Phosphorus release and sediment geochemistry in a low-salinity water bay of the Gulf of Finland

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Sequestration of phosphorus in sediments is critical in controlling the availability of phosphate for algal growth in shallow bays of the Gulf of Finland (Baltic Sea). In the organic-rich, low-salinity-water bay studied, the release of phosphorus from the sediments was sensitive to bioirrigation and oxygen conditions in the water. This was explained by the importance of hydrated iron oxides in binding phosphorus at the sediment surface, the sensitivity of iron-bound phosphorus to redox conditions, and the presence of soluble iron and sulphate. Chemical forms of phosphorus, especially phosphorus bound by redox-sensitive hydrated iron oxides, are regulated by the amount of degradable organic matter, availability of oxygen, iron and sulphate as well as bioirrigation by benthic fauna. To improve the short-term prediction of the water quality and particularly the dynamics of algal blooms in the coastal areas of the Gulf of Finland, sediment phosphorus and especially hydrated iron oxides should be included in water quality models.

Introduction

Eutrophication of coastal waters is of growing concern worldwide and is one of the main problems of the Gulf of Finland (GoF) (Baltic Sea) (HELCOM 2009). In coastal waters, the elevated supply of nutrients and organic matter from riverine inputs cause increased primary production and lead to a shift from diatom towards non-diatom species, resulting in a loss of diversity (e.g. Billen and Garnier 1997, Weckström 2006). Phosphorus (P) plays a key role in eutrophication of coastal waters because blue-green algae (Cyanobacteria) are not limited by nitrogen (N) but benefit from additional P (e.g. Smith 1983, Vahtera et al. 2007, Eilola et al. 2009). Moreover, N fixation by Cyanobacteria is not limited in low-salinity waters (salinity < 10–12 PSU, Howarth and Marino 2006) as opposed to more saline environments. Therefore, coastal waters located at the crossroads of fresh and brackish waters, characterised by low salinities and high external organic matter and nutrient loading, are very sensitive to eutrophication. Although efforts
have been made to reduce external nutrient loading to the GoF, the recovery of its water quality to a good status has been delayed (Pitkänen et al. 2001, HELCOM 2009). In coastal ecosystems, up to 50% of the primary production is remineralised at the surface of the sediments (e.g. Nixon 1981, Sundby et al. 1992), providing a substantial amount of dissolved inorganic P (PO$_4^{3-}$) to the water. Indeed, whereas P mainly enters the ecosystem as particulate P (e.g. Ekholm and Kallio 1996, Uusitalo et al. 2001), which is poorly available to algae, a large proportion of the soluble P released from the sediments, from the degradation of organic matter or as a result of reduction of iron oxy-hydroxides, is readily available for algal growth (Ekholm 1998, Uusitalo 2004). Thus, the sequestration of P by the sediments is critical in controlling the productivity of coastal waters (Caraco et al. 1990, Vahtera et al. 2007).

Phosphorus is present in the sediment in various forms that can be coarsely divided into reactive and immobile using a phosphorus fractionation method (e.g. Ruttenberg 1992, Jensen and Thamdrup 1993). Depending on the methods used, reactive P, which may be or become available for bacteria and algae, may include loosely-bound and pore-water P, P from hydrated oxides of reducible metals [mainly iron (Fe)], and labile organic (or biogenic) P. Immobile P, which is presumed to act as sink for P, can consist of P bound to oxides of aluminium (Al) and non-reducible Fe, apatite P, and residual, mainly refractory organic P.

In iron-rich sediments, the redox-sensitive part (mainly P bound to hydrated oxides of iron) is significant and can play an important role in the release of P from the sediments (Carman and Jonsson 1991, Hartikainen et al. 1996, Lukkari 2008). In the sediments, both P included in the organic matter (Ingall et al. 1993) and iron-bound P, are subject to the fluctuation of the oxygen (O$_2$) conditions (e.g. Boström et al. 1982, Sundby et al. 1992, Mort et al. 2010). The P outflux at the sediment–water interface is usually enhanced when the surface sediments become anoxic (Mortimer 1941, Eilola et al. 2009).

Slomp et al. (2002) suggested that sulphate reducers can enhance the release of P from organic matter under anoxic conditions. The increase of the P flux from the sediments to the water column can also be explained by the reduction of ferric iron [Fe(III)] in hydrated oxides to ferrous iron [Fe(II)], leading to the release of Fe-bound P. In high-Fe(II) and PO$_4^{3-}$ (and low-sulphide, S$_2^-$) environments, ferrous phosphate can precipitate in the sediments as vivianite (e.g. Gächter and Müller 2003). However, in brackish waters that have high concentrations of sulphate (SO$_4^{2-}$), the reduction of SO$_4^{2-}$ into S$_2^-$ reduces the availability of Fe compounds to bind PO$_4^{3-}$ (Caraco et al. 1989) because ferrous iron precipitates into ferrosulphides (FeS or FeS$_2$; Berner 1970). The interaction of iron and sulphur promotes the build-up of PO$_4^{3-}$ in sediment pore-water (e.g. Boström et al. 1982, Caraco et al. 1989, Roden and Edmonds 1997, Emeis et al. 2000). According to the hypothesis by Caraco et al. (1989) in brackish waters (SO$_4^{2-}$ concentrations above 3000 µmol l$^{-1}$), P can be released from the sediments under both oxic and anoxic conditions at the sediment–water interface by three mechanisms:

1. SO$_4^{2-}$ competes with phosphate for anion sorption sites.
2. S$_2^-$ can bind reactive sediment Fe compounds to Fe sulphides, leading to a reduced availability of Fe to bind P.
3. SO$_4^{2-}$ reduction can elevate the pH, which would inhibit the sorption of P onto hydrated iron oxides.

