The internal load was also calculated for the period 1960–1998 using the mean values for anoxic and hypoxic areas given by Hansson et al. (2011) for that time period. An assumption in this calculation is that the inventories of organic matter in the sediments were not significantly different in 1960–1998 compared to the later time period.
for which we calculated internal load. The internal load estimate for the earlier period is thus probably an overestimate. The internal load was 100 kton yr\(^{-1}\) lower during the earlier period (Table 3), when the average anoxic and hypoxic areas covered 5\% and 22\% of the total bottom area in the Baltic Proper, respectively, compared to 15\% and 28\% of the total Baltic Proper area during the later period.

Our estimate of the annual internal load for the period 1999–2011 is 7–12 times higher than the external load of 12–20 kton yr\(^{-1}\) estimated by HELCOM (2011), and 10 times higher than the external load of 18 kton yr\(^{-1}\) reported by Savchuk (2005), Savchuk et al. (2008) and Vahtera et al. (2007). This clearly highlights the dominating role of sediments as a P source in the Baltic Proper, and confirms the positive feedback (or the vicious circle Vahtera et al., 2007) between enhanced phytoplankton production, higher rates of organic matter sedimentation, spread of anoxia, stimulated benthic P flux, and intensified cyanobacterial blooms and N fixation. Further efforts to find cost-efficient solutions to decrease the internal P load in the Baltic should thus be seriously considered.

### 4.5 Burial rates and burial efficiency

Long-term removal of P from biogeochemical cycling in the sea takes place through burial in sediment. Burial rates can be calculated from sediment accumulation rates (SAR) and TP concentration at a depth in the sediment below which it does not change noticeably. Sediment accumulation rates in the EGB are highly spatially variable, ranging from 10.5 to 527 gm\(^{-2}\) yr\(^{-1}\) with the highest rates in the north-eastern part of the EGB (Hille et al., 2006). This high variability in sediment accumulation rate is reflected in the TP burial rates, because the TP content at depth in sediment was less variable than the sediment accumulation rate. Using the mean sediment accumulation rate of 129 gm\(^{-2}\) yr\(^{-1}\) found by (Hille et al., 2006) and a sediment TP concentration of 30 µmolg\(^{-1}\), which was the measured concentration at depth in the sediment cores from this study, we calculated a TP burial rate of 0.011 mmolm\(^{-2}\) d\(^{-1}\). This was within the same range as the TP burial rate calculated by Mort et al. (2010) for a site (the so
called Northern Gotland site) in the Northern Baltic Proper (0.018 mmol m$^{-2}$ d$^{-1}$), and the mean TP burial rate given by Hille et al. (2005) for the EGB (0.018 mmol m$^{-2}$ d$^{-1}$). Hille et al. (2005) refer to this as the net TP deposition rate. For the anoxic bottoms (>124 m) of our study the total input (or gross sediment deposition rate) of P to the sediment was calculated as the sum of our average measured DIP efflux (0.376 ± 0.214 mmol m$^{-2}$ d$^{-1}$) and the TP burial rate. Because Hille et al. (2005) have a larger data set of TP burial rates than we can calculate from our sedimentary TP contents in the anoxic part of the EGB, their average TP burial rate of 0.018 mmol m$^{-2}$ d$^{-1}$ was used. Through this mass balance approach, a total input of P to the sediment in the anoxic part of the EGB of 0.40 mmol m$^{-2}$ d$^{-1}$ was calculated. The burial efficiency, i.e. the fraction of the P input to sediment which underwent long-term burial, was thus 4%. This burial efficiency agrees well with that of 3% calculated with the same method for anoxic parts of the Gulf of Finland (Viktorsson et al., 2012). These low burial efficiencies suggest that anoxic Baltic sediments are very efficient in recycling P, and they are consistent with previous findings of enhanced P recycling in anoxic marine sediments as discussed above. Our burial efficiency of 4% in the EGB is approximately eight times lower than that of 33% estimated for the EGB by Hille et al. (2005). These authors measured P burial rates, but likely overestimated the burial efficiency since they calculated diffusive benthic DIP fluxes from pore water gradients, an approach which tends to underestimate the DIP flux as explained above. This leads to a too low estimate of the input of P to sediment, and thus to a too high burial efficiency.

