Nutrient exchange across the sediment-water interface in the eastern Gulf of Finland

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Benthic nutrient fluxes (sedimentation, degradation and burial within the sediment, and release to the water column) were estimated for a series of stations in the Neva Bay and different areas of the eastern Gulf of Finland (GOF). It was shown, that the Gulf sediments act as an efficient trap for both nutrients: 20%-50% of P and 40%-65% of N in the Neva estuary and in the open Gulf, and up to 100% in the Neva Bay are buried within the accumulating sediment. The rest is released to the overlying water. Minor portion of dissolved nutrients is released by molecular diffusion from the deep sediment layers. The diffusion from immediate sediment-water interface and convective transport seem to be of greater importance in nutrient release. The variations in the intensity of benthic processes of nutrient sedimentation, adsorption, minerals formation, nitrification, denitrification and convective transport from the sediments in the sub-areas of the Gulf are generally determined by the chemical composition and amount of sedimenting material, in combination with bottom dynamics. Benthic nutrient flux to the overlying water could supply generally a small fraction of estimated phytoplankton nutrient demand (0%–10% of P and 1%–5% of N).

Introduction

Nutrient exchange across the sediment–water interface is an important process affecting the chemical composition and the trophic level of aquatic systems, particularly in shallow waters such as estuaries and coastal marine environments (e.g. Klump and Martens 1981, Callender and Hammond 1982, Boynton and Kemp 1985, Koop *et al.* 1990). Due to the generally high productivity and shallow water depth a large part of the sedimenting particulate organic matter reaches the bottom and substantial amounts of dissolved nutrients rapidly liberate as a result of bacterial decomposition and mineralization, autolysis, and desorption. The exchange of nutrients between sediment and water can, therefore, significantly affect local primary production within the shallow water area as well as lateral transport of nutrient compounds out to the deeper waters (Fisher *et al.* 1982, Hopkinson and Wetzel 1982).

The present study was carried out in the eastern Gulf of Finland (GOF), the state of which has been deteriorating steadily during recent decades



Fig. 1. The sampling stations and the sub-area division. — I: The inner Neva estuary. — II: the outer Neva estuary. — III: the open north-eastern Gulf. — IV: the Finnish archipelago.

due to anthropogenic eutrophication caused by increased nutrient (nitrogen and phosphorus) loading from the Neva River (St. Petersburg, NW Russia).

The purpose of the present study was to quantify nutrient (phosphorus and nitrogen) fluxes across the sediment–water interface in order to assess the relative importance of benthic nutrient recycling to the water quality and to the requirements of primary producers in different areas of the eastern Gulf of Finland.

Study area

This research was conducted in the Neva Bay and different sub-areas of the north-eastern GOF according to division given in Pitkänen (1991) (Fig. 1).

Fine-grained sediments with high values of water content are typical of the outer estuary and the open Gulf, while the sediments of the inner estuary and the Neva Bay vary from the sands and sandy silts to gyttja clays. The sediment accumulation rate varies widely from 0.5 mm yr⁻¹ in the sandy areas to 10–20 mm yr⁻¹ in some nearshore bays and accumulation bottom in the open basin of the GOF (Niemistö and Voipio 1981, Pitkänen 1994). It is suggested that the eastern Gulf acts as an effective trap for nutrients and autochthonous particulate organic matter, thus regulating trophic conditions in the whole Gulf (Pitkänen 1991, Pitkänen *et al.* 1993).

Materials and methods

Sampling procedure

The study is based on the data from 24 stations (4–65 m in depth) sampled in August 1993 and September 1996 during the cruises of R/V Professor Multanovsky and Talan (Fig. 1).

Near-bottom water (4–5 cm above the sediment surface) and intact sediment cores were taken with a gravity corer. Onboard the cores were immediately divided into 4–9 subsamples, the uppermost usually about 0.1–0.2 cm and the deeper ones 1 to 5 cm in thickness down to a depth of 15–17 cm, and were extruded into small plastic bags. At each site, at least three cores were similarly sliced, and the slice replicates were pooled together. All samples were stored in a refrigerator at temperature about 4 °C.

