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Recycling and burial of phosphorus in sediments of an anoxic fjord—the By Fjord, western Sweden

by Lena Viktorsson,1 Mikhail Kononets,2 Per Roos3 and Per O.J. Hall2,4

ABSTRACT

Recycling and burial of sediment phosphorus were studied in the By Fjord, western Sweden, during the years 2009 to 2010 using autonomous benthic landers and sediment sampling. The By Fjord is a small fjord with a shallow sill at its narrow mouth, which limits water exchange of the fjord’s basin water. The water in the basin is exchanged only every 3 to 5 years and the water below sill level is anoxic or sulfidic between water renewals. Five sites were examined in the By Fjord; three shallow sites above the sill level with oxic bottom waters and two deeper sites with anoxic bottom waters. Contents of sediment organic carbon, total nitrogen and organic phosphorus were higher at deep stations when compared to shallow ones, whereas the contents of sediment inorganic phosphorus was higher at shallow than at deep stations both in surficial and buried sediment. One shallow oxic site and one deep anoxic site were also examined in the adjacent Koljo Fjord having similar characteristics as the By Fjord. In situ measurements of benthic fluxes of dissolved inorganic phosphorus (DIP) showed that the fluxes from sediments with oxic overlying water (0.05–0.23 mmol m$^{-2}$ d$^{-1}$) were much lower than fluxes from sediments with anoxic overlying water (1.25–2.26 mmol m$^{-2}$ d$^{-1}$). The DIP flux increased with increasing flux of dissolved inorganic carbon (DIC) not only at anoxic but also at oxic bottoms, which is different from observations in brackish water environments. The average ratio between the DIC and DIP fluxes at oxic bottoms was almost 10 times higher than the Redfield C:P ratio indicating partial immobilization of P in oxic sediments. In contrast, the C:P ratio in fluxes was on average 1.5 times lower than Redfield at the anoxic bottoms. The benthic fluxes from anoxic bottoms were P rich not only in relation to C, but also to N. The low C:P flux ratio at anoxic sites coincided with an about 2.5 times higher than Redfield C:P ratio of organic matter in the sediment solid phase clearly suggesting preferential regeneration of P at anoxic bottoms. Burial of inorganic P was higher than organic P burial at both anoxic and oxic sites; the former made up 59 to 60% of the total P burial at the deep anoxic stations, and 80% at the main shallow oxic station. The burial efficiency for organic P at anoxic bottoms was estimated to be only 1 to 3%, which indicates extremely efficient recycling of deposited organic P under anoxic conditions in this fjord environment.

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1. Introduction

The productivity in the coastal ocean is primarily controlled by the supply of nitrogen (N) and phosphorus (P). In contrast to N, which can be made bioavailable through N\textsubscript{2} fixation, the ultimate source of P is weathering. Thus, P reaches the system through rivers and, to a minor extent, atmospheric deposition. Primary production is not only supported by nutrient supply from land and atmosphere, but is also dependent on recycling of nutrients within the system. In the shallow coastal oceans an important part of the remineralisation takes place in the sediment, because a large part of the primary produced organic matter reaches the sea floor without being much degraded (e.g. Wollast 1991). Thus, the nutrient exchange between sediment and water is an important factor influencing primary productivity in the coastal zone. Since the start of the 20\textsuperscript{th} Century the use of fertilizers, and thus the supply of nutrients from land, increased dramatically. This enhanced supply resulted in eutrophication of many coastal oceans and an increase in the number and area of sites with hypoxic bottoms (Diaz and Rosenberg 2008; Conley et al. 2011). Anoxia can cause severe damage to marine ecosystems that sometimes is irreversible (Rabalais et al. 2010; Zhang et al. 2010). Not only is anoxia by itself a threat to the ecosystem causing death of higher life, it also increases the flux of P from sediment to water (e.g. Balzer et al. 1983; Sundby et al. 1986; Ingall and Jahnke 1997). This increase fuels P limited primary production and results in higher sedimentation rates of organic matter, which in turn sustains the anoxia and a continuous enhanced P flux (Van Cappellen and Ingall 1996; Slomp and Van Cappellen 2007; Vahtera et al. 2007; Howarth et al. 2011; Jilbert et al. 2011). In contrast to the enhanced P flux found at anoxic bottoms, oxic bottoms generally have a P flux much lower than what would be expected from decomposition of organic matter with Redfield C:P composition (Jensen et al. 1995; Ingall and Jahnke 1997; McManus et al. 1997; Viktorsson et al. 2012; Viktorsson et al. 2013). This difference in fluxes means that the bottom water oxygen conditions have profound effects on the benthic nutrient exchange and can influence the ratio between the nutrients that are released from the sediment (e.g. Karlson et al. 2007). There are several different processes that can explain the P rich (in relation to C) fluxes at anoxic bottoms and the P poor fluxes at oxic bottoms.

Starting with processes affecting P fluxes at oxic bottoms, the process most commonly referred to is the adsorption of phosphate on iron oxyhydroxides (Mortimer 1942). This mechanism will both act to decrease the flux of P when the bottom-water and the upper sediment is oxic, as well as increase the P flux when the sediment turns anoxic and the iron oxyhydroxides reductively dissolve. This mechanism thus results in C:P ratios in fluxes above (oxic) or below (anoxic) what would be expected from the C:P composition of the organic matter being degraded. The C:P ratio of solutes produced diagenetically within the sediment pore water may not, however, differ from that of the degrading organic matter, unless there is preferential P regeneration (in relation to C). The C:P ratio of solute production in the pore water can be different from that in the benthic flux, since the adsorption of P to iron oxides is a secondary effect, taking place after DIP has been produced in the pore water during the decomposition of organic matter. Another secondary and redox dependent
mechanism is storage of polyphosphates in bacteria under oxic conditions (Gachter et al. 1988; Sannigrahi and Ingall 2005; Goldhammer et al. 2010). It has been shown that sulfur bacteria use intracellularly accumulated polyphosphates as an energy source during anoxic conditions (Schulz and Schulz 2005). Accumulation, and subsequent hydrolysis, of polyphosphates in bacteria could possibly have a similar, or even a larger, influence as iron adsorption-desorption on the benthic P flux in environments with changing redox conditions (Jilbert et al. 2011). However, it is still uncertain if these bacteria are widespread and how large impact they can have on the flux.