Finally, estuaries and shallow coastal areas of the GoF that are at the crossroads of fresh and brackish waters are subject to changes in P processes that may result in P release from the sediment due to the abundance of organic matter, Fe and SO$_4^{2-}$. These zones may be particularly sensitive to elevated PO$_4^{3-}$ concentrations in the water column. Especially shallow areas where wind secures good mixing of the water allowing dissolved P released from the sediments to reach the surface of the water and be available for algal growth. Presently, modeling of P release from the sediment of the GoF focuses on either the water column or the sediment–water interface by using oxygen conditions in the water column or decomposition of
organic matter at the sediment surface to define P release from the sediments (Kiirikki et al. 2006). However, chemical forms of P define how much of the sediment P can be released and biogeochemistry of Fe and SO₄²⁻ can play an important role in the ability of sediments to retain P. Therefore, a solid understanding of sediment geochemistry is an important prerequisite to the development of coupled water-sediment models.

In this study, we investigated the distribution and interaction of Fe, sulphur (S) and P in the sediments of a shallow, organic-rich, brackish bay of the GoF to understand the processes affecting P release from the sediments in an environment with low salinity and high external organic-matter input.

**Töölönlahti**

**Catchment**

Töölönlahti is a shallow and very eutrophic brackish bay with turbid water (Tikkanen et al. 1997). The bay is located on the northern coast of the GoF, in the northeastern part of the brackish Baltic Sea. The bay lies in the centre of Helsinki (ca. 575 000 inhabitants), the capital of Finland (60°10´N, 24°56´E; Fig. 1). It is around 2 m deep and covers 20 ha. The mean salinity of the bay (4.4 PSU) lies in the lower range of the salinity of the Baltic (1–25 PSU; HELCOM 2009). The original catchment area was 5 km² but nowadays, as a result of the diversion of stormwaters, it only gathers rainwater from 0.4 km² (Tikkanen et al. 1997). A rapid increase in the population around the bay took place in the late 19th and early 20th centuries. The pollution load was significantly reduced in the mid-1940s, when the wastewaters were diverted elsewhere (Tikkanen et al. 1997). The bay is connected to the GoF (Eläintarhanlahti) on its eastern side (Fig. 1). Since 2005, additional water has been pumped (0.5 m³ s⁻¹) from the Humallahti (Fig. 1) to improve the water quality of the bay. The additional pumping decreased the amount of water flowing into the bay from Eläintarhanlahti, which reduced the input of sediments from the Vantaanjoki during flooding periods (Fig. 1).

**Sediment and water quality properties**

According to Virkanen (1998), the sedimentation rate in the bay is 0.6 cm yr⁻¹ for the topmost 55 cm (¹³⁷Cs dating method) and the loss-on-ignition (LOI) remains constant in the range of 13%–14% from the depth of 20 cm upwards. This layer represents sediment accumulation from the mid-1970s, i.e., deposition after the removal of the wastewater inputs to the bay. Therefore, we focused our analysis of the sediment on the top 20 cm.

According to the national classification scheme by the Finnish Environment Institute, the water quality of the bay before coastal seawater...
was pumped into it was poor (analysed between 2000 and 2003; see Kajaste 2003). The water was turbid throughout the year as a result of sediment entering the bay from the Vantaanjoki (Fig. 1) during flooding periods and plankton biomass developing during the summer months. The O$_2$ state remained relatively good as a result of mixing (shallow bay and windy area) but dead algae caused O$_2$ deficiencies near the bottom sediments in late summer (Kajaste 2003). The benthic fauna is clearly dominated by Chironomidae followed by Oligochaeta, Marenzelleria spp. and Potamopyrgus antipodarum (Munne et al. 2008). Munne et al. (2008) reported an improvement in the water quality after the pumping had begun in 2005. Turbidity was reduced and the average summer nutrient concentrations decreased between 2005 and 2007. However, PO$_4^{3-}$ concentration decreased only from 0.55 to 0.51 µmol l$^{-1}$. During the summer months, N rather than P becomes the limiting nutrient for algal growth in the bay. From April to October 2000–2007, the monthly average ratio of dissolved inorganic N to dissolved inorganic P (DIN/DIP) was practically zero.

