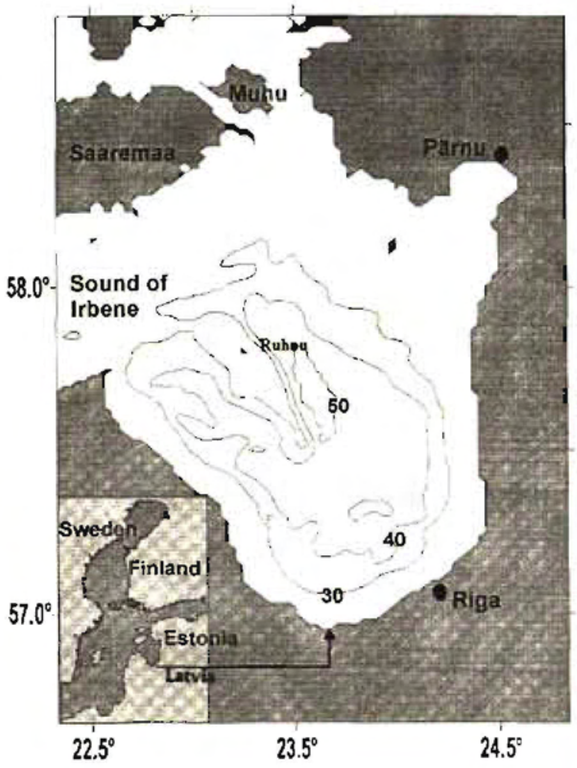
MEDDELANDEN från STOCKHOLMS UNIVERSITETS
INSTITUTION för GEOLOGI OCH GEOKEMI

AVHANDLING för
FILOSOFIE DOKTORSEXAMEN

No. 311

The role of sediments in the biogeochemical cycles of nutrients in the Gulf of Riga

Juris Aigars



Stockholm 2001
Department of Geology and Geochemistry
Stockholm University
S-106 91 Stockholm
Sweden

A dissertation for the Doctor's Degree in Natural Science
Department of Geology and Geochemistry
Stockholm University
S-106 91 Stockholm
Sweden

Abstract

The sediment biogeochemistry of C, N, P and biologic silica (BSi) plays an important role in cycling of these elements in aquatic ecosystems. In shallow coastal and estuarine systems, water-sediment nutrient dynamics can influence biological processes (e.g., primary production) in overlying waters.

The objectives of this study are:

- characterize C, N, P and BSi geochemistry of the surface sediments in the Gulf of Riga,
- estimate the spatial distribution, including net flux and sink, for organic C, N and P in the Gulf of Riga,
- examine if there are any appropriate bulk, regional and/or vertical relationships between the nutrients,
- examine if nutrient biogeochemistry in surface sediments vary as a response to naturally occurring processes i.e., intensity of sedimentation and bioturbation, oxygen deficiency, variation of temperature

Spatial and vertical distribution reveals that organic C and N ratio is almost independent of sediment characteristics and location, and exhibit a stable value down the sediment core. Over 90 % of carbon and nitrogen in sediments is organic. In contrast, organic P constitutes less than 50 % of the total phosphorus pool. The organic C:N:P ratio in sediments indicate that N and P are decomposed preferentially to C, whereas P is decomposed preferentially to N. The stable C:N ratio in sediments indicates that preferential N decomposition occurs in water column and/or immediately upon settling at sediment surface. Distribution pattern of BSi suggests that accumulation rate of sediments controls BSi concentration. Although nutrient loading from drainage area increased drastically over the past 100 years, vertical profiles of C, N and BSi show no variation in element concentrations except in the top few centimeters. A corresponding increase of benthic biomass most likely results in low elemental accumulation in these sediments.

Although Gulf of Riga is one of the most productive areas in the Baltic Sea, seasonal alterations of C and N levels were limited. However, during spring and autumn algae blooms total C and N concentrations increased in the study area. Limited data suggests that burrowing amphipods directly impact the C and N concentrations in the top 2-3 cm of sediments. The vertical distribution of P is more dependent on oxygen concentration, which is largely controlled by bioturbation and sedimentation rates. Moreover, the results suggest that bioturbation is largely responsible for temporal accumulation of inorganic P in surface sediments.

The low unidirectional fluxes of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) in early spring is consistent with low water temperature and poor nutritional quality of experimentally added material. The high water temperature and better nutritional quality of material added in summer, comparatively to winter, resulted in large DIN and DIP fluxes. Moreover, flux experiments under low oxygen conditions and pulse input of large quantities of settling seston suggest that sediment surface might experience lack of oxygen despite availability of oxygen in the overlying water column.

ISBN 91-7265-076-1, pp. 1-11
ISSN 1101 - 1599
Tryck: Sandlund and Co Grafiska, Stockholm 2001

The role of sediments in the biogeochemical cycles of nutrients in the Gulf of Riga

Juris Aigars

Department of Geology and Geochemistry, Stockholm University, S-106 91 Stockholm, Sweden

---

The doctoral thesis consist of a summary and the following papers:

Paper I
Carman, R., Aigars, J. and Larsen, B. 1996. Carbon and nutrient geochemistry of the surface sediments of the Gulf of Riga, Baltic Sea. *Marine Geology* 134: 57-76.

Paper II
Carman, R. and Aigars, J. 1997. Vertical and spatial distribution of biogenic silica in the sediment of the Gulf of Riga, Baltic Sea. *Toxicological and Environmental Chemistry* 60: 245-259.

Paper III
Danielsson, Å., Carman, R., Rahm, L. and Aigars, J. 1998. Spatial estimation of nutrient distributions in the Gulf of Riga sediments using cocriging. *Estuarine, Coastal and Shelf Science* 46: 713-722.

Paper IV
Aigars, J. and Carman, R. 2000. Seasonal and spatial variations of carbon and nitrogen distribution in the surface sediments of the Gulf of Riga, Baltic Sea (Accepted by *Chemosphere*)

Paper V
Aigars, J. 2000. Redox-dependent seasonal variations of the phosphorus geochemistry in the surface sediments of the Gulf of Riga. (Submitted to *Chemosphere*)

Paper VI
Aigars, J. and Carman, R. 2001. Sediment-water phosphorus fluxes in the Gulf of Riga, Baltic Sea: seasonal approach (Manuscript)

Paper I is reprinted with kind permission from Elsevier Science.
Paper II and Paper III is reprinted with kind permission of editors of *Toxicological and Environmental Chemistry* and *Estuarine, Coastal and Shelf Science*, respectively.

Stockholm, May 2001

Juris Aigars

Introduction

On geological time scales, sedimentary processes in oceans play a critical role in distribution of C, N and P (e.g., *Berner et al.* 1993, *Kump* 1993). On shorter time scales, however, sediment biogeochemistry plays a significant role in cycling of C, N and P in shallow aquatic ecosystems e.g., lakes, estuaries, coastal bays and seas, continental shelves (*Callender* 1982, *Wulff et al.* 1990, *Wollast* 1993). Sediments can be a temporary source of some compounds, a terminal sink for others or an interface of biogeochemical transformations (e.g., *Hallberg et al.* 1972, *Blackburn and Henriksen* 1983). In many cases the magnitude of these sediment-water processes is sufficient to be a major component in calculating oxygen or nutrient (C, N and P) fluxes/sinks, and hence, important in formulating estuarine management strategies.

The nutrient and oxygen dynamics of surface sediments in shallow coastal and estuarine systems can influence conditions in overlying waters and sediments (e.g., *Holm* 1978, *Zeitzschel* 1980, *Nixon and Pilson* 1983). The dissolved nutrient fluxes from sediments to the overlying water column may fluctuate on a seasonal to annual basis as a response to various factors e.g., settling of organic detritus, effect of temperature on microbial reactions (*Klump and Martens* 1989, *Scudlark and Church* 1989). In addition, biogeochemical processes in sediments may be coupled to the microbial degradation of organic matter deposited from the overlying water column.

Several environmental factors have been mentioned to be of significance for nutrient and oxygen dynamic in surface sediments e.g., quantity and quality of organic matter reaching the sediment surface (*Wassmann* 1984, *Jensen et al.* 1988), infaunal community characteristics (*Blackburn and Henriksen* 1983), and chemical characteristic of surfical sediments and overlying water (*Henriksen and Kemp* 1988). However, these variables are highly interactive and therefore, it is often difficult to identify cause and effect relationships.

The loading of nutrients into the Baltic Sea has increased four-fold in N and eight-fold in P since 1900 (*Larsson et al.* 1985). However, calculations of overall nutrient budgets (e.g., *Larsson et al.* 1985, *Andersen* 1986) indicate that N and P concentrations in water do not increase at a corresponding rate. The budget calculations generally assume that increased burial in sediments results in this discrepancy (e.g., *Larsson et al.* 1985, *Wulff et al.* 1990). The burial of C, N, P and other elements in sediments may reflect changes in element loading and environmental conditions that are on time scales from years to millennia (*Schneider et al.* 1990, *Wollast* 1992). However, the scarcity of sediment data in budget calculations calls for additional studies of sedimentary processes.

Wulff and Stigebrandt (1989) discussed that empirical studies of large-scale ecological processes are a widely accepted approach in limnology. The results from such empirical studies are expected to be similar to those of marine systems. However, in lakes it is more straightforward to determine the system boundaries and transfer of energy and material what makes lake system studies easier comparing to marine systems. Therefore, it is logical to focus on comparatively small marine basins such as the Gulf of Riga to understand these biogeochemical indications.

The present thesis is a summary of six articles dealing with distribution and relationships of nutrients in surface sediments, and between nutrient biogeochemistry and environmental parameters.

Study area

The Gulf of Riga is a shallow and semi-enclosed basin of the Baltic Sea. The total area and volume for the Gulf of Riga are 19 000 km^2 and 420 km^3, respectively. The drainage area covers 136 000 km^2 and consists of Quaternary, Devonian, Cambrian deposits and (*Yurkovskis et al.* 1993). The maximum and mean depths are 62 and 20 m, respectively. Continuous deposition of fine material (mainly at 40-50 m depth) comprises about 28 % of the total area. These accumulation bottoms are mostly situated in the south and southwestern parts of the Gulf of Riga (*Juskevics et al.* 1993). The northern part of the Gulf of Riga (north of Ruhnu Island) is dominated by transportation/erosion bottoms (*Raudsep et al.* 1993) consisting of sand and pebbles/boulders at the surface, and underlying stiff glacial clay/clayey silt. Similar lithology also dominates in the southwestern part of the Gulf with water depths shallower than 35 m.

Water exchange with the Baltic Sea occurs at the north of Gulf through the Irbene and Muhu Straits with sill depths of 35 m and 5 m, respectively. Freshwater runoff is mainly located to the south/southeast of the Gulf and averages at 36.2 km^3 yr^{-1} (*Laznik et al.* 1999). The Gulf of Riga is usually thermally stratified from April/May through September/October. The location of the thermocline is normally situated between 20 and 30 m. Consequently, fine-grained material, which settles on transportation bottoms beneath the spring-summer thermocline, is resuspended in autumn when thermal stratification breaks down.

Results and discussion

Distribution of nutrients and their relationships (Papers 1, 2 and 3).

Spatial and vertical distribution of nutrients, and relationships among them are important factors for assessing the impact of sedimentary biogeochemical processes on the ecosystem. Such information is useful for additional studies i.e., laboratory, statistical, and model approaches of the response on the distribution and composition within the sediments during natural and anthropogenic changes.

The first article deals with the physical structure and carbon- and nutrient geochemistry of sediments in the Gulf of Riga. Loss on ignition (LOI) measurements, used in this study, is frequently used to estimate organic C concentrations in surface sediments. Although LOI does not represent a well-defined chemical parameter (i.e., heating removes most of organic C, organic N, crystal water, and volatile compounds), it gives a fairly stable bulk average ratio of 3.0 between LOI and organic C. In contrast, very weak correlation is observed between LOI and organic N. Previous studies indicate that LOI correlates well with the water content (WC) in sediments (*Håkanson and Jansson* 1983). Consistent with this, data from the Gulf of Riga also exhibit a strong logarithmic correlation (R^2=0.96) between WC and LOI almost independently of sediment location and burial depth (Fig. 2, paper 1). The largest deviations from WC and LOI correlation occur at sites with glacial clay (i.e., old sediments).

The C:N:P ratio of marine organic particulate matter is quite stable (*Redfield et al.* 1963). However, organic C:N ratio exhibits higher values for brackish water in the Baltic Sea i.e., molar ratio varies between 7-10 (*Hendrikson* 1975, *Ituriaga* 1979, *Shaffer* 1987). The Gulf of Riga sediments exhibit very strong linear correlation (R^2 =0.97) between organic C and N, which is almost independent of water depth, depth below seafloor, carbon content, sediment characteristics, and location (Fig. 3, paper 1). The average molar organic C:N ratio is 10.2, and it is consistent with those in similar sediment regions (e.g., *Balzer* 1984; *Froelich et al.* 1988; *Koop et al.* 1990). The average organic C:N ratio in sediments is slightly higher than the average ratio of living organisms in the Baltic Sea (7-10), and suggests preferential N decomposition and/or admixture of old organic matter.

In contrast to the strong linear correlation between organic C and N, the organic C:P and N:P ratios exhibit weak correlation. This suggests that organic P is practically independent of the concentrations of organic C and N. The average organic C:N:P ratio is 230:22.5:1. This elemental ratio suggests that N and P are decomposed preferentially to C, and P is decomposed preferably to N. The average organic C:P ratio is between 228 and 236. This ratio is quite similar with the ratio of organic C:P=125 reported by Balzer (1984) from Kiel Bight. However, organic C:P ratio from our study considerably differs from the average C:P ratios (490, 552 and 1200) reported by Mach et al. (1987), Ingall and Van Cappellen (1990) and De Lange (1992), respectively. The settling time in shallow sub-estuaries of the Baltic Sea is short compared to more pelagic systems. As a result, degradation of organic material is less complete in shallow basins compared to more pelagic basins prior to settling.