The aim of this study was to describe the marine benthic P cycling in two small sill fjords, the By Fjord and the Koljo Fjord on the Swedish west coast. The basin water in the fjords is almost permanently anoxic and sulfidic, and the water above the sill depth is permanently oxic. The fjords are thus well suited for studies comparing the P cycling at anoxic and oxic bottoms, and for measuring DIP and DIC fluxes to better understand the differentiated benthic recycling of P relative to C under anoxic and oxic conditions. The in situ measured P fluxes were enhanced at anoxic bottoms (C:P ratios in fluxes lower than the Redfield ratio), while the C:P ratio in fluxes mostly was higher than Redfield at oxic bottoms. Nevertheless, the DIP flux correlated positively with the DIC flux at both oxic and anoxic bottoms. We also investigated the relation between C:P ratios in fluxes and C:P ratios in sedimentary organic matter; organic and inorganic P burial rates and their relative importance; and the burial efficiency for organic P.

2. Materials and methods
   a. Study site

   The By Fjord is a small fjord on the west coast of Sweden with a shallow sill at the mouth. The By Fjord is situated on the inside of the double-ended fjord system of Havsten Fjord, Hake Fjord and Koljo Fjord (Figure 1). The By Fjord is 4 km long, has a maximum depth of ca 50 m and a sill-depth of 13 m. At the head of the fjord the small city of Uddevalla is located where the small Bäve River discharges into the fjord. This river has a mean flow of 4 m$^3$ s$^{-1}$, and at high flows of 10 m$^3$ s$^{-1}$ a thin surface layer of 1 to 2 m thickness with low salinity develops in the fjord. The sewage treatment plant serving Uddevalla and its surroundings also discharges into the fjord at the same location as the Bäve River enters. The Bäve River supplies the major part of the fresh water to the fjord, whereas the river and the sewage treatment plant supply about 50% each of the nutrients N and P to the system (Viktorsson 2007). Due to the fresh water input, the narrow and shallow sill and the deep basin of the fjord, there is a strong vertical density gradient and the basin water is completely exchanged only every 3 to 5 years (Hansson et al. 2013, and references therein). The strong vertical density gradient is reflected in a strong gradient of nutrients and oxygen (nutrients increase with depth and oxygen decreases). As a consequence of the basin water’s long residence time and the respiration taking place in water and sediment, the basin water is oxic only a short time (weeks to months) after the water has been renewed. After that, the basin
water becomes increasingly reducing and a large oxygen debt is built up. In-between water renewals the basin water is therefore anoxic and most of the time also sulfidic. Even though strict rules for terminology have been proposed (Canfield and Thamdrup 2009), we will use the term anoxic for oxygen free water with and without sulfide, although sulfidic conditions are dominant.

The By Fjord and the Koljo Fjord are parts of the Swedish national marine monitoring program led by the Swedish Meteorological and Hydrological Institute. Measurements of salinity, temperature, oxygen and nutrients have been made since 1962 and monthly data of good quality are available from 1990. Investigations of the By Fjord in the early 1970s showed that the status of the fjord at that time was similar to the present conditions, with anoxic water and with no or very little fauna in the sediments below sill depth (Rosenberg 1977; Rosenberg et al. 1977).

The sampled stations of the present study were spread between the anoxic basin (BF25 at 25 m and BF35 at 35 m water depth) and the oxic intermediary water of the By Fjord (BF7 at 7 m, October 2009 and all the following expeditions; BF10 at 10 m, August 2009; and BF15 at 15 m, June 2009; Table 1). A station in the anoxic basin of the adjacent Koljo Fjord (KF43 at 43 m depth) and a shallow one in oxic water of the Koljo Fjord (KF14 at 14 m) were also included in the study (Table 1).

This study is based on data collected during six field campaigns to the By Fjord between June 2009 and November 2010. The two stations in the Koljo Fjord (Figure 1) were visited in June and November 2010, respectively. Benthic solute fluxes were measured in situ at both oxic and anoxic stations using benthic chamber landers. On the first two cruises the
Table 1. Stations where measurements were made in the By Fjord and Koljo Fjord. Stations are named with two letters indicating the fjord name (By Fjord = BF, Koljo Fjord = KF) and a number for the bottom depth at the station.

<table>
<thead>
<tr>
<th>Station</th>
<th>Depth, m</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
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<td>7</td>
<td>11 51.779' E, 58 19.499' N</td>
</tr>
<tr>
<td>BF10</td>
<td>10</td>
<td>11 52.619' E, 58 19.782' N</td>
</tr>
<tr>
<td>BF15</td>
<td>15</td>
<td>11 54.345' E, 58 20.152' N</td>
</tr>
<tr>
<td>BF25</td>
<td>25</td>
<td>11 52.135' E, 58 19.559' N</td>
</tr>
<tr>
<td>BF35</td>
<td>35</td>
<td>11 52.259' E, 58 19.608' N</td>
</tr>
<tr>
<td>KF14</td>
<td>14</td>
<td>11 35.070' E, 58 14.500' N</td>
</tr>
<tr>
<td>KF43</td>
<td>43</td>
<td>11 35.113' E, 58 14.161' N</td>
</tr>
</tbody>
</table>

oxic station in the By Fjord was at 15 m and 10 m water depth, respectively. These depths were found to experience periods of anoxia and the oxic station was therefore moved to a shallower depth (7 m). Pore water samples (DIP) and sediment samples (total carbon [TC], organic carbon [Corg], total nitrogen [TN], total and inorganic phosphorus [TP and P_inorg], water content, and radionuclides [to determine sediment accumulation rates]) were collected on cruises in 2009 and 2011. A description of sampling procedures and methods is given below.

b. In situ measured fluxes

Benthic fluxes of DIP were measured in situ using one or two of the Gothenburg benthic landers (e.g. Stahl et al. 2004; Brunnegård et al. 2004; Tengberg et al. 2004; Almroth et al. 2009; Viktorsson et al. 2013). DIC and dissolved inorganic nitrogen (DIN; the sum of ammonium, nitrite and nitrate) fluxes were measured during the same lander deployments, but these results will be reported elsewhere (Nilsson et al. in prep.; Hall et al. in prep.). Sediment and overlying water were incubated in the chambers of the lander for 20 to 36 hours during which nine samples were taken autonomously with syringes from each chamber. The lander was then recovered and water samples were collected from the syringes. Nutrient samples were filtered through pre-cleaned 0.45 μm pore size cellulose acetate filters onboard immediately after sampling and then stored at 4 to 6°C until analysis on land. DIP was determined with a standard colorimetric method (modified after Koroleff 1983) applied in segmented-flow analysis (SFA) with a reported uncertainty of 0.5 μg P L⁻¹ for the concentration range 0.5–20 μg P L⁻¹, and 3% for >20 μg P L⁻¹.