**Material and methods**

**Sediments**

Sediments were sampled twice, in May and in September 2007, at three locations in the bay (T$_1$, T$_2$, and T$_3$, Fig. 1) to a depth of 20 cm using a Limnos gravity corer. During both campaigns, redox potentials (SenTix ORP) and pH (SenTix Sur) in the sediment cores were monitored immediately after sampling. During the May campaign, sediment cores for metals and organic carbon analyses were sectioned into 1-cm subsamples from the depth intervals of 0–4, 9–10, 14–15, and 19–20 cm. The subsamples were frozen (–18 °C) after sampling. The total concentrations of total organic C (TOC) and total S (Stot) were determined with a LECO CNS-2000 analyser. Freeze-dried and homogenised sediment samples were analysed for total P, Fe, Al, and manganese (Mn) by inductively coupled plasma optical emission spectrometry (ICP-OES) after combined fluoric acid, aqua regia, and boric acid digestion (Leivuori 2000, modified from Loring and Rantala 1992).

**Phosphorus fractionation**

Six different chemical binding and solubility forms of sediment P were separated using a sequential extraction (Lukkari et al. 2008: table 1; see also Jensen and Thamdrup 1993, Lukkari et al. 2007a, 2007b) with the following steps:

1. NaCl-iP: loosely-bound and pore-water P extracted with sodium chloride,
2. NaBD-iP: P bound to hydrated oxides of Fe extracted with sodium dithionite in bicarbonate buffer (pH 7),
3. NRP: P from labile organic matter extracted with sodium hydroxide,
4. NaOH-iP: P from hydrated oxides of non-reducible metals, mainly Al, extracted with sodium hydroxide,
5. HCl-iP: apatite P extracted with hydrochloric acid,

The sediment cores for the P fractionation taken from the same depth intervals as the cores for total P and metals and organic carbon were transported tightly-capped to the laboratory before being cut into 1-cm sections (see ‘Sediments’ above) under N$_2$. For each sampling site, the subsamples from two cores were pooled and sealed into a plastic container in N$_2$ atmosphere, vacuum-packed into gas-tight plastic bags (with N$_2$ as the shielding gas), and stored at +5 °C until analysis. Handling of sediment samples and the first two steps of the extraction procedure were carried out in N$_2$ atmosphere in a glove box (keeping the O$_2$ content below 5%) because the influence of atmospheric O$_2$ has been shown to cause serious errors in P fractioning (Lukkari et al. 2007b). The extracts were analysed spectrophotometrically for PO$_4^{3-}$ (detection limit 0.05 µmol l$^{-1}$) and P$_{tot}$ using the molybdenum-blue method (Koroleff 1983). In addition, the extracts from the NaBD-iP and NRP assays (steps 2 and 3, see above) were analysed for total soluble Fe, Mn, and Al by ICP-OES.
Pore-water analyses

Pore water from the sediment samples was collected using centrifugation and equilibration. For centrifugation, applied to samples taken from sites T1, T2 and T3 in May and T1 in September, the sediment cores were handled under N2 atmosphere. The cores were sectioned into 1-cm subsamples from the depth intervals of 0–10 cm and 2-cm subsamples from the depths 10–20 and 24–26 cm. The subsamples were sealed in a plastic container and vacuum-packed into gas-tight plastic bags (with N2 as the shielding gas) prior to their transfer under N2 atmosphere into centrifugation tubes. The samples were centrifuged for 30 min at 3000 rpm, after which supernatants were filtered, under N2 atmosphere, using a membrane with a pore size of 0.40 µm and placed into acid-washed sample bottles. The bottles were closed tightly and frozen at –20 °C until analysis.

In the equilibration method, a device made of Plexiglas™ cells based on Hesslein’s design (1976) was used at sites T2 and T3 in September. The device consisted of 27 to 30 cells covered with a nitrocellulose transfer-membrane (pore size 0.2 µm) and filled with deoxygenated water. The cells were placed in the sediments for a minimum of 4 days. Immediately after the device had been taken out of the water, 4 ml of water was extracted from the 14-ml cells and 4 µl of H2SO4 (4M) was added. This step allowed the sample to be preserved and the soluble Fe (SFS 3028 1976) and soluble Mn (SFS 3033 1976) to be determined. The rest of the sample (not acidified but filtered) was stored at +4 °C for 24 h before the analysis of NH4+ (detection limit 1 µmol N l–1; SFS-EN ISO 11732 2005) and PO4\textsuperscript{3–} (detection limit of 1 µmol P l–1; SFS-EN ISO 15681-1 2005), and thereafter frozen at –20 °C until the SO4\textsuperscript{2–} analysis which was carried out using an ionic chromatographer ICS-1500 (column IonPac AS9-HC; SFS-EN ISO 10304-1 1995). This method is fast enough to prevent oxidation of ferrous Fe into the insoluble ferric Fe. Results from these analyses were thus used to compare soluble Fe, PO4\textsuperscript{3–} and SO4\textsuperscript{2–}.