5 Conclusions

This study is the first to report in situ measured benthic DIP fluxes in the open Baltic Proper. It also provides the most comprehensive data set of benthic DIP fluxes in the Baltic Proper existing to date. One general finding of this study is that the DIP flux in the EGB increased with increasing water depth and with decreasing bottom water oxygen concentration. The average DIP flux on anoxic bottoms (>124 m) was
0.376 ± 0.214 mmol m\(^{-2}\) d\(^{-1}\) and on oxic bottoms it was \(-0.003 ± 0.040\) mmol m\(^{-2}\) d\(^{-1}\). The in situ measured fluxes were ca. 5–10 times higher than previous ex situ estimated fluxes on anoxic bottoms. This difference may be explained by uncertainties with estimating fluxes from pore water gradients (e.g. Sundby et al., 1986) and difficulties in maintaining strictly anoxic conditions when working ex situ (Tengberg et al., 1995; Viktorsson et al., 2012). In contrast to the mismatch with ex situ measurements on anoxic bottoms, the in situ measured fluxes in this study agree well with previous estimates of benthic fluxes from changes in the DIP pool in the Baltic Proper basin water (Conley et al., 2002; Schneider et al., 2002), and with the previous estimates of DIP fluxes on oxic bottoms in the Baltic (Koop et al., 1990; Viktorsson et al., 2012). We suggest that previous ex situ estimates of anoxic benthic DIP fluxes in the open Baltic Proper often are underestimates.

The DIP flux was positively correlated with the organic carbon inventory of sediment. The DIP flux also correlated well with the DIC flux on anoxic stations, but these fluxes correlated poorly on oxic stations. The positive correlation between DIP and DIC fluxes suggests that the benthic DIP flux on anoxic bottoms in the Baltic Proper is controlled by rates of deposition and degradation of organic matter. This in turn indicates that the vicious circle (Vahtera et al., 2007) is not only triggered by increased sedimentation of organic matter, causing expanded oxygen depletion which causes increased P fluxes from sediment, but that increased sedimentation of organic matter per se causes a higher benthic P flux. This in turn stimulates cyanobacterial growth and blooms, which causes higher export of organic matter from surface to bottom making the benthic P flux higher, and so on.

The flux from anoxic sediment was very P rich in relation to both C and N, and the average C : P ratio in fluxes on anoxic accumulation bottoms was \(69 ± 15\) (mean ± 1\(\sigma\)), which is well below the Redfield C : P ratio of 106 : 1. On oxic stations, however, the C : P flux ratio was much higher than the Redfield ratio, consistent with well-known P retention mechanisms associated with Fe and bacteria in oxidized sediment.
Using a benthic mass balance approach, a burial efficiency of 4% was calculated for the anoxic part of the EGB, which suggests that anoxic Baltic sediments are very efficient in recycling deposited P.

Based on the measured DIP fluxes, an internal P load to the Baltic Proper water column of 146 kton yr\(^{-1}\) was calculated for the period 1999–2011, and of 53 kton yr\(^{-1}\) for the period 1960–1998 (assuming the average benthic DIP flux on oxic, hypoxic and anoxic bottoms has not changed in-between these two time periods). Thus, the present internal load is about 100 kton yr\(^{-1}\) higher than in 1960–1998, which is due to the expansion of hypoxic and anoxic areas in the Baltic Proper. Our estimated contemporary internal load is 7–12 times higher than recent estimates of the external load. This clearly highlights the dominating role of sediments as a P source in the Baltic Proper.

Supplementary material related to this article is available online at: [http://www.biogeosciences-discuss.net/9/15459/2012/bgd-9-15459-2012-supplement.pdf](http://www.biogeosciences-discuss.net/9/15459/2012/bgd-9-15459-2012-supplement.pdf).

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References


Faganeli, J. and Ogrinc, N.: Oxic-anoxic transition of benthic fluxes from the coastal marine environment (Gulf of Trieste, Northern Adriatic Sea), Mar. Freshwater Res., 60, 700–711, 2009. 15462


Phosphorus recycling in sediments of the Central Baltic Sea

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Table 1. Description of stations. The water content is the mass percent in the uppermost centimeter of the sediment. The bottom types A, T and E refers to Accumulation, Transport and Erosion bottoms, respectively (Håkanson and Jansson, 2002). Temperature and salinity were measured in ambient bottom water; averages are shown when more than one deployment was made at the same station. The bottom water O\(_2\) concentration, in µM, was measured approximately 10–20 cm above bottom with an optode inside each chamber just before start of incubation (except at stations X and Z, where it was measured with a Seabird SBE 911 sensor on the CTD); the values given are mean values from 2–12 chambers depending on how many deployments were made at the same station the same year; the number of chambers used are given in the last column, n. ND means no sediment coring in 2010 at the station J.

