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JOUNI LEHTORANTA

Dynamics of sediment phosphorus in the brackish  
Gulf of Finland

MONOGRAPHS  
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Boreal Environment Research

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MONOGRAPHS OF THE BOREAL ENVIRONMENT RESEARCH

**24**

Jouni Lehtoranta

**Dynamics of sediment phosphorus  
in the brackish Gulf of Finland**

Yhteenveto: Fosforin vapautuminen pohjasedimentistä Suomenlahdella

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## List of original publications and author's contribution

This study synthesizes the following original publications, which are referred to by their Roman numerals in the text. The author's contribution is given separately for each article. Previously unpublished results are also presented.

**I** Lehtoranta J., Pitkänen H. and Sandman O. 1997. The sediment accumulation of nutrients (N,P) in the eastern Gulf of Finland (Baltic Sea). *Water, Air and Soil Pollut.* 99: 477–486.

**II** Lehtoranta J. 1998. Net sedimentation and sediment-water nutrient fluxes in the eastern Gulf of Finland (Baltic Sea). *Vie et Milieu* 48: 341–352.

**III** Pitkänen H., Lehtoranta J. and Räike A. 2001. Internal nutrient fluxes counteract decreases in external load: the case of the estuarial eastern Gulf of Finland. *Ambio* 30: 195–201.

**IV** Lehtoranta J. and Heiskanen A.-S. 2003. Dissolved iron:phosphate ratio as an indicator of phosphate release to oxic water of the inner and outer coastal Baltic Sea. *Hydrobiologia* (in press).

**V** Lehtoranta J. and Pitkänen H. 2003. Binding of phosphate in sediment accumulation areas of the eastern Gulf of Finland, Baltic Sea. *Hydrobiologia* (in press).

**VI** Lehtoranta J., Heiskanen A.-S. and Pitkänen H. 2003. Particulate N and P characterizing the fate of nutrients along the estuarine gradient of the River Neva (Baltic Sea). Submitted manuscript.

Author's contribution to the papers:

**I** J. Lehtoranta was responsible for the examination of previously unpublished data (sediment nutrient concentrations in the eastern Gulf of Finland) and for performing the data analysis. The paper was written jointly by J. Lehtoranta, Heikki Pitkänen and Olavi Sandman.

**II** J. Lehtoranta is fully responsible for this paper.

**III** The study was planned by H. Pitkänen and J. Lehtoranta. Antti Räike was responsible for the data processing and H. Pitkänen wrote the paper. J. Lehtoranta was responsible for the sediment analyses and nutrient flux measurements and for the interpretation of those results.

**IV** J. Lehtoranta and Anna-Stiina Heiskanen planned the study. J. Lehtoranta carried out the sediment analyses, benthic flux measurements and data processing. He also wrote the paper, which was commented on by A.-S. Heiskanen.

**V** The study was planned by J. Lehtoranta and H. Pitkänen. J. Lehtoranta wrote the paper, which was commented on by H. Pitkänen.

**VI** All authors (J. Lehtoranta, A.-S. Heiskanen, H. Pitkänen) took part in the planning of the study. J. Lehtoranta did the data processing and wrote the paper, which was commented on by A.-S. Heiskanen and H. Pitkänen.

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## **List of abbreviations**

AAS	Atomic absorption spectrophotometry
Al-P	Al-bound P extracted with $\text{NH}_4\text{F}$
Ca-P	Ca-bound P extracted with $\text{H}_2\text{SO}_4$
DFe	Dissolved iron
DIN	Dissolved inorganic nitrogen
DIP	Dissolved inorganic phosphorus
DM	Dry mass
DP	Dissolved phosphorus
DUP	Dissolved unreactive phosphorus
Fe-P	Fe-bound P extracted with NaOH
LOI	Loss on ignition
POC	Particulate organic carbon
PON	Particulate organic nitrogen
PTP	Particulate total phosphorus
TPM	Settling total particulate matter
TFe	Total iron
TN	Total nitrogen
TP	Total phosphorus

# Dynamics of sediment phosphorus in the brackish Gulf of Finland

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*Lehtoranta, J. 2003. Dynamics of sediment phosphorus in the brackish Gulf of Finland, Monographs of the Boreal Environment Research No. 24, 2003.*

One of the main threats facing the Baltic Sea is eutrophication due to an excess supply of nutrients. In the Gulf of Finland, primary productivity and biomasses of autotrophic and heterotrophic organisms are among the highest in the Baltic. The high biomasses are attributed mainly to the eutrophying effects of the large land-derived nutrient inflow from St. Petersburg and via the River Neva. The role of sediment phosphorus (P) in eutrophication is, however, poorly understood in the Gulf. The aim of this study was to obtain information on the regional levels of sediment P and to specify the pools of P. Efforts were also made to define the sediment retention ability of P along the estuarine gradient, to establish the factors that affect the benthic flux of P and to assess whether sulphur (S) is a significant factor in sediment P cycling. On the basis of the results it was possible to quantify and consider the ecological implications of the benthic flux of P. The sediments of the Gulf are rich in organic matter, nitrogen (N) and P. A large portion of the mobile pool of P in these sediments consists of iron (Fe)-bound P, which is released when Fe(III) oxides are reduced under anoxic conditions. The increase in the sediment organic matter concentration along the estuarine gradient seems to impair the sediments' ability to retain P. The highest benthic P efflux was measured in summer and the lowest in winter. The decrease in the near-bottom oxygen concentration in summer may favour anaerobic sulphate reduction followed by iron sulphide (FeS) formation close to the sediment-water interface. In the sediment, the key role in preventing P from entering the water is played by the binding ability of P related to diffusing Fe. In the brackish Baltic Sea, in contrast to most lake systems, the diffusion of Fe may be inactivated by FeS formation. Thus, high effluxes of P to oxic water were measured on bottoms where black sediment indicating the presence of FeS extended to the surface of the sediment. The P released from the sediments of the Gulf itself may largely explain the high P concentrations and low N:P ratios in near-bottom waters in summer and, after autumn mixing, in the entire water column. However, the input of P from the main Baltic basin may also lead to an increase in P concentrations in the Gulf. The high release rates of P measured – rather than denitrification – largely explain the N limitation of the primary production. A relationship seems to exist between the increase in near-bottom salinity and the weakening of the sediment oxidation state of the Gulf since 1996. The inflow of saline water to the Gulf strengthens density stratification, thus favouring the release of P to water. Therefore, the variations in hydrological factors may produce a marked between-year variation in the benthic P efflux and counteract the reduction in the external P load. The ability of sediment to retain P could most likely be promoted by decreasing the sedimentation of labile organic matter on the bottom. Organic matter sedimentation could be lowered by cutting the amount of bioavailable N and P from an anthropogenic sources.

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**Keywords:** eutrophication, sedimentation, sediments, pore water, nutrients, phosphorus, nitrogen, iron, benthic flux, internal loading, River Neva, Gulf of Finland, Baltic Sea

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## 1 Introduction

### 1.1 Background

Eutrophication, *i.e.* an excess supply of nutrients leading to increased biological productivity, is considered one of the main problems in aquatic environments (Boers and van der Molen 1993). Phosphorus (P) in the form of phosphate ( $\text{PO}_4^{3-}$ ) is an important nutrient in eutrophication and a limiting nutrient for primary production in most lakes and many estuaries (Fisher *et al.* 1995). Furthermore, when nitrogen (N) is the limiting nutrient in water, a high concentration of P relative to that of N enhances N fixation by blue-green algae (Smith 1983).

Eutrophication increases the amount of new particulate organic matter in water and the subsequent sedimentation. In estuaries, coastal areas and shallow open sea areas a large portion of the autochthonous – and allochthonous – particulate organic matter reaches the surface of the bottom sediment. Organic matter and nutrients and their processes in sediments therefore play an important role in the nutrient dynamics of these systems. Increased concentrations of sediment organic matter leading to higher sediment  $\text{O}_2$  consumption and the eventual depletion of dissolved  $\text{O}_2$  in bottom water are a common consequence of eutrophication. The exhaustion of  $\text{O}_2$  weakens the ability of sediments to retain nutrients, which further accelerates eutrophication.

The sensitivity of water masses to an excess nutrient load and subsequent eutrophication is largely determined by the geomorphological and hydrographic properties of an area. The longer the residence times of the water and the stronger the stratification due to changes in water density, the greater is the sensitivity. In the Baltic Sea, a brackish water body, the main factors controlling water density are temperature and salinity. These result in strong stratifications, namely thermocline and halocline, in the water column. As a consequence, the separate surface and deeper layers may prevent the mixing of  $\text{O}_2$ -rich surface water with the bottom water for years or parts of a year. Due to its unique stratification properties, the Baltic Sea is sensitive to hypoxia and the high release rates of P from the sediments (Conley *et al.* 2002).

Signs of increased eutrophication in the Baltic Sea are frequent outbreaks of harmful blue-green algal blooms (Kahru *et al.* 1994, Alg@line 2002) and changes in benthic communities in shallow

bottom areas owing to the growth of filamentous algae (Bonsdorff *et al.* 1991). Thus, it is likely that natural removal processes such as sedimentation and nutrient burial are not sufficient to retain the increased nutrient supply to the Baltic Sea (*e.g.* Rosenberg *et al.* 1990, Conley *et al.* 2002). Changes in hydrographic features affecting stratification in the Baltic Sea have an effect on biogeochemical processes in the sediments, which may, in turn, affect the pool of P in the water without changes in the external P load (Conley *et al.* 2002).

The Gulf of Finland is one of the most eutrophied parts of the Baltic Sea. The greatest external source of nutrients in the Gulf is the River Neva catchment, which includes the St. Petersburg region. Primary productivity and biomasses of auto- and heterotrophic organisms are therefore higher in the eastern than in the western part of the Gulf (Pitkänen *et al.* 1993, Kauppi *et al.* 1995, Pitkänen and Tamminen 1995). Further, dense accumulations of macroalgal mats have been reported from the easternmost part of the Gulf (Telesh *et al.* 1999). Under summer conditions, dissolved inorganic nutrients are fixed in new particulate organic matter (autochthonous production) in the euphotic zone of the water column within close range of the source. Therefore, maximum primary and secondary productivities and biomasses are usually found in the Neva estuary, where both physical and chemical conditions favour biological production. Due to recycling and secondary effects, however, the large nutrient load from the River Neva and the St. Petersburg region may increase the productivity of the whole eastern Gulf (Pitkänen *et al.* 1993). It has been suggested that N and P are efficiently retained in the Neva estuary (Pitkänen 1994) and that the role of the estuary is decisive in regulating the overall nutrient balance of the entire Gulf of Finland (Pitkänen and Tamminen 1995, Heiskanen *et al.* 1999).

Sediment P studies on the Gulf of Finland are sparse despite widespread knowledge of the high external P load and high trophic state of the Gulf. With the exception of small-scale studies of local interest (*e.g.* Töölönlahti Bay, Kymijoki estuary, harbour dredgings), few sediment P studies have, however, been published in the West. Even fewer studies related to P in sediments of the Gulf of Finland have been published in peer-reviewed

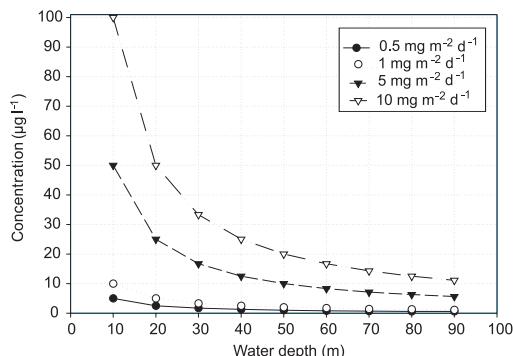
journals. The only recorded studies are those by Conley *et al.* (1997) and Ignatieva (1999), which give some sediment, pore water and benthic P flux data. A sampling site for the benthic P flux was also presented in the doctoral thesis of Stockenberg (1998), who focused on sediment N cycling.

Clearly, then, the fate of particulate P after sedimentation is poorly understood in the Gulf of Finland. Sediments are considered to act as “sinks” for particulate P. However, a portion of the P is released back into the water as a result of the biogeochemical processes undergone by settled particulate P during burial. The released P may significantly increase the biologically available pool of P in water, counteracting decreases in the external load. In terms of P in sediments, two issues are related to the fate of P: the fraction of settled P that will eventually be buried in the sediments, and the fraction of P that will be transformed into an available form, *i.e.* one that may potentially contribute to eutrophication, before permanent burial.

## 1.2 Origin of phosphorus in water

The bioavailable P in the water column is external in origin. External P derives from non-point (*e.g.* runoff from the drainage basin) and point sources (industrial and domestic effluents), groundwater seepage or atmospheric fallout. When P enters the aquatic system, internal processes affect the cycling of P in both water and sediment. In sediments some of the internal processes increase but some decrease the pool of bioavailable P in water. The benthic P efflux (“internal P load”) originates from bottom sediments when dissolved P is released from particles to the pore water and subsequently to the overlying free water. Note that the benthic P efflux can only be based on P transported from external sources. The present study concentrates on the release of dissolved P and thus does not cover the effect of resuspension (*i.e.* transport of settled particles back to the water column).

Sediments can, however, bind and release P. A net flux of P into sediments occurs when net sedimentation of P is above zero and P release is lower than gross P sedimentation. A net flux of P from sediment to water, in turn, occurs when net sedimentation of P is below zero and release is higher than gross P sedimentation. The flux in and out of the sediments may vary seasonally as well as between years, depending, among other



**Fig. 1.** Effect of benthic solute efflux ( $\text{mg m}^{-2} \text{d}^{-1}$ ) on concentration in water column above this square metre calculated for the 100 d time period.

things, on hydrological features. The retention of P in sediments is considered to be largely dependent on (1) net sedimentation of particulate P, (2) early diagenetic cycling and transformations of reactive P compounds, and (3) burial of immobilizable P compounds in deeper sediment layers (Boers *et al.* 1998).

The increase in the concentration of dissolved substances in water after their release is controlled by the flux rate of the substances from sediment to water and the volume of water. In a shallow area, for example, where the water depth is 10 m, an average flux rate of  $1 \text{ mg m}^{-2} \text{d}^{-1}$  during the summer period (100 d) increases the concentration of dissolved substances in the whole water column above this square metre to  $10 \mu\text{g l}^{-1}$  after complete mixing (Fig. 1). A similar increase in concentration is achieved at an average flux rate of  $5 \text{ mg m}^{-2} \text{d}^{-1}$  for water at a depth of 50 m. In the case of nutrients, the issue of whether the benthic flux is high or low depends on the consequences of the efflux related to primary production. For example, the bioavailable P released from the sediments contributes to new production, *i.e.* is a fraction of total primary production. In relatively shallow aquatic environments such as estuaries, continental shelves and bays, the P efflux may support a large proportion of total primary production (Callender 1982, Fisher *et al.* 1982). In the upper Potomac River estuary, for example, efflux of P can meet 27% of the gross primary production requirements (Callender and Hammond 1982). In Narragansett Bay, efflux of P contributes about 50% (Nixon 1981), in the Kiel Bight 20% (Balzer 1984) and

in Århus Bay, Denmark, 15% (Jensen *et al.* 1995) of the amount needed to support primary production. Owing to P released from the bottom, the total external load of P does not correspond fully to the pool of algal-available P in water. Thus, reducing the external load of P does not necessarily lead to rapid recovery of the system. In lakes, the benthic flux of P can temporarily equal or even exceed the input of P from external sources (Boström *et al.* 1985) and can delay recovery of the lakes for decades or even longer.

### 1.3 Binding of phosphorus in sediments

The phosphate ion ( $\text{PO}_4^{3-}$ ) is a highly particle-reactive molecule and thus the sorption properties of sediment are crucial for P-retention capacity. Generally, aerobic conditions are considered to promote P sorption and anoxic conditions to favour P release. After the dissolution of particulate P into inorganic form in sediments, P is easily sorbed into inorganic particulate form. The storage of surplus P by microorganisms can, however, compete with the chemical immobilization of P (Hupfer and Uhlmann 1991). Normal bacteria have a low P content in living cells ( $\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P}$ ) but some bacteria accumulate polyphosphate (poly-P) intracellularly in very large amounts, up to ~ 20% of their dry weight (Deinema *et al.* 1980). These bacteria store P under aerobic conditions and release intracellular P via enzymatic hydrolysis when conditions turn anaerobic (Deinema *et al.* 1985). In organic-rich lake sediments, microorganisms are able to take up and release P, depending on redox conditions, and sterilization of oxic sediments can reduce the microbial take up of P (Gächter *et al.* 1988). Microbial processes can govern the release of P in organic-rich sediments and in sandy sediments poor in metal oxides (Gächter *et al.* 1988, Van Duyl *et al.* 1993). Chemical mechanisms seem to control the release of P when high concentrations of metal oxides are present (Kairesalo *et al.* 1995). However, both nonbiological and biological binding mechanisms of P are able to keep the pore water P concentration low and reduce the release of P from sediment to water.

Owing to surface area effects, the sorption reactions of P caused by inorganic particles are enhanced as a function of decreasing sediment grain size. The main fine-grained ( $\varnothing < 2 \mu\text{m}$ ) constituents of sediments are silicates, *i.e.* clays,

carbonates, Fe and Al oxides, and humic acids. Of the clay minerals, illite adsorbs more P than does montmorillonite, which adsorbs more P than does kaolinite (Edzwald *et al.* 1976). This pattern is analogous to a decrease in the Fe, Al and Mn, but not the Ca, content of these minerals. Silicates and carbonates in larger particles such as sand adsorb P poorly (Brinkman 1993). Due to carboxyl ( $\text{COOH}^-$ ) groups, humic substances have a high affinity to adsorb cations but not anions such as  $\text{PO}_4^{3-}$ . Humic compounds containing Fe and Al can, however, sorb P. The surfaces of fine-grained minerals such as Fe and Al oxides, clay minerals with surficial Fe and Al (hydr)oxides, and possibly also Mn oxides adsorb P efficiently. In general, the importance of Al oxides, aluminosilicates and Ca minerals in regulating sediment P mobilization is likely to depend on their abundance relative to Fe(III) oxides.

It is widely accepted that sedimentary P cycling is linked mainly to the Fe cycle in lake (*e.g.* Einsele 1938, Mortimer 1941, 1942, Campbell and Torgersen 1980) and marine systems (Yamada and Kayama 1987, Sundby *et al.* 1992, Jensen *et al.* 1995). In marine sediments, however, most of the total Fe (60–80%) is bound to sheet silicates (*e.g.* chlorite; Canfield 1988, Thamdrup *et al.* 1994). Adsorption of P by silicate-bound Fe is insignificant compared to that by Fe(III) oxides, which are considered to be the main Fe compounds in P binding. Sediments contain a multitude of Fe(III) oxides, often in complexed mixtures, that range widely in degree of crystallinity, particle size, available surface area, reactivity and oxidation state (Lovley 1991). Although most of the Fe(III) is in the form of insoluble oxides, organically complexed and colloidal forms may also be abundant in sediments (Lovley 1991). The P sorption capacity of amorphous, *i.e.* poorly crystallized,  $\text{Fe}(\text{OH})_3$  and lepidocrocite ( $\gamma\text{-FeOOH}$ ), is about 20 times that of crystalline Fe(III) oxides such as goethite ( $\alpha\text{-FeOOH}$ ) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ; McLaughlin *et al.* 1981).

Other negatively charged anions can also compete with the  $\text{PO}_4^{3-}$  of adsorption sites in sediments. For example, the effect of pH can be related to competition for adsorption sites, because desorption of P from clay minerals and Fe and Al (hydr)oxides is based on ligand exchange, in which P is substituted for by  $\text{OH}^-$  (Bolt 1982). An increase in pH can also increase the negative charge of the sorbing oxides (Hartikainen 1981,

Hartikainen ja Yli-Halla 1996). A significant decrease in P sorption to Fe(III) oxides occurs at  $\text{pH} > 6.5$  (Stumm 1992), values that are often observed in the sediments of the Baltic Sea. It has also been suggested that competition between  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  for Fe(III) oxide surface binding sites could promote P release at high  $\text{SO}_4^{2-}$  concentrations (Caraco *et al.* 1989). However, no difference has been found in the P concentration of pore water between low  $\text{SO}_4^{2-}$  and  $\text{SO}_4^{2-}$  amended sterile treatments (Roden and Edmonds 1997). Nor has any decrease been found in the adsorption capacities of clays determined in seawater  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations (Edzwald *et al.* 1974). Silicon (Si) may also compete with P for adsorption sites (Hartikainen *et al.* 1996, Tuominen *et al.* 1998a, Tallberg 2000). Silicate ( $\text{SiO}_4$ ) and P are sorbed onto the surfaces of hydrated Al and Fe oxides by the same specific mechanism (Obihara and Russell 1972) and, thus,  $\text{SiO}_4$  may chemically compete with  $\text{PO}_4^{3-}$  for adsorption sites.

#### 1.4 Release mechanisms of phosphorus from sediment to water

After settling, particulate P begins to undergo chemical and biological reactions that will lead to dissolution of P. Two mechanisms have to occur simultaneously or within a short period before P is released from sediment to water: first, dissolution of P bound to particles or aggregates and its transfer to the pool of dissolved P in the pore water and, second, a transport process responsible for the release of dissolved P from sediment to water (Boström *et al.* 1982). In sediments, P bound to particles is mobilized into dissolved form in desorption, dissolution, ligand exchange and enzymatic hydrolysis (Boström *et al.* 1982). The driving force behind the released P may be the rate at which dissolved P is generated in the pore water by splitting mechanisms of particulate P. In sediment, the dissolved P generated can be adsorbed, complexed with (in)organic cations, precipitated as authigenic minerals, and taken up by bacteria and benthic microalgae before being released to water.

The main physical factors enhancing the exchange of P between sediment and water are diffusion, temperature, water turbulence, gas ebullition and bioturbation (Boström *et al.* 1982). In stagnant anoxic hypolimnetic and non-bioturbated

sediments, diffusion is considered to be the main mechanism for P release. There is usually a pronounced difference in P concentrations between the overlying water and the surface pore water. The steeper the concentration gradient of P between the free water and the sediment pore water, the higher is the rate of diffusion. An increase in sediment solid matter content decreases free diffusion owing to the increase in collisions of molecules with the particles in sediments.

Temperature can have a major effect on the release rate of P from sediment to water (Holdren and Armstrong 1980, Kelderman and Van der Repe 1982, Psenner 1984). An increase in temperature accelerates the diffusion rate as a result of increased Brownian movement. However, temperature also has an indirect effect on P release, because an increase in temperature raises the metabolic rate of bacteria and subsequently the mineralization rate and microbial redox reactions in sediments.

Physical water movement is a much faster transport mechanism than diffusion. Physical pore water movement is increased by water currents at the sediment-water interface and by gases formed in microbial reduction processes in sediments. In addition, bioturbation promotes physical water movement and affects the binding capacity of P in sediments. Marine sediments are often inhabited by abundant and diverse populations of burrowing macroinvertebrates; these influence nutrient binding and release. A significant variation exists in the behaviour of different burrowing macroinvertebrate species, and so the effect of solute transport in and out of the sediments may vary considerably between species (Matisoff and Wang 1998). The most common mechanism by which they promote sediment-water exchange is, however, thought to be physical: by digging and through their pumping movements and irrigation in burrows the animals increase the contact between interstitial water and the overlying water. Further, benthic macroinvertebrates can alter sediment properties and chemical exchange between sediment and water by their respiration, feeding and defecating activities.

Bioturbation has a three-way effect on the cycling of P in sediments: first, the transport of water increases the concentration of  $\text{O}_2$  in the burrows, thereby improving the P-binding capacity of sediment, but it also promotes the transport of pore water P from sediment to water; second, an abundance of macroinvertebrates increases the rate of

mineralization (Hansen *et al.* 1998) and the acceleration of their digestive and excretory processes (Gardner *et al.* 1981) furthers the dissolution of P; and third, burrowing animals move particulate oxidized compounds down to the reduced zone and reduced compounds up to the oxic zone, thus affecting Fe(III) oxide reduction and re-oxidation in sediments (Canfield *et al.* 1993).

## 1.5 Early diagenetic cycling and transformations of phosphorus compounds in marine sediments

### 1.5.1 Settling of phosphorus in sediments

The main transport mechanism of P to sediments is the settling of particulate matter, although influx of DIP to sediment may also occur. The surface of the sediments receives a mixture of particulate inorganic and organic compounds containing P. In sediments, the settled particulate inorganic P can be divided into Fe-, Mn-, Al- and Ca-bound P, whereas the particulate organic P consists of living and dead algae, plant debris, zooplankton, bacteria and detritus. Part of the settled particulate P behaves as inert material and is buried in its original form, whereas part of the P (*i.e.* mobile P) is involved in various physico-chemical and biological reactions in sediments (*i.e.* diagenesis of P). In Århus Bay, mobile pools of loosely sorbed P, Fe-bound P and fresh organic P constitute nearly 50% of the surface TP but are largely depleted below a depth of 3 cm (Jensen *et al.* 1995). The nonmobilized, buried P consists mostly of stable minerals such as apatite and refractory organic P (Sundby *et al.* 1992, Jensen *et al.* 1995), whereas the Fe-bound P constitutes only a minor proportion of the burial flux of P (3.5%; Jensen *et al.* 1995).