Flux measurements

In situ measurements of nitrate (NO3\textsuperscript{−}), PO4\textsuperscript{3–}, and O2 fluxes at the sediment–water interface were carried out using a benthic chamber at all locations (T1, T2, and T3; Fig. 1) in September 2007. The chamber enclosed 15 l of water above 0.12 m² of sediments. The water in the chamber was circulated through a pump, the O2 was measured in situ using a dissolved oxygen meter (YSI 550A) and water samples were taken every 30 min over a period of 4 to 5 h. The total volume of samples taken accounted for less than 2% of the initial volume in the chamber.

In the laboratory, the release of PO4\textsuperscript{3–} and soluble Fe during hypoxic (O2 < 0.01 mmol l\textsuperscript{−1}) conditions was measured at the in situ temperature. Two cores were collected during the September campaign. N2 gas was gently bubbled to provoke hypoxic conditions in the water and mix the water column without disturbing the sediment–water interface. Water samples were collected periodically during the experiment and analysed in the laboratory for PO4\textsuperscript{3–} and soluble Fe after filtration through a membrane with a 0.45-µm pore size.

Statistical analyses

We used Pearson’s correlation (rP) to detect dependence between two variables. Unless otherwise stated, the coefficients were calculated using the data from the three locations and the two sampling campaigns. We further used a paired t-test to determine seasonal changes of a variable between May and September at a single location. A paired t-test gives an indication of how separate two sets of measurements are when the data from the two groups can be presented in pairs. Normality of the data was verified with the Shapiro-Wilk test.

Results

Sediment properties

The sediments sampled from the bay were fluffy at the top, with porosity decreasing with depth from 0.9 at the surface to 0.75 at the depth of 15 cm (rP = –0.77, n = 21, p < 0.001). The brown oxidised layer was about 2 cm thick. Black sec-
tions and dots were observed in the sediments below 5–10 cm, and also on the surface of the sediments. At all sites, pH in the sediments decreased significantly with depth from 7.5 at the surface to 7.0 at the depth of 10 cm ($r_p = -0.61$, $n = 66$, $p < 0.001$). However, the TOC concentration did not vary significantly with sediment depth (Fig. 2). Redox potential in the sediments decreased significantly with depth ($r_P = -0.76$, $n = 64$, $p < 0.001$) and from May to September at sites T2 (paired $t$-test: $t_9 = 12.96$, $p < 0.001$) and T3 (paired $t$-test: $t_{10} = 23.67$, $p < 0.001$).

Phosphorus and nitrogen

At all sites, the total P concentration in the sediment decreased with depth, from 65 µmol g$^{-1}$ DW at the depth of 0–5 cm to 50 µmol g$^{-1}$ DW at 10–20 cm ($r_p = -0.59$, $n = 42$, $p < 0.001$; see also Fig. 2). On average, over the entire depth profile, $P_{tot}$, was distributed almost equally between various solid-phase fractions (Res-P, HCl-iP, NaBD-iP, NaOH-iP, and NRP; excluding NaCl-iP) (see Fig. 3). However, in contrast to Res-P, HCl-iP and NRP that did not significantly vary with depth, the concentration of NaBD-iP decreased ($r_p = -0.88$, $n = 42$, $p < 0.001$), whereas the concentrations of NaOH-iP and NaCl-iP significantly increased with depth ($r_p = 0.62$, $n = 42$, $p < 0.001$; and $r_p = 0.62$, $n = 42$, $p < 0.001$; respectively). NaBD-iP was correlated with $PO_4^{3-}$ ($r_p = -0.89$, $n = 92$, $p < 0.001$; and $r_p = -0.86$, $n = 92$, $p < 0.001$; respectively), whereas $PO_4^{3-}$ was strongly positively correlated with $NH_4^+$ ($r_p = 0.96$, $n = 95$, $p < 0.001$).

Iron, sulphur, manganese and aluminium

Concentration of total Fe did not change with depth (900–1000 µmol Fe g$^{-1}$ DW). However, reductant-soluble Fe [(i.e. Fe in the NaBD extract (Fe-NaBD)] decreased significantly with depth ($r_p = -0.70$, $n = 42$, $p < 0.001$). At all sites, the concentration of soluble Fe increased up to a
Fig. 3. P fractionations in sediments at the three sites in Töölönlahti in May and September. Res-P (residual, mainly recalcitrant organic P), HCl-iP (apatite-P), NaBD-iP (P bound to hydrated oxides of Fe), NRP (P in labile organic matter), NaOH-iP (P bound to hydrated oxides of non-reducible metals, mainly Al), and NaCl-iP (loosely-bound and pore water P).

peak value located around the depth of 5 cm and reached a maximum concentration of up to 200 µmol l⁻¹ at site T₃ in September (Fig. 5).

Regarding the behaviour of total S (S₅₀₂) and SO₄²⁻ at different depths, we found that the concentration of SO₄²⁻ significantly decreased
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Fig. 5. Soluble iron concentration profiles in the sediment pore water at locations T1, T2, and T3 in May and September.