Most of the C and N in sediments are organically bound. In contrast, inorganic P is usually the dominant fraction, and constitutes more than 50 % of the total P pool. Generally the vertical distribution of apatite phosphorus (AP-P) is quite even. In contrast, the redox-controlled fraction i.e., mobile phosphorus (MOB-P) exhibits high concentration in uppermost oxic centimeter with subsequent sharp decrease deeper in sediment column. The high linear correlation (R^2=0.96) between total inorganic P and MOB-P (Fig. 7, paper 1) indicates that sequestering mechanisms other than redox dependent adsorption is kinetically slow and unimportant during early diagenesis. However, on long time scales it seems that sequestering to other than redox dependent P-compounds are diagenetically more important.

Increase in nutrient levels in the Baltic Sea due to enhanced loading from drainage basin leads to eutrophication (*Larsson et al.* 1985). However, enhanced loading from drainage basins did not increase accumulation of C and N in the Gulf of Riga sediments. This is in contrast to recent study in other regions of the Baltic Sea (*Carman et al.* 2000). One possible explanation might be the dramatic increase of mean benthic biomass. Gaumiga and Lagzdinsh (1995) indicated that the mean benthic biomass increased from 36 g m^{-2} between 1946-51 to 208 g m^{-2} between 1984-85 in the open part of the Gulf. This suggests a 6-fold increase of nutrient recycling by biota during that period. However, the biomass of macrozoobenthos has decreased significantly since the eighties (*Cederwall et al.* 2000). Therefore, in future, we may expect accumulation of organic C and N in sediments to increase.

Wulff and Rahm (1988) indicated that decrease of Si coupled to increase of N and P concentrations in the water column during winter indicates increase of primary production in the Baltic Sea. Because sinking velocity for diatoms is high, cells reach the bottom in an intact state. Furthermore, previous studies indicate that temperature and salinity mostly regulates regeneration of BSi and dissolved silica flux from sediments to the overlying water column (e.g., *Werner* 1977, *Williams and Crerar* 1985. The long-term hydrological study by Berzinsh (1995) indicates that the temperature and salinity is rather stable in the Gulf of Riga. Therefore, it was expected to observe enhanced accumulation of BSi in recent sediments. However, as discussed in the second article, increase in BSi concentrations only occurs in surface sediments (Table 2, paper 2). The expected larger concentrations of BSi in subsurface sediments are not observed most likely because of bioturbation. However, it cannot be excluded that the effect of increased sedimentation of diatoms may be lost due to dilution by large amount of settling allochthonous material. Moreover, the cores analyzed (5-10 cm deep) may be too short to see real background values.

A weak correlation between BSi concentration and distance from the main nutrient source (e.g., river Daugava), and small temporal and spatial variation in parameters affecting the dissolution of BSi during halmyrolysis (e.g., salinity, temperature) suggest that the surfical concentrations of BSi depend on sediment accumulation rates (paper 2). BSi concentrations vary inversely with sedimentation rates because a large portion of allochthonous material is added to the sinking diatom cells near the coast. This is consistent with conclusions by Conley et al. (1986) for sediments in Lake Michigan, and by Pattan et al. (1992) for sediments in Indian Ocean.

A good correlation (R^2=0.77) exists between all measured concentrations of organic C and BSi (Fig. 2, paper 2). However, the ratios obtained from transition/erosion and from accumulation areas vary considerably between and within these groups. It indicates that dissolution of BSi and degradation of organic C are separate processes and have different magnitudes. This is consistent with studies by Martin et al. (1991) and DeMaster et al. (1992).

The third article in this dissertation estimates the spatial distribution and standard deviation of organic C, N, and P in sediment surface (0-2 cm) by using the cokriging method. The advantage of using the cokriging interpolation technique is inclusion of covariables. This gives a possibility to improve spatial interpolation estimates with additional available information from different parameters, which are easier and cheaper to measure.

Organic C, N, and P concentrations indicate similar horizontal distribution patterns with high concentrations in accumulation areas (Fig. 3(a); 4(a); 5(a), paper 3). It is possible that river Daugava may cause high sediment organic content in the southeast of the Gulf. However, the direct reason for most of concentration patterns in surface sediments is sediment type and thus sedimentation conditions. The standard deviations for concentration estimates (Fig. 3(b); 4(b); 5(b), paper 3) are high because data are sparsely available, and there are large variations within the data. In the middle of the basin, mean standard deviation is lower mostly due to smaller variations in sediment type.

Variations of C, N, and P concentrations with seasonally fluctuating factors (papers 4 and 5)

A large fraction of organic matter in coastal and estuarine waters eventually end up in sediments. Rapid transfer of organic particles from the water column to sediments may leave a significant fraction of the nutrient pool as metabolizable organic compounds that are subject to further decomposition. Remineralization of these organic compounds and release of dissolved nutrients into the water column is a major nutrient recycling pathway in nearshore environments and can supply more than 50 % of the requirements for primary producers (*Zeitzschel* 1980, *Klump and Martens* 1987).

In shallow temperate systems deposition of organic matter, and rates of benthic nutrient regeneration and release can undergo a pronounced seasonality due to altered environmental conditions (e.g., *Smetacek* 1980, *Aller and Benninger* 1981).

The fourth and fifth articles deal with nutrient profiles in sediments and their seasonal variability.

Similar vertical profiles of TC and TN were generally observed at both sites (G5 and T3) in the study area. However, during autumn-spring considerable differences of TC and TN concentrations in 0-2 cm between sites were observed (Fig. 4, paper 4). Most likely, this was caused by differences in abundance of macrozoofauna between the sites (Table 1, paper 4). Moreover, establishing of stronger vertical gradient of TC and TN concentrations in 0-2 cm in May at site G5 and disruption of vertical gradient in November at site T3 (Fig. 5 and 6) corresponded to fluctuation in amphipod numbers reported by Cederwall and Jermakovs (1999).

Monthly sedimentation rates in the Gulf of Riga are absent. Therefore, it is impossible to correlate sediment nutrient concentrations with sedimentation rates. However, it can be assumed that significantly higher TN values during April and November at site T3 (Fig. 6, paper 4) result from settling of spring and autumn blooms, respectively. This is consistent with the findings of Smetacek (1980), who indicated that spring and autumn blooms in Baltic forms and deposits in March-April and October-November, respectively. However, only alterations of TN at one sampling site are significant while alterations of concentrations of TC at both sites and TN at second site were small and not significant. The sediment accumulation rates are fairly high in the Gulf of Riga (*Larsen* 1995). This implies deposition of large amount of allochthonous material, which most likely diminish the signal of bloom sedimentation. However, we should also consider the importance of benthic macrozoofauna, which can lower spring and autumn bloom deposition signal intensity by redistributing material within the upper 0-2 cm.

In contrast to C and N concentrations, P does not correlate with the sedimentation pattern of phytoplankton and bioturbation intensity. The temporal increase of inorganic P at site G5 (Fig. 5, paper 5) resulted from increase in MOB-P pool. Einsele (1936) indicated that abiotic binding of P by ferrous complexes control redox-dependent P pools. However, redox measurements (Fig. 4, paper 5) in the study area suggests that controlling factors other than ferrous complexes are more important. It is possible that temporal accumulation of MOB-P results from accumulation of P by microorganisms. This assumption is consistent with the recent findings by Gächter and Meyer (1993), Kerrn-Jespersen and Henze (1993), Van Veen et al. (1993). These authors indicated that several bacteria and protozoa have the capability to accumulate and store excess P as polyphosphates under oxic conditions. The microorganisms use polyphosphates during metabolic processes if oxygen availability decreases. Orthophosphate produced during metabolism is released into the overlying water column or pore-water.

There is evidence that certain fractions of P cycled by bacteria are transformed into refractory organophosphorus compounds (*Gächter and Meyer* 1993). Presence of organophosphorus compounds have been reported in several studies on marine organic matter (*Ingall et al.* 1990, 1993). Thus, P cycling mediated by bacteria may increase the burial efficiency of nonmetabolizable P-rich organic material. This implies that oxic sediments decrease the residence time for P in a basin while reduced sediments increase it. Therefore, the oxic layer in surface sediments is important not only as a short-term buffer zone for P, but also as a zone for P transformation.

The Gulf of Riga is a small basin compared to the Baltic Sea. However, a high variability of accumulation rates occur in the Gulf of Riga (*Larsen* 1995). The accumulation rates and intensity of bioturbation are major factors controlling the redox conditions in surface sediments. Accumulation rates define the amount of material deposited at sediment surface, and therefore, intensity of oxygen consumption by microbially mediated processes. Benthic macrozoofauna also consumes oxygen. However, surface sediment mixing by benthic macrozoofauna enhances delivery rates of oxygen to the deeper layers of surface sediments compared to delivery rates of oxygen controlled by diffusion. Therefore, areas with high sedimentation rates and low bioturbation activity have low oxygen levels in surface sediments, and are not expected to act as a temporary trap for P. In contrast, areas with low accumulation rates and high abundance of macrozoofauna can act as temporary traps for P.

Fluxes of inorganic N and P (paper 6).

The sixth paper deals with experimental fluxes of dissolved inorganic N and P. Nutrient fluxes were measured after adding seston (sinking plankton plus detritus) with the aim of simulating sediment responses to organic matter deposition between spring and autumn phytoplankton blooms.

Smetacek (1980) indicated that in the Baltic Sea relatively intact cells of pelagic biota may reach the sediments after spring and autumn blooms. In contrast, particles that settle during winter consist mostly of resuspended material with low nutritional value, and particles that settle during summer consist mostly of amorphous detritus (*Smetacek* 1980). The availability and quality of food and temperature generally controls the activity of benthic biota. These factors ultimately influence remineralization rates for organic matter settled at the bottom, and subsequent release of dissolved nutrients.

The seston was added to both columns with and without sediments. The fluxes measured in columns without any sediments were assumed to originate from sediment-water interface "sediment surface". The fluxes measured in columns with sediments were assumed to consist of both "sediment surface" fluxes, and fluxes originating

MEDDELANDEN
från
STOCKHOLMS UNIVERSITETS INSTITUTION
för
GEOLOGI OCH GEOKEMI
No. 311

The role of sediments in the biogeochemical cycles of nutrients in the Gulf of Riga.

Juris Aigars

Stockholm 2001

Department of Geology and Geochemistry, Stockholm University
S-106 91 Stockholm
Sweden

A dissertation for the Doctor's Degree in Natural Science
Department of Geology and Geochemistry
Stockholm University
S-106 91 Stockholm
Sweden

Abstract

The sediment biogeochemistry of C, N, P and biologic silica (BSi) plays an important role in cycling of these elements in aquatic ecosystems. In shallow coastal and estuarine systems, water-sediment nutrient dynamics can influence biological processes (e.g., primary production) in overlying waters.

The objectives of this study are:

- characterize C, N, P and BSi geochemistry of the surface sediments in the Gulf of Riga,
- estimate the spatial distribution, including net flux and sink, for organic C, N and P in the Gulf of Riga,
- examine if there are any appropriate bulk, regional and/or vertical relationships between the nutrients,
- examine if nutrient biogeochemistry in surface sediments vary as a response to naturally occurring processes i.e., intensity of sedimentation and bioturbation, oxygen deficiency, variation of temperature

Spatial and vertical distribution reveals that organic C and N ratio is almost independent of sediment characteristics and location, and exhibit a stable value down the sediment core. Over 90 % of carbon and nitrogen in sediments is organic. In contrast, organic P constitutes less than 50 % of the total phosphorus pool. The organic C:N:P ratio in sediments indicate that N and P are decomposed preferentially to C, whereas P is decomposed preferentially to N. The stable C:N ratio in sediments indicates that preferential N decomposition occurs in water column and/or immediately upon settling at sediment surface. Distribution pattern of BSi suggests that accumulation rate of sediments controls BSi concentration. Although nutrient loading from drainage area increased drastically over the past 100 years, vertical profiles of C, N and BSi show no variation in element concentrations except in the top few centimeters. A corresponding increase of benthic biomass most likely results in low elemental accumulation in these sediments.

Although Gulf of Riga is one of the most productive areas in the Baltic Sea, seasonal alterations of C and N levels were limited. However, during spring and autumn algae blooms total C and N concentrations increased in the study area. Limited data suggests that burrowing amphipods directly impact the C and N concentrations in the top 2-3 cm of sediments. The vertical distribution of P is more dependent on oxygen concentration, which is largely controlled by bioturbation and sedimentation rates. Moreover, the results suggest that bioturbation is largely responsible for temporal accumulation of inorganic P in surface sediments.

The low unidirectional fluxes of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) in early spring is consistent with low water temperature and poor nutritional quality of experimentally added material. The high water temperature and better nutritional quality of material added in summer, comparatively to winter, resulted in large DIN and DIP fluxes. Moreover, flux experiments under low oxygen conditions and pulse input of large quantities of settling seston suggest that sediment surface might experience lack of oxygen despite availability of oxygen in the overlying water column.

ISBN 91-7265-076-1, pp. 1-11
ISSN 1101 - 1599
Tryck: Sandlund and Co Grafiska, Stockholm 2001

The role of sediments in the biogeochemical cycles of nutrients in the Gulf of Riga

Juris Aigars

Department of Geology and Geochemistry, Stockholm University, S-106 91 Stockholm, Sweden

---

The doctoral thesis consist of a summary and the following papers:

Paper I
Carman, R., Aigars, J. and Larsen, B. 1996. Carbon and nutrient geochemistry of the surface sediments of the Gulf of Riga, Baltic Sea. *Marine Geology* 134: 57-76.

Paper II
Carman, R. and Aigars, J. 1997. Vertical and spatial distribution of biogenic silica in the sediment of the Gulf of Riga, Baltic Sea. *Toxicological and Environmental Chemistry* 60: 245-259.

Paper III
Danielsson, Å., Carman, R., Rahm, L. and Aigars, J. 1998. Spatial estimation of nutrient distributions in the Gulf of Riga sediments using cocriging. *Estuarine. Coastal and Shelf Science* 46: 713-722.