Chemical analyses

Temperature, pH and near-bottom water oxygen concentration using the Winkler titration, were measured immediately after sampling. Water content and porosity of the wet sediments were determined by drying a subsample at 105 °C, until no further weight loss was observed. For pore water extraction, vacuum filtration through Nuclepore membrane filter (0.45 μ m) was used.

Dissolved inorganic phosphorus (DIP) was

determined using the molybdate method (Murphy and Riley 1962). Dissolved total P (DTP) was obtained in the same manner following digestion of water samples with persulphate-sulphuric acid mixture for 1 hour at 105 °C. Colorimetric methods served to determine ammonium-nitrogen (NH_4^+), and the sum of nitrite- and nitrate-nitrogen ($NO_2^-+NO_3^-$) with Nessler and Griss reagents, respectively (Triphonova 1979, Wood *et al.* 1967). Dissolved total metals, iron and manganese, were measured spectrometrically using ICP in Chemical Laboratory of Geological Survey of Finland.

The forms of phosphorus in the sediment solids — total P (TP) and total inorganic P (TIP) were determined by sequential acid and alkali extractions of the dry sediment and analysis of inorganic P and total P in the pooled extracts (Mehta *et al.* 1954). Organic P content was calculated as a difference between appropriate total and inorganic P content.

Results

Near-bottom water

During the sampling the temperature of near-bottom water varied from 3.0–4.4 °C in the deep waters to 12.8–13.2 °C in the shallow Neva Bay. Dissolved oxygen content 4–5 cm above the sediment– water interface ranged from 2.55 to 9.14 mg $O_2 l^{-1}$ that corresponded to 21%–90% saturation.

The values of pH varied from 6.94 to 7.52. The highest values were found in the Neva Bay.

DIP, DTP and NH_4^+ concentrations varied from 0.010 to 0.118, 0.037 to 0.127 mg P l⁻¹, and 0.020 to 0.201 mg N l⁻¹, respectively. A general tendency for an increase in DIP, DTP and NH_4^+ concentrations from east to west was found. Concentration of $NO_2^-+NO_3^-$ ranged between 0.065 and 0.205 mg N l⁻¹ with highest values in the Neva estuary. These data indicate an intensive nitrification in the near-bottom water of the GOF. In the estuary this process seems to occur more intensively than in the open Gulf.

Physico-chemical characteristics of sediments

Water content and porosity of the bulk sediment

samples varied from 18% and 0.35 for sands to 92% and 0.97 for fine-grained sediments.

The upper few centimetres of sediment were oxygenated as judged from the presence of oxidized forms of inorganic nitrogen. An oxidized layer was found down to 4–5 cm in the open Gulf, 1–2 cm in the outer estuary and 1–5 cm in the inner estuary and the Neva Bay. The sole exception was St. F41 where only the uppermost layer of about 0.1 cm was oxygenated.

The values of pH varied widely from 6.08 to 7.84. The lowest values were found in the Neva Bay and the inner estuary.

Particulate nutrients in sediments

The spatial distribution of sediment P in the eastern GOF is generally governed by increasing gradient of primary production towards the Neva estuary (Pitkänen *et al.* 1993) and bottom dynamics. As a result, TP content in the uppermost 0.1– 0.2 cm surficial sediment layer in the outer estuary is higher than in other sub-areas (Table 1). The spatial distributions of total inorganic and organic sediment phosphorus were similar to that of total phosphorus.

Some typical vertical distributions of particulate P in the sediment cores taken at the stations lo-

Table 1. The ranges of TP content (mg P g^{-1} D.W.) inthe uppermost (0.1–0.2 cm) surficial sediment layer inthe Neva Bay and different sub-areas of the easternGOF.

Sub-area of the GOF	TP
Neva Bay	0.47-0.91
Outer estuary	2.58–3.42
Open GOF F41*)	1.90–2.08 4.88
Near-shore bays	0.23-2.99

^{*)} Station F41 is set aside because it is located on the bottom of accumulation type (according to Jonsson *et al.* 1990), while other stations are located on erosion or transition ones, where not only sedimentation but erosion and resuspension take place. As a result, the sediment at St. F41 differs sharply in physico-chemical and chemical characteristics from those at other sampling sites.



cated at different sub-areas of the GOF are given in Fig. 2.