Soluble iron concentration profiles in the sediment pore water at locations T1, T2, and T3 in May and September. (r_p = -0.79, n = 92, p < 0.001; see also Fig. 4), whereas the S_{tot} concentration significantly increased (r_p = 0.92, n = 21, p < 0.001) with depth. At the surface of the sediments, the SO_{4}^{2-} concentration was \approx 4000 \mu mol l^{-1}, decreasing to \approx 1000 \mu mol l^{-1} at the depth of 20 cm. S_{tot} concentration increased from 350 \mu mol g^{-1} DW at the surface to 1000–1200 \mu mol g^{-1} DW at the depth of 20 cm. When the concentration of SO_{4}^{2-} was below 3000 \mu mol l^{-1}, soluble Fe and PO_{4}^{3-} were strongly correlated with SO_{4}^{2-} (September campaign, equilibration method, T2 and T3 only r_p = 0.96, n = 24, p < 0.001; and r_p = -0.91, n = 24, p < 0.001; respectively). Moreover, PO_{4}^{3-} was significantly correlated with soluble Fe (T2 and T3 only r_p = -0.85, n = 24, p < 0.001). Soluble Fe reached a peak concentration in the pore water at SO_{4}^{2-} \approx 3000 \mu mol l^{-1}, whereas the PO_{4}^{3-} increase started at SO_{4}^{2-} \approx 2000 \mu mol l^{-1} when the soluble Fe concentration decreased by half.

The total Mn and reducant-soluble Mn (i.e. Mn in the NaBD-extract) were 100-fold lower than the total Fe and Fe-NaBD, respectively. Moreover, soluble Mn in pore water decreased significantly with depth (r_p = -0.34, n = 95, p < 0.001) and varied between 1 and 7 \mu mol l^{-1}. The total Al concentration did not change with depth and ranging from 2400 to 2750 \mu mol g^{-1} DW. At the surface, the average molar ratio of Al-NaOH/Fe-NaBD (i.e. Al in the NaOH-extract) was 3, whereas the molar ratio of Al-NaOH/(NaCl-iP + NaBD-iP) was 7.

Benthic fluxes

The data from Töölönlähti allowed us to compare P fluxes from in-situ measurements with those calculated using a mass-balance approach. The results from the in-situ benthic-chamber experiments during the September campaign revealed an active sediment with an average O_{2} and NO_{3}^{-} consumption of \approx 23 mmol O_{2} m^{-2} d^{-1} and \approx 32 \mu mol N m^{-2} d^{-1}, respectively, over the three locations. Phosphorus, on the other hand, was released from the sediments at an average (three locations) rate of 51 \mu mol P m^{-2} d^{-1}. During the experiment under artificially created hypoxic conditions, 1100–1300 \mu mol P m^{-2} d^{-1} was released from the sediments.

The phosphorus fluxes from the sediments can also be calculated from solid-phase data using a mass-balance approach similar to Krom and Berner (1981), either for P_{tot} or reactive phosphorus from the fractionation data. The average difference in the concentration of P_{tot}, over the three locations, between the surface and the layer at the 15-cm depth was 10 \mu mol g^{-1} DW in May and 15 \mu mol g^{-1} DW in September. We considered a dry density of the sediments equal to 2.5 g cm^{-2}, a sedimentation rate of 0.6 cm yr^{-1}, and a porosity of 0.9 (at the surface). Using the Krom and Berner (1981) approach, we obtained sediment P fluxes of 42–62 \mu mol m^{-2} d^{-1}. Using the fractionation data, we could separate the immobile fraction from the reactive fraction and use only the change in the latter to calculate the long-term P release from the sediment (between the surface and the layer at 15 cm depth). In this approach, we calculated that P fluxes varied between 33 and 113 \mu mol m^{-2} d^{-1}.

Discussion

Importance of sediment processes for the water quality

High molar ratios of organic carbon and nitrogen (TOC/TON = 13–15) and organic carbon and
phosphorus (i.e., the sum of Res-P and NRP) (TOC/TOP = 210–300) in the surface layer of the sediments indicated a high input of terrestrial material (Ruttenberg and Goñi 1997, Carman 1998) into the bay (sediment accumulation rate ~1500 g m m–2 yr–1). The sediments of the bay had similar TOC/TON and TOC/TOP as an organic-rich estuary in the eastern GoF (Ahvenkoskenlahti; Lukkari 2008). As a consequence of the high organic matter concentration in the top sediments (TOC = 65–75 g kg–1 DW), O2 consumption (~23 mmol m m–2 d–1) was registered at the sediment surface. Moreover, redox potentials were found to strongly decrease with depth which was associated with a typical reduction-induced colour change [light brown at the top (oxidised) and black deeper down (reduced)].

NRP increased at the surface of the sediment between May and September at stations T1 and T2. This increase could represent the settling of dead algae at the end of the summer, increasing the organic matter, and therefore the organic-P pool, at the top of the sediments. Mineralisation of NRP contributes to the increase of the pore water PO4 3– concentration. During early diagenetic processes, mineralisation of the organic matter releases NH4+ and PO4 3– into the sediment pore-water, which could also explain a strong correlation between PO4 3– and NH4+.