Paper IV
Aigars, J. and Carman, R. 2000. Seasonal and spatial variations of carbon and nitrogen distribution in the surface sediments of the Gulf of Riga, Baltic Sea (Accepted by *Chemosphere*)

Paper V
Aigars, J. 2000. Redox-dependent seasonal variations of the phosphorus geochemistry in the surface sediments of the Gulf of Riga. (Submitted to *Chemosphere*)

Paper VI
Aigars, J. and Carman, R. 2001. Sediment-water phosphorus fluxes in the Gulf of Riga, Baltic Sea: seasonal approach (Manuscript)

Paper I is reprinted with kind permission from Elsevier Science.
Paper II and Paper III is reprinted with kind permission of editors of *Toxicological and Environmental Chemistry* and *Estuarine, Coastal and Shelf Science*, respectively.

Stockholm, May 2001

Juris Aigars

Introduction

On geological time scales, sedimentary processes in oceans play a critical role in distribution of C, N and P (e.g., *Berner et al.* 1993, *Kump* 1993). On shorter time scales, however, sediment biogeochemistry plays a significant role in cycling of C, N and P in shallow aquatic ecosystems e.g., lakes, estuaries, coastal bays and seas, continental shelves (*Callender* 1982, *Wulff et al.* 1990, *Wollast* 1993). Sediments can be a temporary source of some compounds, a terminal sink for others or an interface of biogeochemical transformations (e.g., *Hallberg et al.* 1972, *Blackburn and Henriksen* 1983). In many cases the magnitude of these sediment-water processes is sufficient to be a major component in calculating oxygen or nutrient (C, N and P) fluxes/sinks, and hence, important in formulating estuarine management strategies.

The nutrient and oxygen dynamics of surface sediments in shallow coastal and estuarine systems can influence conditions in overlying waters and sediments (e.g., *Holm* 1978, *Zeitzschel* 1980, *Nixon and Pilson* 1983). The dissolved nutrient fluxes from sediments to the overlying water column may fluctuate on a seasonal to annual basis as a response to various factors e.g., settling of organic detritus, effect of temperature on microbial reactions (*Klump and Martens* 1989, *Scudlark and Church* 1989). In addition, biogeochemical processes in sediments may be coupled to the microbial degradation of organic matter deposited from the overlying water column.

Several environmental factors have been mentioned to be of significance for nutrient and oxygen dynamic in surface sediments e.g., quantity and quality of organic matter reaching the sediment surface (*Wassmann* 1984, *Jensen et al.* 1988), infaunal community characteristics (*Blackburn and Henriksen* 1983), and chemical characteristic of surfical sediments and overlying water (*Henriksen and Kemp* 1988). However, these variables are highly interactive and therefore, it is often difficult to identify cause and effect relationships.

The loading of nutrients into the Baltic Sea has increased four-fold in N and eight-fold in P since 1900 (*Larsson et al.* 1985). However, calculations of overall nutrient budgets (e.g., *Larsson et al.* 1985, *Andersen* 1986) indicate that N and P concentrations in water do not increase at a corresponding rate. The budget calculations generally assume that increased burial in sediments results in this discrepancy (e.g., *Larsson et al.* 1985, *Wulff et al.* 1990). The burial of C, N, P and other elements in sediments may reflect changes in element loading and environmental conditions that are on time scales from years to millennia (*Schneider et al.* 1990, *Wollast* 1992). However, the scarcity of sediment data in budget calculations calls for additional studies of sedimentary processes.

Wulff and Stigebrandt (1989) discussed that empirical studies of large-scale ecological processes are a widely accepted approach in limnology. The results from such empirical studies are expected to be similar to those of marine systems. However, in lakes it is more straightforward to determine the system boundaries and transfer of energy and material what makes lake system studies easier comparing to marine systems. Therefore, it is logical to focus on comparatively small marine basins such as the Gulf of Riga to understand these biogeochemical indications.

The present thesis is a summary of six articles dealing with distribution and relationships of nutrients in surface sediments, and between nutrient biogeochemistry and environmental parameters.

Study area

The Gulf of Riga is a shallow and semi-enclosed basin of the Baltic Sea. The total area and volume for the Gulf of Riga are 19 000 km^2 and 420 km^3, respectively. The drainage area covers 136 000 km^2 and consists of Quaternary, Devonian, Cambrian deposits and (*Yurkovskis et al.* 1993). The maximum and mean depths are 62 and 20 m, respectively. Continuous deposition of fine material (mainly at 40-50 m depth) comprises about 28 % of the total area. These accumulation bottoms are mostly situated in the south and southwestern parts of the Gulf of Riga (*Juskevics et al.* 1993). The northern part of the Gulf of Riga (north of Ruhnu Island) is dominated by transportation/erosion bottoms (*Raudsep et al.* 1993) consisting of sand and pebbles/boulders at the surface, and underlying stiff glacial clay/clayey silt. Similar lithology also dominates in the southwestern part of the Gulf with water depths shallower than 35 m.

Water exchange with the Baltic Sea occurs at the north of Gulf through the Irbene and Muhu Straits with sill depths of 35 m and 5 m, respectively. Freshwater runoff is mainly located to the south/southeast of the Gulf and averages at 36.2 km^3 yr^{-1} (*Laznik et al.* 1999). The Gulf of Riga is usually thermally stratified from April/May through September/October. The location of the thermocline is normally situated between 20 and 30 m. Consequently, fine-grained material, which settles on transportation bottoms beneath the spring-summer thermocline, is resuspended in autumn when thermal stratification breaks down.

Results and discussion

Distribution of nutrients and their relationships (Papers 1, 2 and 3).

Spatial and vertical distribution of nutrients, and relationships among them are important factors for assessing the impact of sedimentary biogeochemical processes on the ecosystem. Such information is useful for additional studies i.e., laboratory, statistical, and model approaches of the response on the distribution and composition within the sediments during natural and anthropogenic changes.

The first article deals with the physical structure and carbon- and nutrient geochemistry of sediments in the Gulf of Riga. Loss on ignition (LOI) measurements, used in this study, is frequently used to estimate organic C concentrations in surface sediments. Although LOI does not represent a well-defined chemical parameter (i.e., heating removes most of organic C, organic N, crystal water, and volatile compounds), it gives a fairly stable bulk average ratio of 3.0 between LOI and organic C. In contrast, very weak correlation is observed between LOI and organic N. Previous studies indicate that LOI correlates well with the water content (WC) in sediments (*Håkanson and Jansson* 1983). Consistent with this, data from the Gulf of Riga also exhibit a strong logarithmic correlation (R^2=0.96) between WC and LOI almost independently of sediment location and burial depth (Fig. 2, paper 1). The largest deviations from WC and LOI correlation occur at sites with glacial clay (i.e., old sediments).

The C:N:P ratio of marine organic particulate matter is quite stable (*Redfield et al.* 1963). However, organic C:N ratio exhibits higher values for brackish water in the Baltic Sea i.e., molar ratio varies between 7-10 (*Hendrikson* 1975, *Ituriaga* 1979, *Shaffer* 1987). The Gulf of Riga sediments exhibit very strong linear correlation (R^2 =0.97) between organic C and N, which is almost independent of water depth, depth below seafloor, carbon content, sediment characteristics, and location (Fig. 3, paper 1). The average molar organic C:N ratio is 10.2, and it is consistent with those in similar sediment regions (e.g., *Balzer* 1984; *Froelich et al.* 1988; *Koop et al.* 1990). The average organic C:N ratio in sediments is slightly higher than the average ratio of living organisms in the Baltic Sea (7-10), and suggests preferential N decomposition and/or admixture of old organic matter.

In contrast to the strong linear correlation between organic C and N, the organic C:P and N:P ratios exhibit weak correlation. This suggests that organic P is practically independent of the concentrations of organic C and N. The average organic C:N:P ratio is 230:22.5:1. This elemental ratio suggests that N and P are decomposed preferentially to C, and P is decomposed preferably to N. The average organic C:P ratio is between 228 and 236. This ratio is quite similar with the ratio of organic C:P=125 reported by Balzer (1984) from Kiel Bight. However, organic C:P ratio from our study considerably differs from the average C:P ratios (490, 552 and 1200) reported by Mach et al. (1987), Ingall and Van Cappellen (1990) and De Lange (1992), respectively. The settling time in shallow sub-estuaries of the Baltic Sea is short compared to more pelagic systems. As a result, degradation of organic material is less complete in shallow basins compared to more pelagic basins prior to settling.

Most of the C and N in sediments are organically bound. In contrast, inorganic P is usually the dominant fraction, and constitutes more than 50 % of the total P pool. Generally the vertical distribution of apatite phosphorus (AP-P) is quite even. In contrast, the redox-controlled fraction i.e., mobile phosphorus (MOB-P) exhibits high concentration in uppermost oxic centimeter with subsequent sharp decrease deeper in sediment column. The high linear correlation (R^2=0.96) between total inorganic P and MOB-P (Fig. 7, paper 1) indicates that sequestering mechanisms other than redox dependent adsorption is kinetically slow and unimportant during early diagenesis. However, on long time scales it seems that sequestering to other than redox dependent P-compounds are diagenetically more important.

Increase in nutrient levels in the Baltic Sea due to enhanced loading from drainage basin leads to eutrophication (*Larsson et al.* 1985). However, enhanced loading from drainage basins did not increase accumulation of C and N in the Gulf of Riga sediments. This is in contrast to recent study in other regions of the Baltic Sea (*Carman et al.* 2000). One possible explanation might be the dramatic increase of mean benthic biomass. Gaumiga and Lagzdinsh (1995) indicated that the mean benthic biomass increased from 36 g m^{-2} between 1946-51 to 208 g m^{-2} between 1984-85 in the open part of the Gulf. This suggests a 6-fold increase of nutrient recycling by biota during that period. However, the biomass of macrozoobenthos has decreased significantly since the eighties (*Cederwall et al.* 2000). Therefore, in future, we may expect accumulation of organic C and N in sediments to increase.

Wulff and Rahm (1988) indicated that decrease of Si coupled to increase of N and P concentrations in the water column during winter indicates increase of primary production in the Baltic Sea. Because sinking velocity for diatoms is high, cells reach the bottom in an intact state. Furthermore, previous studies indicate that temperature and salinity mostly regulates regeneration of BSi and dissolved silica flux from sediments to the overlying water column (e.g., *Werner* 1977, *Williams and Crerar* 1985. The long-term hydrological study by Berzinsh (1995) indicates that the temperature and salinity is rather stable in the Gulf of Riga. Therefore, it was expected to observe enhanced accumulation of BSi in recent sediments. However, as discussed in the second article, increase in BSi concentrations only occurs in surface sediments (Table 2, paper 2). The expected larger concentrations of BSi in sub-surface sediments are not observed most likely because of bioturbation. However, it cannot be excluded that the effect of increased sedimentation of diatoms may be lost due to dilution by large amount of settling allochthonous material. Moreover, the cores analyzed (5-10 cm deep) may be too short to see real background values.

A weak correlation between BSi concentration and distance from the main nutrient source (e.g., river Daugava), and small temporal and spatial variation in parameters affecting the dissolution of BSi during halmyrolysis (e.g., salinity, temperature) suggest that the surfical concentrations of BSi depend on sediment accumulation rates (paper 2). BSi concentrations vary inversely with sedimentation rates because a large portion of allochthonous material is added to the sinking diatom cells near the coast. This is consistent with conclusions by Conley et al. (1986) for sediments in Lake Michigan, and by Pattan et al. (1992) for sediments in Indian Ocean.

A good correlation (R^2=0.77) exists between all measured concentrations of organic C and BSi (Fig. 2, paper 2). However, the ratios obtained from transition/erosion and from accumulation areas vary considerably between and within these groups. It indicates that dissolution of BSi and degradation of organic C are separate processes and have different magnitudes. This is consistent with studies by Martin et al. (1991) and DeMaster et al. (1992).

The third article in this dissertation estimates the spatial distribution and standard deviation of organic C, N, and P in sediment surface (0-2 cm) by using the cokriging method. The advantage of using the cokriging interpolation technique is inclusion of covariables. This gives a possibility to improve spatial interpolation estimates with additional available information from different parameters, which are easier and cheaper to measure.

Organic C, N, and P concentrations indicate similar horizontal distribution patterns with high concentrations in accumulation areas (Fig. 3(a); 4(a); 5(a), paper 3). It is possible that river Daugava may cause high sediment organic content in the southeast of the Gulf. However, the direct reason for most of concentration patterns in surface sediments is sediment type and thus sedimentation conditions. The standard deviations for concentration estimates (Fig. 3(b); 4(b); 5(b), paper 3) are high because data are sparsely available, and there are large variations within the data. In the middle of the basin, mean standard deviation is lower mostly due to smaller variations in sediment type.

Variations of C, N, and P concentrations with seasonally fluctuating factors (papers 4 and 5)

A large fraction of organic matter in coastal and estuarine waters eventually end up in sediments. Rapid transfer of organic particles from the water column to sediments may leave a significant fraction of the nutrient pool as metabolizable organic compounds that are subject to further decomposition. Remineralization of these organic compounds and release of dissolved nutrients into the water column is a major nutrient recycling pathway in nearshore environments and can supply more than 50 % of the requirements for primary producers (*Zeitzschel* 1980, *Klump and Martens* 1987).

In shallow temperate systems deposition of organic matter, and rates of benthic nutrient regeneration and release can undergo a pronounced seasonality due to altered environmental conditions (e.g., *Smetacek* 1980, *Aller and Benninger* 1981).

The fourth and fifth articles deal with nutrient profiles in sediments and their seasonal variability.

Similar vertical profiles of TC and TN were generally observed at both sites (G5 and T3) in the study area. However, during autumn-spring considerable differences of TC and TN concentrations in 0-2 cm between sites were observed (Fig. 4, paper 4). Most likely, this was caused by differences in abundance of macrozoofauna between the sites (Table 1, paper 4). Moreover, establishing of stronger vertical gradient of TC and TN concentrations in 0-2 cm in May at site G5 and disruption of vertical gradient in November at site T3 (Fig. 5 and 6) corresponded to fluctuation in amphipod numbers reported by Cederwall and Jermakovs (1999).