Particulate organic P is considered to be the main compound transporting P to sediments (Froelich *et al.* 1982). In regions with marked seasonality such as at northern temperate latitudes, the settling of the spring bloom with its high P content (Gardner *et al.* 1985) carries a large portion of the organic particulate P to the surface of the sediment. In the Baltic Sea, for example, seasonal short-term changes in the phytoplankton biomass in the water mass are due to the rapid sedimentation of phytoplankton (Laakkonen *et al.* 1981, Heiskanen 1998). A large part of phosphorus may be stripped from the entire water column by this event (Wulff

and Rahm 1988). Although organic matter is mineralized during sinking (Laakkonen *et al.* 1981, Leppänen 1988), a substantial portion of the settled particulate organic matter decomposes within the sediments in relatively shallow environments such as estuaries and coastal waters (Fisher *et al.* 1982, Wassman 1990). In estuaries, however, the sedimentation of particulate matter may be accentuated by salt-induced flocculation of colloidal and particulate matter containing P (Edzwald *et al.* 1974, House *et al.* 1998); further, the P in estuarine water may precipitate on Fe(III) oxides (Gunnars *et al.* 2002).

Labile organic matter rich in P tends to increase the release of P from sediment to water within a period of days after settling in brackish (Conley and Johnstone 1995) and marine environments (Slomp *et al.* 1993). It does not, however, necessarily lead to the immediate release of P from sediment to water owing to the sorption capacity of P in sediments. A major portion of the organic P in sedimentation flux can be mineralized in sediments, but the mineralized P is partitioned between the pore water and adsorption sites of the sediment (Sundby *et al.* 1992, Jensen *et al.* 1995). The proportion of organic P may then decrease but that of Fe(III) oxide-bound P increase in surface sediment. In Århus Bay, a large part of the P immobilised by biota in spring is mineralized at the sediment surface and subsequently retained in the pool of Fe-bound P (Jensen *et al.* 1995). Efficient release of Fe(III) oxide-bound P has nonetheless been observed later, that is, in August. In the study of Sundby *et al.* (1992), the settling matter had a much higher proportion of organic P (35% of TP) and a lower proportion of P bound to metal oxides (25% of TP) than was measured on the sediment surface (6% and 50% of TP, respectively).

Therefore, although the settling of particulate organic P is an important transport mechanism of P into sediment, the P is partly bound to inorganic compounds after mineralization in sediments. However, neither fresh organic P nor Fe(III) oxide bound P is efficiently buried, because organic P is mineralized and Fe-bound P is dissolved in the reduction of Fe(III) oxides in sediments (Jensen *et al.* 1995). In the Gulf of St. Lawrence, for example, approximately half of the sedimentation flux of particulate P is released from sediment back to water (Sundby *et al.* 1992), whereas in Århus Bay, 65% of the net sedimentation of P is released back to water (Jensen *et al.* 1995).

**Table 1.** Microbial mineralization processes by which organic matter is oxidized by electron acceptors in marine sediments (Richards 1965, Stumm and Morgan 1970, Froelich *et al.* 1979).

	Reduction reaction	Formula	type	Depth in sediment
oxic	Aerobic respiration	$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$	biologic	mm
anoxic	Denitrification	$5\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+ \rightarrow 5\text{CO}_2 + 2\text{N}_2 + 7\text{H}_2\text{O}$	biologic	mm
anoxic	Manganese reduction	$\text{CH}_2\text{O} + \text{MnO}_2 + 4\text{H}^+ \rightarrow \text{CO}_2 + 2\text{Mn}^{2+} + 3\text{H}_2\text{O}$	biologic	cm
anoxic	Iron reduction	$\text{CH}_2\text{O} + 4\text{FeOOH} + 8\text{H}^+ \rightarrow \text{CO}_2 + 4\text{Fe}^{2+} + 7\text{H}_2\text{O}$	biologic	cm
anoxic	Sulfate reduction	$2\text{CH}_2\text{O} + \text{SO}_4^{2-} + 2\text{H}^+ \rightarrow 2\text{CO}_2 + \text{H}_2\text{S} + 2\text{H}_2\text{O}$	biologic	m
anoxic	Methanogenesis	$\text{CH}_2\text{O} \rightarrow \frac{1}{2}\text{CH}_4 + \frac{1}{2}\text{CO}_2$	biologic	m

### 1.5.2 Biological and nonbiological iron oxide reduction in sediments

Heterotrophic microbial reduction of electron acceptors during mineralization is considered to be a controlling factor in sediment P cycling (Berner 1974, Froelich *et al.* 1979, Billen 1982, Bender and Heggie 1984). The redox potential in sediment differs drastically from that in the oxic water mass, which affects P equilibrium between the solid and solution phases, *i.e.* sorption capacity of sediment. Thus, the transformation of previously unavailable forms of P into available ones may necessitate a temporary benthic step. In nature, P is predominantly in the oxidation state +V and does not significantly change the valence state in natural biological or nonbiological chemical reactions (Stevens 1980, Frossard *et al.* 1995). Thus, the  $\text{PO}_4^{3-}$  ion itself does not participate in redox reactions in sediments but redox conditions affect the binding capacity of P in sediments.

Heterotrophic microorganisms that reduce oxidized compounds using organic matter as an energy source are directly or indirectly responsible for most of the redox reactions in sediments.  $\text{O}_2$ ,  $\text{NO}_3^-$ , Mn(IV) and Fe(III) oxides,  $\text{SO}_4^{2-}$  and  $\text{CO}_2$  serve as electron acceptors in the respiratory degradation of organic matter mediated by heterotrophic microorganisms (Table 1). The vertical sequence of  $\text{O}_2$ ,  $\text{NO}_3^-$ , Mn, Fe and  $\text{SO}_4^{2-}$  respiration (in this order from the oxic sediment surface towards the deeper layers) probably occurs in aquatic sediments although there is no sharp distinction between these processes (Sørensen and Jørgensen 1987, Canfield 1992).

A vertical respiration sequence may occur in sediment due to the fact that reducing microorganisms maintain the concentration of electron

donors (*i.e.*  $\text{H}_2$  and substrates) at levels too low for other reducers to metabolize them (Lovley 1991, Achtnich *et al.* 1995). Therefore,  $\text{O}_2$ -reducing bacteria inhibit the reduction of  $\text{NO}_3^-$ , which in turn inhibits the reduction of Mn and Fe oxides. Mn reduction can also partially inhibit Fe reduction (Lovley and Phillips 1988). In addition, Mn- and Fe-reducing bacteria competitively inhibit  $\text{SO}_4^{2-}$  reduction when sufficiently reactive Mn and Fe oxides are present (Lovley and Phillips 1987). The  $\text{SO}_4^{2-}$ -reducing bacteria can also inhibit  $\text{CH}_4$  formation, which is generated by methanogenic bacteria in fermentation and  $\text{CO}_2$  respiration. The main difference between freshwater and marine sediments thus lies in the amount of  $\text{SO}_4^{2-}$  in the marine system, resulting in dominance of the sulphur cycle, whereas in fresh waters, methane formation is the terminal step, which dominates carbon metabolism (Nealson 1997).

Phosphorus dissolved in pore water originates mainly from both Fe(III) oxides and organic matter, which constitute the main mobile P-binding pools in coastal sediments (Krom and Berner 1981, Jensen *et al.* 1995, Ingall and Jahnke 1997). The bulk of the P, however, is thought to be released in sediment from Fe(III) oxides undergoing reduction (Yamada and Kayama 1987, Sundby *et al.* 1992, Jensen *et al.* 1995). There are two main processes that can reduce Fe(III) oxides in sediments: first, enzymatic microbial dissimilatory reduction and, second, nonenzymatic reduction by the sulphide formed in microbial dissimilatory  $\text{SO}_4^{2-}$  reduction (Lovley 1991).

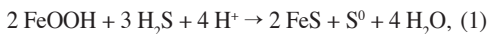
Microorganisms are important in the reduction of Fe(III) oxides, because the storage under anaerobic conditions of readily reducible, synthetic, poorly crystalline Fe(III) oxides or sterilized sediment containing poorly crystalline Fe(III) oxides does



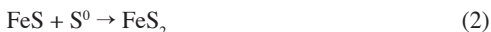
not result in detectable Fe(III) reduction, even after long periods (Bromfield 1954, Ehrlich *et al.* 1973, Lovley and Goodwin 1988, Lovley *et al.* 1990). As well as anaerobic conditions, the Fe(III) oxide-reducing bacteria need direct contact with particles to reduce Fe(III). When direct contact is prevented, Fe(III) oxides are not reduced (Lovley 1991). In microbial dissimilatory Fe(III) oxide reduction, Fe(III) is used as an external electron acceptor and Fe(III) is reduced to soluble Fe(II), organic C being the electron donor (Table 1). In this reaction, organic C is oxidized to CO<sub>2</sub>. Dissimilatory microbial Fe(III) reduction leads to the simultaneous accumulation of Fe(II) and P in anoxic pore water.

Although the concentration of O<sub>2</sub> in near-bottom water is high, the anoxic zone develops within a few millimetres beneath the sediment-water interface in organic-rich, fine-grained marine sediments (Jørgensen and Revsbech 1985). O<sub>2</sub> may be depleted, but the nitrate (NO<sub>3</sub><sup>-</sup>) present can still inhibit Fe(III) reduction in sediments (Ellis-Evans and Lemon 1989, Obuekwe *et al.* 1981, Jones *et al.* 1983, Sørensen 1982) and so prevent the release of P from Fe(III) oxides to anoxic water (Andersen 1982). Extensive release of P may occur after depletion of O<sub>2</sub> due to the fact that nitrification is inhibited after the exhaustion of O<sub>2</sub>, leading rapidly to depletion of nitrate.

At neutral pH, H<sub>2</sub>S formed in microbial dissimilatory SO<sub>4</sub><sup>2-</sup> reduction can nonenzymatically reduce Fe(III) oxides in sediments. Fe(III) oxide minerals are crucial phases in early diagenetic monosulphide (FeS) and pyrite (FeS<sub>2</sub>) formation, which are important sinks of Fe(II) in marine environments (Canfield 1989, Thamdrup *et al.* 1994). The most efficient way to precipitate sulphides in which Fe is involved is through the reaction (Pyzik and Sommer 1981):



with possibly a further reaction to pyrite (Berner 1970):



The evidence for Fe(III) reduction by sulphide is the accumulation of S<sup>0</sup> and FeS<sub>2</sub> in the zones in which dissolved Fe(II) accumulates in the pore water in marine sediments (Canfield 1989, Thamdrup *et al.* 1994). Therefore, the Fe(III) oxides are depleted while the pools of FeS and FeS<sub>2</sub> increase

with sediment depth (Thamdrup *et al.* 1994). When Fe(III) oxides are present in relatively high concentrations, dissolved sulphide is virtually absent from sediment pore waters due to FeS formation, even in the presence of active sulphide production by SO<sub>4</sub><sup>2-</sup> reduction (Canfield 1989). The presence of dissolved sulphide in sediments indicates that reactive Fe(III) oxides towards sulphide has become consumed (Canfield 1989). In marine systems, Fe(III) oxides are probably reduced mostly by H<sub>2</sub>S, because SO<sub>4</sub><sup>2-</sup> reduction is the dominant anaerobic respiration process. In Århus Bay, for example, partial oxidation of H<sub>2</sub>S accounts for 63% of the estimated Fe(III) reduction, whereas the contributions of microbial Fe reduction to carbon mineralization are considered to be small (Thamdrup *et al.* 1994). A significant portion of the Fe(III) reduction was involved in the precipitation and partial oxidation of H<sub>2</sub>S to S<sup>0</sup>, FeS, and FeS<sub>2</sub>.

The rate and extent of microbial Fe(III) oxide reduction is controlled by the surface area and site concentration of the solid phase. Microbial reduction of poorly crystalline Fe(III) oxide is about 20 times that of goethite, which is about 50 times that of hematite (Roden and Zachara 1996). This result is consistent with the decrease in particle size and increase in surface area and crystallinity of these oxides. In accordance with microbial Fe(III) oxide reduction, poorly crystalline Fe(III) oxide minerals are more reactive towards sulphide than are crystalline goethite and hematite. Thus, Fe(III) oxides that effectively adsorb P (see section 1.3) are the same forms as those that are effectively reduced by Fe(III) oxide-reducing microorganisms and by H<sub>2</sub>S formed in microbial SO<sub>4</sub><sup>2-</sup> reduction in sediments.

### 1.5.3 Cycling of phosphorus in marine sediments

A classic P cycling model is based on the Fe cycle in sediment: insoluble Fe(III) oxides are reduced to soluble Fe(II) ions, after which the P bound to Fe(III) oxides is released into pore water. When reduced soluble Fe(II) is diffused to an oxic environment (sediment surface or near-bottom water) it is oxidized to Fe(III) oxides having a high capacity to sorb P. Hence, sediments overlain by aerobic waters often have an Fe(III) oxide-rich surface layer. The precipitated Fe(III) oxides present in

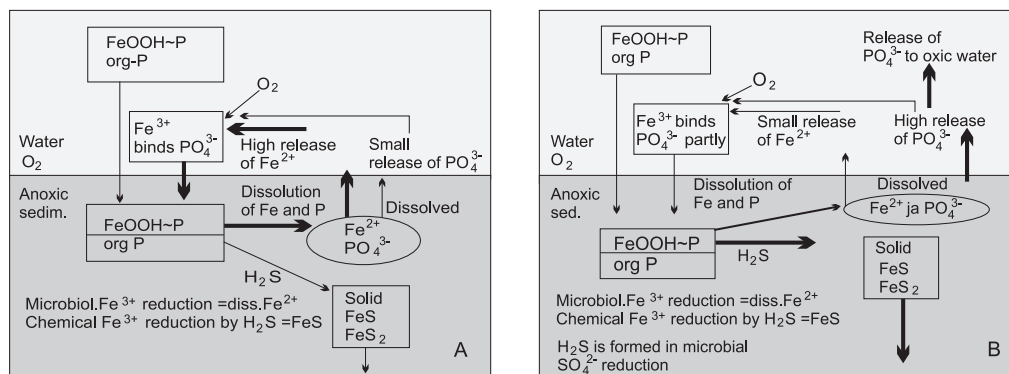


Fig. 2. Cycling of Fe, S and P in a (a)  $\text{SO}_4^{2-}$ -poor and (b)  $\text{SO}_4^{2-}$ -rich aquatic environment.

the surface layer are considered to effectively prevent P from entering the euphotic surface of water (Tessenow 1975, Mayer *et al.* 1982, Gallagher 1985, Ellis-Evans and Lemon 1989). Adsorption of P onto Fe(III) oxides may occur rapidly, because Fe(II) is oxidized within minutes or hours in the presence of  $\text{O}_2$  (Davison and Seed 1983, Millero *et al.* 1987, King *et al.* 1995). As well as chemically, Fe(II) is oxidized by lithotrophic Fe(II) oxidizing bacteria in surficial sediments (Sobolev and Roden 2001). Due to the cycling of Fe in sediments, P can be desorbed and adsorbed several times before its permanent burial or release to water. The P-rich surface layer is in a dynamic state and over time moves upwards as new sediment accumulate.

However, back in 1948, Hasler and Einsele suggested that  $\text{SO}_4^{2-}$  increases the availability of P, a hypothesis that was later substantiated by Sugawara *et al.* (1957). Recent studies have also revealed the tight coupling between Fe, S and P in marine sediments (Jensen *et al.* 1995, Roden and Edmonds 1997, Anschutz *et al.* 1998, Rozan *et al.* 2002). The coupling of Fe with S leads to differences in P cycling between  $\text{SO}_4^{2-}$ -poor and  $\text{SO}_4^{2-}$ -rich systems (Fig. 2). As pointed out earlier,  $\text{SO}_4^{2-}$  reduction does not itself release P, but it indirectly promotes P mobilization and reduces the P retention capacity.  $\text{SO}_4^{2-}$  has a double effect on the P cycle via reactions with Fe: first, Fe(III) oxides are effectively reduced by sulphide formed in microbial  $\text{SO}_4^{2-}$  reduction (Thamdrup *et al.* 1994) and, ultimately, even very stable crystalline Fe(III) oxides are converted to  $\text{FeS}_2$  in sulphidic sediments (Canfield 1989); second, dissolved Fe(II) is

quickly and effectively removed from pore waters by the precipitation of solid  $\text{FeS}$ , and the formation of  $\text{FeS}_2$  in the presence of  $\text{H}_2\text{S}$  formed in  $\text{SO}_4^{2-}$  reduction (Taillefert *et al.* 2000). Coprecipitation of Fe and S leads to permanent burial of FeS minerals (Canfield 1989, Jensen *et al.* 1995). The FeS minerals formed adsorb P poorly at neutral pH (Bebie *et al.* 1998). As a consequence, the upward flux of dissolved Fe(II) is decreased, thereby reducing or preventing the re-formation of an Fe(III) oxide-rich surface layer able to adsorb P efficiently. However, the P solubilized from Fe(III) oxides is maintained in pore water (Rozan *et al.* 2002).

Due to FeS formation, the dissolved Fe:P ratio is higher in freshwater than in brackish-marine systems under anoxic conditions (Gunnars and Blomqvist 1997). When conditions turn oxic, the newly formed colloidal Fe(III) oxides scavenge P ions in lake-water sediment. In marine sediments, though, P is less efficiently scavenged, and significant amounts remain dissolved in the overlying water (Gunnars and Blomqvist 1997). It has been suggested that the ratio of Fe:P dissolved in pore water governs the fate of P when these elements are transported to the oxic zone in sediment. The predominant Fe:P surface complexation molar ratio of Fe(III) oxide is suggested to be about 2, which corresponds to a mass ratio of 3.6 (Gunnars and Blomqvist 1997, Gunnars *et al.* 2002). When the dissolved Fe:P ratio is under 3.6 by mass, the available Fe is in too short supply to bind all the dissolved P. In marine systems, the Fe:P ratio is under 3.6 by mass and in lake-water systems (calcareous lakes not included) almost invariably above



3.6 under anoxic conditions (review by Gunnars and Blomqvist 1997).

The benthic flux of P increases when conditions turn from oxic to anoxic in lake (e.g. Einsele and Vetter 1938, Mortimer 1941, 1942, Mayer *et al.* 1982, Ellis-Evans and Lemon 1989), brackish-marine (Koop *et al.* 1990, Gunnars and Blomqvist 1997) and marine systems (e.g. Balzer 1982, 1984, Balzer *et al.* 1983, Sundby *et al.* 1986). Several studies have, however, confirmed the occurrence of significant aerobic P release in both lake and marine systems (e.g. Lee *et al.* 1977, Bates and Neafus 1980, Holdren and Armstrong 1980, Boström and Petterson 1982, Boers *et al.* 1984, Boers 1986, Sinke and Cappenberg 1988, Löfgren and Boström 1989, Conley *et al.* 1997). In  $\text{SO}_4^{2-}$  rich systems, a low concentration of dissolved Fe(II) may lead to insufficient Fe(III) oxide formation. The Fe(III) oxides formed can then only partially retain the flux of P, and the benthic efflux of P may occur even though the overlying water is oxic. In  $\text{SO}_4^{2-}$  poor lakes, however, a portion of the P released to oxic water may originate from P bound to organic matter in sediments.

Owing to the low reserves relative to the requirements of algae in most lakes, P is a key factor in lake-water eutrophication (Vollenweider 1968). In marine and brackish systems, including the Gulf of Finland, however, primary production in the photic zone tends to be N limited (Hecky and Kilham 1988, Howarth 1988, Källqvist 1988, Vitousek and Howarth 1991, Kivi *et al.* 1993). The difference in nutrient limitation can be attributed to the lower sediment P-binding ability due to the higher  $\text{SO}_4^{2-}$  concentrations in brackish and marine sediments than in lake waters (Caraco 1991a and b, Roden and Edmonds 1997, Gunnars and Blomqvist 1997).

### 1.6 Objectives of this study

The release of P from the bottom sediments may contribute markedly to the P budget of the Gulf of Finland, and consequently on its trophic state. Information on the external P load is spatially and temporally much more accurate than is that on the release of P from sediment to water in the Gulf of Finland (HELCOM 1998). More information is needed on the release and burial of P in sediments if we are better to understand the water ecosystem of the Gulf of Finland. Thus, there is a clear need

to include sediment nutrient processes when assessing the further needs of protection strategies for the Gulf of Finland. The structure of this study is presented in Fig. 3. The aims of the study are:

- to obtain basic information on regional levels of particulate and dissolved nutrients in sediments (I–VI, this paper);
- to define the mobile and refractory pools of P in sediments (II, VI);
- to define the spatial sediment retention ability of P along the estuarine gradient (VI);
- to provide insight into annual variability in the benthic flux of P and to establish which factors have an effect on the flux (IV, this paper);
- to assess whether sulphur is a significant factor in sediment P cycling (II, III, IV, VI, this paper); and
- to quantify and consider the ecological implications of benthic fluxes of N and P (III, IV, V, VI, this paper).

## 2 Study area

### 2.1 Hydrography

The Gulf of Finland (area 30 000 km<sup>2</sup>, average depth ca. 37 m; Fig. 4) lies between 59°11'N, 22°50'E and 60°46'N, 30°20'E and is geomorphologically a direct continuation of the main basin of the Baltic Sea. The absence of sills permits free flow of the saline deep water of the Baltic into the Gulf of Finland, a process that largely controls the deep water salinity in the Gulf. The salinity stratification, in turn, largely controls the residence time of deep water and thus O<sub>2</sub> concentration in the deep parts of the Gulf of Finland. There is positive water exchange between the Gulf and the main basin of the Baltic Sea, the approximate volume of exchange being 600 km<sup>3</sup> out of and 480 km<sup>3</sup> into the Gulf (Alenius *et al.* 1998). The permanent halocline at 60–80 m depth in the western Gulf of Finland prevents the vertical mixing of water down to the bottom (Fonselius 1969, Alenius *et al.* 1998). In shallower areas, and especially in the eastern Gulf, the halocline is usually weak or totally absent (Hela 1966, Niemi 1975).

In the shallow areas and in the eastern Gulf, salinity increases from the surface towards the

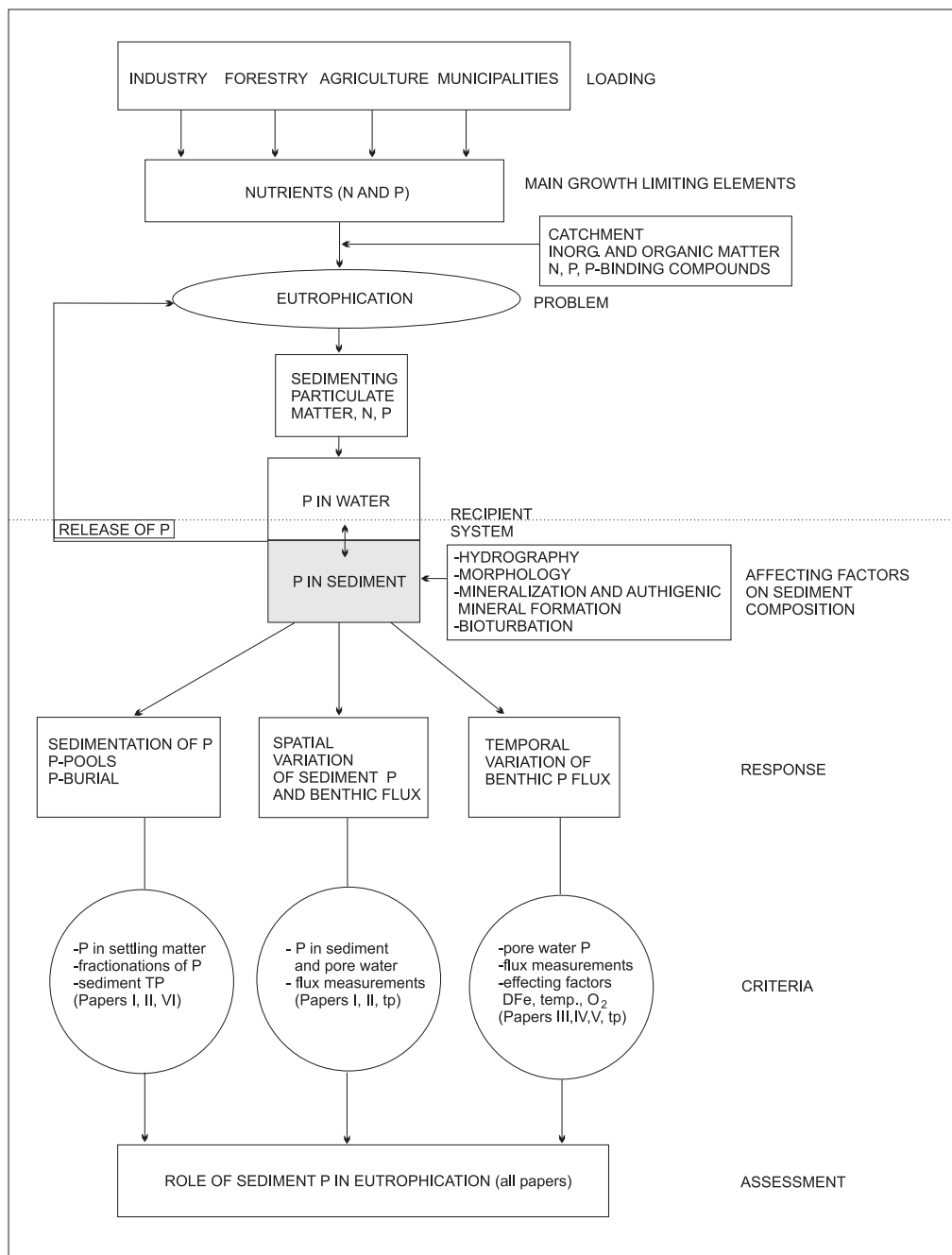


Fig. 3. Structure of this study. Roman numerals refer to the original papers (I–VI), and to this paper. The concept is modified from Mannio (2001).

deeper water layers. The gradual increase in salinity towards the bottom, below the mixed surface layer, indicates slow, but almost continuous, vertical mixing between the outflowing surface and the inflowing deeper water layers. The vertical mixing of water is particularly marked in the Neva estuary, where both the water depth and the vertical salinity difference are smaller than elsewhere in the Gulf. The density stratification in summer is enhanced by the vertical temperature stratification as well as by the increase in salinity towards the bottom. The thermocline is usually at 10–20 m depth. The water-mass mixes after the surface water has cooled in late October–early November, and in winter the water is almost isothermal down to a depth of 60 m (Niemi 1975, Alenius *et al.* 1998).