Ptot concentrations in the sediments of the bay (~50 µmol g–1 DW at a depth of 15 cm, and 65 µmol g–1 DW at a depth of 0–1 cm) were within the range of Ptot concentrations in the GoF (averaged over the GoF: 45 µmol g–1 DW in the topmost 25-cm, but 67 µmol g–1 DW at the sediment surface (0–1 cm); Lukkari 2008). In the Töölönlahti sediment, ~20% of the total extractable P in the surface sediments was in forms that could in the long term be released to the water column. As a comparison, in the surface sediments of the GoF corresponding percentages ranged from 10% to 50% (Lukkari 2008). Therefore, Töölönlahti represents an organic-rich brackish-water environment with active, early diagenetic processes potentially influencing the water quality by e.g. consuming oxygen and releasing phosphate and ammonium to the water column. This highlights the importance of including sediment geochemistry into the water quality modelling.

**Phosphorus fluxes**

Sensitivity of the sediments to variable O2 conditions was clearly shown by the difference between the P fluxes measured in situ (~50 µmol m m–2 d–1) and during an artificially-created anoxia (1100–1300 µmol m m–2 d–1). In our experiment, P release rate was at its maximum over 20 times higher during artificial anoxia than when the water above the sediment remained oxic. Similar values were reported by e.g. Boström et al. (1982). However, the laboratory experiment might have overestimated the P flux because of the intensive deoxygenation and disturbance of the sediment structure by the core walls. When we calculated the P loss in terms of Ptot and reactive P reserves of the sediments with depth, the long-term P effluxes were 42–62 µmol m–2 d–1 and 33–113 µmol m–2 d–1, respectively. These values were in the range of our direct measurements in the field (~50 µmol m–2 d–1), whereas the differences were considerably larger when the values were compared with those obtained under artificially-created anoxia in the laboratory. All our results were within the broad range of P fluxes derived from incubation flux measurements in the GoF (Conley et al. 1997: 38 to 684 µmol m–2 d–1, Lehtoranta 2003: –6 to 1000 µmol m–2 d–1, Lukkari 2008: –245 to 1774 µmol m–2 d–1).

During a low-O2 event (down to 0.18 mmol l–1 at 1-m depth) which took place in Töölönlahti in August 2002, high chlorophyll-a and PO4 3– concentrations were measured in the water (Fig. 6). During the year 2002, PO4 3– in the water column increased with decreasing oxygen levels (rP = –0.57, n = 30, p < 0.001; calculated using the data provided by the Environment Centre of the City of Helsinki). The water (and PO4 3–) input from the GoF to the bay could not justify the elevated PO4 3– levels, as water was flowing out of the bay at the time (decreasing water levels in the GoF; Fig. 6). Instead, it could only be explained by the internal PO4 3– loading from the sediments of the bay. During this event, over a two-week period the concentration of PO4 3– in the bay increased abruptly (Fig. 6) by more than 1 µmol l–1. A similar increase has been reported in the Gotland Basin (~2 µmol l–1; Emeis et al. 2000) and linked to the iron-bound
P liberated during the anoxic event. Similarly, Mort et al. (2010) demonstrated that P release from seasonally hypoxic sediments in the Baltic is due to Fe-P release.

In addition to the rapid release of \( \text{PO}_4^{3-} \) during anoxic turnover, it was slowly released from the sediments of the bay during oxic conditions in the water column. Although, it is interesting to notice that the diffusive fluxes across the sediment–water interface, calculated using Fick’s first law and the pore-water \( \text{PO}_4^{3-} \) concentrations, were close to zero. Therefore, under oxic conditions, the release of P could be explained by bioirrigation. We did not collect benthic fauna during sampling campaigns but indirect evidence strongly supports this conclusion. The \( \text{NH}_4^+ \) profiles from the Töölönlahti sediments present a typical bioirrigation shape (Boudreau and Marinelli 1994). Maximum depth of bioturbated sediment changed from 15 cm to 8 cm between May and September (Fig. 4). This depth is similar to the maximum penetration depth of bioturbation (15 cm) in the soft-bottom sediments surrounding the Åland islands (Bonsdorff et al. 1996). In the Åland islands sediments, Macoma balthica, amphipods, polychaetes and chironomid larvae are responsible for bioturbation (Bonsdorff et al. 1996). The shrinking of the bioturbated layer can be partly explained by the disappearance of the dominating species, chironomid larvae, from the sediments during the summer months. Bioirrigation oxidizes the surface sediments improving their ability to bind P but it can also mix dissolved \( \text{PO}_4^{3-} \) from the pore-water of deeper reduced layers to the sediment surface (e.g. Hietanen et al. 2007). Therefore, the availability of oxygen in the water column and hydrated iron oxides at the sediment surface controlled but could not completely prevent the phosphate release from the sediment.