Salinity, temperature, depth/pressure and oxygen sensors that continuously measured ambient conditions in the bottom water during the incubations were mounted on the landers. Each chamber was also equipped with oxygen (optodes), salinity and temperature sensors for calculation of chamber volume (salinity), detection of possible leakage (salinity and oxygen) and measurement of total oxygen uptake rates. Chamber volume, a necessary parameter when calculating the benthic flux, was calculated by injection of a known volume
of MQ water (around 56 to 59 mL, which normally is 0.5 to 1% of the chamber volume), and the chamber volume was then calculated from the measured salinity decrease and the MQ volume injected (Nilsson 2008). Using data from sensors inside and outside chambers, occasional leakage of chambers could easily be detected. Flux data from leaking chambers were discarded.

To calculate the benthic flux in each chamber, a linear regression of the nine DIP concentrations versus time was made. All data points were corrected for the small dilution that occurred when ambient bottom water entered the chamber, through a metal loop, as a sample was withdrawn from the incubated water. For the flux to be considered significant the p-value of the linear regression had to be less than 0.05 (95% significance level). To avoid biasing towards high fluxes, a second condition for low fluxes was used; all insignificant fluxes that were lower than the lowest significant flux on the same deployment were re-evaluated. These low fluxes were considered significant if their error of slope was less than five times larger than the slope; otherwise they were discarded. A more detailed description of the flux calculations is given in Almroth et al. (2009), of the landers in e.g. Stahl et al. (2004), and of the chambers and their hydrodynamics in e.g. Tengberg et al. (2004). Examples of the evolution of DIP concentration during chamber incubations are shown in Figure 2.

c. Pore water

In June and August 2009, pore water was sampled at the 10 m (August), 15 m (June), 25 m and 35 m stations. Sediment cores were collected with a multiple corer, stored at in situ temperature and then vertically sectioned a few hours after sampling. The cores were sliced in a glove bag, which was filled with nitrogen gas (filled and emptied three times before slicing to evacuate all oxygen) to avoid oxidation of the samples. The sediment was put into 50 mL centrifuge tubes, which then were taken out from the glove bag and centrifuged at
2500 rpm (670 G) for 30 minutes. The tubes were then placed in a new glove bag, filled with nitrogen gas, where the pore water (supernatant) was collected and filtered through pre-cleaned 0.45 μm pore size cellulose acetate filters. The samples were then stored at 4 to 6°C until they were analyzed for DIP after the cruise (same method as for lander samples).

d. Sediment

Sediment solid phase samples for TC, C_\text{org}, TN, TP, P_{\text{inorg}} and water content were collected on all of the expeditions in 2009, and samples for sediment accumulation rate determinations were collected in 2009 and 2011. Samples for these parameters were also collected with a multiple corer and the cores were sliced in a cold room on-board. C/N/P samples were immediately frozen and then freeze-dried on land. Samples for TC, C_\text{org} (after treatment with HCl fumes) and TN were analyzed with a Carlo ERBA N1500 gas chromatograph (Verardo et al. 1990). From the same freeze-dried and carefully grinded sediment samples, 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 DIP, which was detected with SFA. The repeatability was ±5%. P_{\text{inorg}} was determined on the same sediment samples according to Aspila et al. (1976). Organic phosphorus (P_\text{org}) was calculated as the difference between TP and P_{\text{inorg}}. Water content samples were first stored at 4 to 6°C on-board the ship, and the weight of water loss calculated after drying at 70°C until constant weight on land. Sediment accumulation rates (SAR) were determined at the BF25 and BF35 stations. For these determinations aliquots of dried sediment samples were analyzed for 137Cs by gamma spectrometry using n-type HPGE-detectors and counting times between 2 to 3 days per sample. Due to the relatively well-defined peaks of Chernobyl and nuclear weapon testing fallout, SAR were determined in cores collected in 2009 using the Chernobyl and fallout 137Cs peaks, and taking the salt corrected dry mass accumulated per unit area between the two peaks (Figure 3). In the core collected in 2011, SAR at the BF25 station was determined using the Chernobyl peak, and taking the salt corrected dry mass accumulated per unit area between that peak and contemporary time.

3. Results and discussion

It is well known that the sediment-water exchange of P is influenced by bottom water oxygen conditions (e.g. Sundby et al. 1986; Jensen et al. 1995; Ingall and Jahnke 1997; Slomp et al. 2002). Not only oxygen, but also other parameters like sediment accumulation rate, fauna and amount and degradation rate of organic matter in the sediment can affect benthic P cycling (e.g. Ingall and Van Cappellen 1990; Van Cappellen and Ingall 1994; Eilola et al. 2009; Ekeroth et al. 2012; Viktorsson et al. 2012; Viktorsson et al. 2013). To investigate the effects of bottom water oxygen, and sedimentary organic matter content, on the sediment-water fluxes of DIP in the two fjords, we will describe the differences between shallow oxic and deep anoxic bottoms with higher contents of organic matter. We will also present a benthic mass balance for P based on the measured benthic fluxes and burial rates.
Figure 3. Depth distributions of $^{137}$Cs in sediment of the BF25 (at 25 m water depth) and BF35 (at 35 m water depth) stations in the By Fjord obtained from cores collected in 2009. Data refers to dry sediment weight. The first peak at around 5 cm depth corresponds to inputs from the Chernobyl accident in 1986 while the deeper peak at 13–15 cm corresponds to fallout from nuclear weapon tests, which peaked around 1962.

a. Pore water DIP and sediment characteristics

The concentration of DIP in the pore water increased steadily with sediment depth at all stations (Figure 4). However, the pore water DIP reached generally higher concentrations at the anoxic stations than at the oxic ones. Also, the concentration gradients across the sediment-water interface were generally steeper at the anoxic compared to the oxic stations. These differences between sediments overlain by oxygenated and anoxic bottom water are well known. They were also consistent with differences in measured DIP flux rates between the oxic and anoxic stations of this study.

The oxic shallower stations were more exposed to turbulence and this was reflected in the water content (WC). The sediment WC on the BF7 station was 57 wt% (average for the top 0–3 cm of sediment) and increased with bottom depth to 87–89% on stations BF25 and BF35 (Table 2). According to the classification of bottom type from water content by Håkanson and Jansson (2002), this indicates that BF7 was a transport bottom while BF25 and BF35 were accumulation bottoms.

From the data at hand it is not possible to exactly determine the quality of the organic matter in the sediment at the different stations, but the $C_{org}/TN$ ratio can give an indication. The $C_{org}/TN$ ratio at both oxic and anoxic bottoms was 10 in the surficial sediment of all stations and increased with sediment depth to about 12 to 13 (Figure 5), i.e. elevated from the Redfield ratio of 6.6. There are mainly two reasons for elevated $C_{org}/TN$ ratios in sediments. First, N is often preferentially remineralized in organic matter in relation to C, explaining the commonly found elevated C:N ratio in aged organic matter (Burdige 2007). The second reason for elevated C:N ratios may be input of terrestrial organic matter, which has a higher
C:N ratio than fresh marine organic matter. Even though the C:N ratios in sediment of all stations were similar, the benthic DIC flux, which is a measure of the C$_{org}$ oxidation rate in sediments where dissolution of carbonate minerals is negligible (Anderson et al. 1986), was higher at the anoxic bottoms than at the oxic ones (Nilsson et al. in prep.).