<table>
<thead>
<tr>
<th>Year, month</th>
<th>station</th>
<th>depth (m)</th>
<th>Position Lat. N</th>
<th>Lon. E</th>
<th>Sediment water content (%) WM</th>
<th>Bottom type</th>
<th>Bottom temperature (°C)</th>
<th>BW S</th>
<th>BW T</th>
<th>BW O(_2) (µM)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 to A 60 57°23.06′</td>
<td>19°05.02′</td>
<td>39</td>
<td>E</td>
<td>4.4</td>
<td>7.5</td>
<td>284 ± 6</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26 Sep B 75 57°28.34′</td>
<td>19°16.00′</td>
<td>82</td>
<td>A</td>
<td>4.6</td>
<td>8.7</td>
<td>125 ± 11</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2008 C 90 57°28.04′</td>
<td>19°26.01′</td>
<td>69</td>
<td>T</td>
<td>5.3</td>
<td>10.0</td>
<td>6 ± 1</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D 129 57°19.65′</td>
<td>19°19.26′</td>
<td>95</td>
<td>A</td>
<td>6.2</td>
<td>12.0</td>
<td>anoxic</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E 170 57°07.45′</td>
<td>19°30.60′</td>
<td>93</td>
<td>A</td>
<td>6.3</td>
<td>12.6</td>
<td>anoxic</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F 210 57°17.24′</td>
<td>19°48.02′</td>
<td>94</td>
<td>A</td>
<td>6.3</td>
<td>12.7</td>
<td>anoxic</td>
<td>4</td>
<td></td>
<td></td>
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<tr>
<td>20 Sep to 2009 U 49 57°30.01′</td>
<td>20°56.03′</td>
<td>24</td>
<td>E</td>
<td>6.0</td>
<td>7.6</td>
<td>191 ± 4</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Oct V 64 57°26.50′</td>
<td>20°43.62′</td>
<td>55</td>
<td>T</td>
<td>4.7</td>
<td>9.4</td>
<td>36 ± 4</td>
<td>2</td>
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<td>X 90 57°20.73′</td>
<td>20°35.35′</td>
<td>94</td>
<td>A</td>
<td>6.4</td>
<td>11.0</td>
<td>0–3</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y 124 57°18.87′</td>
<td>20°33.07′</td>
<td>90</td>
<td>A</td>
<td>6.6</td>
<td>11.3</td>
<td>anoxic</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z 170 57°20.86′</td>
<td>20°28.34′</td>
<td>95</td>
<td>A</td>
<td>6.7</td>
<td>12.1</td>
<td>anoxic</td>
<td>0</td>
<td></td>
<td></td>
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<tr>
<td>16 Aug to 2010 J 30 57°28.83′</td>
<td>18°59.51′</td>
<td>ND</td>
<td>ND</td>
<td>4.5</td>
<td>7.4</td>
<td>274 ± 4</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Sep H 44 57°31.11′</td>
<td>19°05.25′</td>
<td>30</td>
<td>E</td>
<td>2.9 ± 0.1</td>
<td>7.8 ± 0.1</td>
<td>248 ± 17</td>
<td>12</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>A 59 57°23.11′</td>
<td>19°04.92′</td>
<td>58</td>
<td>T</td>
<td>4.2 ± 0.1</td>
<td>8.4 ± 0.9</td>
<td>164 ± 60</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B 75 57°28.36′</td>
<td>19°16.26′</td>
<td>88</td>
<td>A</td>
<td>5.5</td>
<td>9.9 ± 0.1</td>
<td>2 ± 2</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>D 128 57°19.65′</td>
<td>19°19.29′</td>
<td>91</td>
<td>A</td>
<td>6.8</td>
<td>12.0</td>
<td>anoxic</td>
<td>4</td>
<td></td>
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<tr>
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<td>19°30.60′</td>
<td>94</td>
<td>A</td>
<td>6.5</td>
<td>12.3</td>
<td>anoxic</td>
<td>4</td>
<td></td>
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<tr>
<td>F 210 57°17.23′</td>
<td>19°48.02′</td>
<td>94</td>
<td>A</td>
<td>6.4</td>
<td>12.45</td>
<td>anoxic</td>
<td>4</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Table 2. Mean values of the DIP flux (mmol m\(^{-2}\) d\(^{-1}\)) for the different depth ranges and bottom with oxic, hypoxic and anoxic bottoms water (BW) conditions. Standard deviation (\(\sigma\)), confidence interval (CI) and number of incubations (\(n\)) are given in the last three columns.