**Iron, sulphur and phosphorus**

Under anoxic conditions, soluble iron is usually in the ferrous state [Fe(II)]. Therefore, we assumed that soluble Fe in the sediment pore-water represented Fe(II). Usually, the Fe(II) peak is located near the transition zone between the oxidised and reduced conditions (e.g. Carman and Rahm 1997). In the sediment of the bay, the peak of Fe(II) was observed between 0 and 5 cm. The strong relationship (below a sulphate concentration of 3000 \( \mu \text{mol l}^{-1} \)) between \( \text{SO}_4^{2-} \) and Fe(II) supported our assumption that iron oxides were reduced to Fe(II), and \( \text{SO}_4^{2-} \) was transformed into \( \text{S}^{2-} \) that further precipitated Fe(II) into FeS or FeS\(_2\) (black sections below a depth of 5 cm). This is in accordance with the increase of the solid-phase S pool (see Results). Moreover, phosphate was strongly correlated with \( \text{SO}_4^{2-} \) and Fe(II) in the sediments of the bay (see Results). The reduction by half of the Fe(II) ions in the sediment pore water coincided with the increase in the \( \text{PO}_4^{3-} \) concentration and the subsequent decrease in the reactive P fractions, mainly that of Fe-bound P in the sediments. In fact, Fe-bound P (NaBD-iP) was correlated with \( \text{PO}_4^{3-} \) and \( \text{SO}_4^{2-} \) (see Results). Under anoxic conditions, \( \text{SO}_4^{2-} \) can become a predominant oxidant, and its reduced form \( \text{S}^{2-} \) can, in turn, rapidly precipitate Fe(II) (Rickard 1995), consequently reducing its concentration in the pore-
water and its capacity to be oxidised again and bind P (Figs. 4 and 5, also see Results). Therefore, the P-binding ability of the sediments in our study area was also dependent on the diagenetic sulphate reduction, as noted by e.g. Caraco et al. (1989). Interaction between Fe(II) and S\(^{2-}\) indirectly supports also P release in oxic conditions, because built up of PO\(_4^{3-}\) in the pore water keeps it vulnerable for bioirrigation-induced mixing to the water column.

In brackish sediments, sulphate reduction is the predominant pathway of anaerobic metabolism (Jørgensen 1982) whereas in freshwater sediments, methanogenesis is predominant (Capone and Kiene 1988). Caraco et al. (1989) suggested that SO\(_4^{2-}\) competition with PO\(_4^{3-}\) for anion sorption sites can be an important mechanism when SO\(_4^{2-}\) concentrations in the water column are above 3000 µmol l\(^{-1}\), as in our study, and that elevated pH resulting from SO\(_4^{2-}\) reduction can explain the reduction in P sorption onto Fe-oxyhydroxides. However, anions of weak acids (for example, phosphate and silicate) are much more effective in binding onto the surfaces of metal oxyhydroxides via ligand-exchange reaction than anions of strong acids, such as SO\(_4^{2-}\) (Hingston et al. 1967). Moreover, in our study, the concentration of PO\(_4^{3-}\) continued to increase in the pore-water of the sediments when SO\(_4^{2-}\) decreased below 1000 µmol l\(^{-1}\) and the pH decreased with depth in the sediments of the bay. Therefore, we concluded that in this brackish bay, binding of Fe by S\(^{2-}\) was the main mechanism by which SO\(_4^{2-}\) inhibits P uptake by sediments.

Bioirrigation and bioturbation

Bioirrigation and bioturbation increase the surface of the oxic–anoxic boundary in the sediments and affect biogeochemical reactions in several ways (Aller 1988). For example, increasing solute exchange between the surface water and the sediment pore-water (Revsbech et al. 1980) and mixing particulate species in the top layers of the sediments (Mermillod-Blondin et al. 2004). Oxygen is transported to deep sediments (down to 5–15 cm depth) by bioirrigation rather than molecular diffusion or turbulence (Revsbech et al. 1980). Activity of benthic fauna redistributes the organic matter deposited onto the surface to deeper sediments, increases microbial activity (Aller 1988), and increased availability of oxygen in the sediments enhances aerobic degradation of the organic compounds (Kristensen 1988). Mixing of oxidized particulate species in reduced sediment layers can, for example, result in reduction-induced P release from hydrated oxides of Fe (Lewandowski and Hupfer 2005). Contrary, recycling of reduced species formed during anaerobic respiration — e.g. Fe and manganese ions as well as sulphides — is increased in the sub-oxic zone by their placement in contact with oxidized species (Berner and Westrich 1985). Lewandowski and Hupfer (2005) analysed the impact of macrozoobenthos on pore-water phosphate concentrations in lake sediments and found that they were mainly redox-controlled by association of P with Fe oxyhydroxides precipitating along oxidized burrow walls, and not a consequence of mineralization processes occurring in organic-rich “hot spots” of increased P turnover.

The burrowing and irrigation activity and depth of the benthic fauna varies through the year depending on the feeding type, mobility and life cycle of the species (Kristensen 1988). Chironomidae, the dominating benthic species in Töölölähti, can catapult the water they filter far into the overlying water (Morad et al. 2010) and burrow down to 20 cm depth (Gingras et al. 2007). In our study, the bioirrigated layer of the sediments shrank in the autumn when relatively deep-burrowing chironomids had left. Thus, less oxygen reached the deep layers of the sediments. When Chironomidae return and deepen the bioirrigated layer again, the release of dissolved nutrients like PO\(_4^{3-}\) may temporarily increase before the increased amount of oxidized Fe species start to bind PO\(_4^{3-}\) in the bioirrigated surface sediments.