Another indicator of the quality of sedimentary organic matter, as well as diagenetic alteration of it, is the C$_{org}$:P$_{org}$ ratio. The C$_{org}$:P$_{org}$ ratio in sediment was around 250 at the anoxic stations BF25 and BF35 with no clear change with depth into sediment (Figure 5). This ratio was thus almost 2.5 times higher than the Redfield C:P ratio of 106. Sedimentary C$_{org}$:P$_{org}$ ratios several times higher than the Redfield ratio (and often higher than 250) are common in anoxic sediments, and have been observed e.g. in sapropel of the eastern Mediterranean Sea (Slomp et al. 2002), the Black Sea (Teodoru et al. 2007), the Baltic Sea (Jilbert et al. 2011), and the oxygen minimum zone of the northern Arabian Sea (Kraal et al. 2012). The high C$_{org}$:P$_{org}$ ratios in anoxic sediments have been explained with preferential P regeneration, i.e. P is released from organic matter faster than C during microbial degradation. The C$_{org}$:P$_{org}$ ratio in sediment of the shallow station BF7 with oxygenated bottom water was lower (about 160 to 200) in the top part of the sediment core than at the anoxic stations BF25 and BF35, while below about 3 cm sediment depth the C$_{org}$:P$_{org}$ ratios at the shallow oxic
Table 2. Measured variables given as mean values (when multiple measurements were made) for each field campaign. Bottom water oxygen in $\mu$M with standard deviation of the mean (std) and number of measurements made (n); DIP flux in mmol m$^{-2}$ d$^{-1}$, with standard deviation of the mean (std), 95% confidence interval (CI) for the mean, and number of measurements made (n); TC, C$_{org}$, TN, P$_{org}$ and P$_{inorg}$ inventories in the upper 3 cm of the sediment given in mmol cm$^{-2}$ (C, N) or $\mu$mol cm$^{-2}$ (P); and average water content (WC) in the upper 3 cm of the sediment given as weight/weight. Eff stands for the efficiency of P recycling and is the DIP flux divided by the sediment carbon inventory in the top 3 cm. Stations are named with two letters indicating the fjord name (By Fjord = BF, Koljo Fjord = KF) and a number for the bottom depth at the station. Bottom water salinity and oxygen were measured inside the incubation chambers at the beginning of incubations. Bottom water temperature was measured in ambient bottom water with a CTD sensor mounted on the lander frame (model 3231, AADI, Norway). ND means not determined.

<table>
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<th>Station</th>
<th>Year</th>
<th>Month</th>
<th>S</th>
<th>T (°C)</th>
<th>BW O$_2$ ($\mu$M)</th>
<th>Mean std n</th>
<th>DIP flux (mmol m$^{-2}$ d$^{-1}$)</th>
<th>Mean std Cl n</th>
<th>Inventory (mmol cm$^{-2}$)</th>
<th>Inventory (mmol cm$^{-2}$)</th>
<th>WC (w/w)</th>
<th>Eff (d$^{-1}$)</th>
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<td>47 18 8</td>
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<td>ND ND</td>
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<tr>
<td>BF25</td>
<td>2010</td>
<td>April</td>
<td>31</td>
<td>7.7</td>
<td>0 – – –</td>
<td>1.88 0.41 0.33 6</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
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<tr>
<td>BF35</td>
<td>2010</td>
<td>April</td>
<td>32</td>
<td>7.6</td>
<td>0 – – –</td>
<td>1.44 0.34 0.30 5</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
<td></td>
<td></td>
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<tr>
<td>KF14</td>
<td>2010</td>
<td>June</td>
<td>27</td>
<td>7.0</td>
<td>86 8 3</td>
<td>−0.02 0.01 0.01 3</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
<td></td>
<td></td>
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<tr>
<td>BF25</td>
<td>2010</td>
<td>June</td>
<td>31</td>
<td>7.7</td>
<td>0 – – –</td>
<td>1.35 0.34 0.33 4</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
<td></td>
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<tr>
<td>BF35</td>
<td>2010</td>
<td>June</td>
<td>32</td>
<td>7.3</td>
<td>0 – – –</td>
<td>1.28 0.19 0.22 3</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BF7</td>
<td>2010</td>
<td>Nov</td>
<td>23</td>
<td>10</td>
<td>187 31 12</td>
<td>0.05 0.02 0.01 12</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KF43</td>
<td>2010</td>
<td>Nov</td>
<td>28</td>
<td>6.8</td>
<td>0 – – –</td>
<td>1.08 0.24 0.21 5</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
<td>ND ND</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The given C inventory is for C$_{org}$, not TC.
and the deeper anoxic stations were not significantly different (although the BF7 station showed some scatter of the ratio; Figure 5). Our interpretation is that preferential P regeneration took place in sediment of all stations in this study, but more rapidly after deposition and more intensively at the long-term anoxic stations. Oxygen only penetrates 3 to 4 mm into the sediment at the shallow oxic station (Kononets et al. unpublished results), which means that sedimenting organic matter will be exposed to an anoxic environment relatively fast after deposition. Despite this, high $C_{org}:P_{org}$ ratios were not observed above 3 cm depth in this sediment. Thus, organic matter at the shallow oxic station apparently requires longer time of accumulation in anoxic sediment before the preferential P regeneration shows up in as high C:P ratios in organic matter as at the long-term anoxic stations. Unfortunately we did not determine sediment accumulation rate at the shallow oxic station, so we are not able to estimate the time of exposure to anoxia required to produce $C_{org}:P_{org}$ ratios at this station similar to the long-term anoxic stations. Nevertheless, this study has shown that organic
matter deposited in sediment under oxygenated bottom water had lower \( \text{C}_{\text{org}}:\text{P}_{\text{org}} \) ratios (but still higher than Redfield) than organic matter deposited in sediment under anoxic bottom water for some time after deposition. However, the sedimentary \( \text{C}_{\text{org}}:\text{P}_{\text{org}} \) ratio at sites with oxygenated bottom water approached with time (or depth into sediment) that of sites with long-term anoxic bottom water.