Monthly sedimentation rates in the Gulf of Riga are absent. Therefore, it is impossible to correlate sediment nutrient concentrations with sedimentation rates. However, it can be assumed that significantly higher TN values during April and November at site T3 (Fig. 6, paper 4) result from settling of spring and autumn blooms, respectively. This is consistent with the findings of Smetacek (1980), who indicated that spring and autumn blooms in Baltic forms and deposits in March-April and October-November, respectively. However, only alterations of TN at one sampling site are significant while alterations of concentrations of TC at both sites and TN at second site were small and not significant. The sediment accumulation rates are fairly high in the Gulf of Riga (*Larsen* 1995). This implies deposition of large amount of allochthonous material, which most likely diminish the signal of bloom sedimentation. However, we should also consider the importance of benthic macrozoofauna, which can lower spring and autumn bloom deposition signal intensity by redistributing material within the upper 0-2 cm.

In contrast to C and N concentrations, P does not correlate with the sedimentation pattern of phytoplankton and bioturbation intensity. The temporal increase of inorganic P at site G5 (Fig. 5, paper 5) resulted from increase in MOB-P pool. Einsele (1936) indicated that abiotic binding of P by ferrous complexes control redox-dependent P pools. However, redox measurements (Fig. 4, paper 5) in the study area suggests that controlling factors other than ferrous complexes are more important. It is possible that temporal accumulation of MOB-P results from accumulation of P by microorganisms. This assumption is consistent with the recent findings by Gächter and Meyer (1993), Kerm-Jespersen and Henze (1993), Van Veen et al. (1993). These authors indicated that several bacteria and protozoa have the capability to accumulate and store excess P as polyphosphates under oxic conditions. The microorganisms use polyphosphates during metabolic processes if oxygen availability decreases. Orthophosphate produced during metabolism is released into the overlying water column or pore-water.

There is evidence that certain fractions of P cycled by bacteria are transformed into refractory organophosphorus compounds (*Gächter and Meyer* 1993). Presence of organophosphorus compounds have been reported in several studies on marine organic matter (*Ingall et al.* 1990, 1993). Thus, P cycling mediated by bacteria may increase the burial efficiency of nonmetabolizable P-rich organic material. This implies that oxic sediments decrease the residence time for P in a basin while reduced sediments increase it. Therefore, the oxic layer in surface sediments is important not only as a short-term buffer zone for P, but also as a zone for P transformation.

The Gulf of Riga is a small basin compared to the Baltic Sea. However, a high variability of accumulation rates occur in the Gulf of Riga (*Larsen* 1995). The accumulation rates and intensity of bioturbation are major factors controlling the redox conditions in surface sediments. Accumulation rates define the amount of material deposited at sediment surface, and therefore, intensity of oxygen consumption by microbially mediated processes. Benthic macrozoofauna also consumes oxygen. However, surface sediment mixing by benthic macrozoofauna enhances delivery rates of oxygen to the deeper layers of surface sediments compared to delivery rates of oxygen controlled by diffusion. Therefore, areas with high sedimentation rates and low bioturbation activity have low oxygen levels in surface sediments, and are not expected to act as a temporary trap for P. In contrast, areas with low accumulation rates and high abundance of macrozoofauna can act as temporary traps for P.

Fluxes of inorganic N and P (paper 6).

The sixth paper deals with experimental fluxes of dissolved inorganic N and P. Nutrient fluxes were measured after adding seston (sinking plankton plus detritus) with the aim of simulating sediment responses to organic matter deposition between spring and autumn phytoplankton blooms.

Smetacek (1980) indicated that in the Baltic Sea relatively intact cells of pelagic biota may reach the sediments after spring and autumn blooms. In contrast, particles that settle during winter consist mostly of resuspended material with low nutritional value, and particles that settle during summer consist mostly of amorphous detritus (*Smetacek* 1980). The availability and quality of food and temperature generally controls the activity of benthic biota. These factors ultimately influence remineralization rates for organic matter settled at the bottom, and subsequent release of dissolved nutrients.

The seston was added to both columns with and without sediments. The fluxes measured in columns without any sediments were assumed to originate from sediment-water interface "sediment surface". The fluxes measured in columns with sediments were assumed to consist of both "sediment surface" fluxes, and fluxes originating from deeper sediment layers "sub-surface". Subtracting the fluxes from columns without sediments from fluxes measured in sediment bearing columns resulted in fluxes, which originate from deeper sediment layers "sub-surface".

The low temperature and nutritionally poor seston added in March resulted in low and unidirectional fluxes of measured compounds (Fig 3, paper 6). No clear correlation between amount of seston added and fluxes was observed.

During summer, N-NO$_3^-$ fluxes mostly were directed into the sediments and P-PO$_4^{3-}$ and N-NH$_4^+$ fluxes out of sediments (Fig. 4, paper 6). The highest fluxes were observed in columns without sediments, thereby indicating that organic matter degradation most actively occurs at sediment surface within freshly settled material. The release of ammonia and phosphate from "sediment surface" increased after oxygen concentration decreased from 11 mg/l to 4mg/l. In contrast, "sub-surface sediment" accumulates dissolved compounds after oxygen decreases. Most likely, release of large quantities of dissolved nutrients from "sediment surface" increase pore water concentrations in "sub-surface" through diffusion. The increase of pore water concentration, in turn, shifts adsorption equilibrium and large amounts of dissolved nutrients are adsorbed on particles.

As discussed in paper 5, redox-dependent P concentration in sediments may be controlled by biota. The release of phosphate from "sub-surface" (Fig. 4, paper 6) most likely, results from depletion of oxygen in "sub-surface" by biota, five days after low oxygen conditions are established. In contrast, five days of low oxygen level in the overlying water column did not result in release of ammonia from "sub-surface".

The early autumn experiment (Fig. 5, paper 6) indicates large increase of phosphate and ammonia fluxes after pulse additions of seston. Similarly to summer experiment, the "sub-surface" sediments accumulate part of dissolved nutrients released from "sediment surface". The fluxes shifted to low level in our experimental system much faster (48 h) than in the experiment conducted by Conley and Johnstone (1995). Conley and Johnstone (1995) used intact phytoplankton cells in their experiment. In contrast, we used seston (partly degraded organic matter), which may have changed the flux rates.

Acknowledgments

There are number of people in the Department of Geology and Geochemistry, SU, Department of Systems Ecology, SU and Institute of Aquatic Ecology, LU whom I would like to express my gratitude. I would like to especially thank Hans Cederwall, Rolf Carman, Andris Andrushaitis, Rolf Hallberg, Lars-Erik Bagander, and Carin Larsson for their invaluable support and help. I would also like to thank Agneta Hagberg for helping me with the administrative paperwork and Joyanto Routh for helping me with preparation of this thesis.

References

Aller, R.C. and Benninger, L.K. (1981) Spatial and temporal patterns of dissolved ammonium, manganese, and silica fluxes from bottom sediments of Long Island Sound, U.S.A. *J. Mar. Res.* 39: 295-314.

Andersen, J.M. (1986) Reversal of the eutrophication of the Baltic Sea. *Vatten*. 42: 36-40.

Balzer, W. (1984) Organic matter degradation and biogenic element cycling in a near shore sediment (Kiel Bight). *Limnol. Oceanogr.* 29: 1231-1246.

Berner, R.A., Ruttenberg, K.C., Ingall, E.D. and Rao, J.-L. (1993) The nature of phosphorus burial in modern marine sediments. In: *Interactions of C, N, P and biogeochemical Cycles and Global Change.* (Edited by Wollast, R., Mackenzie, F.T. and Chou, L.). NATO ASI Series, Springer-Verlage, Berlin.

Berzinsh, V. (1995) Hydrology. In: *Ecosystem of the Gulf of Riga Between 1920 and 1990.* (Edited by Ojaveer, E.). Estonian Academy Publishers, Tallinn.

Blackburn, H. and Henriksen, K. (1983) Nitrogen cycling in different types of sediments from Danish waters. *Limnol. Oceanogr.* 28: 477-493.

Callender, E. (1982) Benthic phosphorus regeneration in the Potomac River estuary. *Hydrobiologia*, 92: 431-446.

Carman, R., Aigars, J., Danielsson, Å. and Rahm, L. (2000) Recent paleoecological sediment records of biogenic silica as an indication of the eutrophication in the Baltic Sea. *Marine Geology* (submitted).

Cederwall, H., Jermakov, V. and Lagzdins, G. (2000) Long term changes in the soft bottom macrofauna of the Gulf of Riga. ICES, *Journal of Marine Science*, 56: 000-000.

De Lange, G. J. (1992) Distribution of various extracted phosphorus compounds in the imbedded turbidic/pelagic sediments of the Madeira Abyssal Plain, eastern North Atlantic. *Mar. Geol.* 109: 115-139.

DeMaster, D.J., Dunbar, R.B., Gordon, L.I., Leventer, A.R., Morrison, J.M., Nelson, D.M., Nittrouer, C.A. and W.O. Smith Jr. (1992) Cycling and accumulation of biogenic silica and organic matter in high-latitude environments: The Ross Sea. Oceanography. 5: 146-153.

Einsele, W. (1936) Uber die Beziehungen des Eisenkreislaufs zum Phosphatkreislauf im eutrofen See. *Arch. Hydrobiol.* 29: 664-686.

Froelich, P. N., Arthur, M. A., Burnett, W. C., Deakin, M., Hensley, V., Jahnke, R., Kaul, L., Kim, K.-H., Roe, K., Soutar, A. and Vathakanon, C. (1988) Early diagenesis of organic matter in Peru continental margin sediments: Phosphorite precipitation. *Mar. Geol.* 80: 309-343.

Gaumiga, R. and Lagzdinsh, G. (1995) Macrozoobenthos. In: *Ecosystem of the Gulf of Riga Between 1920 and 1990.* (Edited by Ojaveer, E.). Estonian Academy Publishers, Tallinn.

Gächter, R. and Meyer, J.S. (1993) The role of microorganisms in sediment phosphorus dynamics in relation to mobilization and fixation of phosphorus. *Hydrobiologia*, 253: 103-121.

Hallberg, R.O., Bågander, L.E., Engvall, A.G. and Schippel, F.A. (1972) Geochemistry of the sediment-water interface. Ambio No. 2.

Henriksen, K. and Kemp, W.M. (1988) Nitrification in estuarine and coastal marine sediments. In *Nitrogen cycling in coastal marine environments.* (Edited by Blackburn, T.H. and Sorensen, J.). John Wiley, Chichester, pp. 207-249.

Holm, N.G. (1978) Phosphorus exchange through the sediment-water interface, Mechanism studies of dynamic processes in the Baltic Sea. Contributions in Microbial Geochemistry, Department of Geology, University of Stockholm. No. 3. Pg. 149.

Håkanson, L. and Jansson, M. (1983) Principles of Lake Sedimentology. Springer, Berlin, 316 pp.

Ingall, E. D. and Van Cappellen, P. (1990) Relation between sedimentation rate and burial of organic phosphorus and organic carbon in marine sediments. *Geochim. Cosmochim. Acta.* 54: 373-386.

Ingall, E.D., Schroeder, P.A. and Berner, R.A. (1990) The nature of organic phosphorus in marine sediments: New insights from ^{31}P NMR. *Geochim. Cosmochim. Acta*, 54: 2617-2620.

Ingall, E.D., Duchamp, J.C. and Zilm, K.W. (1993) ^{31}P and ^{13}C NMR characterization of organic phosphorus and carbon during aerobic decomposition of marine plankton. Am. Chem. Soc., Abstr. Pap. 205: 187-190.

Jensen, M.H., Andersen, T.K. and Sorensen, J. (1988) Denitrification in coastal bay sediment: regional and seasonal variation in Aarhus Bight, Denmark. *Mar. Ecol. Prog. Ser.* 48: 155-162.

Kerrn-Jespersen, J.P. and Henze, M. (1993) Biological phosphorus uptake under anoxic and aerobic conditions. *Water Research*, 27: 617-624.

Klump, V.J. and Martens, C.S. (1989) The seasonality of nutrient regeneration in an organic-rich coastal sediment: Kinetic modeling of changing pore-water nutrient and sulfate distributions. *Limnol. Oceanogr.* 34: 559-577.

Klump, J. V. and Martens C. S.(1987) Biogeochemical cycling in an organic -rich coastal marine basin. 5. Sedimentary nitrogen and phosphorus budgets based upon kinetic models, mass balances, and the stoichiometry of nutrient regeneration. *Geochim. Cosmochim. Acta.* 51: 1161-1173.

Koop, K., Boynton, W. R., Wulff, F. and Carman, R. (1990) Sediment-water oxygen and nutrient exchanges along depth gradient in the Baltic Sea. *Mer. Ecol. Prog. Ser.* 63: 65-77.

Kump, L.R. (1993) The coupling of the carbon and sulfur biogeochemical cycles over Phanerozoic time. In: *Interactions of C, N, P and S Biogeochemical Cycles and Global Change.* (Edited by Wollast, R., Mackenzie, F.T. and Chou, L.). NATO ASI Series, Springer-Verlag, Berlin.

Larsen, B. (1995) Evaluation of sediment pollution data: examples from the Gulf of Riga - status August 1995, *Publications on Chemistry XXIII, Extended abstracts of the Symposium Environmental Analyses*, University of Tartu, Department of Chemistry, pp. 81-92.

Larsson, U., Elmgren, R. and Wulff, F. (1985) Eutrophication and Baltic sea: Causes and consequences. *Ambio*. 14: 9-14.

Laznik, M., Stålnacke, P., Grimvall, A. and Wittgren, H.B. (1999) Riverine input of nutrients to the Gulf of Riga - temporal and spatial variation. *J. of Mar. Syst.* 23: 11-27.

Mach, D. L., Ramirez, A. and Holland, H. D. (1987) Organic phosphorus and carbon in marine sediments. *Am. J. Sci.* 278: 429-441.

Martin, W.R., Bender, M., Leinen, M. and Orchardo, J. (1991) Benthic organic carbon degradation and biogenic silica dissolution in the central equatorial Pacific. Deep Sea Research. 38: 1481-1516.