Owing to the topography of the Gulf of Finland and the mean fresh water inflow (2460 m<sup>3</sup> s<sup>-1</sup>; Bergström and Carlsson 1993) from the River Neva to the easternmost end of the Gulf, the entire Gulf of Finland can be regarded hydrographically as a partially mixed estuary. The Neva is the largest river flowing into the Baltic Sea, accounting for 75% of the total inflow into the Gulf of Finland and for 20% of the total riverine inflow into the Baltic Sea (Ehlin 1981). The surface salinity of the study area increases from 0 in Neva Bay to ca. 6 in the western Gulf, whereas near the bottom the salinity increases from 5 in the east to 9 in the west (Pitkänen *et al.* 1993, Perttilä *et al.* 1995). Owing to the inflow of more saline water from the main basin and the large inflow of fresh water from the Neva, the open waters of the Gulf are divided into deeper western (more marine affected) and shallower eastern (more freshwater affected) parts.

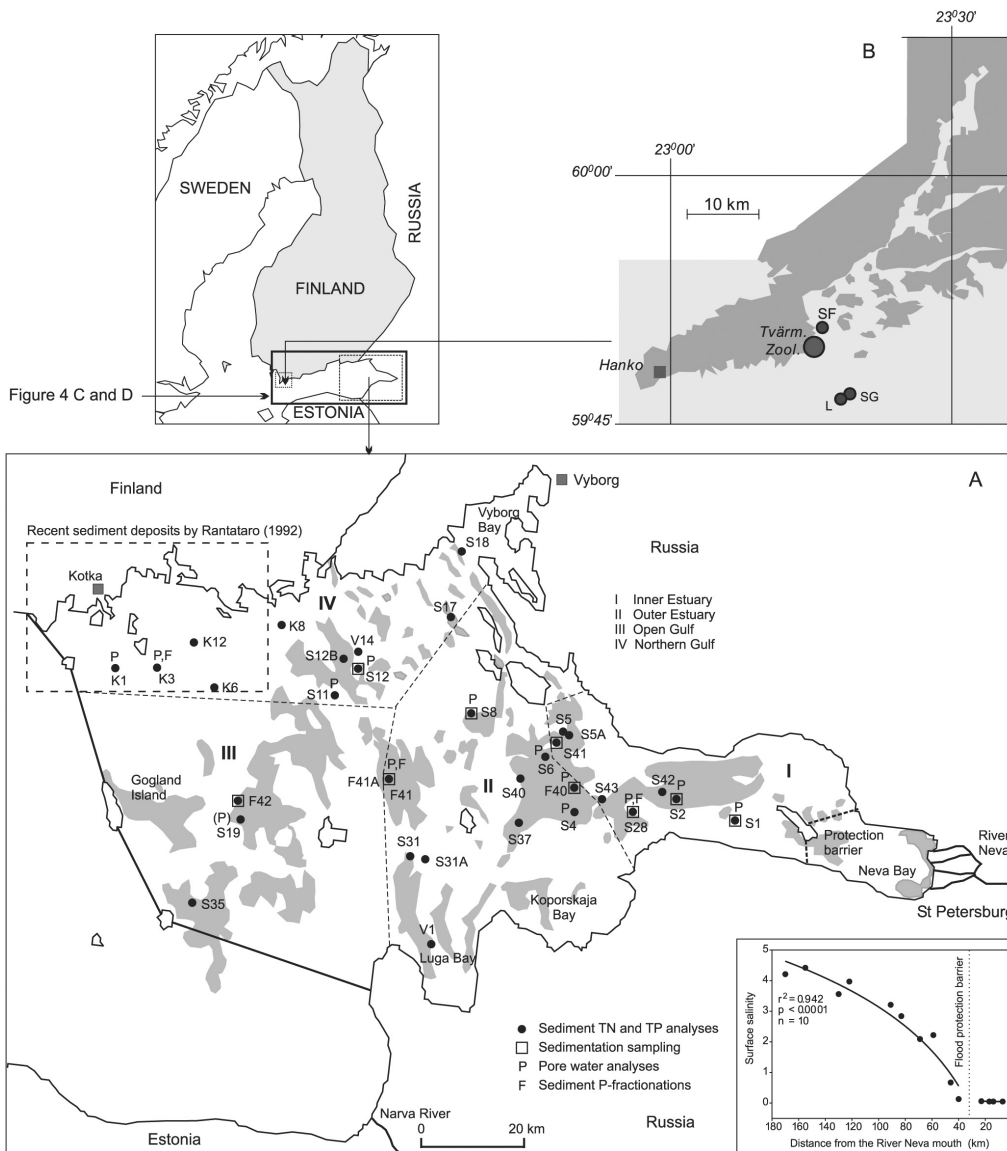
The borderline between the eastern (area 13 000 km<sup>2</sup>) and western parts of the Gulf can be drawn along the belt of reefs and shallows that goes from the coast of Finland to that of Estonia via the islands of Kaunissaari, Gogland and Suuri Tytärsaari and the Narva Bay (Fig. 4a). The average residence time of water in the whole Gulf is ca. 3 a (Alenius *et al.* 1998), whereas it is ca. 1 a in the eastern Gulf and ca. 6 months in the Neva estuary (Pitkänen 1994). Due to the Coriolis effect and prevailing wind directions, the average anti-clockwise circulation of surface water in the Gulf can be calculated, demonstrating that the northern coast is the main recipient of the impact of the Neva and of rivers discharging into the Gulf from Finland.

## 2.2 Geomorphology and characteristics of sediments

In the Gulf of Finland, sediment accumulation is characterized by the greatly variable distribution of bottom types due to the irregular topography and by the numbers of basins filled with deposits of pelitic mud (Emelyanov 1988). No high resolution maps of accumulation areas have been published for the entire Gulf of Finland. Nonetheless, the unpublished data of Winterhalter *et al.* (Fig. 4a) and geological maps of the Kotka–Pyhtää–Vehkalahti (Rantataro 1992) and Espoo–Helsinki–Sipoo regions (Häkkinen and Åker 1991) together with echo soundings conducted for the present study suggest that large accumulation areas do exist in the Gulf of Finland but that these tend to be smaller in the northern than in the open and southern parts of the Gulf. Estimates for the extent of the total accumulation area range from 25% to 35% of the entire Gulf, corresponding to an area of 7500–10 500 km<sup>2</sup> (Kankaanpää 1997, Vallius 1999a). The largest accumulation areas seem to be located in the deep parts of the western Gulf.

Bottom currents, which are largely controlled by bottom topography, have considerable influence on the active sedimentation of fine particulate matter. In the open sea area, active sedimentation (*i.e.* formation of recent sediment deposits) usually occurs at water depths exceeding 60–90 m (Emelyanov and Kharin 1988, Rantataro 1992). The critical depth for permanent sedimentation varies markedly, however, due to the complex hydrography and geomorphology of the Gulf of Finland. Mosaic-like bottoms are particularly common in the coastal waters of Finland, where rock outcrops alternate with till and clay sediments (Häkkinen and Åker 1991, Rantataro 1992). In Finnish coastal waters (Häkkinen and Åker 1991, Rantataro 1992) and in the large area off Vyborg Bay (Winterhalter *et al.* unpubl.), the recent sediment deposits are mainly located in small, steeply sloping basins surrounded by large shallow areas.

The topmost layers of the recent sediment deposits consist of muddy clays or silts (Winterhalter 1992). The thickness of recent sediment may range from a couple of centimetres to several metres from one accumulation basin to another and even within a single basin (Vallius 1999a and 1999b). Grain size distribution studies from the central western Gulf of Finland show that 50% to 75% of the surface sediment matter is of the clay fraction

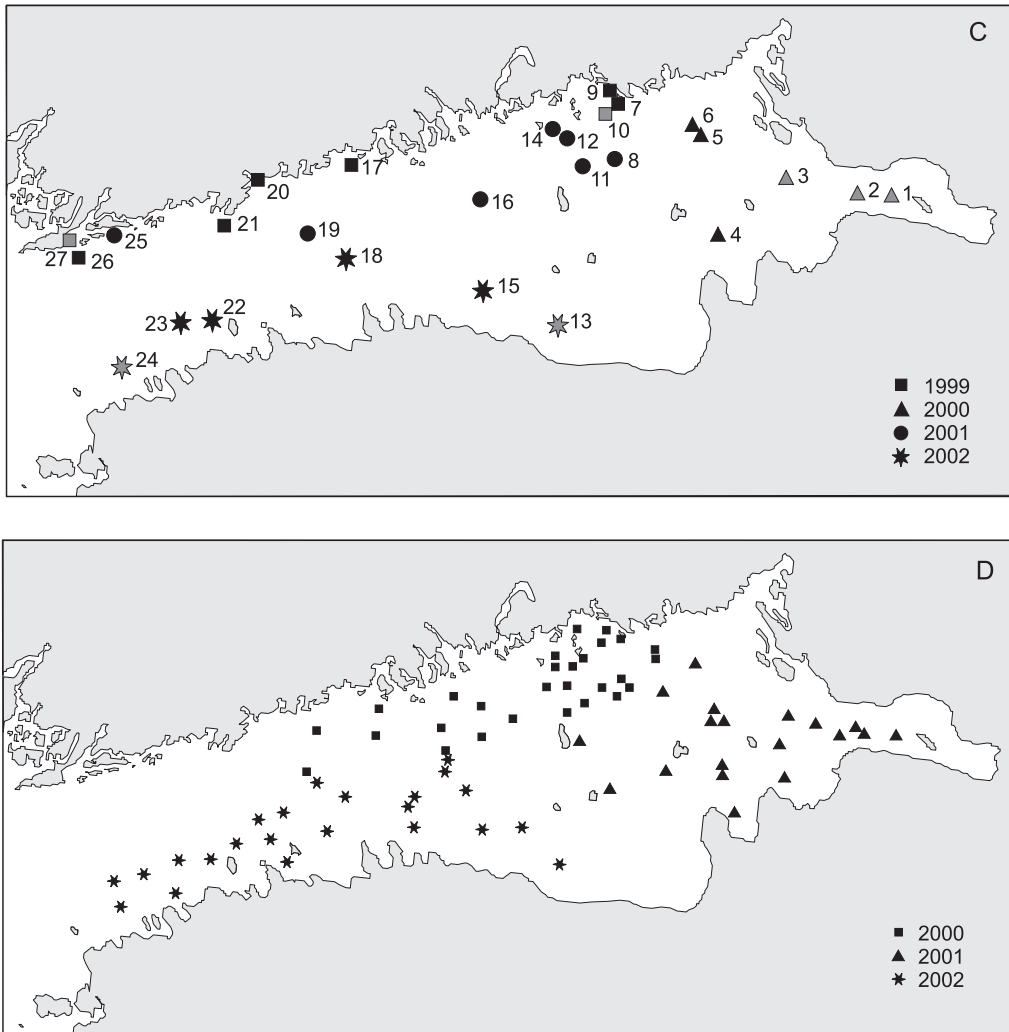


**Fig. 4. (a)** Sub-division of the eastern Gulf of Finland based on cluster analysis (VI) and morphometrical and hydrological features (Pitkänen 1993); and sampling sites for sediment DM, LOI, TN and TP and settling matter POC, PON and PTP measurements. Grey denotes areas of recent sediment deposits (Winterhalter, Rybalko, Butylin and Spiridonov, unpubl.).

**(b)** Sampling sites for seasonal variation in benthic flux and near-bottom water. SF= Storfjärden, SG=Storgadden and L=Längden.

(Vallius 1999a). The most common minerals in the surface sediments of the Baltic Sea are feldspars, quartz and clays (mostly illite) together with authigenic minerals such as Fe sulphides, carbonates, barite, vivianite, Mn oxides and Fe/Mn micronodules (Emelyanov 1995).

The accumulation rate of dry matter ranges from 0.01 to 0.30 g cm<sup>-2</sup> a<sup>-1</sup> (0.5 to 19.4 mm a<sup>-1</sup>) in the basins of the Gulf of Finland (Kankaanpää *et al.* 1997). In the study of Kankaanpää *et al.* (1997), the mean accumulation rate for the entire Gulf was 0.15 g cm<sup>-2</sup> a<sup>-1</sup> (6 mm a<sup>-1</sup>). The accumulation rate



**Fig. 4. cont. (c)** Sampling sites for benthic nutrient flux measurements in 1999–2002. Grey symbols denote oxidized sediments (*i.e.* sampling site with a brown oxidized surface layer) and black symbols anoxic reduced sediments (*i.e.* sampling site where black layer extended to surface of sediment).

**(d)** Near-bottom water DIN:DIP ratio measurements in 2000–2002.

may, however, vary even within one basin. In a large accumulation area covering 1.5 x 2.0 nautical miles in the central Gulf of Finland, for example, the accumulation rate ranges from 2.5 to 15 mm a<sup>-1</sup> (Vallius 1999b).

The benthic animals mainly responsible for bioturbation of the surface layers of soft sediments in the Gulf of Finland are the amphipods *Monoporeia affinis* (formerly *Pontoporeia*), *Pontoporeia femorata* and *Saduria entomon* and the

mollusc *Macoma baltica* (Andersin and Sandler 1991). The bioturbation caused by *M. affinis* is particularly effective due to vertical migration of the amphipod to free water during the night and back into the sediment during the day (Lindström 1992). The alien polychaete *Marenzelleria viridis*, which has spread to the entire Gulf of Finland since 1990, may also have a marked effect on bioturbation.

### 2.3 Southwest coast of Finland

The area where the seasonal variation of benthic flux was studied lies at the entrance of the Gulf of Finland to the northern Baltic Sea (Fig. 4b). Located in the archipelago, the station Storfjärden (water depth 33 m) is surrounded by islands. It represents a well oxygenated accumulation area bioturbated mainly by the bivalve *Macoma baltica*. The bottom topography causes considerable fluctuations in temperature and salinity in the near-bottom water, which originates from Baltic surface water, in deep water upwelling from the layer near the permanent halocline, and in surface water of the inner archipelago (Niemi 1975, Hällfors *et al.* 1983). Storfjärden is also affected by riverine waters in spring (Niemi 1975). The station Storgadden (water depth 51 m) is located in a transitional zone between the outer archipelago and the open sea and is influenced by the surface water flow of the Gulf of Finland and by deep water flow from the layer near the permanent halocline of the main Baltic Sea basin (Niemi 1975, Hällfors *et al.* 1983). There is a clear decrease in the near-bottom O<sub>2</sub> concentration in summer and autumn at Storgadden, although complete O<sub>2</sub> depletion was not detected in 1993–2001. Burrowing animals have not been observed at Storgadden in recent years (A. Laine, pers. comm.).

## 3 Materials and methods

### 3.1 Sediment sampling

The data reported in the present study were collected during eleven research cruises of R/V Muikku in 1992–2002 (Table 2) and one cruise of R/V Akademik Shuleikin in 1994. With the exception of one cruise to the eastern Gulf of Finland in early September 2000, all cruises took place in July and August.

In order to study only recent sediments, samples were collected from the areas of active deposition, *i.e.* soft bottoms, where the sediment is weakly consolidated due to high organic matter concentration (Pieczka 1992). The structure of the bottom sediments was studied during the research cruises with an Atlas Deso 10 echo sounder (30 kHz), which provides deep enough penetration and resolution for soft sediments. The sampling sites were selected on the basis of bathymetric maps and recent sediment deposit maps as well as echographs (Häkkinen and Åker 1991, Rantataro 1992, Kankaanpää 1997, Lehtoranta, unpubl.). Sediment samples were collected with a pistonless lightweight gravity corer (slightly modified from Axelsson and Håkanson 1978) and a Limnos corer (inner diameter 94 mm, Kansanen *et al.* 1991) from below the euphotic zone (Fig. 4a–c). Sediment cores 20–70 cm long were taken at each site, generally from the deep part of the basin.

**Table 2.** Data sets used in studies I–VI and in this summary.

Objectives	Sites		Years of sampling	Location of study area	Paper
	n	type			
Spatial variation of sediment LOI, TN and TP	27	S	1992–1994	EGOF	I, II, VI
Spatial variation of sediment P-pools	5	S	1995, 2000	GOF	II, this paper
Spatial variation in pore water nutrient concentrations	13	PW	1995–1996	EGOF	II, V
Spatial variation in quality of settling SPM	9	T	1992, 1995	EGOF	VI
Seasonal variation in benthic flux and pore water	2	I, PW	1999–2000	WGOF	IV
Long-term variation in quality of near-bottom water	1	W	1995–2002	WGOF	this paper
Spatial variation of benthic nutrient flux	27	I	1999–2002	GOF	III, IV, this paper
Spatial variation of near-bottom water DIN and DIP	73	W	2000–2002	GOF	this paper

S = sediment, T = sediment trap, I = incubation of sediment cores, PW = pore water, W = water samples, GOF = Gulf of Finland, EGOF = eastern Gulf of Finland, WGOF = western Gulf of Finland

The quality of settling particulate matter was studied with sediment traps (height:diameter = 5) deployed below the mixed surface layer (generally 10–15 m from the bottom surface) at nine sites on 9–15 August 1992 and 11–17 August 1995 (Fig. 4a).

The seasonal variation in benthic nutrient flux and pore water concentrations was studied with sediment samples taken between 26 April 1999 and 27 March 2000 from two different coastal accumulation areas, one representing the inner and one the outer coastal area (Storfjärden and Storgadden; Fig. 4b). Both sampling stations were marked with mooring buoys during the study. Sampling was conducted 10 times at Storfjärden and seven times at Storgadden.

## 3.2 Chemical analyses, and pore water and benthic flux measurements

### 3.2.1 Settling particulate matter analyses

Concentrated formaldehyde was used as a preservative in the trap cylinders (Gundersen 1991). The water in the upper part of the cylinder was discarded and the remainder was collected through an opening in the bottom of the cylinder. The total volume of the sample was measured and subsamples for chemical analysis were taken from the homogenous suspension. Total particulate matter (TPM) samples were filtered in duplicate on precombusted (4 h at 450°C) and preweighed Whatman GF/F glass fibre filters. Organic carbon (POC), nitrogen (PON) and phosphorus (PTP) samples were filtered in duplicate on acid-washed and precombusted (4 h at 450°C) Whatman GF/F glass fibre filters. POC and PON filters were dried and analysed with an elemental CHN analyser (LECO & Leeman Labs CHN analysers) and PTP using acid hydrolysis after high temperature combustion (Solorzano and Sharp 1980). The orthophosphate produced was determined according to Koroleff (1983).

### 3.2.2 Organic matter, total N, P and metal analyses, and fractionations of P

For sediment analyses of DM, LOI, TN and TP, the cores were cut into 1-cm slices from the surface to 10-cm depth in 1992–1994 (I, II, VI). In 1995,

deeper layers were sectioned at 5–7 cm, 7–10 cm and 10–15 cm (V). Each slice was frozen (–18 °C) in an air-sealed plastic bag for further sediment analyses (Table 3). Freeze-dried and homogenized sediment samples were analysed for Fe, Mn, Ca and Al by microwave-assisted (20 min) nitric acid (65%) and hydrogen peroxide (30%, 2 ml/100 ml) digestion for physico-chemical analyses according to the EPA 3051 method (V). Sediment Fe, Mn, Ca and Al concentrations were determined by AAS.

The sediment P-pools were fractionated according to the method of Hartikainen (1979) from five sites (Fig. 4a). The sediment samples, which were preserved at +4°C in sealed glass jars or plastic bags before analysis, were wet when fractionated. The fractionation method is based on the ability of certain reagents to dissolve phosphate minerals:  $\text{NH}_4\text{Cl}$  is considered to extract labile, loosely adsorbed phosphates,  $\text{NH}_4\text{F}$  Al bound phosphates (Al-P), NaOH Fe bound phosphates (Fe-P) and  $\text{H}_2\text{SO}_4$  Ca bound phosphates (Ca-P). Residual phosphate (Res-P) is obtained by calculating the difference between TP (determined by the digestion method of Zink-Nielsen (1975)) and the sum of reactive phosphate in the fractions. The organic P and refractory P compounds are included in the Res-P fraction. However, the pool of Res-P may become too high as some of the particulate P may be lost when the extracted sample is decanted for P analysis during the fractionation procedure. The fractionation method used here has been criticized for not extracting P compounds specifically. The  $\text{NH}_4\text{F}$  step in fractionation of P, for example, is known to extract Fe-P as well (Pettersen *et al.* 1988), and the NaOH step may extract organic P such as humic P compounds (Klapwijk *et al.* 1982) and phytate (Golterman *et al.* 1998). Moreover,  $\text{H}_2\text{SO}_4$ -P may contain Fe-bound P such as  $\text{FePO}_4$  (Khin and Leeper 1960, Frink 1969).

### 3.2.3 Pore water

The spatial variation in pore water nutrient concentrations was studied by vacuum filtering the sediment pore water through Nuclepore polycarbonate membranes (pore size 0.4  $\mu\text{m}$ ) under  $\text{N}_2$ -gas atmosphere in the temperature-adjusted laboratory (+6 to +9°C) of R/V Muikku immediately after sampling (II, V). To obtain a sufficient pore water volume for the analyses, the 0–1 to 3–5 cm layers were filtered for 15 to 20 min and the

**Table 3.** Variables and analyses used in sediment, pore water and benthic flux measurements.

Material	Element/variable	Methods	Used in
Settling particulate matter	POC and PON PTP	CHN analyser (POC, PON), acid hydrolysis (PTP)	paper VI
Sediment	dry weight, loss on ignition	freeze drying, ignition in muffle furnace by standard method SFS 3008 (1981)	papers I, II, IV, V, VI
Sediment	TN, TP	co-digestion by Zink-Nielsen (1975), strong sulphuric acid	papers I, II, IV, V, VI
Sediment	P-fractions	sequential extractions by Harti- kainen (1979)	paper II
Sediment	Fe, Mn, Ca, Al	microwave assisted digestion, AAS, EPA 3051	paper V
Sediment	redox-potential, pH	platinum electrode comb. electrode, PHM62 Standard pH-meter	paper V
Pore water	SO <sub>4</sub> <sup>2-</sup>	EN ISO 10304-1 (1995)	paper IV
Pore water	DFe	AAS	paper V
Near-bottom and pore water, benthic flux	DP, DIP, NH <sub>4</sub> <sup>+</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , DFe	Spectrofotometrically by methods of Koroleff (1983), Murphy and Riley (1962)	papers II, III, IV, V
Near-bottom and pore water, benthic flux	NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , NO <sub>2+3</sub> <sup>-</sup>	Automatic Ion Analyser (LaChat QuickChem 8000) based on the technology of flow injection analy- sis (FIA) colorimetry	papers III, IV, this paper
Near-bottom water, benthic flux (reservoir)	O <sub>2</sub>	Winkler method (O <sub>2</sub> ) colorimetry, WTW Microprocessor Oximeter OXI96 electrode	papers II, III, IV, V, VI, this paper

deeper layers for 20 to 50 min. After the filtration, the pore water samples were decanted into HCl-washed and Milli-Q water-rinsed 100-ml polyethylene bottles. The samples were stored in the dark at +4°C for 1–15 h before analysis. The pore water samples from the surface layer were usually diluted with Milli-Q water by a factor of 25 and those from the deeper layers by a factor of 50 due to the high nutrient concentrations. The pore water DIP and NH<sub>4</sub><sup>+</sup>-N were analysed according to Koroleff (1983). The nitrate-nitrite sum (NO<sub>2+3</sub><sup>-</sup>-N) was determined on non-diluted samples with an Automatic Ion Analyzer (LaChat QuickChem 8000), based on the technology of flow injection analysis (FIA) colorimetry. In the eastern Gulf of Finland, the samples for pore water DFe analyses were collected into Nalgene bottles from four sites in August 1995 (Fig. 1 in V). The samples (~20 ml)

were preserved with 2–3 drops of Suprapur HNO<sub>3</sub> acid (Merck) and stored in the dark at +4°C.