In contrast to the \( \text{C}_{\text{org}}:\text{TN} \) ratios that were similar at oxic and anoxic bottoms, the profiles of \( \text{C}_{\text{org}} \) and TN in the sediments showed that concentrations and inventories of these compounds were higher at the deeper anoxic bottoms (Figure 6 and Table 2). This was probably the reason for the higher measured \( \text{C}_{\text{org}} \) oxidation rates at the deep anoxic stations than at the shallow oxic ones (Nilsson et al. in prep.). The more energetic benthic hydrodynamic conditions at shallow bottoms are likely to have caused a transport via resuspension of particulate organic matter from these transport bottoms to the less hydrodynamically energetic deep accumulation bottoms explaining the higher content of sedimentary organic carbon and nitrogen, and higher \( \text{C}_{\text{org}} \) oxidation rates, there than at shallow bottoms.

The total phosphorus (TP) content of the sediment was, except for the top centimeter at the shallow oxic station, remarkably similar at both oxic and anoxic stations. Below about 1 cm and down to the bottom of the cores, the sediment TP content was 22 to 28 \( \mu \text{mol g}^{-1} \) at all three stations. In this way sediment TP behaved differently compared to sedimentary \( \text{C}_{\text{org}} \) and TN, the concentrations and inventories of which always were higher at stations BF25 and BF35 than at station BF7. However, the distributions of \( \text{P}_{\text{org}} \) and \( \text{P}_{\text{inorg}} \) in sediment were different at oxic and anoxic stations (Figure 6). Whereas both \( \text{P}_{\text{inorg}} \) and especially \( \text{P}_{\text{org}} \) decreased with depth into sediment at the oxic station, both \( \text{P}_{\text{inorg}} \) and \( \text{P}_{\text{org}} \) were quite constant around 14 to 16 \( \mu \text{mol g}^{-1} \) and around 9 to 11 \( \mu \text{mol g}^{-1} \), respectively, down the cores at both anoxic stations. \( \text{P}_{\text{inorg}} \) dominated over \( \text{P}_{\text{org}} \) in sediment of all stations, but to a larger extent at the oxic station. \( \text{P}_{\text{inorg}} \) made up 65 to 90% of TP throughout the core at the oxic station, but less (about 55 to 60%) at the anoxic stations (Figure 6). Hence, \( \text{P}_{\text{org}} \) made up 10 to 35% and about 40 to 45% of TP at the oxic and anoxic stations, respectively. At the deep anoxic stations, and below the surficial layer at the oxic station, sedimentary \( \text{P}_{\text{inorg}} \) probably consisted of refractory P-containing minerals, such as apatite or detrital P, some of which may be of terrestrial origin. Because the sediment was sulfidic and all iron should be in solution or in the form of solid FeS(s) or FeS\(_2\)(s), P associated with Fe(III) (oxyhydr)oxides should be negligible in sediments of stations BF25 and BF35 with anoxic bottom water. The data at hand do not enable us to explain why sedimentary \( \text{P}_{\text{inorg}} \), below the surficial layer, was higher at the shallow oxic station than at the deeper anoxic stations.

At the shallow oxic station the top cm of the sediment contained 22 to 28 \( \mu \text{mol g}^{-1} \) \( \text{P}_{\text{inorg}} \) (Figure 6). This surface enrichment of \( \text{P}_{\text{inorg}} \) at the shallow station was not observed at the deeper anoxic stations, where \( \text{P}_{\text{inorg}} \) concentrations in surficial sediment were 13 to 16 \( \mu \text{mol g}^{-1} \). The surface enrichment of \( \text{P}_{\text{inorg}} \) explains the higher TP content in surficial sediment at the shallow oxic station than at the deeper anoxic ones, and it suggests P retention in sediment under oxic conditions which most likely was due to adsorption on
Figure 6. Profiles of C$_{org}$, TN, P$_{org}$ and P$_{inorg}$ in the solid phase of the sediment in the By Fjord. All concentrations are per dry weight of sediment. P$_{org}$ and P$_{inorg}$ as a percentage of total P in sediment are also presented. Grey squares or crosses indicate 35 m, black triangles 25 m and open circles 7 m bottom depth, respectively.
or coprecipitation with Fe(III) (oxyhydr)oxides and/or bacterial storage of polyphosphates. This P retention at oxic stations is consistent with the difference in measured DIP flux rates between oxic and anoxic stations as explained further in this paper.

b. Benthic DIP fluxes and elemental ratios in fluxes

Fluxes of DIP were measured in situ both at oxic and anoxic stations in the By Fjord in summer, fall and spring during the years 2009 to 2010 (Table 2). DIP fluxes measured at bottoms with oxygenated overlying water were lower than DIP fluxes measured at anoxic bottoms (Figure 7). Fluxes measured at oxic bottoms did not show any correlation with the bottom water oxygen concentration, nor with the benthic oxygen uptake rate (data not shown). In the nearby Koljo Fjord, with similar hydrographic conditions, two lander deployments were made in June and November 2010 at one oxic and one anoxic site, respectively (Table 2). The two Koljo Fjord stations followed the same pattern regarding fluxes as those measured in the By Fjord (Figure 7).
Table 3. Mean flux ratios (atomic) of DIC, DIN and DIP at oxic and anoxic bottom water conditions.

Note that negative DIP or DIN fluxes were not included in calculations of the ratios. Both DIC fluxes lower than 150 mmol m$^{-2}$ d$^{-1}$ (and corresponding DIP and DIN fluxes), and the full range of observed fluxes were used to calculate elemental ratios in anoxic fluxes; see Figure 8. DIC fluxes are from Nilsson et al. (in prep.), and DIN fluxes from Hall et al. (in prep.).

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>std</th>
<th>n</th>
<th>Redfield</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIC:DIP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>anoxic (DIC &lt; 150)</td>
<td>69</td>
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<td>36</td>
<td>106</td>
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<tr>
<td>anoxic</td>
<td>79</td>
<td>30</td>
<td>45</td>
<td>106</td>
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<tr>
<td>oxic</td>
<td>992</td>
<td>1976</td>
<td>20</td>
<td>106</td>
</tr>
<tr>
<td>DIN:DIP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>anoxic (DIC &lt; 150)</td>
<td>5.3</td>
<td>2.6</td>
<td>36</td>
<td>16</td>
</tr>
<tr>
<td>anoxic</td>
<td>7</td>
<td>5</td>
<td>47</td>
<td>16</td>
</tr>
<tr>
<td>oxic</td>
<td>19</td>
<td>16</td>
<td>19</td>
<td>16</td>
</tr>
</tbody>
</table>

The benthic DIC and DIN fluxes were, like the DIP flux, higher at anoxic sites than at oxic ones. Whether the oxygen conditions and the bottom type had a similar influence on the DIP, DIC and DIN flux rates was determined from the elemental ratios in solute fluxes at the oxic and anoxic bottoms. Since almost all carbon in the sediment was organic, and there was no significant difference between oxic and anoxic bottoms, or with sediment depth, in this respect, we assumed that the contribution to the DIC flux from dissolution of carbonate minerals was negligible at all stations.