Nixon, S. W. And Pilson, M.E.Q. (1983) Nitrogen in estuarine and coastal marine ecosystems. In *Nitrogen in marine environment.* (Edited by Carpenter, E.J. and Capone, D.G.). Academic Press, New York, pp. 565-648.

Pattan, J.N., Gupta, S.M., Mudholkar, A.V. and Parthiban, G. (1992) Biogenic silica in space and time in sediments of central Indian Ocean. *Indian J. of Mar. Sci.* 21: 116-120.

Redfield, A.C., Ketchum, B.H. and Richards, F.A. (1963) The influence of organisms on the composition of seawater. In: *The Sea.* (Edited by Hill, M.N.). Wiley, New York, 2, pp. 26-77.

Schneider, J., Röhrs, J. and Jäger, P. (1990) Sedimentation and eutrophication history of Austrian Alpine lakes. In *Large Lakes: Ecological Structure and Function.* (Edited by Tilzer, M.M. and Serruya, C.). Springer-Verlag, Berlin, pp. 316-335.

Scudlark, J.R. and Church, T.M. (1989) The sedimentary flux of nutrients at a Delaware salt marsh site: A geochemical perspective. *Biogeochemistry*, 7: 55-75.

Smetacek, V. (1980) Annual cycle of sedimentation in relation to plankton ecology in western Kiel Bight. *Ophelia*, Suppl. 1: 65-76.

Van Veen, H.W., Abee, T., Kortstee, G.J.J., Konings, W.N. and Zehnder, A.J.B. (1993) Characterization of two phosphate transport systems in *Acinetobacter johnsonii* 210A. *J. Bacteriol.* 175: 200-206.

Wassmann, P. (1984) Sedimentation and benthic mineralization of organic detritus in a Norwegian Fjord. *Mar. Biol.* 83: 83-94.

Wassmann, P. and Andrushaitis, A. (1993) Övergjödsling av Östersjoen og Rigabukten, *Naturen*, 5: 205-213 (in Norwegian).

Werner, D. (1977) Silicate metabolism. In: *The biology of diatoms.* (Edited by Werner, D.). *Botanical monographs*, University of California Press, Berkley and Los Angeles. 13: 110-149.

Williams, L.A., Parks, G.A. and Crerar, D.A. (1985) Silica diagenesis, I. Solubility controls. *J. of Sed. Petrol.* 55: 301-311.

Williams, L.A. and Crerar, D.A. (1985) Silica diagenesis, II. General mechanisms. *J. of Sed. Petrol.* 55: 312-321.

Wollast, R. (1992) Interactions of carbon and nitrogen cycles in the coastal zone. In: *Interactions of C, N, P and S Biogeochemical Cycles and Global Change.* (Edited by Wollast, R., Mackenzie, F.T. and Chou, L.). NATO ASI Series, Springer-Verlag, Berlin.

Wulff, F. and Rahm, L. (1988) Long-term, seasonal and spatial variations of nitrogen, phosphorus and silicate in the Baltic, an overview. *Marine Environmental Research*. 26: 19-37.

Wulff, F., Stigebrandt, A. and Rahm, L. (1990) Nutrient dynamics of the Baltic Sea. *Ambio*, 19: 126-133.

Yamada, S.S. and D'Elia, F. (1984) Silicic acid regeneration from estuarine sediment cores. *Mar. Ecol. Prog. Ser.* 18: 113-118.

Zeitzschel, B. (1980) Sediment-water interactions in nutrient dynamics. In *Marine benthic dynamics.* (Edited by K.R. Tenore and B.C. Coull), pp. 195-218. University of South Carolina, USA.

Paper I

ELSEVIER

Marine Geology 134 (1996) 57–76

MARINE GEOLOGY
INTERNATIONAL JOURNAL OF MARINE GEOLOGY, GEOCHEMISTRY AND GEOPHYSICS

Carbon and nutrient geochemistry of the surface sediments of the Gulf of Riga, Baltic Sea

Rolf Carman [a,*], Juris Aigars [a,b], Birger Larsen [c]

[a] *Department of Geology and Geochemistry, Stockholm University, S-106 91 Stockholm, Sweden*
[b] *Institute of Biology, Marine Biology laboratory, Salaspils, Latvia*
[c] *Geological Survey of Denmark, DK 2400 Copenhagen, Denmark*

Received 23 August 1995; accepted 15 April 1996

Abstract

The distribution of different forms of carbon, nitrogen and phosphorus and standard physical sediment parameters of the surface sediments of the Gulf of Riga, a shallow semi-enclosed brackish bay of the Baltic Sea, has been examined. Several measured parameters were highly correlated. This is valid almost irrespectively of differences in depth below seafloor and sediment characteristics as well as location and extent of burial/diagenesis. Preferential release of nitrogen (N) relative to carbon during organic matter decomposition seems to occur during halmyrolysis and/or almost instantaneously upon settling at the sediment surface because the C_{org}/N_{org} ratio is uniform (10.2) within all types of sediment. Preferential release of phosphorus (P) relative to both C and N also occurs and organic matter decomposition appears independent of the amount of C and N. Inorganic C and N in sediments normally constitute only a small proportion of the total C and N concentrations. The amount of inorganically bound nitrogen depends to a great deal on the surface area of the adsorbing species and the clay mineral composition. Inorganic P usually constitutes more than 50% of the total amounts of P, irrespective of physical and chemical differences between samples. Concerning early diagenesis the amount of inorganic P is controlled mainly by the release/fixation on species prone to oxidation/reduction reactions.

An estimate of the total amount of annually sequestered C, N and P in the accumulation sediments suggests 44,000, 5800 and 1100 ton/year, respectively. For N and P this sequestering constitutes around 6% and 40% of the total annual load.

1. Introduction

The area of the Gulf of Riga (Fig. 1) is 19,000 km^2. Its drainage area covers 136,000 km^2 and consists of Quaternary, Devonian and Cambrian sedimentary deposits (Yurkovskis et al., 1993). The main river inputs are located in the southern and eastern parts of the Gulf. The Gulf of Riga represents a semi-enclosed basin and is a comparatively shallow region of the Baltic Sea. The maximum and mean depth are 62 and 20 m, respectively. There are small areas subjected to continuous deposition of fine material (around 28%). Water exchange with the Baltic proper occurs mainly through the sound of Irbene (Pastors, 1967). The main accumulation bottom zone is at 40–50 m depth, but fine material (<0.01 mm) dominates normally at depths exceed-

---

[*] Corresponding author.

0025-3227/96/$15.00
PII S0025-3227(96)00033-3

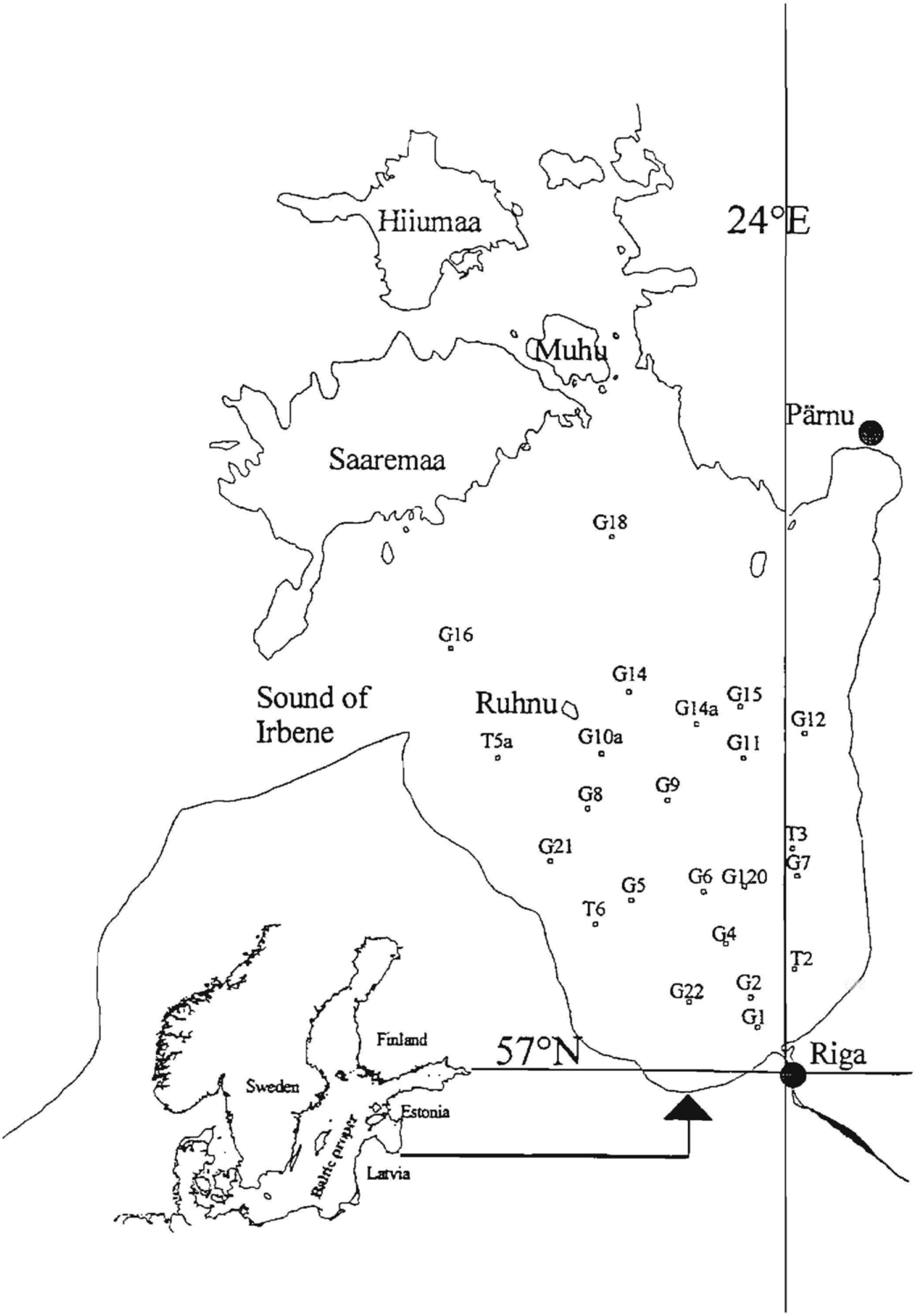


Fig. 1. Outline map showing the sampling sites of the investigated area.

ing 27 m. Almost all of these accumulation bottoms are situated in the southern or southwestern part (Emelyanov, 1988; Juškevičs et al., 1993). The northern parts of the gulf, north of Ruhnu Island, are dominated by transportation/erosion bottoms, with water depths less than 25 m (Emelyanov, 1988; Raudsep et al., 1993). These bottoms are characterized by sand and pebbles at the surface, with underlying stiff glacial clay/clayey silt. Such sediments dominate also in the southwestern part of the gulf with water depths exceeding 35 m. Above 35 m depths ferric concretions occur frequently.

The Gulf of Riga usually is stratified thermally. The location of the thermocline is normally situated between 20 and 30 m. Generally, the thermocline lasts until September/October. Consequently, fine material settled beneath the spring–summer thermocline will be resuspended in the autumn and transported to "true" accumulation bottoms. From a limnological point of view the Gulf of Riga can be classified as monomictic with holomictic mixing (a continuous single mixing). After the holomictic mixing in the autumn–winter, the entire water mass stays saturated with oxygen until summer when oxygen is partly depleted in the deeper parts of the Gulf (Berzinsh et al., 1988, Yurkovskis et al., 1993).

The Gulf of Riga is one of the most eutrophic areas of the Baltic Sea. The annual primary production has been estimated to four million tons/year in 1989. This is about 290 g C m^{-2} yr^{-1} (Andrushaitis et al., 1992) or about twice as much as an average for the entire Baltic proper (Elmgren, 1989). The salinity varies between 4 and 7‰ (Yurkovskis et al., 1993). According to Yurkovskis et al. (1993) the Gulf is strongly limited with respect to phosphorus although a substantial release of phosphorus from the sediments occurs in connection with spring–summer algal blooms (Yurkovskis et al., 1993; Aigars and Andrushaitis, 1993).

The aim of the study was to characterize the carbon- and nutrient geochemistry of the surface sediments of the highly eutrophic and phosphorus limited Gulf with respect to sequestering pattern and capacity. We also wanted to examine if there is any appropriate bulk, regional and/or vertical relationships between the analysed parameters. Such relationships will be useful tools for additional studies (laboratory, statistical and model approaches) of the response on the distribution and composition within the sediments during anthropogenic and oceanographic changes.

2. Materials and methods

Twenty-six soft to semi-soft bottom sediment cores were sampled during summer 1991 and 1993 (Fig. 1 and Table 1) using a modified Kajak gravity corer (Blomquist and Abrahamsson, 1985). Samples from the surface 5 cm where sliced in cm sections except at three stations (G120, G5 and T3) where they were sliced down to 10 cm below sea floor. They where dried to constant weight at 80°C for determination of the water content (WC %) and ground to fine powders in an agate mortar. Loss on ignition (LOI %) was measured by heating sediment samples to 500°C for 2 h. Bulk density is calculated by using the WC- and LOI content and assuming an average inorganic sediment density of 2.6 g/cm^3 (Akal, 1972). Bottom water temperatures (in situ) were also measured (Table 1).