To measure the seasonal variation in pore water nutrient concentrations in the western Gulf of Finland (Storfjärden and Storgadden), two sediment cores (inner diameter 94 mm) were sectioned at the following depths: 0–0.5, 0.5–1, 1–2, 2–3, 3–5, 5–7, 7–10 cm (IV). The slices of the two cores were pooled to yield sufficient pore water volume for the analyses. The samples were sliced, pooled and filtered under N<sub>2</sub> atmosphere in a clove-bag. The pooled samples were placed in air-tight centrifuge tubes, and pore water was separated by centrifugation (10 000 rpm, 10 min) and subsequent vacuum filtration through polycarbonate membranes (0.4 μm) under N<sub>2</sub> atmosphere. After filtration, the pore water samples were decanted into HCl-washed and Milli-Q water-rinsed 100-ml



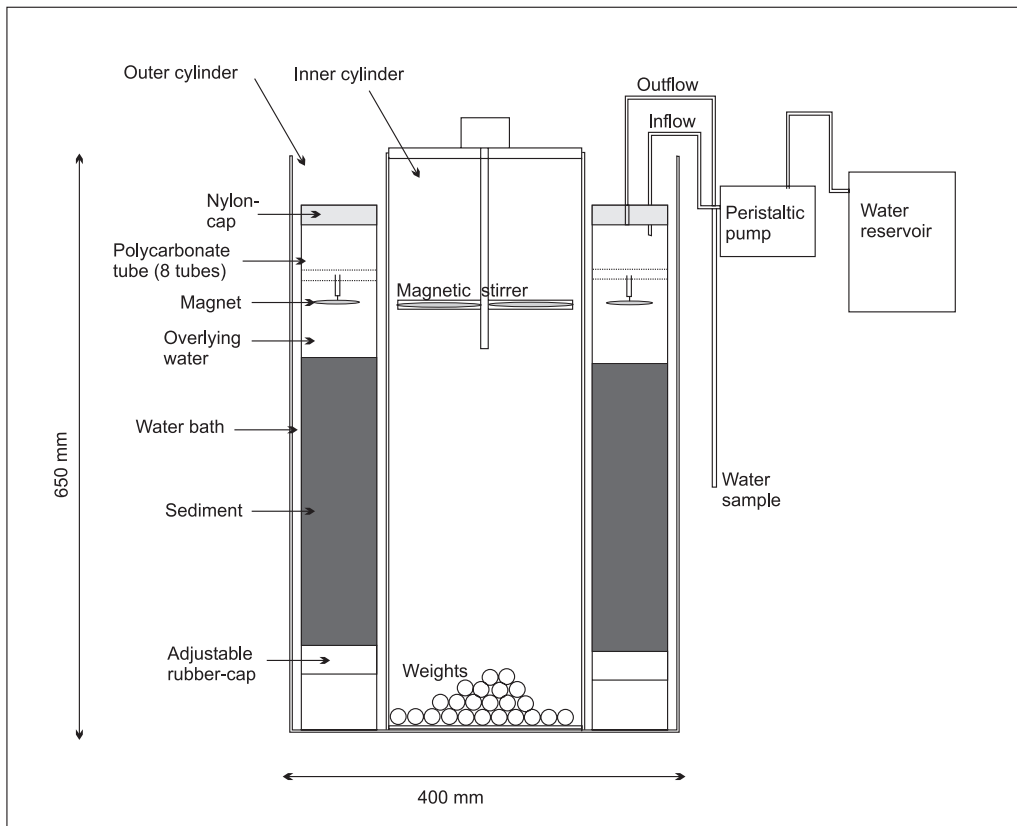


Fig. 5. Sediment incubator used in present study (not in scale).

polyethylene bottles and stored in the dark at +4°C for 10 h before analysis. The surface layer samples were usually diluted with Milli-Q water by a factor of 10 at Storfjärden and 25–50 at Storgadden. The deeper layers were diluted by a factor of 50 at both stations. Concentrations of DFe, DP and DIP in the near-bottom and pore water were analysed according to Koroleff (1983) and the  $\text{SO}_4^{2-}$  concentration according to the standard EN ISO 10304-1 procedure (1995).

### 3.2.4 Benthic flux

The release of solute from sediment to water can be quantified by mass balance analysis at the whole-system level (Ahlgren 1977), by laboratory or *in situ* confinement of sediments in core tubes (Kamp-Nielsen 1975) or benthic chambers

placed on the bottom (Sonzogni *et al.* 1977), or by flux calculations based on observed concentration gradients (diffusion calculations) at the sediment-water interface (Devol 1987). Reliable applications of the diffusion calculations, however, are restricted to environments with low bioturbation and turbulence (Enell and Löfgren 1988). For more dynamic environments such as shallow sea areas, coastal areas and estuaries, direct benthic flux measurements are often necessary.

The sediment for the benthic flux measurements was sampled with a pistonless gravity corer into removable polycarbonate tubes (inner diameter 74 mm, height 500 mm). A similar incubation technique was used to measure the spatial (III, this study) and temporal variation (IV) in the benthic flux. Two to four replicate samples were taken from all stations. The sediment cores were stored at +4°C and placed in a sediment incubator (Fig. 5) within a few

hours of sampling. To obtain similar water volumes (~400 ml), the position of sediment in the core was adjusted by a moveable water-tight bottom cap. A magnetic stirring mechanism was installed inside each core to ensure that the water above the sediment remained homogenous. Resuspension of the fluffy surface layer may decrease the benthic DIP flux during incubation (Holdren and Armstrong 1980) and so the stirring rate (~15 rpm) was kept well below the visible resuspension limit. The samples were incubated in the dark and at *in situ* temperature. The temperature was controlled with a water bath inside the outer cylinder of the incubator. If necessary, crushed ice was added to the water bath to maintain a low temperature during incubation.

The upper end of the polycarbonate tube was sealed with a tight Nylon cap that had holes for the inlet and outlet tubes (Tygon tube). Unfiltered near-bottom water sampled 1 m above the surface of the sediment was used as inflowing water (reservoir water). The continuous flow of water from the reservoir through the cores (0.4–0.5 ml min<sup>-1</sup>) was controlled by a peristaltic pump. The concentration of O<sub>2</sub> in the reservoir was controlled by bubbling the water with N<sub>2</sub> gas to attain the measured near-bottom water O<sub>2</sub> concentration. The O<sub>2</sub> concentration in the reservoir was measured with a WTW Microprocessor Oximeter OXI96 electrode. Steady-state incubation was established by circulating the water for ca. 60 h until water samples were collected for analysis. These samples were then immediately vacuum filtered through a polycarbonate membrane (pore size 0.4 μm). The benthic fluxes of DP, DIP, NH<sub>4</sub><sup>+</sup>-N, NO<sub>2</sub><sup>-</sup>-N, NO<sub>3</sub><sup>-</sup>-N and DFe were calculated from the concentration difference between inflowing and outflowing water, flow rate and sediment surface area. DIN was calculated as NH<sub>4</sub><sup>+</sup>-N + NO<sub>2+3</sub><sup>-</sup>-N, whereas dissolved unreactive phosphorus (DUP) was obtained as DP – DIP for both pore water and benthic flux.

In the seasonal study, total DIN and DIP release for the sampling period could be estimated for Storfjärden and Storgadden by assuming that each flux measurement represented the mean release during the period from the midpoint of the current and previous measurements to the midpoint of the current and following measurements.

Certain disadvantages of the incubation technique used here are difficult to overcome (see Holdren and Armstrong 1980). One of the most serious is the inability to simulate the hydrodynamic properties at the sediment-water interface

during the incubations; flow-through incubation, for example, does not necessarily closely simulate *in situ* water currents, turbulence or advection at the sediment-water interface. The magnetic stirring used may also change the concentration gradient of solute at the sediment water interface, which affects molecular diffusion. An increase in stirring speed may increase the benthic flux of DIP until resuspension occurs (Holdren and Armstrong 1980).

In addition to the difficulty of simulating hydrodynamic properties, the pressure at the bottom is much higher than that in the laboratory during the incubations. When a sediment sample is lifted from the bottom towards the surface, the decrease in pressure increases the gas volume in the sediment. The bubbling gas occasionally observed in the sediment core may have disturbed the concentration gradients between the free water and the sediment-water interface. The effect of the change in pressure can be avoided with a benthic chamber placed on the surface of the bottom. However, the difference in sampling disturbance between benthic chambers and flow-through incubation has been observed to be negligible in a shallow (20 m) marine environment (Miller-Way *et al.* 1994).

### 3.3 Statistical analyses of data

Cluster analysis allows groups to be established that are cognate according to the variables measured. SAS (PROC CLUSTER; SAS Institute, Inc., 1985) was used for statistics. The data were clustered by an average distance method (Sokal and Michener 1958) that tends to join clusters with small variances and is slightly biased towards producing clusters with the same variance. Here, cluster analysis was performed by sampling site (individual directed analysis), and data were normalized to the average of 0 and a variance of 1. In the cluster analysis, DM and the concentrations of LOI, TN and TP for each of the 1 cm sub-layers (1–10 cm) were used as discrete variables (a total of 40 variables). One of the applications of cluster analysis is in studies in which sediment samples have been analysed for several metal concentrations (Hodkinson *et al.* 1986, Albani *et al.* 1989).

Pearson product-moment correlation coefficients, regression and stepwise regression models for a combination of explaining variables were calculated using SAS software (SAS Institute Inc., 1989, 1990).

### 3.4 Supporting data used in interpretation of temporal and spatial variations in benthic flux

The Finnish Environment Institute (SYKE) monitors water quality in the coastal areas of Finland. One of the intensively monitored stations, Längden, is located 4 km southwest of Storgadden (Fig. 4b). In the present study, Längden represents the yearly variation in near-bottom water  $\text{PO}_4^{3-}\text{-P}$ ,  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_{2+3}\text{-N}$  concentrations in 1995–2002. The variation in near-bottom water concentrations is compared to the yearly variation in benthic fluxes of DIP,  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_{2+3}\text{-N}$  at Storgadden measured in 1999–2000. The near-bottom water samples were taken with a Limnos sampler and the nutrient analyses performed by SFS standard methods. The near-bottom water  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_{2+3}\text{-N}$  concentrations measured at 73 sites during research cruises in 2000–2002 (Fig. 4d) have been included in the study to represent the near-bottom DIN:DIP mass ratio in the Gulf of Finland in late summer. As with pore water and benthic flux measurements, the near-bottom water DIN is calculated as  $\text{NH}_4^+\text{-N} + \text{NO}_{2+3}\text{-N}$  for both monitoring station and cruises. The unfiltered near-bottom water  $\text{PO}_4^{3-}\text{-P}$  concentration is given as DIP in the calculation of the near-bottom DIN:DIP mass ratio.

## 4 Results and discussion

### 4.1 Characteristics of surface sediments

On the basis of the organic matter concentrations established in this study (average surface LOI 17.6% DM) and the particle size studies of Vallius

(1999a), recent sediment deposits in the Gulf of Finland can mainly be classified as organic-rich clay and silt. The average surface C concentration in the Gulf of Finland is almost twice that in Bothnian Bay and over twice that in the Bothnian Sea (Leivuori 1998). Here, surface LOI values exceeding 20% DM were common and those exceeding 10% DM covered the whole study area (Fig. 7b in VI). The term “organic-rich sediments” used in the present study refers to sediments in which the surface LOI generally exceeds 20% DM. In the Gulf of Finland, the concentration of sediment organic matter decreases by an average of 48% within the 0–10 cm layer (VI), largely due to mineralization during burial. Furthermore, a large part of the sedimented organic matter may have been mineralized anaerobically, because the dissolved  $\text{O}_2$  is depleted within a few millimetres at the sediment surface in the Gulf (Conley *et al.* 1997).

The surface sediment TN concentration is also significantly higher than in the Bothnian Sea and Bothnian Bay, but comparable to that in the Baltic Proper (Table 4). The average surface TP, in turn, is twice the concentration measured in the Baltic Proper below the permanent halocline. The concentration of TP is also clearly higher than that in the Bothnian Sea and Bothnian Bay. The average TP concentration in the deep layer of the open Gulf ( $1.2 \text{ mg g}^{-1} \text{ DM}$ ), however, is comparable to that in the Baltic Proper ( $1.0\text{--}1.2 \text{ mg g}^{-1} \text{ DM}$ , Carman and Wulff 1989) but lower than that in the Bothnian Sea ( $2.4 \text{ mg g}^{-1} \text{ DM}$ ) as measured at one site, where the oxidized layer is several centimetres thick (Mälkki 2000). The results suggest that in the open Gulf of Finland, the P-binding ability of the deep sediment is comparable to that in the main Baltic basin but poorer than that in the Bothnian Sea. In the Gulf of Finland, the surface TP and TN concentrations are evidently high due to the heavy

**Table 4.** Sediment TN, TP and TFe concentrations as  $\text{mg g}^{-1} \text{ DM}$  in the sub-basins of the Baltic Sea.

Sub-basin	TN	TP	TFe	Number of observations	Sediment layer (cm)	Reference
Gulf of Finland	8.6	3.2	45	30 (Fe=20)	0-1	this study, for Fe Leivuori 1998
Baltic Proper	7.3-7.9	1.3-1.6	19.0-19.5	2	0-2	Carman and Wulff 1989
Bothnian Sea	2	1.3	39	24	0-1, 0-2	Leivuori 2000
Bothnian Bay	4	1.5	55	32 (Fe=29)	0-1, 0-2	Leivuori 2000

N and P loading and the more eutrophied conditions resulting in a high sedimentation rate of particulate N and P (Pitkänen *et al.* 1993, Heiskanen *et al.* 1999, VI).

Of the P-binding elements, the surface sediments of the Gulf of Finland are rich in Fe (mean 45 mg g<sup>-1</sup> DM, Leivuori 1998) and poor in Ca (mean 3.2 mg g<sup>-1</sup> DM; V), which may emphasize the role of Fe compounds in P binding compared to those of Ca. Jensen *et al.* (1992) suggested that when the total Fe:P mass ratio is above 15 in lake sediments, there is enough Fe to control the benthic flux of P from sediment to oxic water. The sediment TFe:TP mass ratio usually exceeds 15 in the Gulf of Finland and so there seems to be sufficient TFe in most of the surface sediments to bind P efficiently (V). The TFe concentration does not, however, reveal the pool of Fe(III) oxides that can bind P efficiently. As a matter of fact, in the surface sediments of the transition zone between the Baltic Sea and the North Sea, Fe is mainly bound to sheet silicates, only about 20% of total Fe being in the form of Fe(III) oxides (Thamdrup *et al.* 1994).

A clear vertical change from brown to black was noted in the colour of the surface sediment in the sampled cores. There was usually a 1- to 10-mm-thick brown oxidized surface layer (coloured by Fe(III) oxides) in the upper sediment of the cores sampled in 1992–1995 and beneath it invariably a black layer coloured by FeS. There has been a good agreement between the depth of H<sub>2</sub>S detection and the depth of the transition from brown to black (Thamdrup *et al.* 1994). In the present study, the black layer is considered to be an anoxic reduced layer, as shown by the low redox potentials measured (< 0 mV, V) and the presence of a smell of H<sub>2</sub>S. The appearance of the brown-black transition zone in the sediments varied, however, from one region to another. The thickness of the oxidized layer generally ranged from 5 to 10 mm in the inner and outer Neva estuary but from only 1 to 2 mm in the organic-rich sediments of the open Gulf and in the semi-enclosed bays of the coastal regions in late summer.

When high abundances of benthic animals such as the amphipods *Monoporeia affinis* and/or *Pontoporeia femorata* or the bivalve *Macoma baltica* were observed, the brown oxidized layer reached a thickness of 20 mm (IV, V). The abundance of *M. affinis* in particular may have a marked effect on the oxidant balance in the sediments. The constant high redox potentials as well as the constant TN

and TP concentrations within the uppermost 5 cm suggested that a large number of amphipods can increase the thickness of the oxidized layer and mix the sediment efficiently (V). In addition, the irrigation of burrows with oxic water may lead to a low DIP concentration due to newly formed Fe(III) oxides (Hansen *et al.* 1998) and to high concentrations of NO<sub>2+3</sub>-N due to enhanced nitrification (Kristensen and Blackburn 1987, Henriksen *et al.* 1983). Thus it is, likely that the effect of bioturbation resulted in low DIP and NH<sub>4</sub><sup>+</sup>-N and high NO<sub>2+3</sub>-N concentrations in the pore waters (V). Moreover, the highest denitrification rates were found in areas bioturbated by amphipods (Gran and Pitkänen 1999).

In the present data, the weakening of the sediment oxidation state between 1992–1995 and 1996–2001 showed up as an increase in the number of sites with reduced anoxic sediments. In 1996–2001, the sediment sampling sites at which the black reduced layer reached the very surface of the sediment occurred at greatly variable water depths, from coastal waters to the open Gulf (Fig. 4c, Lehtoranta, unpubl.). Further, the sediment surface was often colonized by white bacteria (probably filamentous sulphur-oxidizing *Beggiatoa* spp). The absence of the oxidized surface layer is in general related to the high sediment organic matter concentration and hypoxic conditions prevailing in the near-bottom water (Jørgensen 1996a).

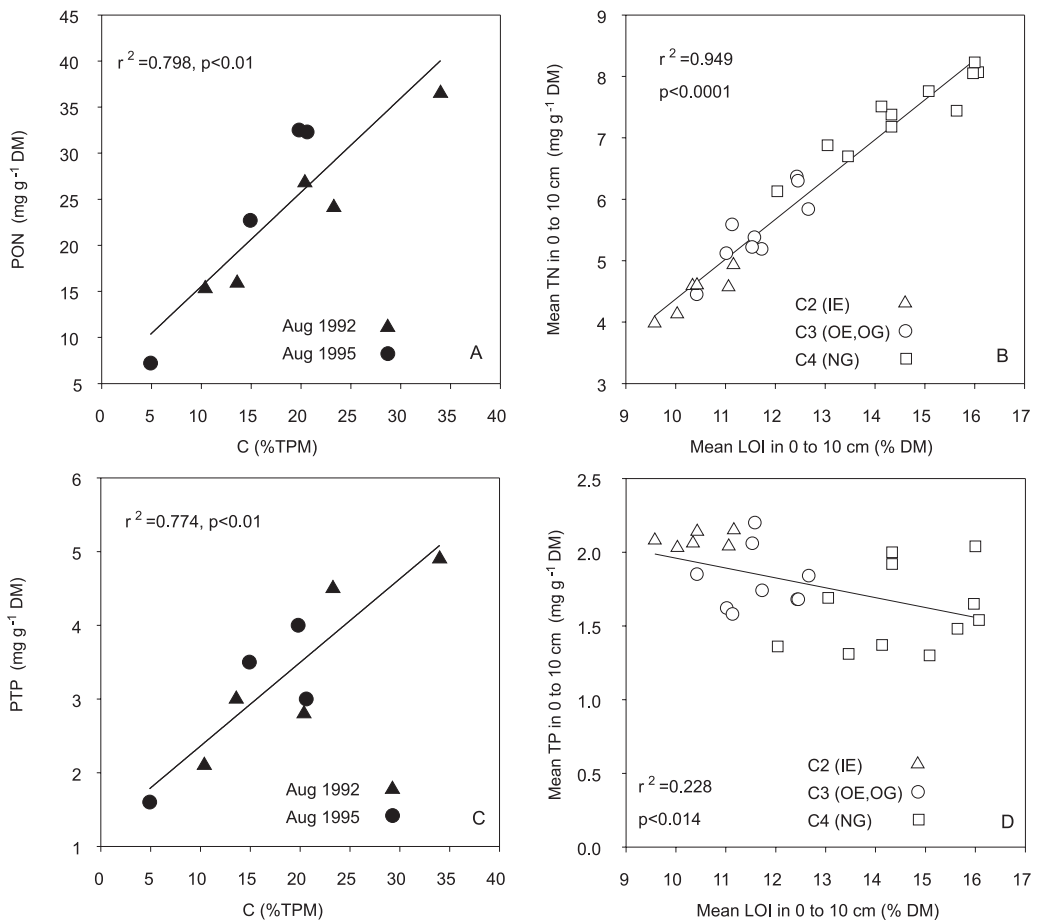
The weakening of the sediment oxidation state in the Gulf of Finland may be related to the medium pulse of seawater to the Baltic that occurred in 1993 and to the intrusion of saline water from the main Baltic basin to the Gulf in 1996. An increase in deep water salinity was observed in the central Gulf in mid-1994, but the highest deep water salinity values, between 8.9 and 9.5, were observed in the central (Alenius *et al.* 1998, Lips and Leppänen 2002) and coastal areas of the western Gulf after 1996 (7.0; III). A corresponding decrease in near-bottom water O<sub>2</sub> concentrations was observed in the central Gulf and coastal waters after 1996 (III, Lips and Leppänen 2002). The increase in deep water salinity may have strengthened the vertical stratification, thus hindering efficient vertical mixing of the water column and leading to the poor conditions observed in the sediments after 1996.

The abundance of burrowing benthic animals seems to be related to the weakening of the sediment oxidation state. Benthic animals were exceptionally abundant in the Gulf of Finland in 1991–

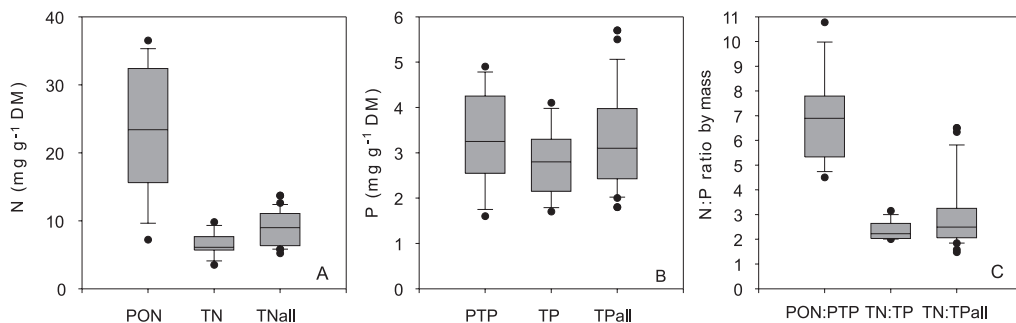
1995 (Kotta *et al.* 2002), but after the high salinity values observed in 1996, there was a dramatic fall in their numbers in 1996–1998 (Kotta *et al.* 2002). Later, in 1999–2002, a very low abundance or total absence of benthic animals was recorded in large areas of the Gulf (A. Laine pers. comm.). Similar poor conditions may, however, have occurred earlier, too. Gripenberg (1934), for example, reported grey or black sediment surfaces with smell of  $\text{H}_2\text{S}$  back in 1924, and Stenij (1929) low  $\text{O}_2$  conditions in the Gulf of Finland in 1928. Changes in hydrographic features as well as eutrophication should therefore be taken into account when seeking the cause of the poor oxidation state of the sediments.

## 4.2 Binding, dissolution and burial of phosphorus in sediments

According to the strong positive relationship between settling matter POC, PON and PTP (Fig. 6a and c), the sedimentation of organic particulate matter is an important mechanism for transporting both N and P into the sediment in late summer. Similar relationships between these factors exist in the western Gulf of Finland (Laakkonen *et al.* 1981). In the water column, though, the chemical precipitation of P with Fe(III) oxides may also play a role (Gunnars *et al.* 2002).



**Fig. 6.** Relationship between concentrations of (a) POC and PON in settling matter, (b) sediment LOI and TN in 0–10-cm sediment layer and corresponding relationship between (c) settling matter POC and PTP and (d) sediment LOI and TP. In (b) and (d) C1, C2 and C3 denote clusters formed in cluster analysis (see Fig. 6 in VI) and corresponding area, *i.e.* IE = Inner Neva Estuary, OE = Outer Neva Estuary, OG = Open Neva Estuary and NG = Northern Gulf.



**Fig. 7.** Average concentrations of (a) settling particulate organic N (PON) and sediment TN and (b) settling particulate P (PTP) and sediment TP at trap sites and at all studied sites (TNall and TPall) in 0–1-cm sediment layer. Box plot shows median, 25th and 75th percentiles and standard deviation.

The PON concentration in settling matter was much higher than the TN concentration in the sediment surface, whereas the PTP and sediment TP concentrations in settling matter were close to each other (Fig. 7a and b). Comparable settling PTP and sediment surface TP concentrations have also been measured from the other sea areas, including the central Gulf of Finland (Jensen *et al.* 1995, Sundby *et al.* 1992, Leivuori and Vallius 1998). The results of the present study suggest that a much larger portion of settling PON than of PTP was lost in the surface sediments after settling. In other words, retention of sedimented P may be more efficient than that of N in surface sediments. The discrepancy between N and P may be explained by the fact that the settled organic matter rich in P was partly mineralized and partitioned between pore water and surface adsorption sites in sediments (see section 1.5.1). However, in addition to the adsorption of newly mineralized P, the surface TP may be increased due to the binding of upward diffusing P from deeper layers onto metal oxides present in the surface layer (Sundby *et al.* 1992). The settled PON is mineralized to  $\text{NH}_4^+$ , which is not, in contrast to P, effectively adsorbed by inorganic compounds.