The benthic DIP flux was positively correlated with the DIC flux at both oxic and anoxic bottoms. However, the ratio between the DIC and DIP fluxes at oxic and anoxic bottoms differed (Table 3 and Figure 8). This indicates that the degradation rate of organic matter controlled the magnitude of the DIP flux at both bottom types, but to a lesser extent at oxic bottoms. This was probably largely (but not necessarily only) due to immobilization of DIP in oxygenated sediment, but the immobilization was not fully effective in this marine environment for reasons explained below. Furthermore, the “efficiency” of P recycling, a parameter which we introduce in this paper and which we define as the DIP flux (mmol m$^{-2}$ d$^{-1}$) divided by (or normalized to) the organic carbon inventory in the top 3 cm of sediment (mmol cm$^{-2}$; Table 2), was several times higher at anoxic bottoms (0.33 to 0.63 d$^{-1}$) compared to oxic ones (0.04 to 0.12 d$^{-1}$; Table 2). Immobilization of DIP in oxidized surface sediments and a more intense preferential regeneration of P in anoxic sediments than in oxic ones (as evidenced by higher C$_{org}$:P$_{org}$ ratios in surficial sediment of anoxic than of oxic stations) likely explain both the higher efficiency of P recycling and the lower C:P ratios in fluxes (Table 3) at anoxic than at oxic bottoms.

The average C:P ratio of fluxes from the anoxic bottoms was 69 ± 18 (Table 3), which is about 1.5 times lower than the Redfield ratio of 106. While the anoxic flux was P rich in relation to C, the sedimentary organic matter was, as explained above, P poor at the anoxic stations with C:P ratios around 250, i.e. about 2.5 times higher than the Redfield C:P ratio. These two independent sets of observations clearly demonstrate that preferential P regeneration (in relation to C) took place in anoxic By Fjord and Koljo Fjord sediments as has
Figure 8. The relation between DIC and DIP fluxes in the By and Koljo Fjords. KF43 belongs to the anoxic stations, and KF14 to the oxic ones. The fluxes presented are from individual chambers, i.e. not mean values as presented in Tables. Fluxes from anoxic bottoms were P enriched while fluxes from oxic bottoms were P depleted in relation to the Redfield C:P ratio of 106:1. The correlation between the DIP and DIC flux from anoxic sediments was much weaker or absent at DIC fluxes $>150$ mmol m$^{-2}$ d$^{-1}$. This was likely caused by anoxic oxidation of methane, which produces DIC without a simultaneous production of DIP. These data points were thus not used in the linear regression or in calculation of flux ratios presented in the text. The linear regression lines are type 1 (least square).

been observed in many other anoxic sediments (e.g. Ingall and Jahnke 1997; Ingall et al. 2005; Viktorsson et al. 2012; Viktorsson et al. 2013). The mechanisms causing preferential P regeneration, which have been presented to date, include the activity of phosphatases. Phosphatases are enzymes, which cleave off phosphate groups from organic matter and are used by C-limited bacteria to increase the bioavailability of the organic matter C moiety (Steenbergh et al. 2011). Another (and likely related) mechanism was presented by Steenbergh et al. (2013), who suggested that high (about 400:1) C:P ratios in microbial biomass contribute to preferential P regeneration. It has been discussed whether preferential P regeneration takes place only in anoxic sediments, both in anoxic and oxic sediments, in both anoxic and oxic sediments but with higher intensity in anoxic sediments, or in both anoxic and oxic sediments but less apparent in oxic sediments because of retention mechanisms removing DIP from pore water there (e.g. Jilbert et al. 2011; Steenbergh et al. 2011). Results from this study (primarily lower C$_{org}$:P$_{org}$ ratios in surficial sediments of oxic than of long-term anoxic stations, but higher than Redfield C$_{org}$:P$_{org}$ ratios in all sediments) indicate that preferential P regeneration took place in both anoxic and oxic sediments, but more intensively in anoxic sediments.
Eutrophication has been proposed to be a self-accelerating process (e.g. Rosenberg et al. 1990; Vahtera et al. 2007) since recycling and removal/retention of both N and P in sediments are oxygen dependent with more bioavailable N and P released from sediments under anoxic than oxic conditions. The simple explanation is that anoxia leads to higher benthic release of N and P, which ultimately leads to stimulated primary productivity (and in the Baltic stimulated cyanobacterial N2-fixation) in surface waters, which leads to higher input of organic matter to bottom waters and sediments, which stimulates oxygen consumption and may cause anoxia, which leads to release of yet more N and P in bioavailable form from sediments, and so on. One environmental implication of preferential P regeneration is that it may strongly contribute to eutrophication being a self-accelerating process. This is not only due to low C:P ratios in fluxes from sediments just after the bottom water has turned anoxic, but also due to sustained low C:P ratios in fluxes from long-term anoxic bottoms and that DIP fluxes from such bottoms are proportional to DIC fluxes, i.e. to input and degradation rate of organic carbon in the sediments as shown by this study and studies in the Baltic Sea (Viktorsson et al. 2012; Viktorsson et al. 2013). In other words, a system does not need to turn from an oxic to an anoxic state to make eutrophication a self-accelerating process. Eutrophication is also in a long-term anoxic system self-accelerating as long as the system receives inputs of organic matter.

The benthic solute flux at anoxic bottoms was P enriched not only in relation to C, but also to N; the average N:P (DIN/DIP) ratio in fluxes from anoxic bottoms was 5.3 ± 2.6 (Table 3), which is 3 times lower than the Redfield ratio of 16. The slightly higher than Redfield average N:P ratio in fluxes at oxic bottoms (19; Table 3) may have been caused by DIP retention being more efficient to lower the benthic solute flux than denitrification, which produces N2 gas which is not included in the measured DIN flux.