<table>
<thead>
<tr>
<th>Group, (Stations)</th>
<th>Depth range</th>
<th>Bottom type</th>
<th>BW O(_2)</th>
<th>DIP flux average</th>
<th>(\sigma)</th>
<th>CI</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (A-08, U-09, J-10, H-10, A-10)</td>
<td>30–60 m</td>
<td>T, E</td>
<td>118–278</td>
<td>−0.003</td>
<td>0.040</td>
<td>0.025</td>
<td>10</td>
</tr>
<tr>
<td>2 (C-08, B-10)</td>
<td>75–90 m</td>
<td>A, T</td>
<td>0–10</td>
<td>0.027</td>
<td>0.068</td>
<td>0.067</td>
<td>4</td>
</tr>
<tr>
<td>3 (D, E, F (-08,-10), Y-09)</td>
<td>124–210 m</td>
<td>A</td>
<td>0</td>
<td>0.376</td>
<td>0.214</td>
<td>0.082</td>
<td>26</td>
</tr>
</tbody>
</table>
Table 3. Calculated internal DIP load to the Baltic Proper, based on in-situ measured benthic DIP fluxes (this study) and the areal extent of hypoxia and anoxia (Hansson et al., 2011) for the two time periods 1999–2011 and 1960–1998. Standard deviation (σ) for the total loads is given as the square root of the quadratic sum of the three individual standard deviations.

<table>
<thead>
<tr>
<th>Time period</th>
<th>Redox condition</th>
<th>Area (km$^2$)</th>
<th>Flux (mmol m$^{-2}$ d$^{-1}$)</th>
<th>Load (kton yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mean</td>
<td>σ</td>
<td>mean</td>
</tr>
<tr>
<td>1999–2011</td>
<td>oxic</td>
<td>117 420</td>
<td>-0.003</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>hypoxic</td>
<td>57 680</td>
<td>0.027</td>
<td>0.068</td>
</tr>
<tr>
<td></td>
<td>Anoxic</td>
<td>30 900</td>
<td>0.376</td>
<td>0.214</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>206 000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1960–1998</td>
<td>oxic</td>
<td>150 380</td>
<td>-0.003</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>hypoxic</td>
<td>45 320</td>
<td>0.027</td>
<td>0.068</td>
</tr>
<tr>
<td></td>
<td>Anoxic</td>
<td>10 300</td>
<td>0.376</td>
<td>0.214</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>206 000</td>
<td></td>
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**Fig. 1.** Map of the central part of the Eastern Gotland Basin. Visited stations are indicated by a cross (2009 cruise), a triangle (2010 cruise only) and an × (2008 and 2010 cruises). Positions and water depths are given in Table 1.
Fig. 2. Total phosphorus (TP) inventory (0–3 cm) (left panel) and profiles (right panel) in sediment from five stations in the Eastern Gotland Basin 2008. Stations with oxic bottom water are shown in a lighter grey colour and those with anoxic bottom water in a darker grey colour.
**Fig. 3.** Pore water DIP profiles at stations ≤ 90 m (top three panels) and stations > 90 m (bottom three panels) 2008–2010. Profiles from stations at similar bottom depths are shown together. Note the different scales on the x-axis.
Fig. 4. Total dissolved Fe and Mn in pore water, together with profiles of sediment TP and pore water DIP from 2008 (also shown in Figs. 2 and 3, respectively). Note the different scales on the x-axis.
Fig. 5. Examples of evolution of the DIP concentration with time in chambers from oxic stations (J, H, A) on the 2010 cruise. The different shades of grey indicate different chambers. Filled squares indicate data points used to evaluate the flux. A full thin line means that the slope of the linear regression was used to calculate the flux ($p < 0.05$). No line indicates that the increase concentration over time in the chamber was too small to be measurable and the flux was set to zero (the procedure to evaluate chamber data and to calculate fluxes is described in the text).
Fig. 6. Examples of evolution of the DIP concentration with time in chambers from the anoxic stations (D, E, F) on the 2010 cruise. The different shades of grey indicate different chambers. A full thin line means that the slope of the linear regression was used to calculate the flux.
Fig. 7. Benthic DIP effluxes and up-take rates presented as station averages from each year. Error bars indicate 95% confidence interval, and its magnitude was mostly related to sediment spatial variability. The fluxes are sorted after bottom depth, with the shallowest station to the left and increasing bottom depth to the right. The labels on the x-axis are from top to bottom; bottom water oxygen concentration in µM, measured at the start of the incubation inside the chambers; bottom depth in m; year of sampling; and station name.
Fig. 8. DIP flux versus bottom water oxygen concentration; the latter was measured just before the start of the incubation inside the chambers. Fluxes are presented as mean values for each lander deployment.
Fig. 9. DIP flux versus organic carbon inventory in the top 3 cm of the sediment. Fluxes are presented as mean values for each lander deployment.
Fig. 10. DIP flux versus DIC flux. Fluxes are presented as mean values for each lander deployment.