The difference in the binding of N and P after settling was supported by the opposite correlations between sediment TN and TP and organic matter, although both PON and PTP correlated strongly and positively with POC in settling matter (Fig. 6a–d). The correlation between sediment organic matter and TN remained strong and *positive* in the 0–10 cm layer (Fig. 6b) but that between sediment organic matter and TP was *negative* (Fig. 6d). The change in the correlation from positive to negative

between organic matter and P is attributed to the participation of inorganic compounds in the binding of P. Unlike P, N is mostly bound to organic matter in sediments, even after the mineralization processes. This is in accordance with the finding that organic N may constitute 99% of the N in marine sediments (Keefe 1994).

In sediments, the TN and TP concentrations increased towards the surface layers (IV, V, VI). The increase may be due to enhanced external loading of N and P and subsequent sedimentation of particulate matter enriched in N and P. Another explanation is that, during burial, the dissolution processes reduce the concentrations of TN and TP. The average accumulation rate of 0.6 cm in the recent deposition areas of the Gulf (Kankaanpää 1997) suggests that the deep layer studied is mostly about 20 years old. Moreover, the steepest decrease in both the TN and TP concentrations was observed within the 0–2 cm layer (IV, V, VI). Hence, the decrease in TN with sediment depth found here is largely attributed to the mineralization of organic N during burial (II), a conclusion supported by the concurrent increase in the  $\text{NH}_4^+$ -N concentration with sediment depth (II, V). The decrease in the TP concentration with the simultaneous increase in pore water DIP is largely attributed to the release of P from both organic and inorganic compounds (II, V).

The processes occurring in sediments during burial seem to lead to more efficient dissolution of P than of N, although after settling the surface sediment retains P more effectively than N. The average sediment surface TN and TP concentrations were higher than those of the deep layer (9–10 cm) by 44% and 61%, respectively (VI).

Thus, in the sediment layers studied the average concentration of TP decreased relatively more with sediment depth than did that of TN. Further, except in the inner Neva estuary, the ratio of TN to TP (ranging from 2.4 to 5.8 by mass; VI) was higher than the pore water DIN:DIP ratio (ranging from 0.8 to 2.0 by mass; II, IV) in the deep layers of the sediments, suggesting that P is dissolved more efficiently than N during burial and thus leads to a low pore water DIN:DIP ratio in sediments.

The measured steep increase in pore water DIP with sediment depth – except in the inner Neva estuary – suggests efficient dissolution of P from a solid to a dissolved phase and consequently a high diffusion rate towards the surface layer of the sediment (II, IV, V). In the organic-rich bottom areas of the Gulf, the pore water DIP concentrations are between 7.4 and 13.7 mg l<sup>-1</sup>, with a maximum value of 16.5 mg l<sup>-1</sup>. These are among the highest values reported from northern temperate marine regions, and are comparable to those recorded in the Baltic Proper (Carman and Rahm 1997) and the German Bight (Slompe *et al.* 1998).

In the present study, the pore water DIP concentration was clearly dependent on the sediment redox potential (V), implying that the dissolution of sediment P was closely coupled with a reduction in metal oxides. Under anaerobic conditions, however, P can also be released from bacteria, which may store very high concentrations of P under aerobic conditions and release intracellular P via enzymatic hydrolysis when conditions turn anaerobic (Deinema *et al.* 1985).

According to the data on P fractionations (Fig. 8a–j) and the use of multiple regression analysis (V), the main mobile P pools in the Gulf of Finland were formed by Fe-bound P and organic P. As a matter of fact, sediment TFe and organic matter concentrations together explained 82% of the variation in the TP concentration in sediments (V). When an oxidized layer was present at the surface, the Fe-P (NaOH-P) concentrations were at their highest, accounting for 30% to 50% of TP (Fig. 8a–d). In the deep black layer, the proportion of Fe-P amounted to only 15% of TP. The decrease in the Fe-P pool and the increase in DIP with sediment depth indicated that a large portion of the P is released from Fe(III) oxides undergoing reduction in sediments (see section 1.5.2). On the basis of the P fractionations and the total accumulation area, estimated to be 9000 km<sup>2</sup>, the Fe-bound P pool would amount to roughly 17 000 t in the 0–2 cm sediment

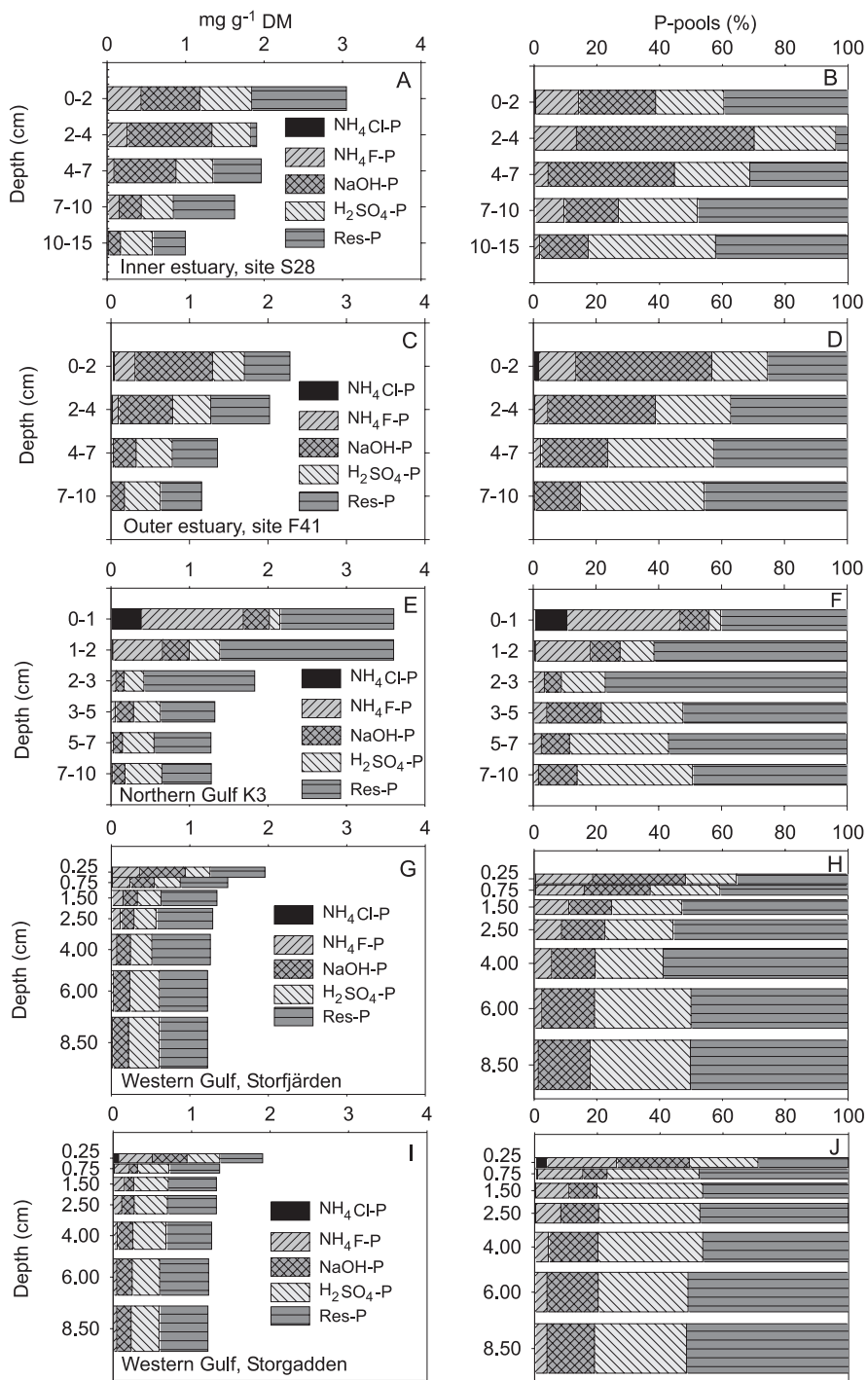
layer. Thus, there is a large pool of mobile P in the surface sediments of the Gulf that can be dissolved into pore water under anoxic conditions.

In the organic-rich sediments of the present study, at sites where the black reduced layer extended right to the surface of the sediment, the pool of Fe-P constituted only 9% of the TP already in the surface layer (Fig. 8f), and the pool of loosely bound P (NH<sub>4</sub>Cl-P) was very high. The result obtained indicates that the degree of P saturation in the organic-rich sediments is high (Boström *et al.* 1988) and that the ability of the sediment to retain P has declined drastically (II).

Al-P (NH<sub>4</sub>F-P) may also play an important role in the binding of P in the surface sediment, as suggested by the rather high concentration of Al-P there (Fig. 8a–j). The increase in the Al-P concentration in comparison to Fe-P is attributed to the fact that Fe(III) oxides have a lower pK<sub>a</sub> value than Al(III) oxides and, thus, at a given pH, Al(III) is surrounded by a higher number of undissociated H<sub>2</sub>O groups, which are more easily replaced by H<sub>2</sub>PO<sub>4</sub><sup>-</sup> anions than are OH<sup>-</sup> groups (Hartikainen 1981). The concentration of Al-P was, however, negligible in the deep layer of the sediment at all the sites studied. Thus, the pool of Al-P does not play a significant role in burial of P. On the other hand, NH<sub>4</sub>F is also known to extract Fe-P (Pettersson *et al.* 1988), which may partly explain the decrease in the pool of NH<sub>4</sub>F-P representing Al-bound P during burial.

In the deep layer of the sediment, a large portion of the sediment P was bound to Ca (H<sub>2</sub>SO<sub>4</sub>-P, Fig. 8a–j). The results suggest that P is buried largely in association with Ca rather than with Fe or Al compounds. No indication of P having converted to authigenic apatite P (Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>OH) was observed during the early diagenesis, the Ca-P concentration being almost constant and unrelated to sediment depth (Fig. 8a and c). In the Finnish coastal area, however, a slight variation was noted in the Ca-P concentration with sediment depth (Fig. 8e), but in general there appears to be little authigenic formation of apatite in the sediment layer studied. In Århus Bay, the apatite-P concentration is also uniform with depth (Jensen *et al.* 1995). Here, only the uppermost 10-cm layer was studied; examination of deeper layers would provide more insight into the role of Ca in sediment P binding. Continental slope sediments, for example, show strong indications of authigenic apatite formation at the expense of Fe-P (van Cappellen and Berner 1988).





**Fig. 8.** Depth distribution of P-fractions (a-f) along the estuarine gradient in the eastern Gulf of Finland and (g-j) in the western Gulf of Finland. Data of sites S28 and F41 are from Paavilainen (1997).



Ruttenberg and Berner (1992) found that the size of the authigenic apatite reservoir increases with sediment depth in the continental margins of Long Island Sound (thickness of studied layer 0–300 cm) and the Mississippi Delta (0–70 cm).

In the eastern Gulf of Finland, the proportions of the three major P-pools in the deep layer were 15% for Fe-P, 40% for Ca-P and 45% for Res-P of TP, whereas in the western coastal Gulf the figures were 17%, 30% and 50%, respectively. Thus, in the entire Gulf of Finland, rather similar proportions of Fe-P, Res-P and Ca-P pools are buried in the sediment. In Århus Bay, Fe- and Mn-bound P constitutes only 3.5% of the buried TP (Jensen *et al.* 1995). In their study, however, Jensen *et al.* (1995) used the P-fractionation method of Jensen and Thamdrup (1993). The use of different methods in the fractionation of P may partly explain the difference in Fe-P pools occurring between Århus Bay and the Gulf of Finland.

### 4.3 Role of settled organic matter in burial and release of nutrients along estuarine gradient

The decrease in the gross sedimentation rate of C, N and P along the estuarine gradient of the River Neva suggests that N and P are efficiently settled in the inner estuary (Fig. 2 in VI; see Heiskanen *et al.* 1999). The observation is consistent with the non-linear dependencies between the total and inorganic N and P concentrations and salinity in the surface water layer (Pitkänen *et al.* 1993, Pitkänen and Tamminen 1995) and the decrease in chlorophyll-*a* and phytoplankton biomass along the estuarine gradient during the summer (Kaupila *et al.* 1995, Pitkänen and Tamminen 1995). In the inner Neva estuary, however, a large portion of the gross sedimentation evidently consists of resuspended matter, as suggested by the low concentration of suspended solids in the waters of the Neva. The annual averages of suspended matter in the five branches of the Neva were 5.1 in 2000 and 7.3 mg l<sup>-1</sup> in 2001 (P. Ekholm, unpubl.). Further, in the coastal area of the Baltic Proper, the proportion of resuspended settling matter commonly exceeds 50% at water depths similar to those of the Gulf of Finland (Blomqvist and Larsson 1994).

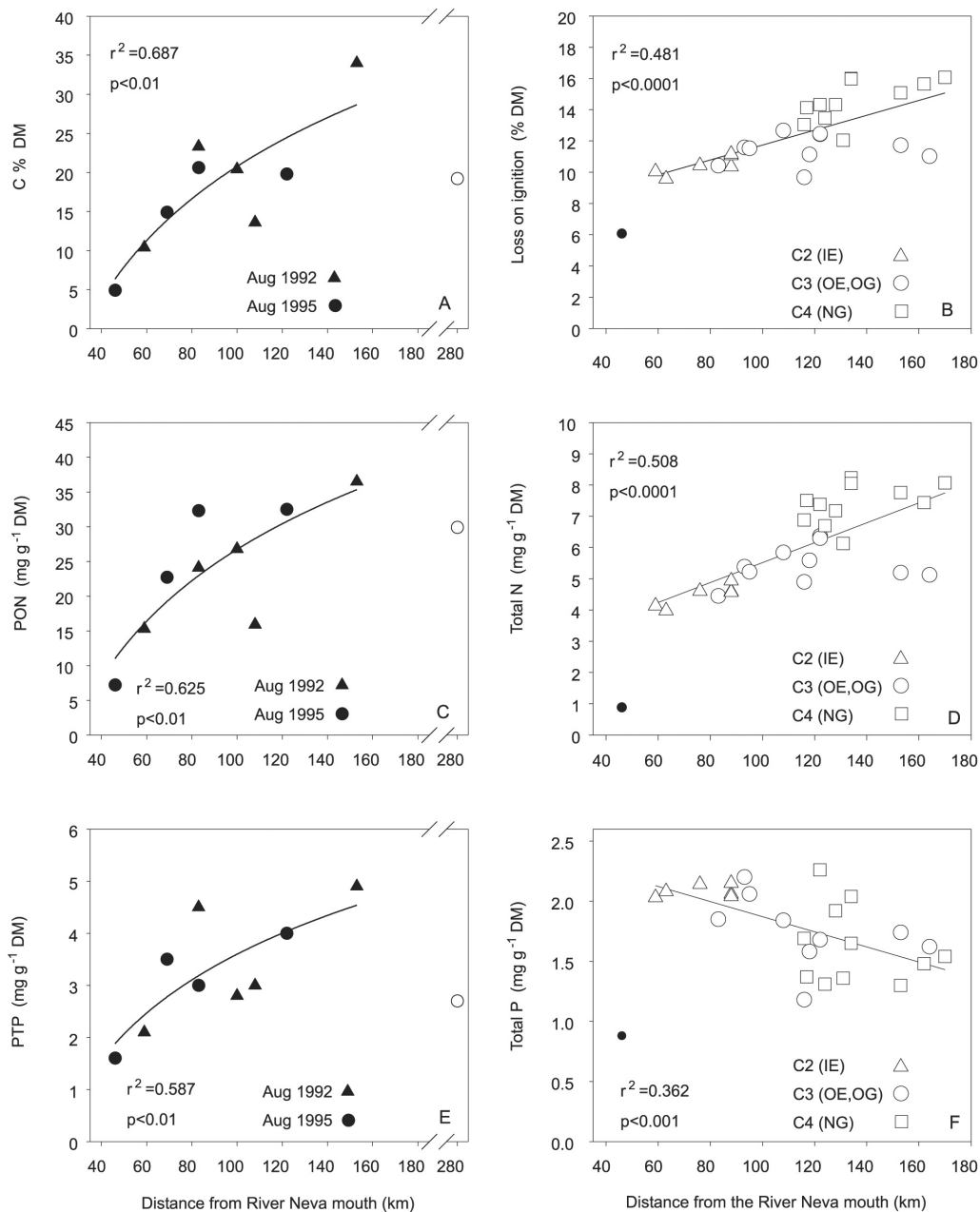
The increase in the proportion of settling POC, PON and PTP in particulate matter along the estuarine gradient (Fig. 9a, c and e) is attributed

to the decrease in the sedimentation rate of inorganic particulate matter supplied by the Neva and the increase in that of autochthonous particulate organic matter. The increase in settling POC and PON seemed to result in an increase in the concentration of sediment organic matter and TN along the estuarine gradient (Fig. 9b and d). However, the increase in PTP along the estuarine gradient resulted in a decrease rather than an increase in the TP concentration in sediment (Fig. 9f). In addition, neither TN or TP concentrations correlated with water depth, even though this increases significantly, from 20 to 60 m, from the inner estuary towards the west (VI).

The increase in the sediment TN concentration along the estuarine gradient appeared to result in enhanced burial of N, because the deep layer TN concentration could be predicted well by the surface TN concentration ( $r^2=0.73$ ,  $p < 0.0001$ ; VI). It is, therefore, probable that the surface TN concentration largely controls the concentration of buried N. Henrichs and Reeburgh (1987) suggested that the burial efficiency of organic matter increases with its deposition rate; the same can be expected to hold for TN.

Unlike TN, however, the deep layer TP concentration could not be predicted by the surface sediment TP concentration ( $r^2=0.09$ ) along the estuarine gradient (VI). This poor dependency is due to the fact that despite considerable variation in the surface TP concentration, the concentration of TP has remained fairly constant in the deep layer; for example, the average TP concentration with a 95% confidence interval varied considerably in the surface layer (TP  $3.2 \pm 0.4$  mg g<sup>-1</sup> DM) but only slightly in the deep layer (TP  $1.2 \pm 0.1$  mg g<sup>-1</sup> DM). The conclusion, then, is that, in the sediments, the dissolution of the mobile P pool during burial eventually leads to fairly similar TP concentrations in the deep layer that are not related to the surface concentration.

In the present study, only the *increase* in the sediment organic matter concentration explained significantly the *decrease* in the mean TP concentration (Fig. 6d). The relationship obtained is analogous to the decrease in the mean TP concentration along the estuarine gradient (Fig. 9f). In the Delaware estuary, the decrease in the sediment Fe(III) oxide concentration explains the decrease in the sediment TP concentration along the estuarine gradient (Strom and Biggs 1982). Here, Fe(III) oxides were not measured, but it can be hypothesized that



**Fig. 9.** Concentrations of particulate (a) POC, (c) PON and (e) PTP in settling matter and average concentrations of (b) organic matter as LOI, (d) TN and (f) TP in 0–10-cm sediment layer vs. distance from the River Neva mouth. Reference concentration for settling matter in the coastal western Gulf of Finland (not included in calculations) is marked with an open circle (Heiskanen and Tallberg 1999). In (b), (d) and (f) C1, C2 and C3 denote clusters formed in cluster analysis (see Fig. 6 in VI) and corresponding area, *i.e.* IE = Inner Estuary, OE = Outer Estuary, OG = Open Gulf and NG = Northern Gulf. Sediment sampling site S1 (black dot) was not included in calculations.

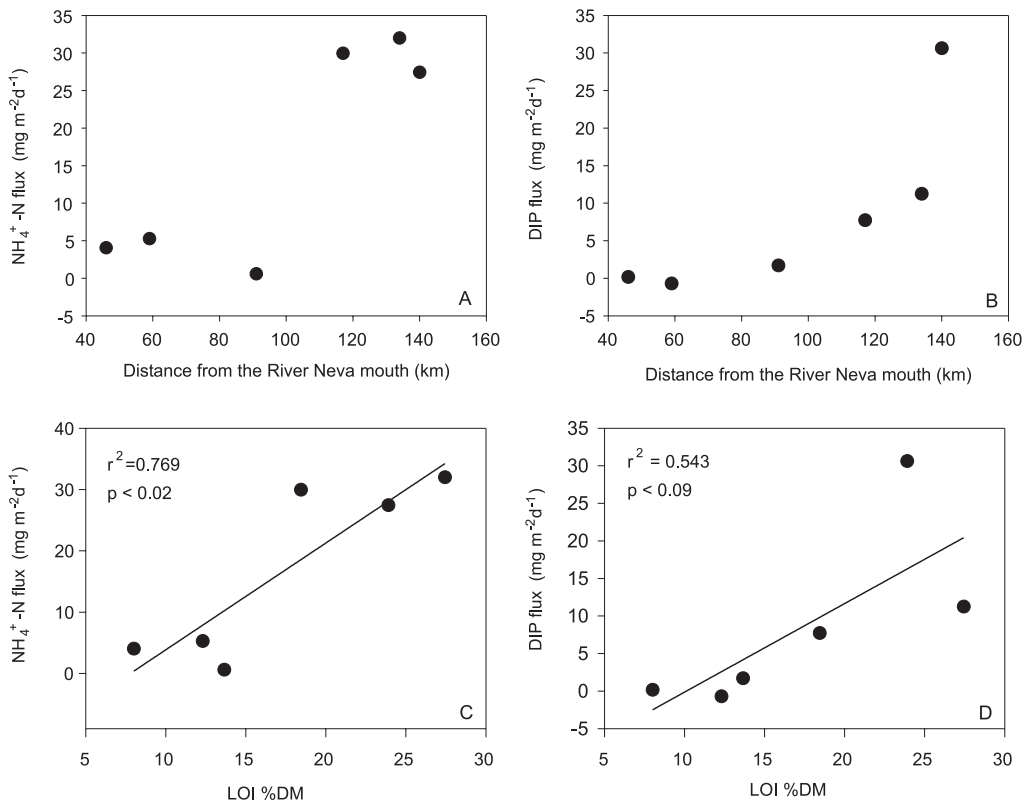
the organic matter concentration is related to the efficiency of Fe(III) oxides to retain P in sediments along the estuarine gradient as follows:

The increase in the sediment organic matter concentration along the estuarine gradient together with changes in hydrodynamic conditions may shift the balance of oxidants towards anaerobic mineralization closer to the sediment-water interface. Thus, it is possible that in organic-rich sediments, Fe(III) oxides are efficiently reduced by Fe(III) oxide-reducing bacteria and by  $H_2S$  in the surface layer of the sediments, whereas in organic-poor sediments efficient Fe(III) oxide reduction does not occur until deeper in the sediment. Accordingly, a decrease in the ability of sediment to retain P with an increase in organic matter was observed along the estuarine gradient. The decrease in the ability of sediment to retain P along the estuarine gradient is supported by the following factors:

– the vertical TP concentration profiles produced by cluster analysis show that in the inner estu-

ary the 0–7 cm layer and in the outer estuary and the open Gulf the 0–5 cm layer can retain P well, whereas in the organic-rich northern areas the layer able to retain P is only 0–2 cm thick (Fig. 7 in VI);

- the sediment Fe-P concentration (NaOH-P) suggests that Fe maintains its ability to bind P deeper in the inner Neva Estuary and the open Gulf than in the organic-rich areas (Fig. 8a–f);
- the pore water DFe:DIP ratio of 4.3 by mass suggests that there is enough DFe to prevent DIP release to water in the inner Neva Estuary, whereas in the organic-rich sediments of the open Gulf the ratio of 0.09 by mass is insufficient to retain diffusing P in sediments in late summer (V, see Ignatieva 1999);
- both the pore water DIP concentrations (II) and the pool of loosely-adsorbed P increase along the estuarine gradient (Fig. 8a–f); and
- the benthic flux of DIP from the sediment to water measured in early September appeared to



**Fig. 10.** Relationship between benthic flux of (a) NH<sub>4</sub><sup>+</sup>-N (b) DIP and distance from the River Neva mouth and between benthic flux of (c) NH<sub>4</sub><sup>+</sup>-N (d) DIP and sediment organic matter concentration.

increase rather than decrease with the sediment organic matter concentration and with the estuarine gradient (Fig. 10b and d).

Clearly, then, the sediments of the inner Neva Estuary retain P better than do the organic-rich sediments of the open eastern Gulf. According to cluster analysis, the majority of the bottoms with high organic matter concentrations are situated in the northern part of the open eastern Gulf (VI).

#### 4.4 Seasonal variation in benthic nutrient flux

There is a clear seasonal pattern in temperature, salinity and concentrations of  $O_2$ ,  $NH_4^+$ -N,  $NO_{2+3}^-$ -N and DIP in the near-bottom water at Längden monitoring station, close to Storgadden (Fig. 11a–f; see Niemi 1975). The near-bottom temperature and salinity usually begin to increase in early spring, before May. Salinity is normally at its highest in summer. The increase in salinity is attributed to the intrusion of more saline water from the water layers near the permanent halocline of the open Gulf after ice-melt and the increase in surface water temperature (Niemi 1975, Alenius *et al.* 1998). Every summer, the  $NH_4^+$ -N and DIP concentrations increase but the  $O_2$  and  $NO_{2+3}^-$ -N concentrations decrease in the near-bottom water. The concentrations of  $NH_4^+$ -N and DIP are usually highest in mid-summer. In autumn, the breakdown of the temperature stratification and the subsequent mixing of water cause a peak in the near-bottom temperature and  $O_2$  concentration and a steep drop in salinity and nutrient concentrations.