In the Neva Bay and the inner estuary, TP content was determined only at three horizons in the sediment column, 0.1–0.2, 0.2–1 and 10–15 cm. At most stations in the Neva Bay, the vertical decrease of TP content with depth in the sediment was insignificant. Obviously, near-bottom currents transport most part of freshly sedimented material to the west in the deeper areas.

Organic P content in the uppermost sediment exhibits rather low percentage of 11%–15% in the Neva Bay and the inner estuary, and 25%–33% in the outer estuary and the open Gulf.

On the average, TP shows more or less constant values with depth below 10 cm. As regards to nitrogen, according to data for the outer estuary and the open Gulf presented by O. Sandman (pers. comm.), the appropriate depth in the sediment is usually about 15–20 cm.

Fig. 2. Vertical distributions of particulate TIP (dashed line) and TP (solid line) in the sediment cores sampled at the stations located in the sub-areas of the eastern GOF.

The N:P ratio in topmost sediment is relatively low: mean estimates are 3 (w/w) and 2 for the open GOF, and the outer Neva estuary and St. F41, respectively. Deeper in the sediment column the N:P ratio tends to increase to about 4–5 (w/ w), that is in line with the general findings of preferential P mineralization (Menzel and Ryther 1964, Seki *et al.* 1968).

Nutrients and metals in pore water

Some typical vertical distribution of DIP, DTP, NH_4^+ -N and NO_2^- + NO_3^- -N in pore water of different sub-areas of the GOF are presented in Fig. 3 and 4. The concentrations of the various nutrient fractions in the sediments exhibit several patterns of concentration with respect to depth.

Interstitial waters of the estuary and the Neva Bay sediments were generally poor in phospho-



Fig. 3. Vertical distributions of DIP (dashed line) and DTP (solid line) in sediment pore waters at the stations located in the Neva Bay and in the subareas of the eastern GOF.





Fig. 5. Vertical distribution of dissolved Fe and Mn in sediment pore waters at the stations located in the sub-areas of the eastern GOF.

rus. At most stations, DTP concentration was about 0.1–0.2 mg P l⁻¹. In the open Gulf, DTP tended to increase from east to west mainly in reduced sediment. It seems likely that this enrichment in P is attributable to the desorption of phosphate from metal hydroxides undergoing reduction as the redox layer within the sediment moves upward. In this case oxic sediment acts as a trap for phosphate diffusing upward and only small portion of it is able to escape to the overlying water. At all stations, most of the interstitial P was in inorganic forms. The highest interstitial P content was found at St. F41.

Pore waters of the eastern Gulf sediments are enriched in dissolved inorganic nitrogen [DIN: $NH_4^++NO_2^-+NO_3^-$]. The concentrations of DIN were as much as 15–16 mg N l⁻¹. Some portion of interstitial N was in oxidized forms, indicating nitrification in the top oxic sediment layer.

It has been found in this study, that interstitial nitrogen concentrations were higher than those in the overlying water. As for phosphorus, in the Neva Bay, the inner estuary and near-shore bays (St. A, 6_L and 3_K) the interstitial concentrations in the upper sediment layers were generally lower than those in the overlying water.

Vertical profiles of some metals such as iron and manganese are important in order to trace the early diagenetic processes, because under certain conditions these metal ions are involved in authigenic minerals formation with phosphate within the sediment. In this study, pore water metal concentrations were determined at stations in the open Gulf and the outer estuary (Fig. 5). Pore waters of the eastern GOF sediments are enriched in Mn, while concentrations of Fe in these subareas were often below detection limit of the applied method of 30 mg Fe l^{-1} . According to data presented by O. Chernykh (pers. comm.) and Melnichuk *et al.* (1991), pore waters of the Neva Bay and the inner estuary exhibit high content of dissolved Fe (up to about 10 mg Fe l^{-1}). An increasing gradient of interstitial Mn and Fe content prevails towards the Neva Bay.

Discussion

Sedimentation and burial of nutrients

Sediment nutrients consist of labile and refractory organic and inorganic compounds. The former decompose or dissolve within the sediment and release phosphate and ammonium-ions to the interstitial water. The latter behave as inert/almost inert material and are buried within the accumulating sediment.

It was shown (Pitkänen 1991), that the eastern GOF acts as an efficient sink for both nutrients. Sedimentation and burial of P and N have been estimated based on data on sediment nutrient content, sediment accumulation rate, porosity and dry solid density.