Sub-samples were taken for total C, N and P analyses and for different subfractions of these elements. Total carbon- (TOT-C) and nitrogen (TOT-N) was measured on a Leco element analyzer with a precision of ±0.5%. Carbonate carbon (IN-C) was determinated on oven ignited (500°C) samples in the same element analyzer (Hedges and Stern, 1984). Organic carbon (ORG-C) was obtained from difference between the total and carbonate carbon values. In order to investigate the significance of the ignition method for determination of carbonate carbon we also measured organic carbon after pretreatment with 1 M HCl (Hedges and Stern, 1984). The ignition method and the acid method gave almost the same results (±3%). Fixed nitrogen (FIX-N) was measured essentially according to the method described by Silva and Bremner (1966) and exchangeable nitrogen (EX-N) according to Mackin and Aller (1984). Organic nitrogen (ORG-N) was obtained from differences between the total and the sum of FIX-N and EX-N. All wet extracts of N were measured according to Parson et al. (1984). Total

Table 1
The sampling site coordinates in the Gulf of Riga and a brief sediment description

Station	Position (Decca)	Depth (m)	Temp. (°C)	Sediment description	Sampling date
G1	N57°06′45″ E23°57′30″	27	2.2	sandy aleurite, light brown down to 2 cm	19.06.91
G2	N57°10′30″ E23°56′0″	40	2.1	aleuritic mud, light brown down to 1.5 cm	19.06.91
G4	N57°17′40″ E23°50′50″	42	3.2	mud, light brown down to 6.5 cm	18.06.91
G5	N57°23′18″ E23°28′30″	44	3	sandy-mud, light brown down to 4.5 cm	17.06.91
G6	N57°24′30″ E23°45′45″	44	1.9	mud, light brown down to 3 cm	18.06.91
G7	E57°26′30″ E24°07′10″	41	2	mud, light brown down to 4.5 cm	18.06.91
G8	N57°35′30″ E23°18′30″	44	3.1	mud, light brown down to 1.1 cm	17.06.91
G9	N57°36′45″ E23°37′0″	54	2.1	mud, light brown down to 4 cm	17.06.91
G10a	N57°42′ 6″ E23°21′ 6″	28	12.1	fine sand (2.5 cm) on stiff clay	30.07.93
G11	N57°42′0″ E23 55′0″	41	1.8	mud, light brown down down to 5 cm	18.06.91
G12	N57°45′20″ E24°09′15″	27	3.5	sandy aleuritic mud on stiff clay light brown down to 1.5 cm	18.06.91
G14	N57°50′7″ E23°28′0″	50	1.9	mud, light brown down to 3.2 cm	17.06.91
G14a	N57°46′ 5″ E23°44′ 0″	42	2.5	muddy aleurite, light brown down to 1.5 cm	30.07.93
G15	N57°48′8″ E23°54′45″	32	1.7	sandy aleurite, light brown down to 3 cm	18.06.91
G16	N57°56′35″ E22°46′15″	34	4	sandy mud, light brown down to 2 cm	17.06.91
G18	N58°11′45″ E23°24′30″	27	7.4	aleuritic sand	18.06.91
G21	N57°28′ 4″ E23°09′ 7″	36	2.6	fine sand (0.5 cm) on muddy sand	31.07.93
G22	N57°09′ 75″ E23°41′ 78″	38	2.6	mud, light brown down to 2 cm	31.07.93
G120	N57°25′ 0″ E23°55′ 0″	43	2.1	mud, light brown down to 2 cm	28.07.93
T2	N57° 14′ 0″ 24°06′ 0″	35	4.2	aleuritic mud on sandy mud, light brown down to 1.5 cm	28.07.93
T3	N57°30′ 0″ E24°06′ 0″	43	3.6	mud, light brown down to 2 cm	28.07.93
T5a	N57°42′ 0″ E22°57′ 4″	32	4.2	aleuritic sand on stiff clay	29.07.93
T6	N57°20′ 0″ E23°20′0″	45	2.4	sandy aleurite, light brown down to 1 cm	29.07.93

phosphorus (TOT-P) and inorganic phosphorus (IN-P) was measured according to Froelich et al. (1988). Mobile phosphorus (MOB-P) was measured according to Carman and Jonsson (1991) without pretreatment with other chemicals. Apatite phosphorus (AP-P) was obtained from the difference between IN-P and MOB-P whereas the amount of organic phosphorus (ORG-P) in the sediment was obtained by the difference between TOT-P and IN-P. All wet extracts of P were measured using standard spectrophotometric technique (e.g. Murphy and Riley, 1962).

3. Results

According to the classification scheme by Håkanson and Jansson (1983), 17 of the 26 sediment cores sampled could be characterized as accumulation bottoms for continuous deposition of fine material (i.e. <medium silt or 0.01 mm). Of the remaining nine stations five could be characterized as transportation bottoms (T6, G1, G1b, G15 and G18) and the rest (T5a, G21, G10a and G12) as intermediates between transportation- and erosion bottoms. Sampling dates, depths and positions are shown in Table 1, together with bottom water temperatures and a brief sediment description. The measured and calculated physical and chemical parameters are compiled in the Appendix.

3.1. Physical sediment parameters

The water content (WC) and the loss on ignition (LOI) (see the Appendix) varied from 90.3% to 23.8% and from 17.4% to 0.7%, respectively. The major portion of the sediment samples had WC values more than 70% and LOI values more than 10%. This preponderance is primarily due to the sampling technique used (gravity core sampling) that make sediment sampling difficult at bottoms with high bulk density. The general trend of the WC and the LOI is that the values decrease with increasing depth in the sediment column. However, some stations with coarser sediment material and/or with stiff glacial clay a few cm down in the sediment profile, displayed different patterns. They had either decreasing values from the top level down to 2–3 cm succeeded by increasing contents (G1, G1b, G12, G18 and G21, T6) or completely inverse patterns, i.e. increasing contents with depth (T5a). The bulk density ranges from 1.05 (e.g. G2, G9) to almost 1.9 at station T6.

3.2. Chemical parameters

3.2.1. Carbon

The measured concentrations range of TOT-C, IN-C and ORG-C are shown in Table 2 together with average concentrations in the uppermost section from both accumulation- and transportation/erosion bottoms. Expressed in % of dry substance (% ds) the carbon content varied between 6.49–0.23, 2.15–0.015 and 6.3–0.2 for TOT-C, IN-C and ORG-C, respectively. The highest concentration of ORG-C was found in a transect north-northwest from the outflow of the river Daugava at depths exceeding 35–40 m with sediment fractions <medium silt. The lowest concentration of ORG-C is detected in sediments located in shallow areas near the coast and in the region north of Ruhnu Island. Both the highest and the lowest amount of IN-C were found at transportation-erosion bottoms. In general the inorganic carbon content increased downwards in the sediment columns.

3.2.2. Nitrogen

The concentration ranges of TOT-N, EX-N, FIX-N and ORG-N are compiled in Table 2. Calculated average concentrations (from level 0–1 cm) of these fractions are also shown in Table 2. Normally most of the total nitrogen is present in organic form. Inorganic nitrogen comprises normally around 10% only. However, at organic-poor transportation-erosion bottoms the percentage of inorganic nitrogen dominates (e.g. G10a, G21, T5a). Nevertheless, the inorganic nitrogen usually is a minor part of the total amount of nitrogen in the sediments of the Gulf of Riga.

3.2.3. Phosphorus

In contrast to carbon and nitrogen a large amount of the phosphorus was sequestered as inorganic phosphorus. It constituted between 45% to almost 100% of the total amount. However, the vertical variation in the sediment columns of the inorganically bound phosphorus is great, mainly depending on the large variations in MOB-P. The concentration ranges of TOT-P, MOB-P, AP-P and ORG-P are shown in Table 2 together with the mean concentrations from the uppermost sec-

Table 2

Concentration range (all levels included) of total- and sub fractions of carbon, nitrogen and phosphorus. The mean values are calculated from the uppermost section from deposition bottoms (dep-btm) and transportation-erosion bottoms (trp-btm). All values are given in μmol/g ds

	TOT-C	ORG-C	IN-C	
Min–Max	192.5–5409	173.5–5267	12.39–1761	
Mean (dep-btm)	4619	4449	157	
Mean (trp-btm)	1792	1489	302	
	TOT-N	ORG-N	FIX-N	EX-N
Min–Max	20.0–520.7	6.21–481	0.53–42.2	0.29–23.48
Mean (dep-btm)	449	409	31.7	7.9
Mean (trp-btm)	135	123	7.2	4.6
	TOT-P	ORG-P	MOB-P	AP-P
Min–Max	7.2–90.5	0.1–35.4	0.28–61.8	3.48–18.6
Mean (dep-btm)	63.4	17.4	36.8	9.2
Mean (trp-btm)	29.3	6.8	15.8	6.6

tion. In general, the amount of MOB-P decreased with increasing burial depth whereas the amount of AP-P normally was quite evenly distributed vertically. As for nitrogen, the highest amount of ORG-P was found at accumulation bottoms near the outflow of the river Daugava.

4. Discussion

4.1. Water content, organic matter (LOI) and bulk density

A strong linear relationship between the ratio WC/porosity and bulk density is obvious because the density of the mineral particles is practically the same (~2.6) for all marine bottoms (Akal, 1972). It is also commonly observed that the organic matter content (defined as LOI) is highly correlated with the WC (Håkanson and Jansson, 1983).

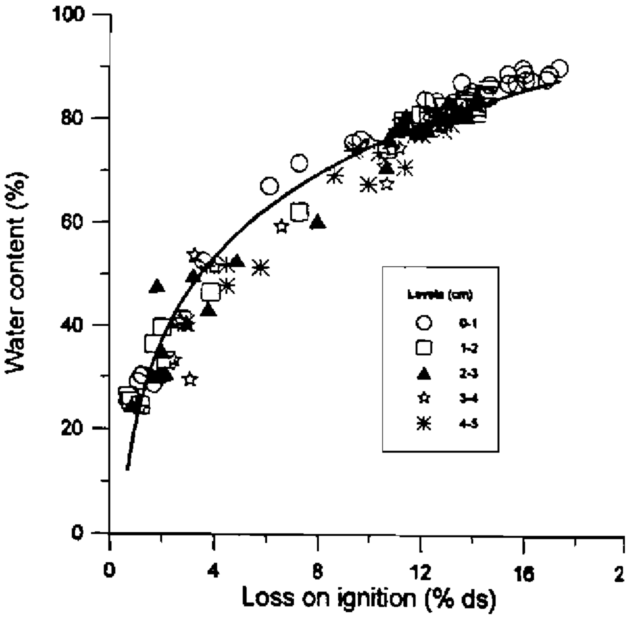


Fig. 2. The relationship between water content (WC, %) and organic matter content (measured as loss on ignition).

Our data on the relationship between the LOI and WC do not diverge from the commonly observed pattern mentioned above and they exhibit a strong logarithmic relationship ($R^2=0.96$) almost independent of other sediment characteristics and depth in the sediment profile (Fig. 2). The largest deviations occurred at stations with glacial clay or coarse sediment material (i.e., old sediment with low quantities of organic matter and different sedimentation conditions).

4.2. Loss on ignition versus organic carbon

Although LOI does not represent a well-defined chemical parameter, it is often used as an approximate measurement of the organic content of sediments and soils (Håkanson and Jansson, 1983). Heating of the sediments (500°C) removes most of the organic substances (C and N) but some crystal water and volatile compounds will also be vaporized. The percentage quotient of LOI/ORG-C varies between 2.04 and 15.3. The lowest and highest ratios originate both from stations with low organic contents, and especially from levels exceeding 2 cm depth of the profile. Vertically the ratio increases at all stations, with the steepest increase on stations with high bulk density (see the Appendix). The average ratios, excluding ratios exceeding four which originate from levels deeper than 2 cm at transportation/erosion bottoms, are 2.77, 3.05, 3.12, 3.14 and 3.15 for level (in cm) 0–1, 1–2, 2–3, 3–4 and 4–5, respectively. The standard deviation of the different levels decreases with increasing sediment depth; 0.26, 0.24, 0.22, 0.20 and 0.18. The increasing ratio with increasing depth in the sediment profile indicates that there is a higher release of crystal water and/or of volatile compounds (e.g. diatoms) than in the surface part of the sediment profile.

If we assume that the organic matter entering the sea floor has a Redfield composition of $[(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)]$ the LOI/ORG-C ratio would be 2.7. This is very close to the measured average ratio for the uppermost section (2.77). If we instead use the calculated average $C_{org}/N_{org}/P_{org}$ ratio of the samples in present study (230:22.5:1; see succeeding headings for interpretation and discussion) the ratio becomes 2.62, i.e. a preferential N and P release. Both ratios are lower than the measured bulk average ratio of 3.0. However, the estimated ratio from the average organic composition does not include loss of other compounds that may be released during ignition. Nevertheless, LOI measurements on the sediments from the Gulf of Riga could be used as a good estimate for the amount of organic carbon at almost all kinds of bottoms.

4.3. *Organic carbon and nutrient ratios*

The C_{org}:N_{org}:P_{org} ratio of marine particulate organic matter is quite consistent (Redfield et al., 1963; Copin-Montegut and Copin-Montegut, 1983). The C:N:P ratio of 106:16:1 has since the middle of this century been accepted to be the average organic molar ratio (henceforth referred to as Redfield ratio) in marine organic matter. The molar composition in fresh water exhibits a more variable composition (Heckey et al., 1993) with both higher and lower ratios than Redfield. Deviation from Redfield ratio seems also to be normal for the brackish Baltic Sea where the C_{org}/N_{org} ratio mostly exhibits higher values, i.e. between 7–10 instead of 6.625 (Hendrikson, 1975; Iturriaga, 1979; Shaffer, 1987). The N_{org}/P_{org} ratio is, on the other hand, commonly lower, between 12–14 (Sen-Gupta and Koroleff, 1973), whereas the ratio between carbon and phosphorus usually has higher ratios than Redfield. Shaffer (1987) suggests that the most likely or "best" average value for this ratio in the Baltic Sea and adjacent areas should be around 130.

In the interpretation of the C_{org}:N_{org}:P_{org} ratio in the sediments it should be remembered that the sediments contain different aged (10 000–100 ^{14}C years) allochtonous matter (precipitated humus, particulate land-derived organic matter) with high C/N ratios. However, measured ratios in sedimenting material and in the sediments are important as a base for characterizing the organic matter with respect to the degree of fractionation during decomposition. Fractionation processes during settling and during benthic degradation usually increases the C_{org}/N_{org} and the C_{org}/P_{org} as well as the N_{org}/P_{org}. This is caused by a preferential N and P utilization (e.g. Froelich et al., 1988).