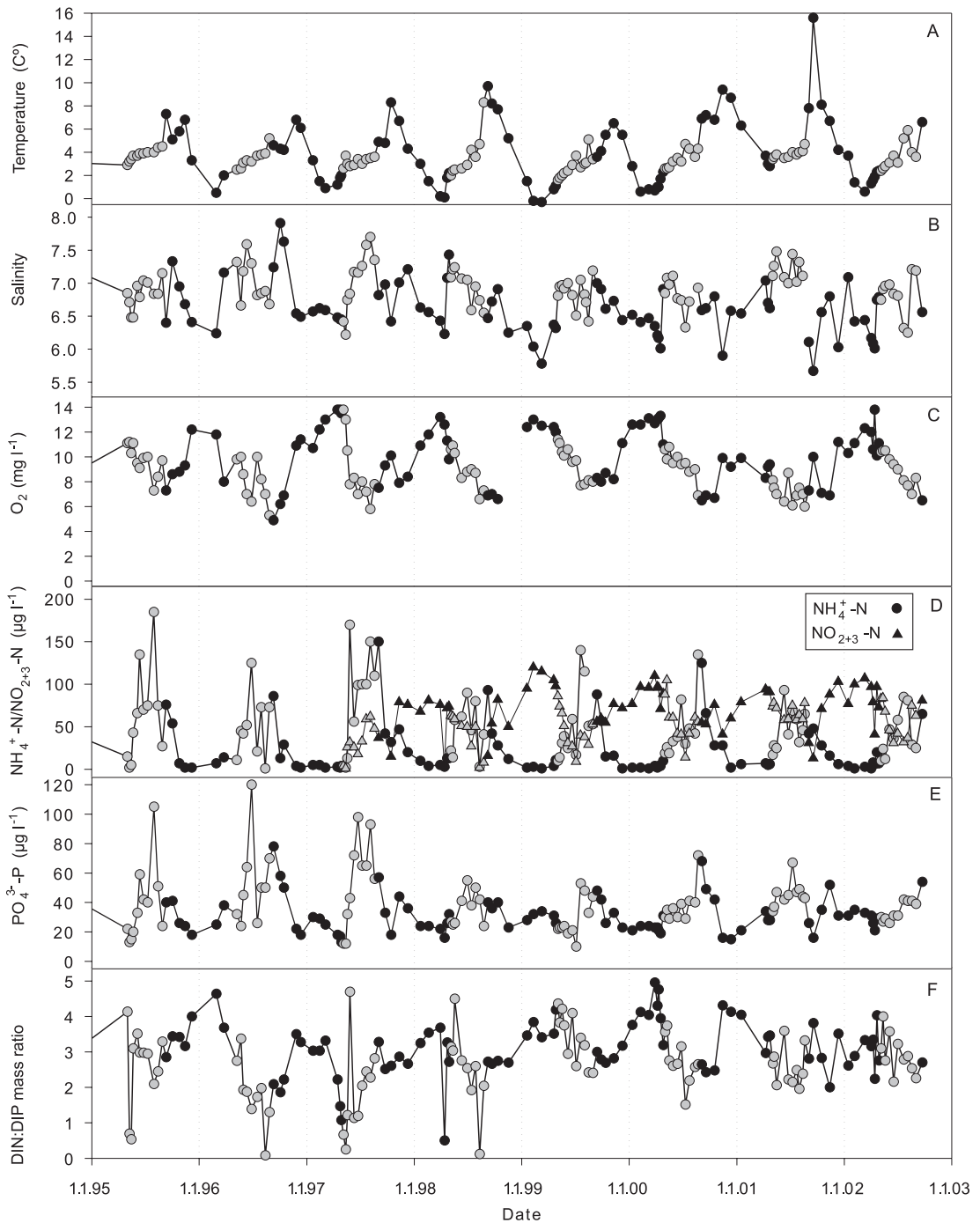
Seasonal agreement between the benthic DIP fluxes measured at Storgadden and the variation in DIP in the near-bottom water at Längden (Fig. 11e and Fig. 12a) is good. High benthic DIP fluxes were recorded between June and late August (maximum  $32 \text{ mg m}^{-2} \text{ d}^{-1}$  in July), whereas only small effluxes and influxes were recorded between October and March (minimum  $-0.2 \text{ mg m}^{-2} \text{ d}^{-1}$  in March). There was a significant efflux of  $NH_4^+$ -N throughout the year (Fig. 13a). However, the seasonal patterns were fairly similar for the release rates of  $NH_4^+$ -N and DIP. The highest  $NH_4^+$ -N flux was measured in July ( $48 \text{ mg m}^{-2} \text{ d}^{-1}$ ) and the lowest in March ( $17 \text{ mg m}^{-2} \text{ d}^{-1}$ ). In contrast to  $NH_4^+$ -N, the benthic  $NO_3^-$ -N flux was always towards the sediment (Fig. 13c). In addition, a small influx of  $NO_2^-$ -N was measured throughout the year, except

in June when a low efflux of  $0.04 \text{ mg m}^{-2} \text{ d}^{-1}$  was recorded (Fig. 13e). Thus, the DIN released from the sediment to water was almost completely in the form of  $NH_4^+$ -N and the influxes of  $NO_3^-$ -N and  $NO_2^-$ -N could only reduce the efflux of DIN slightly.

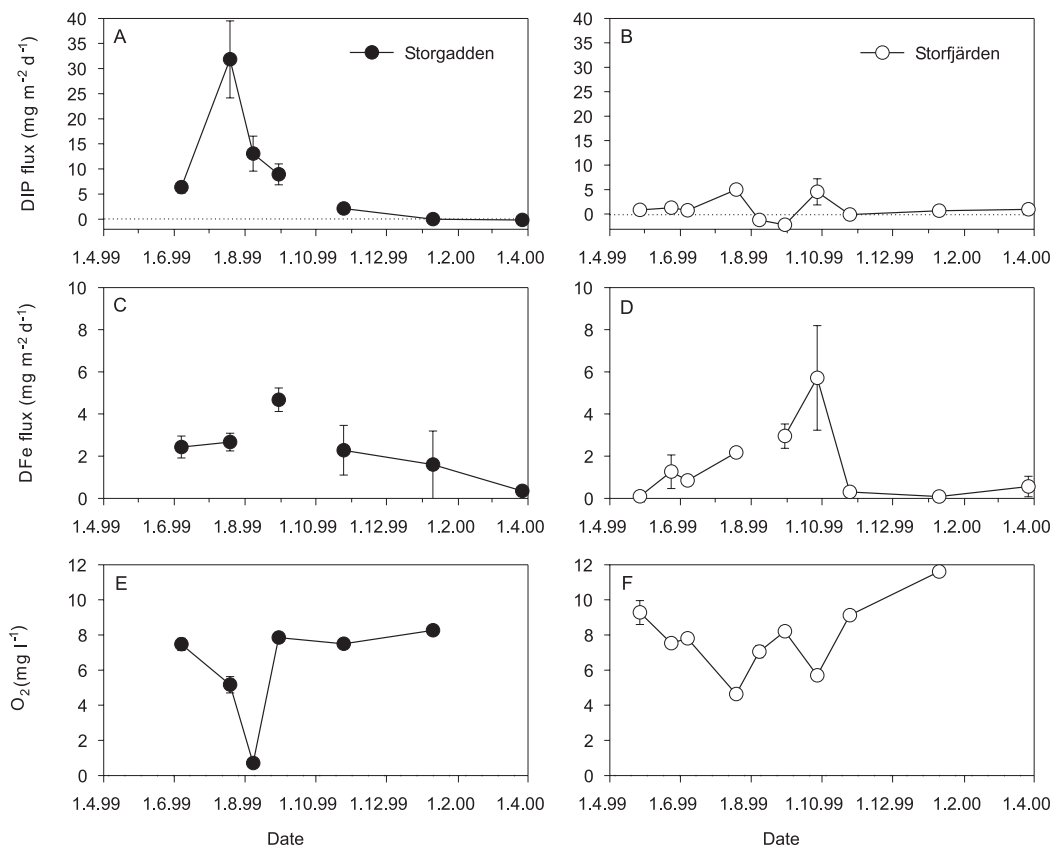
At Storfjärden, the highest DIP flux was measured in summer, but the release rate was clearly lower than that at Storgadden (Fig. 12b). The highest  $NH_4^+$ -N flux was observed in summer, but the release rate was, again, generally lower than at Storgadden (Fig. 13b). In contrast to Storgadden, a significant efflux of  $NO_3^-$ -N and a low efflux of  $NO_2^-$ -N (except in July) were measured at Storfjärden in summer (Fig. 13d and f). The differences between the two stations in the benthic fluxes of DIP,  $NH_4^+$ -N and  $NO_3^-$ -N may be attributed to the bioturbation caused by abundant *Macoma baltica* and the better oxidation state of sediment at Storfjärden than at Storgadden (see section 4.5).

At northern temperate latitudes, seasonal patterns of P release similar to those at Storgadden and Storfjärden have been observed in several coastal and near-shore marine sediments with a marked seasonal variation in near-bottom temperature (*e.g.* Jensen *et al.* 1995, Boers *et al.* 1998, Hopkinson Jr. *et al.* 2001, Rozan *et al.* 2002). At Längden, however, the near-bottom DIP concentration increases even though the temperature only varies between +1 and +4 °C in summer. The highest DIP efflux was measured when the temperature was only +4.0 °C at Storgadden in July. In summer, the temperature was considerably lower at Storgadden (range +2.7–3.5 °C; IV) than at Storfjärden (range +5.0–7.0 °C; IV), but the release rate of DIP was much higher at Storgadden. These results demonstrate that the benthic flux of DIP can be high despite a low temperature above the sediment surface in summer.

Several coinciding factors may explain the increase in benthic flux of DIP in mid-summer and early autumn. The settling of the spring bloom (Laakkonen *et al.* 1981, Heiskanen 1998) serves as a fresh energy source for microorganisms, which in turn enhances microbial activity in sediments during the summer (Meyer-Reil 1983, Graf *et al.* 1983). The release of DIP did not, however, occur in early June, right after the settling of the spring bloom at the end of May at Storfjärden (a comparison with Storgadden cannot be made due to a lack of measurements). As discussed in section 1.5.1, the poor correlation between the settling



**Fig. 11.** Seasonal variation in near-bottom water (a) temperature, (b) salinity, (c)  $O_2$ , (d)  $NH_4^+-N$  and  $NO_{2+3}-N$ , (e)  $PO_4^{3-}-P$  and (f) DIN:DIP ratio at Längden monitoring station. Grey symbols denote measurements between May and August.



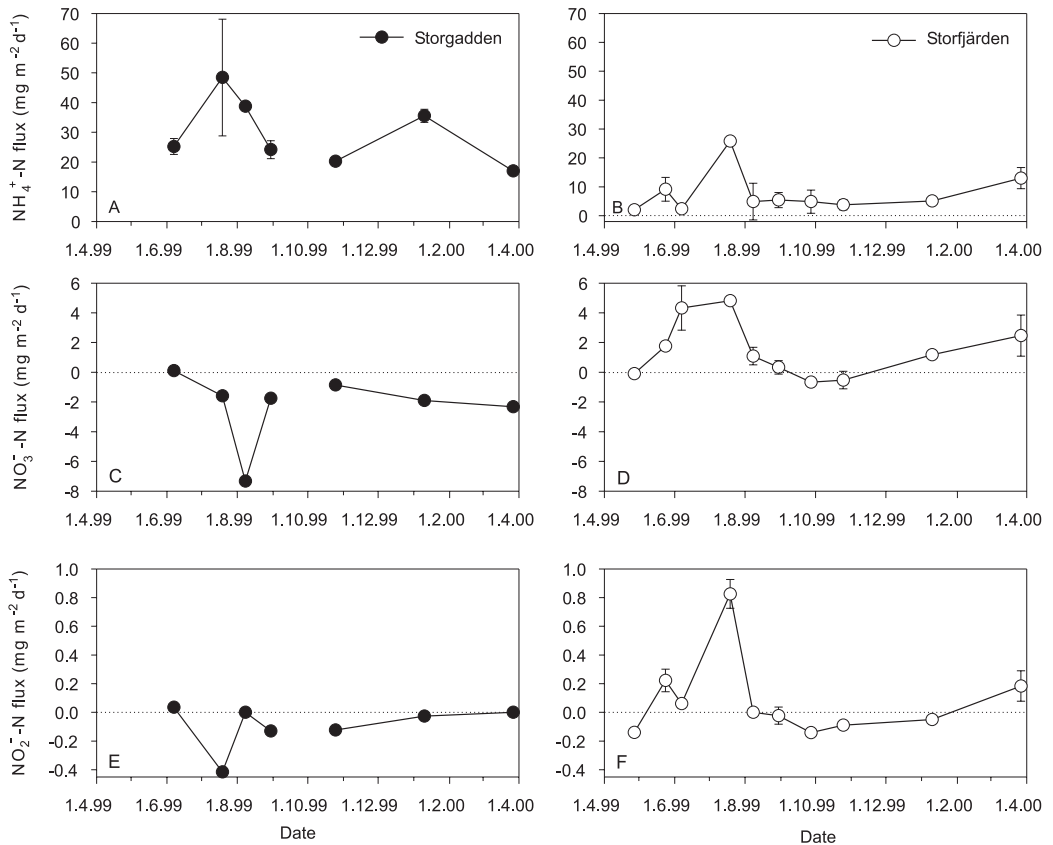
**Fig. 12.** Seasonal variation in benthic flux of (a) DIP, (b) DFe and (c) measured  $O_2$  concentrations in near-bottom water after incubation at Storgadden and Storfjärden. Bars denote standard error of the mean.

of the spring bloom and the efflux of DIP may be attributed to binding of the mineralized org-P to inorganic particulate form. Furthermore, the slight increase recorded in the near-bottom temperature in summer may promote the microbial activity and molecular diffusion of solutes in sediments. The effect of such a slight increase in temperature on molecular diffusion is, however, small.

Seasonal changes in hydrographic features may also increase the benthic flux during the summer period. In summer, density stratification is strengthened due to the formation of the thermocline and the increase in near-bottom salinity (Fig. 11b). Density stratification prevents the efficient mixing of surface and deep water layers, resulting in a prolonged residence time of the near-bottom water. Owing to this prolonged residence time and the high sediment  $O_2$  consumption caused by a high sediment organic matter content, the near-

bottom  $O_2$  concentration decreases in summer (see Fig. 11c). Although  $O_2$  is not depleted from the near-bottom water, the lowered  $O_2$  concentration may cause anoxia at the sediment-water interface (Rahm 1987), thus favouring the release of DIP and  $NH_4^+-N$ . It is also likely that anoxia in sediment in summer permits anaerobic microbial  $SO_4^{2-}$  reduction close to the sediment-water interface (Thamdrup *et al.* 1994, Jørgensen 1996a), which in turn affects the cycling of Fe, S and P in surface sediments.

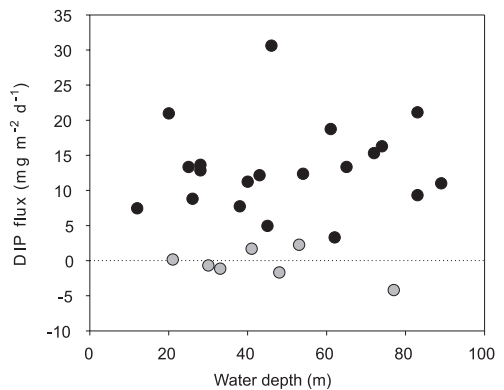
A common feature in all the high effluxes of DIP measured in summer or early September was that the black layer indicating the presence of FeS compounds extended to the very surface of the sediment (Fig. 14). In contrast, only low fluxes were measured at the sediment-water interface at bottoms where a brown oxidized layer was present. One might expect a relationship between



**Fig. 13.** Seasonal variation in benthic flux of (a)  $\text{NH}_4^+\text{-N}$ , (b)  $\text{NO}_3^-\text{-N}$  and (c)  $\text{NO}_2^-\text{-N}$  at Storfjärden and Storgadden. Bars denote standard error of the mean.

water depth and sediment quality; however, the anoxic reduced bottom areas were found at greatly variable water depths (Fig. 14).

The poor correlation between water depth and sediment organic matter, TN, TP (VI) and benthic nutrient flux (Fig. 14) is largely attributed to the complex morphology of the study area. Hence, the sedimentation of fine particulate matter and the renewal of near-bottom water may vary greatly in late summer, regardless of water depth. Sills, islands and headlands form semi-enclosed basins, in Finnish coastal waters in particular. In these basins, the density stratification and prevailing near-bottom water currents may differ from those in the open sea even when the water depths are similar. Thus, the benthic flux of DIP may differ greatly in adjacent basins in late summer (e.g. sites 7 and 10 in Fig. 4c, benthic DIP flux in Fig. 18c).



**Fig. 14.** Correlation between water depth and benthic flux of DIP. Grey symbols denote oxidized sediment (i.e. bottom with brown oxidized surface layer) and black symbol anoxic reduced sediment (i.e. bottom where black layer extended to surface of sediment).



#### 4.5 Pore water iron:phosphorus ratio as an indicator of phosphorus release to oxic water

Although there seemed to be sufficient TFe to retain P in sediments, the pore water DFe concentrations were low compared to those of DIP. At Storfjärden, the pore water DFe concentrations increased with sediment depth within the 0–3 cm layer, but in deeper layers decreased, being near or below the detection limit at 5–10-cm depth (IV). In addition, high DFe concentrations were measured in the brown oxidized layer (excluding the uppermost sediment layer) but only low DFe concentrations in the black sediment layer. Vertical pore water profiles of DFe similar to those at Storfjärden have been reported from the Baltic Sea–North Sea transition area (Thamdrup *et al.* 1994), the Atlantic Canadian continental margin (Anschutz *et al.* 1998), the Neva Estuary (Ignatieva 1999) and the shallow Rehoboth Bay, Delaware (Rozan *et al.* 2002). This vertical profile of the DFe concentration can be attributed to microbial dissimilatory reduction of Fe(III) oxides and FeS formation. In surface layers, microbial Fe(III) oxide reduction leads to the accumulation of DFe in pore water (Canfield 1989, Lovley 1991), whereas in deeper layers FeS formation results in the depletion of DFe (Thamdrup *et al.* 1994, Rozan *et al.* 2002). However, in addition to FeS formation, other authigenic Fe(II) minerals (*e.g.* Fe-rich silicate, Fe-Ca carbonates or siderite) may precipitate in sediments (Thamdrup *et al.* 1994). Pore water profiles of DFe similar to those at Storgadden have been reported from the Baltic Proper, below the permanent halocline (Carman and Rahm 1996) and the organic-rich sediments of the Gulf of Finland (Ignatieva 1999, V).

The change in the oxidation state of the surface sediment shown by the colour of the marine sediments is closely associated with the release of nutrients from the sediment to the water column (Jørgensen 1996a). Furthermore, the seasonal variation in the release of P is linked to changes in the anaerobic microbial  $\text{SO}_4^{2-}$  reduction rate, which is found to be at its highest in summer and lowest in winter, and to subsequent FeS production in marine environments (Thamdrup *et al.* 1994, Jensen *et al.* 1995, Kristensen *et al.* 2000, Rozan *et al.* 2002). In the present study, however, microbial  $\text{SO}_4^{2-}$  reduction was not measured; instead, the presence of efficient  $\text{SO}_4^{2-}$  reduction was indicated

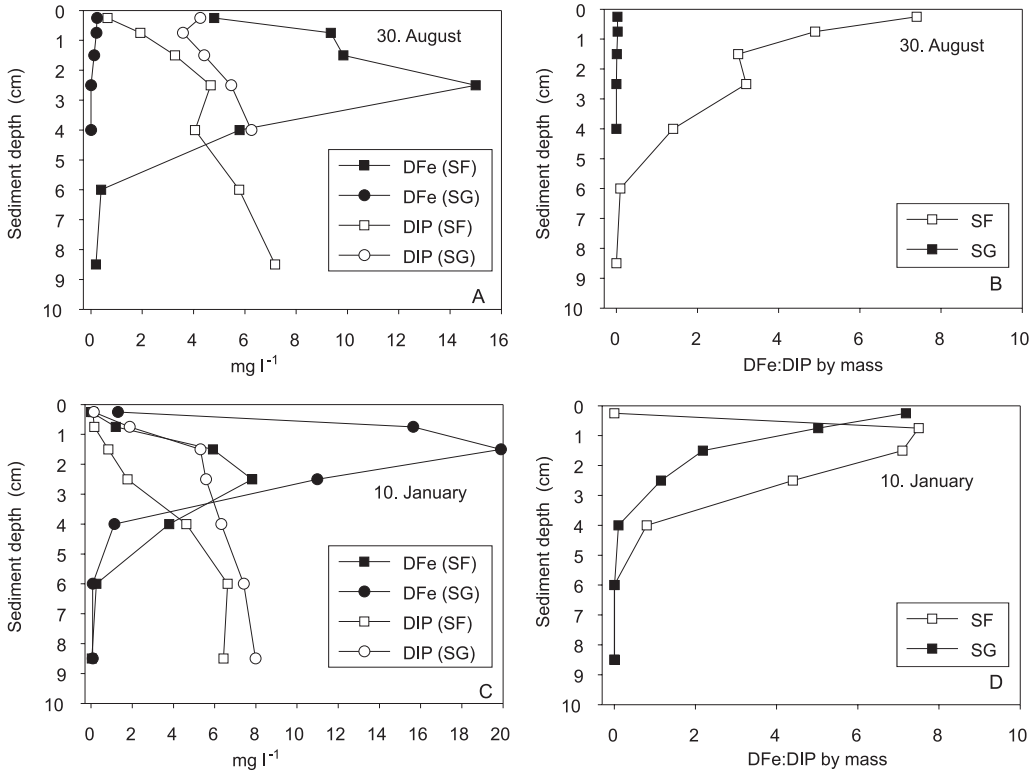
by the steep decrease in pore water  $\text{SO}_4^{2-}$  with sediment depth (IV), the smell of  $\text{H}_2\text{S}$  produced in  $\text{SO}_4^{2-}$  reduction, the low sediment redox potentials (V) and the colour transition from brown to black in sediments.

At Storfjärden, the thickness of the brown oxidized layer in the sediment was relatively constant (~20 mm) throughout the year. At the deeper Storgadden station, however, the black reduced layer indicating the presence of FeS extended to the surface of the sediment in mid-summer and autumn, whereas in winter and early spring the brown oxidized layer was 10 mm thick. The seasonal variation in the colour of the surface sediment at Storgadden may be related to changes in the  $\text{SO}_4^{2-}$  reduction rate, because an increase in the reduction of  $\text{SO}_4^{2-}$  enhances FeS formation in sediments (Rozan *et al.* 2002). Therefore, the  $\text{SO}_4^{2-}$  reduction and subsequent FeS formation probably explain the low pore water DFe concentrations at Storgadden in summer (Fig. 6 in IV). In Århus Bay, an annual variation in the thickness of the oxidized layer similar to that at Storgadden has been attributed to variation in the oxic zone in sediment (minimum 0.4 mm in summer and maximum 6 mm in winter) and to the efficiency of  $\text{SO}_4^{2-}$  reduction (Jørgensen 1996b, Thamdrup *et al.* 1994).

The pore water DFe:DIP mass ratio was related to the release of DIP into oxic water above the sediment during the seasonal cycle. For example, in August the DFe concentration in the surface of the anoxic reduced sediment at Storgadden was only 0.2 mg l<sup>-1</sup> and that of DIP as high as 4.3 mg l<sup>-1</sup> (Fig. 15a). Thus, the surface DFe:DIP ratio was only 0.05 by mass (Fig. 15b) and concomitantly a high DIP efflux, 8.9 mg m<sup>-2</sup> d<sup>-1</sup>, was observed (Fig. 16, see date 30.8). At the same time, in the well oxidized sediment at Storfjärden, the surface layer DFe concentration was 4.8 mg l<sup>-1</sup>, whereas that of DIP was 0.65 mg l<sup>-1</sup>. These values give a high DFe:DIP ratio of 7.4 by mass and a concomitant small influx of DIP (-2.2 mg m<sup>-2</sup> d<sup>-1</sup>, Fig. 16, see date 30.8). In winter, however, high DFe concentrations (> 7 mg l<sup>-1</sup>) and low surface DIP concentrations (0.10–0.87 mg l<sup>-1</sup>) were recorded at both stations (Fig. 15c). The DFe:DIP ratio exceeded 7 by mass at both stations (Fig. 15d), and low benthic fluxes of DIP were observed (0.0 and 0.7 mg m<sup>-2</sup> d<sup>-1</sup>, Fig. 16, see date 10.1).