The estimated values for P and N sedimenta-

tion fluxes presented in Tables 2 and 3 are of the same order with mean estimates calculated on the basis of annual budgets for TP and TN as residuals from the input and output terms of 3.01 mg P m⁻² d⁻¹ and 8.22 mg N m⁻² d⁻¹ (Pitkänen 1991). Nutrients demonstrate more strong sedimentation in the Neva estuary, some bays (St. A and 6_L) and at St. F41.

The average values of the estimated burial fluxes of TP tend to increase from the open GOF to the Neva Bay. At most stations in the Neva Bay (sandy silts) the calculated sedimentation fluxes are equal to the burial ones. As discussed above, freshly sedimented material containing labile phosphorus compounds does not retain at the sediment surface in this area and are transported by near-bottom currents to the estuary. As a result, sediment phosphorus in the Neva Bay represent mainly refractory compounds and, on the average, about 90% of sedimented P are retained by the sediment.

The estimated burial fluxes of TN in the open GOF are close to those in the outer estuary.

From the sediment organic P data, a mean degradation within the top 10 cm of the sediment column taken as a "black box" at steady state

(Balzer 1984) has been estimated (Table 2). The average values of degradation flux tend to increase from the open Gulf to the estuary. The highest values were found at stations 1 and F41. Therefore, the sedimenting particulate organic P at these sites is enriched in labile compounds.

The estimated burial fluxes of N (Table 3) are within the range of values reported in other studies from the Baltic Sea (Kiel Bight and the Baltic's main basin) of 1.68–9.88 mg N m⁻² d⁻¹. As regards to phosphorus, the estimated burial fluxes (Table 2) are somewhat higher as compared with those obtained for other Baltic areas of 0.22–0.67 mg P m⁻² d⁻¹ (data cited by Koop *et al.* 1990). There are at least two explanations for this deviation:

- sedimenting particulate material in the GOF contains more land-based refractory phosphorus compounds than that in the Baltic's main basin and Kiel Bight;
- sinks for inorganic P within the Gulf sediments are of greater importance than in other Baltic sediments. The sinks may include processes of adsorption of phosphates on metal oxides and clayey minerals, and authigenic minerals formation.

Table 2. Sedimentation (S), degradation (D), release and buri	al (B) fluxes of phosphorus (in mg P m ⁻² d ⁻¹) in the
Neva Bay and different sub-areas of the eastern GOF.	

	Open GOF	Outer estuary	Inner estuary	Neva Bay	F41
Sedimentation	2.10±0.20	4.34±0.66	7.99±1.89	3.12±0.22	12.47
Degradation	0.38 ± 0.04	0.66 ± 0.08	0.84 ± 0.28	0.00 ± 0.00	2.31
Release (S-B)*)	1.26 ± 0.11	3.17 ± 0.56	5.40 ± 1.43	0.11 ± 0.06	9.91
Diffusive release	0.17 ± 0.05	0.04 ± 0.02	0.00 ± 0.00	0.00 ± 0.00	5.76
Burial	0.84 ± 0.07	1.17 ± 0.13	2.59 ± 0.71	3.01 ± 0.26	2.56

*) Release calculated as a difference between sedimentation and burial fluxes

Table 3. Sedimentation (S), release, burial (B) and apparent denitrification fluxes of nitrogen (in mg N $m^{-2} d^{-1}$) in the Neva Bay and different sub-areas of the eastern GOF.

	Open GOF	Outer estuary	Inner estuary	Neva Bay	F41
Sedimentation	6.42±0.97	7.21±1.02	_	_	25.15
Release (S-B)*)	2.82 ± 0.39	3.72 ± 0.84	-	-	15.03
Diffusive release	7.52±2.13	24.78±7.27	1.64±0.76** ⁾	0.60±0.19**)	55.28
Burial	3.61 ± 0.63	3.49 ± 0.58	_	-	11.12
Apparent denitrification***)	4.7 ± 1.32	21.06 ± 6.56	-	_	40.25