The average C:P ratio of fluxes from the oxic bottoms (992; Table 3) was, in contrast to the anoxic bottoms, higher than the Redfield ratio of 106, in accordance with the well-known retention mechanisms of DIP in oxygenated sediments (e.g. Mortimer 1942; Aller 1980). However, the DIP flux still correlated with the DIC flux from oxic bottoms in this fjord, as previously mentioned. This suggests that the diagenetic DIP production went up with increasing oxidation rate of organic matter in the sediment, but that the oxygenated sediments of this marine fjord could not retain all of the produced DIP. The DIP, which could not be retained, escaped to the overlying water. The fraction of the produced DIP, which was escaping increased with increased DIP production in the sediment and with increased DIC flux. This behavior is different from brackish environments such as the Gulf of Finland and the Eastern Gotland Basin in the Baltic Sea, where there was no correlation between DIP and DIC fluxes at oxic bottoms (Kiirikki et al. 2006; Viktorsson et al. 2012; Viktorsson et al. 2013). The difference between the brackish Baltic Sea and these marine fjords in P retention in oxygenated sediments may be explained with the classical salt effect (Caraco et al. 1990; Blomqvist et al. 2004). The higher sulfate concentration in the saltier water of the fjords favors bacterial sulfate reduction and sulfide production. Fe is then to a larger extent reduced and removed as iron sulfide and pyrite in this marine environment, and less
Table 4. Sediment accumulation rates (SAR) as well as burial rates of $P_{\text{inorg}}$ and $P_{\text{org}}$, and burial efficiencies (bur. eff.) for $P_{\text{org}}$ at the BF25 and BF35 stations. SAR were determined from sedimentary distributions of $^{137}$Cs. Year is the time of sediment sampling. Time span is the period used to determine SAR. During sampling in 2009, the Chernobyl and fallout peaks were used to estimate SAR, whereas only the Chernobyl peak was used in 2011; see text. Burial rates of $P$ were calculated from SAR, and the $P_{\text{org}}$ and $P_{\text{inorg}}$ concentrations at depth in the sediment cores (Figure 6).

<table>
<thead>
<tr>
<th>Station</th>
<th>Year</th>
<th>Time span</th>
<th>SAR (g m$^{-2}$ y$^{-1}$)</th>
<th>Burial rate $P_{\text{inorg}}$ (mmol m$^{-2}$ y$^{-1}$)</th>
<th>Burial rate $P_{\text{org}}$ (mmol m$^{-2}$ y$^{-1}$)</th>
<th>Bur. eff. $P_{\text{org}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF25</td>
<td>2009</td>
<td>1986–1963</td>
<td>726</td>
<td>10.8</td>
<td>7.2</td>
<td>1.1</td>
</tr>
<tr>
<td>BF35</td>
<td>2009</td>
<td>1986–1963</td>
<td>1070</td>
<td>15.6</td>
<td>10.7</td>
<td>1.8</td>
</tr>
<tr>
<td>BF25</td>
<td>2011</td>
<td>2011–1986</td>
<td>848</td>
<td>12.9</td>
<td>8.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Fe(III) is thus available to scavenge DIP. Because iron adsorption of DIP likely is small in these marine fjords, bacterial accumulation of polyphosphates may play a relatively larger role there compared to brackish environments. Although there are no data from this study to confirm which processes were active in DIP immobilization at oxic bottoms in the By Fjord and the Koljo Fjord, we suggest that storage of polyphosphates by bacteria was potentially more important than scavenging by Fe(III) (oxyhydr)oxides at these marine sites.

c. Burial rate and burial efficiency of $P$

Burial rates of organic and inorganic $P$ in sediments of the two anoxic stations in the By Fjord (BF25 and BF35) were calculated from the measured SAR (Table 4) and the $P_{\text{org}}$ and $P_{\text{inorg}}$ concentration at depth in the sediment. The $P_{\text{org}}$ and $P_{\text{inorg}}$ concentrations below a surface layer of about 4 cm in the sediment of both stations were approximately constant at an average value of 10.0 $\mu$mol g$^{-1}$ (dry weight) and 14.7 $\mu$mol g$^{-1}$ (dry weight), respectively, down to the bottom of the cores at 20 cm depth (Figure 6). Since the $P_{\text{org}}$ and $P_{\text{inorg}}$ generally did not decrease noticeably below these concentrations in the cores, they were assumed to reflect the content of $P$ being buried. The average obtained burial rates at the two anoxic stations were $8.81 \pm 1.78$ mmol P m$^{-2}$ y$^{-1}$ and $13.1 \pm 2.41$ mmol P m$^{-2}$ y$^{-1}$ for $P_{\text{org}}$ and $P_{\text{inorg}}$, respectively (Table 4). Burial of $P_{\text{inorg}}$ was thus more important than burial of $P_{\text{org}}$, and $P_{\text{inorg}}$ made up 59 to 60% of TP burial at the long-term anoxic stations. Hence, $P_{\text{org}}$ constituted 40 to 41% of TP burial at these stations. We did not determine SAR at the shallow oxic station BF7, so we were not able to calculate P burial rates there. However, the distributions of $P_{\text{org}}$ and $P_{\text{inorg}}$ at depth in sediment of this station (Figure 6) made it possible to estimate the relative importance of the two $P$ fractions in contributing to TP burial. We thus found that $P_{\text{inorg}}$ made up about 80%, and $P_{\text{org}}$ about 20%, of TP burial at the shallow site with oxygenated bottom water. The finding of this study that 60–80% of $P$ burial at oxic and anoxic sites in this fjord environment was made up of inorganic $P$ is in contrast to observations that 60 to 80% of reactive $P$ burial at both oxic and anoxic sites in
the Kattegat, Danish Straits and central Baltic Sea (Baltic proper) takes place in the form of organic P (Mort et al. 2010). Still, inorganic P has in many previous studies been found to be an important contributor to P burial. As a recent example, Jilbert and Slomp (2013) reported that authigenic phosphorus minerals (iron(II)-phosphates and manganese-calcium-carbonate-phosphates) constituted major burial phases of P in deep euxinic basins of the Baltic proper, and that authigenic phosphorus minerals other than carbonate fluorapatite may contribute significantly to total P burial in euxinic environments.

Using a mass balance approach and assuming steady state (i.e. no change of the sediment P pool size with time), we estimated the organic P deposition to the sediment of the long-term anoxic stations as the sum of DIP efflux and $P_{org}$ burial to be $617 \pm 19.4 \text{ mmol P m}^{-2} \text{ y}^{-1}$. Since the source of DIP contributing to the flux from these long-term anoxic sediments should be organic matter, we should in this way have estimated sea-floor deposition of organic P. The burial efficiency for organic P (burial rate / deposition rate) thus became 1 to 2% at the two anoxic stations (Table 4). This is a very low burial efficiency and it suggests that as much as 98 to 99% of deposited organic P is efficiently recycled in sediments of these long-term anoxic and sulfidic sites.