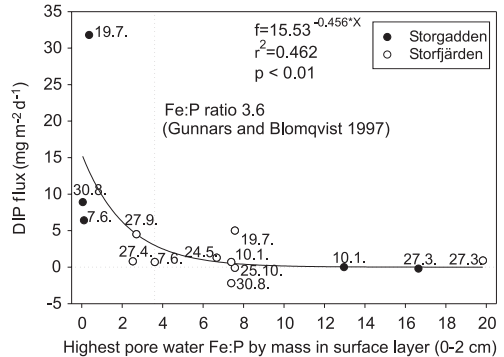
In general, a pore water Fe:P ratio exceeding 3.6 by mass (see section 1.5.3, Gunnars and Blomqvist 1997, Gunnars *et al.* 2002) suggested





**Fig. 15.** Pore water DFe and DIP concentrations and DFe:DIP ratio (a,b) in August 1999 and (c,d) in January 2000. Storfjärden = SF and Storgadden = SG.

good sediment retention ability for P when the near-bottom water was oxic (Fig. 16). In contrast, a low pore water Fe:P ratio (< 3.6 by mass) implied high release of DIP without a corresponding high DFe release from sediment to water (Fig. 12c–d). The poor stoichiometry between the release of DFe and DIP (compare Fig. 12a with c, and b with d) is most likely related to the formation of FeS (Rozan *et al.* 2002). An increase in the anaerobic mineralization of org-P may, however, promote the release of DIP but not of DFe (Golterman 2001). Yet, the low pore water Fe:P ratio in the surface sediment suggested that there was not enough diffusing DFe to form a Fe(III) oxide-rich layer in the sediments to bind all upward-diffusing DIP at the sediment-water interface. When the Fe:P ratio was very low (0.02–0.2 by mass), sediment mechanisms (*e.g.* the DIP formation rate and microbial uptake) other than the sorption of P onto the



**Fig. 16.** Surface pore water Fe:P ratio and benthic flux of DIP. Vertical dotted line denotes Fe:P mass ratio 3.6 (corresponds to molar ratio 2) suggested to be sufficient to effectively bind diffusing DIP. Black symbol denotes Storgadden and blank symbol Storfjärden. Figure beside symbol denotes sampling date.

**Table 5.** Sediment TN, TP and TFe concentrations and pore water DFe and DIP concentrations in the western Gulf of Finland (GOF) and in some small Finnish lakes.

Region	TN (mg g <sup>-1</sup> DM)	TP (mg g <sup>-1</sup> DM)	TFe (mg g <sup>-1</sup> DM)	sediment layer (cm)	DFe (mg l <sup>-1</sup> )	DIP (mg l <sup>-1</sup> )	sediment layer (cm)	n	Reference
GOF (Storfjärden)	7.6	2.2	35.3	0–1	0.1	8.20	7–10	1	this study
Postilampi	9.1	1.3	32.8	0–2	11.0	0.35	7–10	1	Lehtoranta, unpubl.
Kevätön	10.9	2.8	32.3	0–2	89.0	0.01	7–10	1	Lehtoranta, unpubl.
Likolampi	31.0	3.8	41.1	0–2	4.6	0.09	7–10	1	Lehtoranta, unpubl.
Pyhäjärvi	7.7	1.9	37.0	0–2	5.3	0.56	7–10	1	Lehtoranta and Gran 2002
Tottijärvi	13.5	2.0	42.0	0–1	23.9	2.02	7–10	1	Heino 2002

Fe(III) oxides formed must have largely controlled the release of P from sediment to water. Thus, the insufficient ability of Fe(III) to bind DIP and the high surface pore water DIP concentration can explain the measured high efflux of DIP to oxic water. At Storfjärden, unlike Storgadden, the Fe:P mass ratio of pore water could not fully explain the efflux of DIP. The disagreement is attributed to bioturbation (Gallepp *et al.* 1978) or the role of org-P in sediments, or both (Golterman 2001). The bivalve *Macoma baltica* enhances solute transport from sediment to water (Henriksen *et al.* 1983) and, thus, the release of DIP.

In the deep layer of the sediment of some small Finnish mesotrophic and eutrophic lakes, the pore water DFe concentration ranges from 4.6 to 89 mg l<sup>-1</sup> and DIP from 0.01 to 2.0 mg l<sup>-1</sup> (Table 5). In the organic-rich sediments of the western Gulf, the corresponding DFe concentration was only 0.1 mg l<sup>-1</sup> and the DIP concentration as high as 8.2 mg l<sup>-1</sup>. These data suggest that the dissolution of P is more efficient and that the binding ability of P to Fe(III) oxides formed from diffusing Fe(II) in the oxic zone is poorer in the Gulf of Finland than in the lakes. The average pore water SO<sub>4</sub><sup>2-</sup> concentration of about 500 mg l<sup>-1</sup> measured in the organic-rich sediments of the Gulf (IV) is almost 180 times the average, 2.8 mg l<sup>-1</sup>, measured in Finnish lake waters (Mannio *et al.* 2000). Thus, the SO<sub>4</sub><sup>2-</sup> concentration is probably the major cause of the difference in the reduction and burial of Fe and, consequently, in the release and burial of P between the brackish Baltic Sea and freshwater lakes.

The SO<sub>4</sub><sup>2-</sup> concentrations in water are much higher in the brackish Bothnian Bay and Bothnian Sea than in freshwater lakes, but the ability of sediments to retain P is good in these brackish waters. The results of the present study suggest that an increase in sediment organic matter leads to poor retention of P in sediments. Accordingly, it can be hypothesized that the good ability of sediments to retain P in the SO<sub>4</sub><sup>2-</sup> rich Bothnian Sea and Bothnian Bay is linked not only to the sediment TFe concentration, which is higher than that of the Gulf (Leivuori 2000), but also to the low organic matter concentration in sediments (see section 4.1). Moreover, in these waters the organic matter is largely allochthonous (Wikner 2002), which tends to be more refractory than autochthonous organic matter. Most likely, then, the microbial processes are not efficient, and SO<sub>4</sub><sup>2-</sup> reduction and the subsequent FeS formation occur deep in the sediment. This hypothesis is supported by the high sediment redox potentials (Leivuori 2000) and the existence of the brown oxidized layer, which is often several centimetres thick in the Bothnian Bay and the Bothnian Sea (Mälkki 2000).

## 4.6 Quantification and ecological implications of benthic flux of phosphorus

### 4.6.1 Benthic phosphorus flux counteracts decreases in external load

Relative to the surface area of the Gulf of Finland, its external nutrient load is 2 to 3 times the aver-

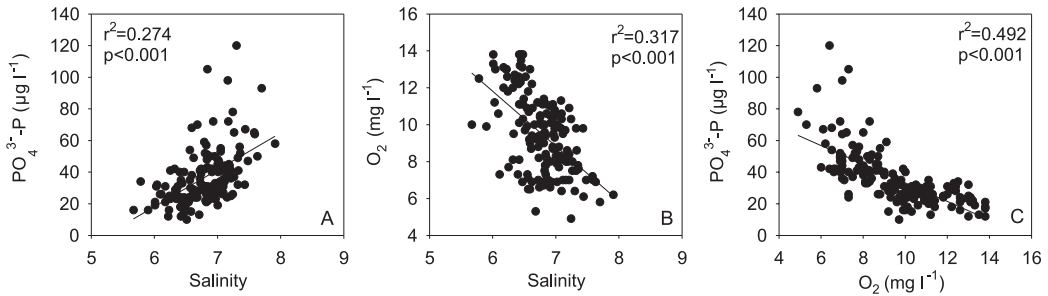


Fig. 17. Relationships between salinity and concentrations of  $O_2$  and  $PO_4^{3--}P$  at Längden monitoring station.

age for the Baltic (III). Although the external P load to the Gulf declined by about 30% during the 1990s, water DIP concentrations increased rather than decreased at the coastal monitoring stations during the same period (III). There are two main reasons for the poor correlation between the external P loading and the P concentration observed in water: first, the benthic flux of DIP has increased in the Gulf itself and, second, the inflow of saline water rich in P has brought a large amount of DIP to the Gulf.

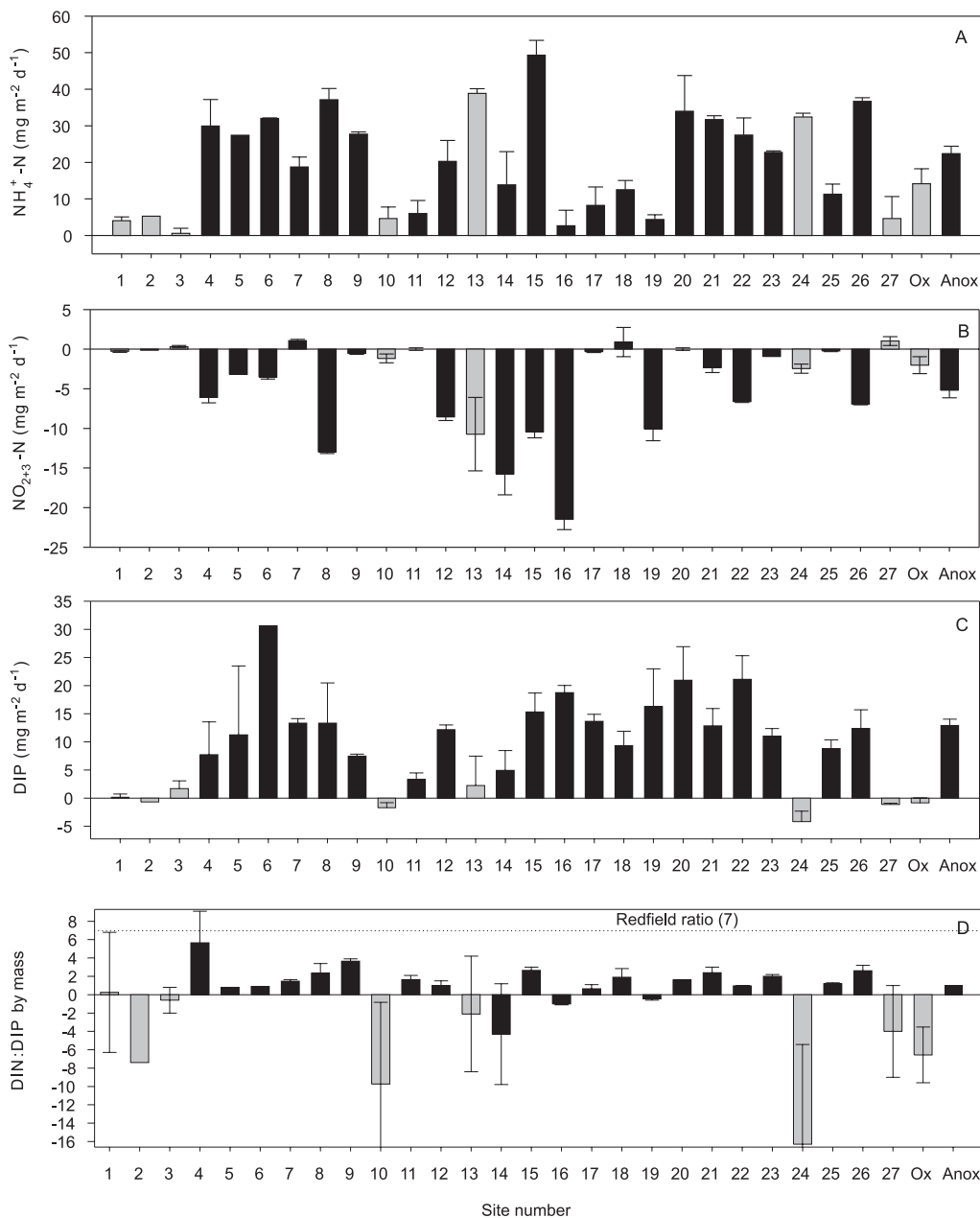
The present study cannot quantitatively distinguish between the P released from the sediments of the Gulf itself and the P entering from the main Baltic basin. At Längden, the significant correlation coefficients observed between salinity and DIP and  $O_2$  concentrations cannot establish the origin of DIP (Fig. 17). The correlations between these factors may be due to two processes occurring concomitantly: first, the inflowing saline water, rich in P and poor in  $O_2$ , may largely control both the DIP and  $O_2$  concentrations in the near-bottom water; second, the intrusion of saline water enhances the density stratification in the water column. The increase in near-bottom salinity together with other factors (*i.e.* settling of organic matter and temperature stratification) may accelerate the release of P from the sediments of the Gulf itself in summer. However, the correlation between near-bottom salinity and the DIP concentration varies regionally; in the eastern Gulf of Finland, for example, salinity and the DIP concentration were poorly correlated ( $r^2 = -0.23$ ) but a strong negative correlation ( $r^2 = -0.75$ ) existed between the near-bottom DIP and  $O_2$  concentration in September 2000 (III).

Based on the Knudsen formula, a simple calculation sensitive to specific water layers (see Enqvist and Omsted 1992, Andersson and Rydberg 1993) suggests that the net input of P from the

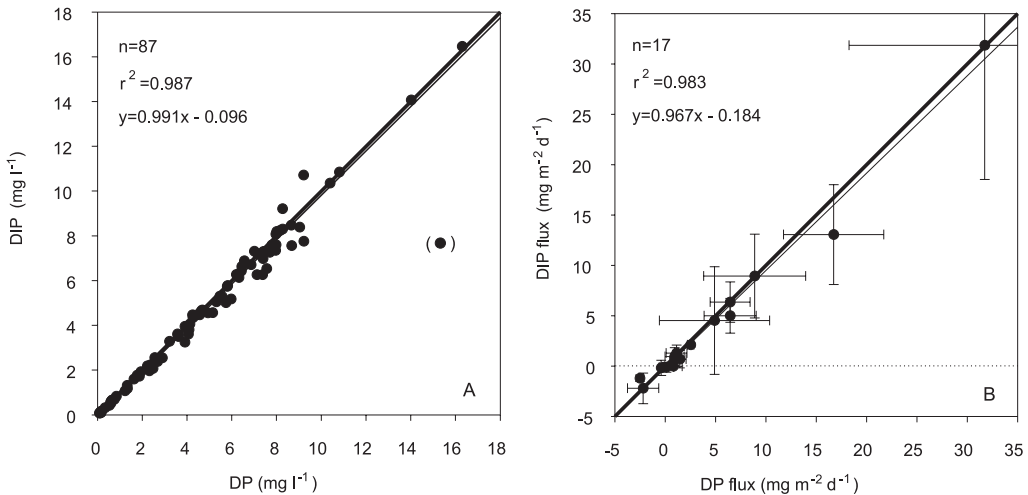
main basin of the Baltic Sea may be 8000 t yr<sup>-1</sup> (Perttilä *et al.* 1995). Furthermore, a mass balance study based on current velocity and water P concentration measurements suggests input of P from the main basin to the Gulf (Stipa 1996, unpubl.). This input (less water flows in than out at the mouth of the Gulf) is explained by the fact that the water from the main basin tends to penetrate into the Gulf along the bottom. In winter, for example, the DIP concentration in the inflowing deep water can be almost twice that in the outflowing surface water (Perttilä *et al.* 1995). The input of P from the main basin calculated by Perttilä *et al.* (1995) is high compared to the external total P load, 7000 t yr<sup>-1</sup>, to the Gulf (III). Thus, the intrusion of P-rich water from the main basin clearly has a marked effect on the DIP concentrations in the near-bottom waters of the Gulf.

The significance of the release of N and P from the sediment of the Gulf is demonstrated by the regional scope of the sampling sites at which benthic nutrient fluxes were measured in 1999–2002. These measurements show high effluxes of  $NH_4^+-N$  and DIP comparable to those at Storgadden in both coastal and open sea areas in the whole Gulf of Finland (Fig. 4c). At the 20 sites where the black layer extended to the sediment surface, the mean release rate for DIN was 20.6 mg m<sup>-2</sup> d<sup>-1</sup> and for DIP as high as 13.1 mg m<sup>-2</sup> d<sup>-1</sup> (Fig. 18a and c). Other studies, too, have measured high  $NH_4^+-N$  and DIP fluxes comparable to those found here in both the eastern and western open Gulf in summer (Conley *et al.* 1997, Johnstone and Stockenberg 1998). Note that the above studies were conducted between June and July in 1993, before the inflow of saline water from the main Baltic basin to the Gulf.

That a large part of the N and P in water may indeed originate from the sediments of the Gulf is in-



**Fig. 18.** Benthic flux of (a)  $\text{NH}_4^+\text{-N}$  (b)  $\text{NO}_{2+3}\text{-N}$  (c) DIP and (d) flux DIN:DIP ratio in the Gulf of Finland as measured on three separate cruises in 1999–2002. Grey bars denote oxidized sediments (*i.e.* bottoms with brown oxidized surface layer) and black bars anoxic reduced sediments (*i.e.* bottoms where black layer extended to surface of sediment). Error bars denote standard error of the mean. Letters Ox denote average benthic flux of DIP on oxidized bottoms and Anox on anoxic reduced bottoms.



**Fig. 19.** Relationship between (a) pore water DP and DIP concentration and (b) benthic flux of DP and DIP at Storfjärden and Storgadden. For pore water, all sediment layers studied, and for benthic flux, all sampling dates are included in calculations. Thick line denotes 1:1 line and thin line regression line. Error bars denote standard error of the mean.

dictated by the total amounts of N and P released to the overlying water on a yearly basis. Calculations show that a total of  $8.4 \text{ g m}^{-2}$  DIN and  $2.0 \text{ g m}^{-2}$  DIP were released to the water at Storgadden and  $3.9 \text{ g m}^{-2}$  and  $0.45 \text{ g m}^{-2}$  at Storfjärden. For P, values ranging from 1 to  $2 \text{ g m}^{-2} \text{ yr}^{-1}$  have been reported from Århus Bay ( $1.0 \text{ g m}^{-2} \text{ yr}^{-1}$ , Jensen *et al.* 1995), and the continental shelf at Massachusetts ( $1.3\text{--}1.9 \text{ g m}^{-2} \text{ yr}^{-1}$ , Hopkinson Jr. *et al.* 2001). Here, the calculated amounts of DIN and DIP released from sediment alone would bring the concentration of DIN up to  $165 \mu\text{g l}^{-1}$  and that of DIP up to  $39 \mu\text{g l}^{-1}$  in the whole volume of water,  $51 \text{ m}^3$ , above the square metre at Storgadden (water depth at Storgadden is 51 m). At Storfjärden, the corresponding figures with a water volume of  $33 \text{ m}^3$  would be  $118 \mu\text{g l}^{-1}$  for N and  $14 \mu\text{g l}^{-1}$  for P. Thus, the sediments can markedly increase the concentrations of DIN and DIP in a large water column not only in the anoxic reduced, but also in the well oxidized, bottom areas during a seasonal cycle. The benthic nutrient fluxes measured (Fig. 18a and c) also indicate that the sediments are locally significant sources of DIN and DIP in shallow and small semi-enclosed basins such as Tammio, Vehkalahti (25 m) and Sandofjärd, Siuntio (26 m) in summer (sites 7 and 25 in Fig. 4c). Owing to the benthic nutrient flux, the trophic state of the small semi-enclosed bays may thus be higher than that in the adjacent sea areas.

Estimating the total accumulation area to be  $9000 \text{ km}^2$  – a figure also used by Kankaanpää

(1997) – and assuming that a well oxidized state of sediment comparable to that at Storfjärden prevails throughout the accumulation area, the total amount of DIP released to water would be  $4100 \text{ t yr}^{-1}$ . Assuming a poor oxidation state similar to that at Storgadden for the whole area, the amount released would be as high as  $18\,000 \text{ t yr}^{-1}$ . This rough calculation highlights the possibility that even under well oxidized conditions in the entire Gulf, the organic-rich sediments are a significant source of P. It can also be calculated that a change of 10% in the accumulation area from a good to a poor sediment oxidation state increases the amount of DIP released in the Gulf of Finland by  $1400 \text{ t yr}^{-1}$ . The above figures suggest that the benthic flux of DIP and the input from the main basin account for a large part of the amount required annually by new primary production in the open Gulf.

The importance of sediment-originated P is emphasized by the great difference in the algal availability of P between the P from external sources and the P released from sediment to water. Based on the algal assays of Ekholm (1998), Ekholm and Krogerus (2003) and the amount of total external P load subdivided into its sources, it can be calculated that about 40% of the total external P load to the Gulf is algal available (Kiirikki *et al.* 2003). The dissolved P in pore water and the dissolved P released into the water column were almost completely in the form of DIP (Fig. 19), which is considered to be totally algal available.

In Århus Bay, on average, 95% of the DP released from the bottom sediment is in the form of DIP (Jensen *et al.* 1995). The input of P from the main Baltic basin is also almost completely in the form of DIP. Thus, the algal availability in the load of TP from external sources is not comparable to the efflux from the sediment to water or to the flux of DIP from the main basin to the Gulf.

#### 4.6.2 Sediment-related explanation for nitrogen limitation of primary production

Sediments do not only act as a significant “source” of nutrients; they may also affect the nutrient limitation of primary production (see section 1.5.3). The high efflux of DIP compared to that of DIN in summer may be related to the fact that primary production in the open Gulf of Finland is mainly N limited (Kivi *et al.* 1993, Pitkänen and Tamminen 1995). The inorganic N:P ratio in the water transported by the River Neva – the largest external source of nutrients in the Gulf of Finland – is about 20 by mass (Pitkänen and Tamminen 1995). The N:P ratio of the total external nutrient load to the Gulf of Finland is about 18 by mass (III). However, in the Gulf of Finland the DIN:DIP ratio in the near-bottom water is about 2 by mass in late summer (Fig. 20b), which is well below the Redfield ratio of 7 by mass, the optimum for phytoplankton production (Redfield *et al.* 1963). Clearly, the external N and P load as such cannot explain the low N:P mass ratios observed in the water column.

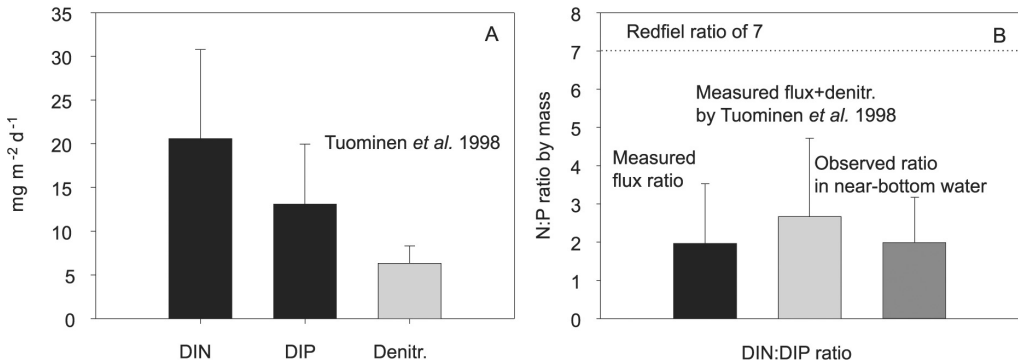
The results of the present study suggest that the low near-bottom water DIN:DIP mass ratio and the marked decrease in this ratio during the summer can be attributed to the benthic effluxes of DIN and DIP. The flux rate of DIP varied more in relation to that of DIN at Storgadden; for example, in January, the release rate of DIN was  $35 \text{ mg m}^{-2} \text{ d}^{-1}$  and the flux of DIP was insignificant, whereas in July the DIN and DIP fluxes were  $47 \text{ mg m}^{-2} \text{ d}^{-1}$  and  $32 \text{ mg m}^{-2} \text{ d}^{-1}$ , respectively. These figures are consistent with the finding that when both the  $\text{NH}_4^+$ -N and DIP concentrations increase in the near-bottom water ( $\text{NO}_{2+3}^-$ -N concentration decreases) in summer, a concurrent decrease usually occurs in the DIN:DIP mass ratio (Fig. 11d–f).

The seasonal flux study showed that the amounts of DIN and, especially, of DIP released in the anoxic sediments were much higher than those

in the oxidized sediments on a yearly basis. Calculated for the whole  $51 \text{ m}^3$  section of the water column, the amounts of DIN and DIP released result in a DIN:DIP ratio of 4.1 by mass at Storgadden. This ratio is close to the winter surface value of 3.8 measured at Längden in 2000, when the whole water column was evenly mixed. For Storfjärden, the corresponding ratio is 8.6 by mass. In the open and coastal surface waters of the western Gulf, DIN:DIP ratios higher than 7 by mass have rarely been measured before the spring bloom (Pitkänen *et al.* 2001). It is, therefore, likely that bottom types comparable to those at Storgadden rather than those at Storfjärden control the water DIN:DIP mass ratio in open coastal areas.

The benthic flux DIN:DIP mass ratio may be lowered mainly by the enhanced release of DIP or the decreased release of DIN, or both. Denitrification reduces the flux of DIN and subsequently lowers the DIN:DIP mass ratio, since during denitrification N, but not P, is removed. Unfortunately, concomitant benthic flux and denitrification rate data are not available here. Nevertheless, a simple calculation of the impact of the denitrification rate on the benthic DIN flux and on the flux DIN:DIP mass ratio can be presented. In areas of recent deposition, the denitrification rate ranges from 4.1 to  $9.1 \text{ mg m}^{-2} \text{ d}^{-1}$  (average value  $6.3 \text{ mg m}^{-2} \text{ d}^{-1}$ ) in summer and early autumn (Tuominen *et al.* 1998b). The rate of  $6.3 \text{ mg m}^{-2} \text{ d}^{-1}$  (Fig. 20a) summed to the average DIN efflux of  $20.6 \text{ mg m}^{-2} \text{ d}^{-1}$  found in the present study (Fig. 20a) brings the total inorganic N efflux only up to  $26.9 \text{ mg m}^{-2} \text{ d}^{-1}$ . Thus, the effect of denitrification on the total inorganic N efflux is not very high. Moreover, the average denitrification rate summed to the measured DIN flux increases the flux DIN:DIP ratio only from 2.0 to 2.6 by mass (Fig. 20b, middle bar), by no means raising it above the Redfield ratio of 7 by mass. It is, therefore, reasonable to suggest that the low benthic flux DIN:DIP mass ratio in the soft bottoms of the Gulf of Finland is due to the enhanced efflux of DIP rather than to the decreased efflux of DIN caused by denitrification. The flux DIN:DIP ratio by mass was thus well below the Redfield ratio of 7 by mass when the release rate of DIP exceeded  $4 \text{ mg m}^{-2} \text{ d}^{-1}$  (compare Fig. 18c and d).