4.4. *The C_{org}/N_{org} correlation*

As can be seen in Fig. 3 the C_{org}/N_{org} ratio is very stable. The ratio is almost independent of water depth, depth below seafloor, carbon content, sediment characteristics, location and extent of diagenesis. Even the topmost section exhibits the same ratio, which suggests that all fractionation mainly occur prior to settling at the sediment surface. Linear correlation analysis gives a very high coefficient of determination ($R^2 = 0.97$) with an average C_{org}/N_{org} ratio of 10.2 (Fig. 3). This ratio is slightly lower than the average ratio of living organisms in the Baltic Sea. It indicates

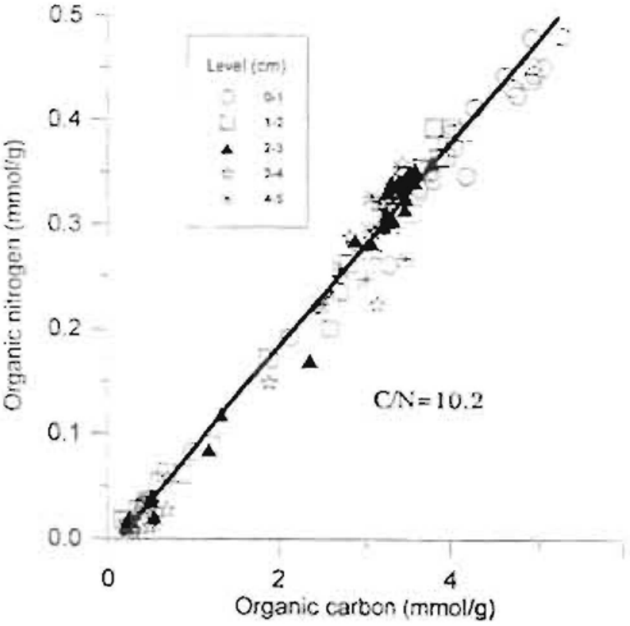


Fig. 3. Correlation between the concentration of ORG-C versus ORG-N ($r^2 = 0.99$). The average molar C/N ratio is 10.2.

preferential N decomposition or admixture of old organic matter. This ratio is consistent with those in similar sediment regions (Müller, 1977; Balzer, 1984; Froelich et al., 1988; Koop et al., 1990). The largest divergences from the "common" ratio appear at transportation/erosion bottoms with coarse material below 2 cm, i.e. very old sediment material.

4.5. The C_{org}/P_{org} correlation

Several studies have shown that preferential fractionated decomposition of P in the organic matter occur during halmyrolysis (Suess and Müller, 1980; Krom and Berner, 1981; Jørgensen, 1983). This is mainly a result of preferential instant autolytic release of easily hydrolysable P compounds (e.g. Froelich et al., 1988). It has also been argued that alteration in C_{org}/P_{org} would occur during diagenesis (Froelich et al., 1988; Ingall and Van Cappellen, 1990; De Lange, 1992b; Ingall et al., 1993; Berner et al., 1993; Berner and Rao, 1994). However, both Mach et al. (1987) and Ramirez and Rose (1992) challenged that diagenetic fractionated decomposition occurs. They claim instead that the C_{org}/P_{org} in sediments are constant and that deviation found were results of analytical defects. Reversed preferential release could also be the case when only refractory P_{org} species remain and during active P accumulation of in situ biota (Balzer, 1984; Gächter et al., 1989; Ingall and Van Cappellen, 1990; Ingall et al., 1990). Furthermore, variations in sedimentation rate seem to affect the preservation and burial of C_{org} (Hartmann et al., 1976; 1989; Jahnke, 1990) while preservation of organic phosphorus seems almost independent of sedimentation rate (Froelich et al., 1982; Ingall and Van Cappellen, 1990). The significance of anoxic versus oxic environment in the fractionation and preservation of C_{org} has been discussed extensively during recent years (e.g. Canfield, 1989, 1994; Jahnke, 1990; Cowie and Hedges, 1992; Ingall et al., 1993; Aller, 1994; Cowie et al., 1995) while the corresponding relevance for preservation of P_{org} has only been paid little attention (Ingall et al., 1993; Ingall and Jahnke, 1994).

A poor linear correlation coefficient ($R^2 = 0.58$) was obtained from the entire set of C_{org} against P_{org} data from this investigation (which include organic matter of very different age). This suggests, even with analytical errors accounted for, that diagenetic processes must affect the C_{org}/P_{org} ratio. This is contradictory to the conclusion presented by Ramirez and Rose (1992) but it is in accordance with the results presented by Ingall and Van Cappellen (1990) and De Lange (1992b). Ingall and Van Cappellen (1990) concluded that diagenetic processes must affect the C_{org}/P_{org} ratio, because they receive totally different linear regression results by combining the results of linear regression analysis on their data set ($R^2 = 0.76$) with division of their samples in carbon rich-($C_{org} > 2$ mmol/g; $R^2 = 0.64$) and carbon poor sediments (<2 mmol/g C_{org}; $R^2 = 0.11$). The slope in their uneven weighting of samples, as in the data presented by Mach et al. (1987), reflects almost solely the samples with high amounts of C_{org}. The same division of our also uneven weighted data reveals the same pattern with a very low coefficient of determination ($R^2 = 0.17$) in samples with more than 2% C_{org} and a coefficient of determination of 0.53 for samples with a content less than 2% C_{org}. The slope of the different lines is, however, almost identical (0.00424, 0.00429 and 0.0438 for all data, $C_{org} > 2\%$ and $C_{org} < 2\%$, respectively). The line intercept crosses very close to the origin. The slope corresponds to an average C_{org}/P_{org} ratio between 228 and 236. It differs from the average ratios obtained by Mach et al. (1987), Ingall and Van Cappellen (1990) and De Lange (1992b) i.e. 490, 552 and 1200, respectively. However, the data are in close connection with the investigation done by Balzer (1984) in Kiel Bight in the southern Baltic proper. It seems, thus, that the fractionation and preservation of carbon and phosphorus in the Baltic Sea, at least in its shallow sub-estuaries, differ from the general pattern found in more pelagic marine environments. One probable explanation for the observed pattern in our case could be that the settling time for organic matter in the Gulf of Riga is short compared to deep-sea sediments, so the fractionated decomposition has not been completed to the same degree when the organic matter finally settles on the sediment surface. Furthermore, preferential C_{org} utilization might also be discerned in the Gulf of Riga sediments, since the highest and most deviating C_{org} versus P_{org} values are traced in the uppermost section of accumulation sediments (Fig. 4). Further down in the profiles of these kinds of sediments the general trend is decreasing C_{org}/P_{org} with increasing burial depth. These stations have a higher accumulation rate (Kuptzov et al., 1984) and consequently comparatively a larger amount of recently settled organic matter. Hence, instant autolytic preferential release of P in the water column and at the sediment surface supersedes preferential C (and N) decomposition further down in the sediment column.

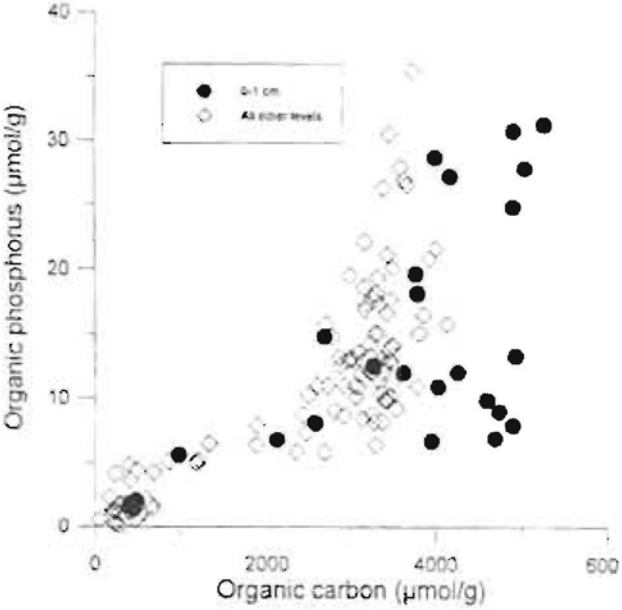


Fig. 4. The relationship between the amount of ORG-C and ORG-P in the sediment.

4.6. The N_{org}/P_{org} correlation

Since there are very small variations in the C_{org}/N_{org} ratio (see above) the N_{org}/P_{org} ratio follows, of coarse, almost the same pattern as the C_{org}/P_{org} ratio. Linear regression analysis gave an average N_{org}/P_{org} of 22.5 which suggest preferential P release from the degradating organic matter.

4.7. Inorganic carbon

The inorganic carbon, as determinated here, is mostly carbonates. In general the sediments of the Gulf of Riga contain less than 1% inorganic carbon (see the Appendix). Such low amount is normal also for the rest of the Baltic Sea (Emelyanov, 1988). This is due to that the brackish Baltic Sea water usually is undersaturated thermodynamically for most carbonates (Carman and Rahm, in prep.) so that abiotic and biotic carbonates dissolve during settling. At accumulation bottoms in the central part of the basin the amount of IN-C in the topmost section gradually decreases with increasing water depth. One plausible explanation for decreasing IN-C concentrations with increasing water depth could be that there is higher density stratification in these parts of the Gulf with lower degree of diapycnal mixing. This in combination with substantial oxic/suboxic respiration preserves an environment with pH close to 7 instead of 8 (e.g. Jahnke, 1990). Thus, settled abiotic and biotic calcium carbonates will dissolve more easily due to enhanced disequilibrium. Vertically in the sediment profiles a slight increases of the carbonate content could be discerned. This could be a result of authigenic precipitation of another carbonate phase caused by raised levels of carbonate alkalinity in the sulfate reducing anoxic part of the sediment profile.

4.8. Inorganic nitrogen

Several authors have reported that a substantial part of the total amount of nitrogen in soils, rocks and sediments is often inorganically bound (e.g. Müller, 1977; Williams and Ferrel, 1991). It is therefore not correct to use ORG-C/TOT-N ratios as a base for characterization of the organic matter, since this ratio does not reflect the chemical composition of the sedimentary organic matter. This is also true for the Gulf of Riga sediments although a substantial part of the total nitrogen is present in organic form. Inorganic nitrogen is reported to be adsorbed on minerogenic particles (preferably on clay minerals) and organic matter in two different ways (e.g. Rosenfeld, 1979), namely as exchangeable ammonium (EX-N) and as fixed ammonium (FIX-N). While EX-N is adsorbed through an ion exchange reaction on the surface of certain organic or mineral surfaces, FIX-N is incorporated in the sediments through adsorption within the clay structure and not easily replaced by other cations. It has been predicted that soluble ammonium, EX-N and FIX-N occur in a sort of equilibrium with each other, both in soils (Nommik, 1965) and in sediments (Rosenfeld, 1979). However, while the ion-exchange behaviour of EX-N, in concentration intervals that are usually found in interstitial waters, could be explained by a simple linear adsorption isotherm (Mackin and Aller, 1984) it seems that FIX-N does not entirely react in this way (Rosenfeld, 1979). Slow reaction kinetics, clay mineral composition, potassium content and prefixation before settling at the sediment surface have been suggested to explain the different behaviour between EX-N and FIX-N (Hartmann et al., 1976; Müller, 1977; Rosenfeld, 1979).

The unitless linear adsorption constant, K, for ammonium is calculated from the relationship expressed by Krom and Berner (1980):

$$K=[K^{*}\rho_{s}(1-\phi)]/\phi \qquad (1)$$

where ϕ = porosity (volume porewater/volume sediment); ρ_s = dry sediment density and K^* is the slope of the linear regression line of adsorbed vs pore water concentration of ammonia. The unitless adsorption isotherm is thus only dependent on changes in the porosity. K^* is dependent on sediment properties, such as grain size and shape of particles but also on content and type of clay minerals (Müller, 1977; Mackin and Aller, 1984). Therefore, both K^* and the adsorbed amount of ammonium should generally increase with decreasing grain size (increasing surface area of particles).

Since the sediment in the present study includes a wide spectrum of grain sizes/porosities we have divided the adsorbed amount of ammonium (EX-N and FIX-N) by $[(1-\phi)/\phi]$ (volume of sediment particles/volume of water; abbreviated in Figs. 5 and 6 as *VOL*). This is an adjustment for alteration in surface area of adsorbing sediment particles. Figs. 5 and 6 display plots of these calculated values versus the total amount of nitrogen. As can be seen both figures exhibit a positive relationship between these variables (although with different shape). Apparently additional sediment properties (e.g. potassium content, clay mineral amount/composition), kinetic aspects and prefixation may affect the concentration of both EX-N and FIX-N. As an example Müller (1977) found relatively high amounts of FIX-N in the southern

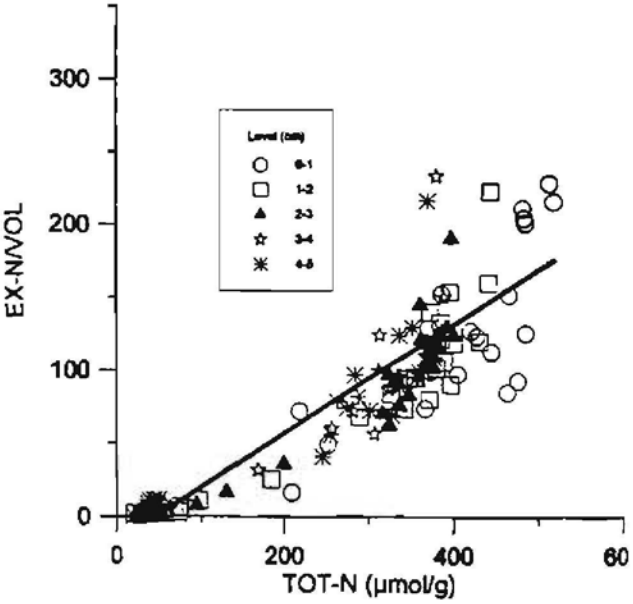


Fig. 5. Estimated importance of mineral surface area on the concentration of EX-N at the different sampling sites.