There are weaknesses with this mass balance approach to estimate burial efficiencies. First, the burial rate corresponds to an integrated accumulation on a decadal time-scale, whereas the benthic flux reflects degradation taking place on a time-scale of weeks-months. Nevertheless, this procedure to equal the deposition flux with the sum of degradation and burial rates has often been used to estimate burial efficiencies for C, N and P (e.g. Canfield 1994; Hulth et al. 1997; Brunnegård et al. 2004; Viktorsson et al. 2013). Second, some of the DIP, diagenetically produced in the pore water during degradation or dissolution of deposited particulate P, may be removed from the pore water due to formation of authigenic P minerals. This process is called sink-switching, and it means that some P is buried in the sediment in another form than that in which it was originally deposited (e.g. Ruttenberg and Berner 1993; Ruttenberg 2003). If sink-switching occurred in the long-term anoxic sediments of our study, it would mean a transfer of P from the $P_{org}$ to the $P_{inorg}$ pool, and that the $P_{org}$ burial rates we report would have to be increased to account for the effect of sink-switching. In an attempt to roughly quantify the influence of possible sink-switching on burial efficiency for organic P in the By Fjord, we assumed that the $P_{org}$ burial rates would be a factor of two higher than those we report (Table 4) if sink-switching was negligible in these sediments. The average $P_{org}$ burial rate would then increase from 8.81 to 17.6 mmol P m$^{-2}$ y$^{-1}$, the average organic P deposition would, hence, increase from 617 to 626 mmol P m$^{-2}$ y$^{-1}$, and the average burial efficiency for organic P would increase from 1.4 to 2.8%. This should be a maximum estimate of the enhancement of burial efficiency as a result of sink-switching, since previous estimates of the transfer of one sedimentary P form (e.g. $P_{org}$) to an authigenic P mineral (e.g. carbonate fluorapatite) due to sink-switching suggest that less than 50% of the original P form is “sink-switched” (Ruttenberg 2003, and references therein). Our simple calculation above suggests that accounting for possible sink-switching in By Fjord sediments would make the burial efficiency only marginally higher than what we report.
The burial efficiency for organic P would still be very low, and more than 97% of deposited organic P would still be recycled in long-term anoxic sediments of this fjord environment.

One complication when comparing the burial efficiency of this study with that of previous ones is that burial efficiencies are reported for different fractions of P (total P, reactive P, and organic P). Nevertheless, using the same type of mass balance approach, Viktorsson et al. (2012) and Viktorsson et al. (2013) reported average burial efficiencies for total P of 3 and 4% in brackish anoxic sediments of the Gulf of Finland and the Baltic proper, respectively. Lukkari et al. (2009) found that burial efficiencies for total P were 41 to 57% at coastal sites with oxygenated bottom water in the northeastern Baltic proper and northern parts of the Gulf of Finland. Burial efficiencies of 7 to 15% for reactive P were reported for eastern Mediterranean sapropel (S1) during its formation (Slomp et al. 2002). In the oxygen minimum zone of the northern Arabian Sea, Kraal et al. (2012) found a burial efficiency of 10% for reactive P, which was claimed to be the lowest burial efficiency reported for the Arabian Sea. Taken together, the range of P burial efficiencies for these low oxygen marine settings is 3 to 15% (excluding the study of sites with oxygenated bottom water by Lukkari et al. (2009)). It thus appears that the P burial efficiency of 1–2% (or about 3% if sink-switching was important) for the long-term anoxic basin of the By Fjord, as reported in this study, may be among the lowest ever reported.

4. Conclusions

In situ lander measurements of benthic DIP fluxes at oxic and anoxic bottoms in the By Fjord, western Sweden (in total 80 flux measurements) showed that DIP fluxes from sediments with oxygenated overlying water (cruise averages ranging from 0.05 to 0.23 mmol m\(^{-2}\) d\(^{-1}\)) were much lower than fluxes from sediments with anoxic overlying water (cruise averages ranging from 1.25–2.26 mmol m\(^{-2}\) d\(^{-1}\)). The same measurements in the adjacent Koljo Fjord showed similar differences in benthic DIP fluxes between oxic and anoxic bottoms. Distributions of DIP in the pore water at oxic and anoxic stations were consistent with the observed difference in fluxes with lower concentrations and less sharp concentration gradients at the sediment-water interface at the oxic than at the anoxic stations.

The DIP flux correlated well with the DIC flux at anoxic bottoms suggesting that the DIP flux in the anoxic part of the fjords to a large extent was controlled by deposition and degradation rate of organic matter. The average C:P ratio of fluxes (DIC flux / DIP flux) from the anoxic bottoms was 69 ± 18, which is about 1.5 times lower than the Redfield ratio. In contrast, the average C\(_{\text{org}}\):P\(_{\text{org}}\) ratio in the solid phase of sediment at anoxic bottoms was around 250, i.e. about 2.5 times higher than the Redfield ratio. The benthic anoxic flux was P rich not only in relation to C, but also to N, and the average anoxic DIN:DIP flux ratio was 5.3 ± 2.6, which is about 3 times lower than the Redfield N:P ratio. All these observations clearly demonstrate that preferential P regeneration took place in anoxic By Fjord and Koljo Fjord sediments.

Burial rates of inorganic P and organic P were 11–16 mmol m\(^{-2}\) y\(^{-1}\) and 7–11 mmol m\(^{-2}\) y\(^{-1}\), respectively, at anoxic bottoms. Burial of inorganic P was more important than burial
of organic P not only at anoxic sites but even more so at oxic ones, and inorganic P made on average up about 80% and 60% of total P burial at oxic and anoxic stations, respectively. The preferential P regeneration was accompanied with very low burial efficiencies for organic P at sites with anoxic bottom water (1 to 3%) suggesting extremely efficient recycling of organic P deposited in these anoxic and sulfidic sediments. This estimate may to our knowledge be among the lowest P burial efficiencies ever reported.

The DIP flux correlated well with the DIC flux not only at anoxic but also at oxic bottoms of these marine fjords, which is different from observations in brackish water environments. However, at the oxic bottoms the DIC:DIP flux ratio was almost 10 times higher than the Redfield ratio suggesting that DIP was partly immobilized in the oxidized sediment. We speculate that because of a salt effect ($SO_4^{2-}$), polyphosphate storage by bacteria may be more important in DIP immobilization than scavenging by Fe(III) (oxyhydr)oxides in these marine settings. Immobilization of DIP in oxidized surface sediments and a more intense preferential regeneration of P in anoxic sediments (than in oxic ones) were likely the reasons for the lower “efficiency” of P recycling (defined as the benthic DIP flux normalized to the carbon inventory in surficial sediment) at oxic bottoms (0.04 to 0.12 d$^{-1}$) than at anoxic bottoms (0.33 to 0.63 d$^{-1}$).

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REFERENCES


Kraal, P., Slomp, C.P., Reed, D.C., Reichart, G.-J. and Poulton, S.W. 2012. Sedimentary phosphorus and iron cycling in and below the oxygen minimum zone of the northern Arabian Sea: Biogeoosciences, 9, 2603–2624.


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