In 1996, Boudreau showed, with an early diagenetic model, that a simulation of organic matter degradation with bioirrigation, reduced the percentage of organic matter degraded by SO\(_4^{2-}\) as compared with a simulation without bioirrigation. Boudreau (1996) explained this with the increasing share of stronger oxidants (oxygen, nitrate, iron oxides and manganese
oxides) that are renewed more quickly under bioirrigation. However, for a sedimentation rate of 0.3 cm yr⁻¹, SO₄²⁻ remained the predominant oxidant of the organic matter even in the irrigated simulation. In our study, the sedimentation rate was double that in Boudreau’s model. Therefore, we assumed that SO₄²⁻ reduction played a major role in the degradation of the organic matter in the bay even under important bioirrigation activity.

Bioirrigation in the sediments of Töölönlähti likely controlled the depth of oxygen penetration and redox conditions, increasing the oxic degradation of the organic matter. However, SO₄²⁻ remained an important oxidant and its reaction with Fe led to the increase of pore-water PO₄³⁻ concentrations in the reduced sediment layers.

**Manganese and aluminium**

Considering the low reductant-soluble Mn concentrations in the sediments we assumed that oxides of Mn did not play as significant role in phosphorus binding in Töölönlähti as hydrated oxides of Fe. For example, Carman (1998) made the same conclusion for the sediments of the GoF. The total Al and Al bound-P (NaOH-iP) concentrations in the sediments of the bay were comparable to those found in some estuary environments in the GoF (NaOH-iP: 3.1–17.5 µmol g⁻¹ DW; Lukkari et al. 2008, 2009a, 2009b). P bound to Al-oxides is not sensitive to redox conditions but pH (Psenner et al. 1984, Portielje and Lijkelma 1993) and therefore provided a relatively permanent storage of P in the sediment as it increased with depth. Kopáček et al. (2005) used the Al-NaOH/Fe-NaBD and Al-NaOH/(NaCl-iP + NaBD-iP) ratios to describe the sensitivity of the sediments to P release during anoxic events. They also suggested, that surface sediments are sensitive to anoxic events if the molar ratios of Al-NaOH/Fe-NaBD, and simultaneously Al-NaOH/(NaCl-iP + NaBD-iP), are below the threshold values of 3 and 25, respectively. Therefore, following Kopáček et al. (2005), the sediments of Töölönlähti were sensitive to P release during hypoxia. In fact, according to this approach, in the GoF area (estuary, coastal, and open sea) all surface sediments would be sensitive to anoxic conditions (Lukkari 2008). However, the research by Kopáček et al. (2005) used the data from freshwater sediments rich in Al, up to 1400 µmol g⁻¹ DW compared with ~150 µmol g⁻¹ DW in our study. Therefore, sensitivity of Töölönlähti and GoF sediments to P release under anoxic conditions can also be partly explained by the low concentration of Al that is not sensitive to reduction. Fe oxy-hydroxides and their sensitivity to fluctuating oxygen conditions played a key role in binding P in the sediments.

**Conclusion**

In the organic-rich, low-salinity water bay presented in this study, phosphate (PO₄³⁻) release from the sediment was determined by high input of organic matter, fluctuating oxygen conditions, as well as iron (Fe) and sulphur (S) chemistry. Anoxic conditions in the near-bottom water were responsible for the rapid release of abundant Fe-bound PO₄³⁻ into the overlying water, as was observed in one event in the field and during artificially created anoxia in the laboratory. The release of phosphorus (P) from the Töölönlähti sediments was clearly sensitive to oxygen conditions in the near-bottom water. The availability of hydrated Fe oxides in the sediments was subject to the re-oxidation of upward diffusing ferrous Fe in the pore water by oxygen. Sulphides (S²⁻) produced during sulphate (SO₄²⁻) reduction can reduce the recycling of Fe into hydrated Fe oxides by precipitating Fe as ferro-sulphides. However, P was released from the sediment also during oxic conditions. This phenomenon was explained by organic-P mineralisation and the burrowing activity of benthic fauna in the bay. The fauna bioirrigated the sediments and mixed dissolved P in the pore water of the reduced layers to the surface. In organic-rich, low salinity environments, located at the crossroads of fresh and brackish waters, i.e. affected by high riverine input and by an increasing availability of SO₄²⁻, the complex early diagenetic processes of P, Fe and SO₄²⁻ can affect the release of P bound to the sediments. These interactions, as well as the effect of bioirrigation, should be included in water quality models to improve the short-term
prediction of the water quality. Indeed, they are essential in predicting the dynamics of algal blooms in the shallow bays of the Gulf of Finland (Baltic Sea), where P plays a key role in the eutrophication process, enhancing especially the Cyanobacteria growth.

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