The benthic flux of DIN and DIP from anoxic reduced sediments may control the near-bottom DIN:DIP mass ratio in large parts of the Gulf of Finland. In anoxic reduced sediments comparable to those at Storgadden, the mean DIN:DIP ratio of



**Fig. 20.** (a) Average DIN and DIP fluxes from the anoxic reduced sediments and measured average denitrification rate by Tuominen *et al.* (1998b), (b) flux DIN:DIP ratio (reduced anoxic bottom sediments) and estimated effect of average denitrification rate of  $6.3 \text{ mg m}^{-2} \text{ d}^{-1}$  by Tuominen *et al.* (1998b) on flux DIN:DIP ratio. Near-bottom water DIN:DIP ratio (separate cruises in 1999–2002,  $n=73$ ) is also given. Bars denote standard deviation.

the measured benthic efflux was 2.0 by mass (20 sites, Fig. 20b). The mean ratio of the efflux is similar to that of near-bottom water samples from 73 sites (Fig. 20b) measured in 2000–2002. The near-bottom water DIN:DIP ratio of  $\sim 1$  by mass measured at the mouth of the Gulf of Finland indicates that the DIN:DIP mass ratio is also low in the inflowing water from the main Baltic basin. It can be concluded that the low DIN:DIP mass ratio in the near-bottom water is a consequence of sediment-related internal processes and that it is mainly the DIP released from the sediment that explains the low near-bottom water DIN:DIP mass ratio recorded in summer.

## 5 Conclusions

There are several sediment-related and hydrodynamic factors that make the Gulf of Finland sensitive to the efficient release of P from sediment to water. The external load of both N and P has been, and still is, high in the easternmost Gulf compared to other parts of the Baltic Sea. Consequently the production of organic matter in that part of the Gulf is higher than elsewhere in the Baltic. The Gulf of Finland is shallow (average depth 37 m) and a large portion of the organic matter containing both N and P reaches the surface of the sediment. As a result, sediments are generally rich in organic matter, N and P. The settled organic matter

forms a large pool of labile C for aerobic as well as anaerobic microorganisms in the sediments. Sediment  $\text{O}_2$  consumption is therefore high, and anoxic conditions develop rapidly in the sediments. The increase in the sediment organic matter concentration, together with changes in hydrodynamic factors, seems to lower the ability of sediments to retain P, which may be related to anaerobic microbial Fe(III) oxide and  $\text{SO}_4^{2-}$  reduction processes.

A large portion of the deposited TP participates in biological and chemical reactions in the sediments. This mobile pool of P consists largely of Fe bound P and organic P, but Al-bound P may also play a role. Thus, if the sediment-water interface is depleted in  $\text{O}_2$ , the Fe(III) oxide-bound P is readily released into near-bottom water after the anaerobic microbial and chemical reduction of Fe(III) oxides. The formation of Ca-P compounds such as apatite, which are considered to be a permanent sink for P, is minor in surface sediments.

A marked seasonal variation in the benthic P flux was noted, the highest flux being measured in summer and the lowest in winter. In summer, salinity and temperature generate density stratification, which may prolong the residence time of near-bottom water. Morphological features also weaken the renewal of the deep-water layers, especially in the northern part of the Gulf. These factors, together with the sediment  $\text{O}_2$  consumption caused by fresh and older organic matter, decrease the concentration of  $\text{O}_2$  in near-bottom water in summer. This may shift the balance of oxidants towards anaerobic mineralization in sediments,



and favour anaerobic microbial Fe(III) oxide and  $\text{SO}_4^{2-}$  reduction and the subsequent FeS formation close to the sediment-water interface.

The high pore water DIP concentrations in both the inner (Storfjärden) and outer coastal areas (Storgadden) indicate efficient diffusion of P towards the sediment-water interface throughout the year. Although there appears to be enough TFe in sediments to retain P, the concentration of dissolved Fe in pore water is very low compared to that of DIP in deep layers of the sediment. In the surface sediment, the binding ability of P related to diffusing dissolved Fe plays a key role in preventing P from entering the oxic near-bottom water during the seasonal cycle. The low dissolved Fe:P ratio ( $< 3.6$  by mass) measured in summer caused a high efflux of DIP from sediment to water, whereas the high ratio measured in winter resulted in a small flux at the sediment-water interface. The dissolved Fe concentrations in pore water are much higher in freshwater lakes than in the brackish Gulf of Finland. The diffusion of Fe in a brackish environment, in contrast to most lake systems, may be inactivated by a high concentration of S, which would increase the mobility of P and subsequently the release of P to oxic water. The classic model describing the coupled cycling of Fe and P in sediments is thus not adequate as such in the brackish Baltic Sea, owing to the coupling of Fe, S and P in the sediments there.

Due to the apparent coupling of Fe and S, high effluxes of DIP were measured on bottoms where the black reduced sediment indicating the presence of FeS extended to the surface of the sediment. Low fluxes at the sediment-water interface were measured on sediments in which a brown oxidized layer indicated the presence of Fe(III) oxides. The inner and the outer parts of the Neva estuary seem to retain P better than the open sea areas and the semi-enclosed basins rich in organic matter. Therefore, in the inner estuary, where the primary production is P limited, phytoplankton production may be largely governed by the bioavailable P supplied by the Neva.

The findings of the present study indicate that the P released from the sediments of the Gulf together with the input of DIP from the main basin of the Baltic Sea may largely explain the high P concentrations and low N:P mass ratios in near-bottom waters in late summer and, after intense autumn mixing, in the entire water column of the Gulf of Finland. Since productivity is low and no intense

influx of P to the sediment was measured in the Gulf in winter, the P concentrations remain high in the water column until the start of the spring bloom. The high release rate of P – rather than denitrification – largely explains the N limitation of primary production in the Gulf of Finland. Owing to N limitation, surplus P may remain in the water column after the spring bloom, which favours N-fixing blue-green algae in late summer.

A relationship seems to exist between the inflow of saline water to the Baltic Sea in 1993 and the weakening of the sediment oxidation state in the Gulf since 1996. Notably, the average DIP concentration in the water column has increased, although the external P load decreased by about 30% (3400 t) in the 1990s. The inflow of saline water, first to the main basin and from there to the Gulf, strengthens the density stratification and weakens the mixing of water in the Gulf. The enhanced stratification may weaken the oxidation state of the sediment and favour the release of P from the sediments of the Gulf itself. The changes in near-bottom salinity related to inflow from the main basin may thus lead to great variation in the benthic P flux in the Gulf from one year to the next. Besides accelerating the benthic P flux, the inflow of saline water from the main Baltic basin may bring a large amount of DIP to the Gulf. These events, which are linked to internal processes, cause a marked between-year variation in the trophic state of the Gulf and so counteract the reduction in the external P load.

The high influx of DIP from the main Baltic basin suggests that the external P load from catchments other than that of the Gulf of Finland alone should be taken into account when considering water protection measures for the Gulf. Even after considerable reductions in the external anthropogenic P load in the drainage basin of the Gulf – excluding the city of St. Petersburg, rapid recovery in the P state cannot be expected outside the direct range of the source, as the P concentration is dependent on internal processes. Even though these processes may markedly increase the P concentration in water, the only realistic way to reduce P in water is to reduce the external P load. The P in sediments has an external source, and eventually a decrease in the benthic efflux of P has to occur when the external P load is reduced. A high sediment organic matter concentration appears to lower the ability of sediments to retain P. This ability could probably be improved by curbing the



deposition of labile organic matter on the bottom. To reduce the sedimentation of autochthonous labile organic matter, the input of bioavailable N and P from anthropogenic sources should be reduced. A decrease in the external load of bioavailable P could rapidly reduce phytoplankton production in the P-limited inner Neva estuary owing to the good ability of sediment to retain P, providing that the eastward inflowing deep water rich in P cannot compensate for the reduction.

It may well be that in the Gulf of Finland the major factor controlling the poor ability of sediments to retain P is microbially mediated. However, at present we know very little about the efficiency of microbial Fe(III) oxide and  $\text{SO}_4^{2-}$  reduction rates in sediments and the factors controlling these microbial processes. The controlling factors may be related to the availability of organic matter or electron acceptors (*i.e.* Fe(III) oxides and  $\text{SO}_4^{2-}$ ) in sediments or to hydrographic features affecting  $\text{O}_2$  conditions and temperature at the sediment-water interface. Large-scale changes in  $\text{O}_2$  conditions and temperature may improve or impair the ability of sediment to retain P due to microbial processes. Therefore, to better understand the between-year variation in DIP concentrations in water, it is essential that we learn more about the sediment processes related to the cycling of P and the exchange of water between the main Baltic basin and the Gulf of Finland.

## Yhteenveto

Suomenlahti on suuren ulkoisen ravinnekuormituksensa vuoksi yksi Itämeren rehevöityneimmistä osa-alueista. Ulappa-alueilla leväbiomassat ovat korkeita ja laajoja sinileväesiintymiä tavataan toistuvasti loppukesällä. Myös rihmalevien massaesiintymiset Suomenlahden itäosien rannoilla ovat yleisiä. Lisäksi runsaana esiintyvät rihmalevät aiheuttavat mm. kalanpyydysten limoittumista. Valtaosa Suomenlahden suuresta ulkoisesta ravinnekuormituksesta on peräisin Neva-joen valuma-alueelta ja Pietarin kaupungista.

Useat sedimenttiin, morfologisiin ja hydrologisiin ominaisuuksiin liittyvät tekijät tekevät Suomenlahdesta alttiin fosforin vapautumiselle sedimentistä pohjanläheiseen veteen. Suomenlahti on merialueeksi matala, sillä sen keskisyvyys on vain 37 m. Tämän vuoksi suuri osa sekä orgaaniseen

että epäorgaaniseen hiukkasmaiseen ainekseen sitoutuneista ravinteista laskeutuu pohjalle. Pitkään jatkuneen ravinnekuormituksen ja sitä seuranneen rehevöitymisen seurauksena Suomenlahden sedimentin eloperäisen aineksen sekä ravinteiden pitoisuudet ovatkin korkeita muihin Itämeren osaluueisiin nähden.

Eloperäisen aineksen pitoisuuden voimakas aleneminen syvyyden kasvaessa sedimentissä viittaa tehokkaaseen mineralisaatioon. Suuri osa tästä mineralisaatiosta on todennäköisesti anaerobista. Fosforin kierron kannalta tärkeimpiä anaerobiseen hengitykseen käytettäviä yhdisteitä ovat sedimentin rautaoksidit ja liukoinen sulfaatti. Huokosveden sulfaattipitoisuuden voimakas pieneneminen syvyyden kasvaessa sedimentissä, rikkivedyn haju ja alhainen redox-potentiaali viittaavat tehokkaaseen mikrobiologiseen sulfaatin pelkistykseen. Anaerobisessa mikrobiologisessa sulfaatin pelkistyksessä muodostuva rikkivety pelkistää tehokkaasti rautaoksideja muodostaen samalla sedimenttiin pysyvästi hautautuvia rautasulfideja, joiden fosforin sitomiskyky on heikko. Sedimentin eloperäisen aineksen suuri määrä näyttää johtavan heikkoon fosforin pidätyskykyyn. Orgaanispitoisilla alueilla ilmeinen tehokas anaerobinen mikrobiaktiivisuus johtaa tehokkaaseen rautaoksidien pelkistymiseen ja heikkoon fosforin pidätyskykyyn. Suomenlahdella pohjia, joiden orgaanisen aineksen pitoisuus on korkea, esiintyy ulkomeren syvillä alueilla, merenlahdilla sekä saarten ja matalikoiden suojaamalla pinta-alaltaan verraten pienillä alueilla.

Biologisiin ja kemiallisiin reaktioihin osallistuva ns. liikkuva fosfori muodostaa suuren osan sedimentin pintakerroksen kokonaisfosforista. Sedimentin pintakerroksen kokonaisfosforipitoisuus on keskimäärin n. 60 % suurempi verrattuna 9–10 cm syvyydestä havaittuun pitoisuuteen. Tämä liikkuva fosfori on sitoutunut lähinnä rautaan ja orgaaniseen ainekseen. Tosin fosforin fraktiointien mukaan myös alumiini sitoo fosforia, ja myös tämä fosforin osa vapautuisi hautautumisen aikana. Kun syvyys sedimentissä kasvaa, rautaan sitoutuneen fosforin pitoisuus alenee rautaoksidien pelkistyessä, ja huokosveden liukoksen fosforin pitoisuus vastaavasti suurenee. Suomenlahdella huokosvedestä havaittiin yleisesti korkeita liukoksen fosforin pitoisuuksia, jotka vaihtelivat yleensä välillä 3–10 mg l<sup>-1</sup>, mutta jopa yli 10 mg l<sup>-1</sup> pitoisuuksia tavattiin. Suuren liukoksen fosforin pitoisuuden vuoksi fosforin diffuusio kohti sedimentti-vesi rajapintaa on voimakasta.

Suomenlahden ulkokeräalueella sedimentin syvän kerroksen (9–10 cm) kokonaisfosforipitoisuus vaihtelee alueellisesti hyvin vähän. Tämä osoittaa, että liikkuvan fosforin vapautuminen hautautumisen aikana johtaa samankaltaisiin kokonaisfosforin pitoisuuksiin tutkitussa sedimenttikerroksessa. Syvän kerroksen heikko fosforin pidätyskyky on todennäköisesti yhteydessä rautaoksidien pelkistymiseen. Kalsiumiin sitoutunutta fosforia puolestaan pidetään yhtenä merkittävimmistä hautautuvan fosforin jakeista. Suomenlahden sedimentissä kalsiumiin sitoutunut fosfori muodostaa merkittävän osan hautautuvasta fosforista, mutta sen muodostuminen hautautumisen aikana on ilmeisesti vähäistä.

Sedimentin kiintoaineen rauta-fosforisuhteen perusteella Suomenlahdella näyttäisi yleisesti olevan riittävästi rautaa sitomaan tehokkaasti fosforia. Kokonaisrautapitoisuutta tärkeämpi tekijä fosforin pidätyksessä on kuitenkin huokosveden liukoisen raudan pitoisuus. Suomenlahdella ilmeisen mikrobiologisen sulfaatin pelkistymisen aiheuttama rautasulfidien muodostuminen alentaa huokosveden liukoisen raudan pitoisuuksia. Suomenlahdella liukoisen raudan pitoisuudet olivat suuria (7–20 mg l<sup>-1</sup>) vain kun sedimentin hapetustila oli hyvä eli kun pintakerroksessa havaittiin ruskea rautaoksidi-kerros. Syvemmissä, paljon rautasulfideja sisältävissä kerroksissa huokosveden liukoisen raudan pitoisuudet olivat aina pieniä, jopa alle määrittäysrajan. Kesällä koko sedimenttikerroksesta mitattiin vain pieniä liukoisen raudan pitoisuuksia mustan rautasulfidi-kerroksen ulottuessa aivan sedimentin pintaan saakka.

Fosforin vapautumisessa oli selvä vuodenaikainen vaihtelu: suurimmat vapautumismäärät mitattiin kesällä ja pienimmät talvella. Loppukevällä ja alkukesällä kevätkukinnan sedimentaatio tuo sedimentin pinnalle uutta, helposti hajoavaa orgaanista ainesta. Kesällä lämpötilakerrostuneisuus ja pintakerrokseen nähden suurempi suolapitoisuus johtaa tehokkaaseen pohjanläheisen vesikerroksen eristymiseen muusta vesimassasta. Myös morfologiset ominaisuudet erityisesti Suomenlahden pohjoisosissa suosivat pohjanläheisten vesikerrosten pitkää viipymää kesäisin. Tämä yhdessä sedimentin suuren hajotuskelpoisen eloperäisen aineksen pitoisuuden kanssa johtaa liukoisen hapen pitoisuuden alenemiseen pohjan läheltä ja jopa loppumiseen sedimentistä. Tämä puolestaan aiheuttaa sen, että eloperäisen aineksen hajotus tapahtuu anaerobisesti mahdollistaen mikrobiologisen rautaoksidien ja sulfaatin pelkistymisen

sekä sitä seuraavan rautasulfidien muodostumisen sedimentin pintakerroksessa.

Sedimentin pintakerroksessa huokosveden liukoisen raudan suhde liukoiseen fosforiin on tärkeä fosforin vapautumista säätelevä tekijä. Liukoisen raudan ja fosforin välinen massasuhte  $< 3,6$  johtaa liukoisen fosforin vapautumiseen sedimentistä veteen, kun taas tätä suurempi suhdearvo ilmentää sedimentin hyvää fosforin sidontakykyä. Vuosi-kierron aikana kesäisistä happiongelmista kärsivän sedimentin pintakerroksen liukoisen raudan ja fosforin välinen suhde oli pieni kesällä ja suuri talvella. Tämä huokosveden raudan ja fosforin välinen massasuhteen vaihtelu oli hyvin yhteydessä fosforin vapautumisen vaihteluun. Vähäinen liukoisen raudan diffuusio kohti sedimentti-vesi rajapintaa vähentää rautaoksidien muodostumista sedimentin hapellisessa pintaosassa. Äskettäin muodostuneiden rautaoksidien vähäinen määrä ei kykene sitomaan kaikkea diffundoituvaa liukoista fosforia, jota vapautuu sedimentin yläpuoliseen veteen, vaikka siinä olisi liuennutta happea. Tämän vuoksi Suomenlahdelta mitattiin suuria vapautuvan fosforin määriä hapelliseen pohjanläheiseen veteen sellaisilta pohjilta, joilla rautasulfideja ilmentävä musta sedimenttikerros ulottui aivan sedimentin pintaan saakka. Sen sijaan pieniä vapautumismääriä tai jopa fosforin sitoutumista vedestä sedimenttiin mitattiin pohjilta, joilla oli ruskea rautaoksidi-kerros.

Suomenlahden murtovesisedimenteissä liukoisen raudan pitoisuudet ovat merkittävästi pienempiä järvisedimentteihin verrattuna. Sulfaattipitoisessa ympäristössä raudan, rikin ja fosforin kierrot ovat läheisessä yhteydessä toisiinsa. Suomenlahden korkea sulfaattipitoisuus (~500 mg l<sup>-1</sup>) verrattuna suomalaisiin järvesisiin (keskiarvo 2,8 mg l<sup>-1</sup>) johtaa siihen, että hapettomassa murtovesisedimentissä raudan diffuusio tulee suurelta osin tehottomaksi rautasulfidien muodostumisen vuoksi. Rautasulfidien muodostuminen estää raudan tehokkaan kierron ja lisää liukoisen fosforin liikkuvuutta ja vapautumista sedimentistä veteen. Siten perinteinen järvisedimentille soveltuva rauta-fosforimalli ei sellaisenaan toimi Itämeren sulfaattipitoisessa sedimentissä.

Suuri ulkoinen fosforikuormitus on aina primaari syy suurelle pohjasta veteen vapautuvalle fosforimäärälle. Kuitenkin sedimentin hapetustilaan vaikuttavilla hydrografisilla tekijöillä on suuri merkitys fosforin pidätyksessä, kun suuri osa sedimentin liikkuvasta fosforista on sitoutunut

rautaoksideihin. Suomenlahden pohjanläheisen veden kerrostuneisuus-, ja happiolosuhteita säätelee suolaisen veden tunkeutuminen Itämeren pääaltaasta Suomenlahdelle. Itämeren pääaltaaseen 1993 tullut suuren suolaisen veden määrä nosti Suomenlahden pohjanläheisen veden suolapitoisuutta vuonna 1994, mutta korkeimmat suolapitoisuudet mitattiin vuonna 1996. Vuoden 1996 aikana ja sen jälkeen pohjaeläinkannat heikentyivät merkittävästi ja hapetustilaltaan heikkoja sedimenttejä havaittiin koko Suomenlahden alueella. Samoilta alueilta mitattiin myös suuria veteen vapautuvan fosforin määriä. Suurella Itämereen tulevalla suolapulssilla, Suomenlahden sedimentin hapetustilan heikkenemisellä ja fosforin vapautumisella sedimentistä veteen näyttäisi olevan yhteys toisiinsa. Suolaisen veden tunkeutuminen Suomenlahdelle voimistaa kerrostuneisuutta ja heikentää pohjanläheisten vesikerrosten happivarojen täydentymistä. Tämä puolestaan aiheuttaa sedimentin hapettomuutta mahdollistaen anaerobisen sulfatien pelkistykseen ja rautasulfidien muodostumisen sedimentin pintakerroksessa ja suuren fosforimäärän vapautumisen. Lisäksi Itämeren pääaltaan syvän veden veden fosforipitoisuus on korkea ja se tuo mukanaan suuren määrän fosforia pääaltaasta Suomenlahteen.

Suomenlahden pohjasta vapautuva fosfori yhdessä Itämeren pääaltaalta tulevan fosforin kanssa selittää suurelta osin pohjanläheisen veden korkean fosforipitoisuuden loppukesällä. Loppusyksyllä ja talvella tapahtuvan vesimassojen sekoittumisen jälkeen fosforipitoisuus nousee myös pintakerroksessa. Talvella merkittävää fosforin pidättymistä vedestä sedimenttiin ei mitattu ja myös fosforia sitova levätuotanto on tuolloin heikkoa. Veden fosforipitoisuus pysyy korkeana aina kevätkukinnan alkuun saakka. Pohjasta vapautuva suuri fosforimäärä selittää myös suurelta osin pohjanläheisen veden alhaisen epäorgaanisen typpi-fosfori suhteen – ei niinkään denitrifikaatio. Vuosikierron aikana pohjasta vapautuva fosfori kykenee alentamaan epäorgaanisten ravinteiden typpi-fosforisuhdetta suuressakin vesitilavuudessa, mikä osaltaan selittää Suomenlahden levätuotannon typpirajoitteisuutta. Pohjasta vapautuneen fosforin suuri määrä voi johtaa myös siihen, että pintakerrokseen jää kevätkukinnan jälkeen käyttökelpoista fosforia, joka suosii typeä sitovien sinilevien kasvua kesäisin.

Suomenlahden pohjasta vapautuvan fosforin sekä Itämeren pääaltaalta tulevan fosforimäärien vaihtelut aiheuttavat merkittävää pitoisuusvaihtelua koko Suomenlahden vesimassassa. Nämä fosforin lähteet voivat kumota ulkoisen fosforikuormituksen vähennyksen vaikutukset pitkälle aikajaksolle. Sisäisten prosessien hallitsevasta osuudesta osoituksena on se, että Suomenlahden fosforipitoisuudet ovat keskimäärin kasvaneet 1990-luvun puolivälin jälkeen, vaikka Suomenlahden valuma-alueen ulkoinen fosforikuormitus väheni 1990-luvun alkupuoliskolla noin 30 % (3 400 t). Suomenlahden sedimentistä tehty fosforin vapautumismittaukset sekä taselaskelmat osoittavat, että sedimentin heikon hapetustilan vallitessa pohjasta voi vapautua fosforimäärä, joka ylittää selvästi vuotuisen ulkoisen fosforikuormituksen määrän. Tämän vuoksi suurelta osin vähennykset ihmistoiminnan aiheuttamassa fosforikuormituksessa eivät välttämättä johda nopeaan palautumiseen päästölähteen välittömän vaikutusalueen ulkopuolella. Jos Suomenlahden fosforipitoisuutta halutaan alentaa, ulkoista fosforikuormitusta on vähennettävä myös muilla valuma-alueilla, kuin Suomenlahden omalla valuma-alueella.

Pitkällä aikavälillä fosforin sedimentaatio ja myös vapautuminen sedimentistä vähenee kun ulkoista kuormitusta vähennetään. Suomenlahdella ainoa keino vähentää fosforipitoisuutta pitkällä aikavälillä on ulkoisen fosforikuormituksen vähentäminen, vaikka fosforin vapautuminen sedimentistä veteen näyttää tällä hetkellä hallitsevasti säätelevän fosforipitoisuutta. Sedimentin eloperäisen aineksen pitoisuuden lisääntyminen näyttää heikentävän sedimentin fosforin pidätyskykyä ja lisäävän fosforin vapautumista. Tämän vuoksi voidaan olettaa, että sedimentin tilaa voidaan parantaa vähentämällä pohjan pinnalle laskeutuvan eloperäisen aineksen l. leväbiomassan määrää ts. poistamalla ulkoisesta kuormituksesta biologisesti käyttökelpoista typeä ja fosforia. Itäisimmän Suomenlahden sedimentti pidättää hyvin fosforia ja täten fosforin poisto voi nopeasti pienentää levätuotantoa Nevan fosforirajoitteisessa estuaarissa edellyttäen, että lännestä tuleva syvän veden virtauksen mukana tuleva fosfori ei kykene korvaamaan tätä vähennystä.

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What, then, could be a more appropriate toast than 'bottoms up'.

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Jouni Lehtoranta

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### Book chapters

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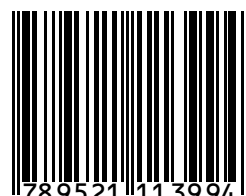
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