*) Release calculated as a difference between sedimentation and burial fluxes

**) Diffusive release of NH4+-ions

***) Apparent denitrification calculated as a difference between diffusive release and release

The presence of adsorbing agents is supported by the constant phosphate concentration in the pore water within the surficial oxic sediment. On the other hand, the calculations conducted in this study allowed to suppose the possibility of vivianite $Fe_3(PO_4)_2 \times 8H_2O$ and reddingite $Mn_3(PO_4)_2 \times 3H_2O$ formation in anoxic sediments that is in line with results of previous study (Melnichuk *et al.* 1991). Saturation degrees are 10^{3} – 10^{10} for vivianite and 109-1014 for reddingite with highest values in the more freshwater estuary sediments. This result is in agreement with the findings of Caraco et al. (1990), who have shown that sediments of most freshwater systems act as more efficient sink for P than those of saline-water ones. However, oversaturation does not necessarily mean presence of the mineral, due to kinetic factors or interfering ions.

Diffusive nutrient release

The portion of the sedimenting nutrients that is not buried must be solubilized and returned to the overlying water. The diffusion is considered to be the main transport mechanism of dissolved nutrient release from the sediment.

The diffusive fluxes of phosphate, ammonium, and a sum of nitrate and nitrite were calculated by application of Fick's first law.

As can be seen from the Table 2, the difusive P fluxes tend to decrease from the open GOF to the estuary. At most stations in the Neva Bay, the inner estuary and the near-shore bays (St. A, 6_L and 3_K), concentration gradient of phosphate at sediment–water interface was found either zero or directed into the sediment, indicating impossibility of diffusive release from the sediment to the overlying water.

The calculated P fluxes agree with values recorded from the Baltic's main basin (Koop *et al.*, 1990) and Kiel Bight (Balzer 1984) of 0.07–1.93 mg P m⁻² d⁻¹. The only exception is St. F41, which exhibits the highest flux value.

In contrast to phosphorus, the N fluxes in the outer estuary are higher than those in the open Gulf (Table 3). The highest values of NH_4^+ -flux of 55–59 mg N m⁻² d⁻¹ were found at stations F41 and A, $NO_2^-+NO_3^-$ -flux of 44 mg N m⁻² d⁻¹ at St. SL 41. The NH_4^+ -fluxes at most stations agree with

those from the Baltic Sea of 0.07–9.34 mg N m⁻² d⁻¹ cited by Koop *et al.* (1990), while the calculated NO₂⁻⁺NO₃⁻-fluxes are mainly much higher than those (up to 3.36 mg N m⁻² d⁻¹) in other Baltic areas. Despite values of NH₄⁺-flux up to about 19 mg N m⁻² d⁻¹ found in the coastal waters of West Sweden, it is possible, that such high values of DIN-flux are hypothetical, because the portion of nitrate will be lost due to denitrification.

There are no published direct measurements of denitrification rate from the study area, though considerable denitrification intensities have been measured or calculated indirectly both in the water column and the sediments in the Baltic's main basin and in coastal waters of the Baltic Sea (Balzer 1984, Rönner 1985, Jørgensen and Sørensen 1988, Koop *et al.* 1990).

Sediment denitrification has been proposed as a major process for the depletion of N in coastal marine ecosystems (Seitzinger *et al.* 1980). Nixon (1981) has shown that denitrification in sediments leads to the characteristically low N:P ratio and may be responsible for nitrogen being the major nutrient limiting primary production.

Nutrient sediment budget in terms of sedimentation, degradation, burial and release

In order to compile a nutrient budget within the sediment–water boundary zone, the terms of sedimentation, degradation within the sediment column, release and burial must be compared (Tables 2 and 3).

In the case of phosphorus, the release calculated as a difference between the sedimentation and the burial terms is always far greater than diffusive fluxes predicted from pore water profiles (Table 2). It is clear that one or more processes are operating in the eastern Gulf to enhance the effect of molecular diffusion on benthic exchange. This enhancement may be attributed to such processes as bioturbation, physical stirring of sediments by currents and wave actions, and gas ebullition. The action of these processes is most pronounced in shallow waters, where the real nutrient fluxes can be one or two orders of magnitude higher than those obtained from molecular diffusion consideration (Hammond et al. 1977, Aller 1978, 1980, McCaffrey et al. 1980, Klump

and Martens 1981, Rutgers van der Loeff et al. 1984).

Mainly due to convective transport the retention efficiency of fine-grained sediments with respect to P tends to increase with depth from the estuary towards the open GOF: 19% of sedimented P is buried within the sediment at St. 1 in the inner estuary, $28\% \pm 3\%$ in the outer estuary and $41\% \pm 2\%$ in the open Gulf.

Furthermore, some experiments conducted in the course of this study provide support for the view that in environments which are characterized by a comparatively low sediment accumulation rate, mineralization of nutrients, nitrification and denitrification occur primarily in the uppermost flocculent sediment layer, rather than throughout the sediment column (Balzer 1984). Therefore, the sediment– water interface may play a key role in these processes, that will substantially reflect on nutrient release to the overlying water.

One more evidence for the importance of diffusion from immediate sediment–water interface and convective transport in P release from the sediments is the tendency for a decrease from west to east of the contribution of P, released to the pore water as a result of decomposition of organic matter within the sediment column (D), in the total P release from the sediment (S-B): $31\% \pm 2\%$ in the open Gulf, $22\% \pm 2\%$ in the outer estuary, $13\% \pm$ 3% in the inner estuary and 0% in the Neva Bay.

As for nitrogen as compared with phosphorus, a more essential portion (50%–55%) of the particulate material reaching the bottom via sedimentation is buried within the fine-grained sediments.

If it is supposed that above-mentioned processes, which are able to enhance the release from the sediments, effect in much the same manner on both nutrients, the underestimation of nitrogen release would also be expected. However, the fluxes calculated as a difference between sedimentation and burial terms are always lower than those estimated as a sum of NH_4^+ - and $NO_2^-+NO_3^-$ fluxes on the basis of pore water concentrations. Obviously, this result may be explained by process of denitrification, which goes more efficiently in the estuary and leads to the loss of inorganic nitrogen. As a result, the real content of nitrogen, which is able to escape to the overlying water in soluble forms, is much less than that predicted from the pore water concentration.

Therefore, in slowly accumulated sediments of the eastern GOF, where immediate interface is a major site of decomposition, nitrification and denitrification, an average annual nutrient exchange across the sediment–water interface can be estimated most correctly by comparison of settling with burial fluxes.

Influence of sediment processes on nutrient cycles in the Gulf

An effective mixing of water column in the eastern GOF (Pitkänen 1991, Pitkänen et al. 1993) is of great importance in returning the part of sedimented and remineralized nutrients to the euphotic layer. In order to estimate the potential influence of sediment-water exchange in the nutrient cycles in the Gulf, the magnitude of P and N release fluxes from the sediments has been compared with phytoplankton demand for these nutrients (Gutelmakher et al. 1987, Pitkänen et al. 1993). The sediments of the GOF are able to supply generally a small fraction of the required nutrients: 2%-10% of P and 1%-5% of N in the Neva estuary and the open Gulf, and less than 1% of P in the Neva Bay during the late summer and early autumn. Only at stations F41 and 26, benthic regeneration of nutrients seems to provide a significant fraction of the daily phytoplankton requirement, 55%-60% of P and about 16% of N.

Conclusion

The results of this study indicate that the sediments of the eastern Gulf of Finland act as an efficient trap for phosphorus and nitrogen. An essential portion of the particulate nutrient material reaching the bottom via sedimentation is buried within the sediment, the rest is released to the overlying water. Due to significant land-based inputs of Mn and Fe to the Gulf, large portion of phosphorus is probably adsorbed on metal oxides in oxic sediment and occurs in authigenic minerals in reduced sediment. As for nitrogen, a substantial portion of ammonium-ions, which is produced during mineralization, is likely oxidized to nitrate-ions accompanied by subsequent denitrification and loss of nitrogen from the sediment. These processes partly counteract eutrophication of the eastern Gulf.

The uppermost millimetres of sediment can play a key role in rapid degradation of labile organic matter, nitrification and denitrification. Minor portion of dissolved nutrients is released by molecular diffusion from the deep sediment layers. The diffusion from immediate sediment– water interface and convective transport seem to be of greater importance in nutrient release from the sediments.

The variations in the intensity of benthic processes in the sub-areas of the Gulf are generally determined by the chemical composition and amount of sedimenting material, in combination with bottom dynamics. Benthic nutrient flux to the overlying water could generally supply a small fraction of estimated phytoplankton nutrient demand in the GOF.

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