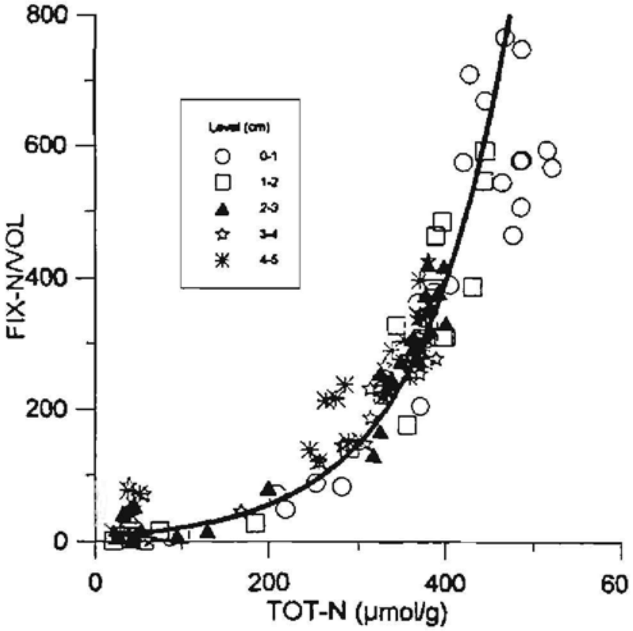


Fig. 6. Estimated importance of mineral surface area on the concentration of FIX-N at the different sampling sites.

Baltic proper, where the high capacity fixation clay mineral illite dominates (Seibold et al., 1971). The importance of illite for the fixation of ammonia has also been established from other marine areas and from freshwater environments (Müller, 1977; Comans et al., 1989; De Lange, 1992a). The lines drawn in Figs. 5 and 6 represent the best fitted lines of the data. For EX-N a fair linear correlation is obtained ($R^2 = 0.87$) while the best fit for FIX-N is represented by an exponential function ($R^2 = 0.80$). The largest digression from calculated regression lines for both EX-N and FIX-N is found in the uppermost section of almost all stations. Organic matter content versus clay mineral amount may explain the divergences (Rosenfeld, 1979; Mackin and Aller, 1984). A closer scrutiny of Fig. 6 reveals that some data points in the lower concentration field of TOT-N display distinctly higher FIX-N/[$(1-\phi)/\phi$] values. These points are from levels beneath 3 cm depth at stations with course sediment material at the top underlain by glacial clay (G10a, T5A, G21 and G12). This additionally confirms the importance of mineral composition for the fixation of inorganic nitrogen.

4.9. Inorganic phosphorus

As can be seen in Fig. 7 there is a high linear correlation ($R^2 = 0.96$) between the total amount of inorganic phosphorus and the amount of MOB-P, almost independently of sediment characteristics and redox condition. The high linear correlation between IN-P and MOB-P is an apparent indication on that sequestering mechanisms other than adsorption on compounds prone to reduction are kinetically slow and unimportant, concerning early diagenesis, for the inorganic phosphorus cycle in the Gulf. However, since lower amounts of AP-P than the calculated average value almost always arise from samples in the uppermost section from sediments located in the deep central part of the Gulf (young sediments) and higher values often originate from the bottommost level at stations with high bulk density (old sediments) it seems that sequestering to other than redox dependant compounds P-bearing elements are diagenetically important in a longer diagenetic perspective. Furthermore, the high amount of P, sequestered to substances prone to reduction in the surficial accumulating sediments of the Gulf of Riga will, however, to a large extent be liberated during an

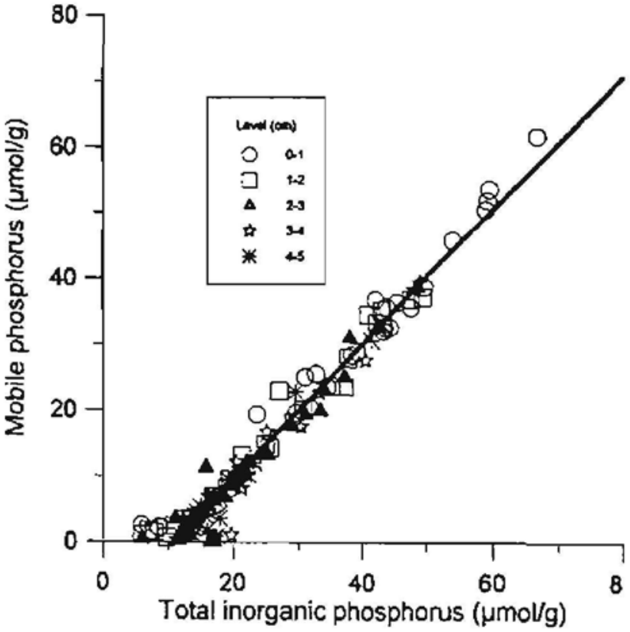


Fig. 7. Concentration of MOB-B in relation to the total inorganic P concentration.

increasing burial rate (in the reduced zone). The liberated P in the reduced zone will then either be sequestered as another P-bearing phase (Froelich et al., 1982; Ruttenberg and Berner, 1993) or be transported upwards through the redox cline by diffusion where it again can be reabsorbed to ironoxyhydroxides (e.g. Shaffer, 1986). To varying degrees, it will even be transported back into the water mass.

4.10. *Total annually sequestering amounts of carbon and nutrients in the sediments of the Gulf of Riga*

Up to now, all measurements have been discussed in terms of amount/dry weight (mol/g ds). A simple recalculation to amount/area (using calculated bulk densities) is, however, necessary when the objective is to estimate time related sequestering versus released amount. Generally, it seems that the normal coring length of 5 cm is too short to achieve a reliable measurement of the "final" sequestering amount. This since both the organic and inorganic amounts of all three elements do not attain constant concentrations within this depth below the sea floor. Based on a first inspection of samples for ^{210}Pb dating the TOT-C content decreases from 1.0 to 0.0% dw (mostly 0.5% dw) from 5 to 25 cm below the seafloor but is quite constant between 10 and 25 cm below the seafloor (on average a decrease of 0.1% dw). It indicates that a further breakdown of the organic matter and release/sequestering of inorganic carbon and nutrient fractions will occur beneath 5 cm but that most of the diagenetic processes have been completed at 10 cm below the seafloor. This is also seen in the analysis of the total amount from station G120, G5 and T3 where the concentration levels out markedly below 6 cm in the profiles.

Using ^{210}Pb dating technique Kuptzov et al. (1984) estimated the sedimentation rate in the deep central muddy part (a station comparable with G9 of this study) to be 2.2 mm/yr. The corresponding value for the muddy southwestern and southeastern part of the Gulf (comparable with station G2 and T2, respectively) is little less than one mm/year (covering the last 100 years). This is comparable with the preliminary results of recent determinations of accumulation rates (using ^{210}Pb). Stations G5, G120 and T3 (Fig. 1) include TOT-C, TOT-N and TOT-P measurements down to 10 cm and consist of sediments from approximately at least the last 50 years. As has been pointed out earlier most of the organic matter accessible to oxidation has already been processed within this period. Further, both inorganic carbon and nitrogen embrace only a minor part of the total concentration and the diagenetic processes affecting its release/sequestering with increasing burial rate varies within less than 5% of the total concentration. Therefore, its alteration could almost be neglected for estimates of total annual sequestering amounts. Finally, although the amount of inorganic phosphorus usually comprises 50% or more of the total concentration its alteration with increasing burial rate depend mainly on release/sequestering on substances prone to oxidation/reduction (see previous discussions). The amount of IN-P below the redox boundary layer is therefore nearly constant (see the Appendix). Hence, by using an average total concentration/area of C, N and P (from levels beneath the redox boundary from station G5, G120, T3 and some additional data from cores taken for ^{210}Pb dating) and assuming an average sedimentation rate of 1 mm/yr (consolidated sediment) one can make a good assessment of the total annual sequestering amount/area. For estimation of the total area of accumulation bottoms we have used the sedimentation map produced by the Geological Survey of Latvia (Juškevičs et al., 1993; south of 58°N) and Estonian Geological Survey (Raudsep et al., 1993; north of 58°N). The sediments are divided in 10 different sediment classes (Table 3), of which three could be assigned to be "true" accumulation bottoms for fine material (i.e. <0.01 mm; medium silts or sediment classes: sandy mud, aleuritic mud and mud). Almost half of the total area of the gulf is covered with sand of different grain sizes. Accumulation bottoms cover only 28% of the total area.

Calculated average total concentration of C, N and P are 2950, 335 and 29 μmol/g, respectively. The average sediment weight/m^2 (representing 1 mm thickness) is estimated at 0.23 kg. Based on

Table 3
Estimated areas of different sediment types of the Gulf of Riga

Sediment type	Estimated area (km^2)	Percent
Sand (various)	8330	44
Aleuritic sand	915	4.8
Muddy sand	470	2.5
Aleurite	840	4.4
Sandy aleurite	551	2.9
Muddy aleurite	744	3.9
Mud	3800	20
Sandy mud	160	0.8
Aleuritic mud	1330	7
Mixed sediments	1860	9.7
$\sum$	19,000	100

an estimate of the total amount of fine grained sediment material deposited in the Gulf of Riga the mean long term accumulation rate is estimated at 0.285 kg m^{-2} yr^{-1}. This is in good agreement with the estimate above. New ^{210}Pb determinations suggest that this estimate may be on the low side. Based on 0.23 kg/m^3 we can calculate that 678, 77 and 6.7 mmol/m^2 of C, N and P are annually sequestered at the bottoms in the accumulation areas. Yurkovskis et al. (1993), based their estimate on an average sequestering amount over the entire Gulf area. Recalculation to the entire area it becomes that 190, 21.6 and 1.9 mmol/m^2 are on average sequestered in the Gulf sediments of C, N and P, respectively. These values are lower than Yurkovskis et al. (1993) estimate for both N and P (255 and 2.6 mmol for N and P, respectively). For P it is comparable with what Wulff and Stigebrandt (1989) estimated for the Bothnian Bay (2 mmol/m^2 yr), and only half of what they estimated for the Baltic proper (4 mmol/m^2 yr). The explanation for the large differences between our estimate and Yurkovskis et al. (1993) total net sinks of N are most likely because our estimate only considers sequestering of N in the sediment while Yurkovskis et al. (1993) estimation embraces the total net sink of N, i.e. sediment sequestering and denitrification. They suppose that the net sink, within the Gulf, is about 80% of the total load of 92,000 tonnes, i.e. 74,000 tonnes or 255 mmol/m^2 year. Our calculation reveals that about 6% (5700 tons) of this sink is due to sequestering of N in the sediment, mainly as organic nitrogen. The remaining sink could thus be due to denitrification.

5. Summary and conclusions

The physical structure and carbon- and nutrient geochemistry of the sediments of the Gulf of Riga, Baltic Sea, have been examined. Several subfractions of carbon and nutrients have been analysed in order to determine sequestering efficiency and patterns but also how and to what extent these elements regenerate and fractionate during burial. Annual net sinks of C, N and P in the sediments have also been estimated.

A good correlation between the physical parameters WC and LOI are obtained almost irrespectively of sediment location, -type and burial depth.

There is a very strong linear correlation between the amount of organic carbon and organic nitrogen. The average C_{org}/N_{org} ratio is 10.2. This ratio is lower than the average ratio of living species in the Baltic Sea area and thus implies a preferential N release. The stable ratio indicates clearly that the preferential N release occurs during halmyrolysis and/or almost instantly upon settling at the sediment surface. Further diagenetic breakdown of the organic matter proceeds thus by utilization of C and N in 10.2 proportionality.

In contrast to the strong linear correlation between C_{org} and N_{org} the C_{org}/P_{org} and N_{org}/P_{org} ratios exhibit weak correlation to each other. This suggests that P_{org} is practically independent of the concentration of C_{org} and N_{org}. A calculated average organic C:N:P ratio is 230:22.5:1 which shows that both N and P are preferentially decomposed compared to C but also that P is preferentially fractioned compared to N.

While most of the carbon and nitrogen is organically bound, inorganic P is usually the dominant P fraction. The amount of inorganic carbon seldom exceeds 10% of the total carbon content, while inorganic nitrogen normally ranges between 4–10%. For both C and N the highest inorganic amount is measured at transport and erosion bottoms. Inorganic P usually constitutes more than 50%. The amount of AP-P is quite uniform irrespective of burial depth and other biogeochemical factors. MOB-P on the other hand varies within a wide range. This is mainly dependant on alteration in redox conditions and adsorption capacity. Thus, at least with respect to early diagenesis, all changes in the total inorganic P pool determine of the changes of MOB-P. This is evidenced by the strong linear correlation between the total inorganic P amount and MOB-P (Fig. 7).

The amount of inorganic nitrogen (FIX-N and EX-N) depends to a great extent on the surface area of adsorbing species, but also on factors such as clay mineral composition, amount and prefixation.

An annual net sink on the accumulation bottoms of 678, 77 and 6.7 mmol/m^2 is estimated for C, N and P, respectively. For N and P this comprises about 9% and 40% of the total annual load (Yurkovskis et al., 1993).

The high correlation between both the physical and chemical measured parameters obtained in the present study will facilitate exploitation of additional sediment data from the Gulf of Riga. For example, the sediment carbon- and nutrient studies performed by the Estonian Geological Survey and the Latvian Geological Survey could be used, but also other physical and chemistry data from other studies with totally different aims, as long as they at least contain data on, for instance, WC and/or LOI content. By certain calculations one can receive good estimates of many selective carbon and nutrient fractions with small errors compared with analytically measured concentrations. This will pave a way to improve the accuracy of future nutrient transformation budgets and calculations of distribution- and annual sequestering amounts in the sediments. Proved strong correlations will also make future sediment analysis less complex since several tedious and time-consuming analyses could be excluded and still preserve good accuracy.

Acknowledgment

We would like to express our gratitude to Prof. R. Hallberg, Prof. L. Rahm, Dr. N. Holm and Prof. F. Wulff for constructive comments. This work was supported by the Swedish Environmental Protection Agency, Nordic Council of Ministers and Stockholm Marine Institute (SMF).

References

Aigars, A. and Andrushatis, J., 1993. Nutrient transport through the water–sediment interface in the Gulf of Riga, Baltic Sea. Latv. Zin. Akad. Vestis (Latvian Sci. Acad. News, Riga), 10(B): 73–78.

Akal, T., 1972. The relationship between the physical properties of underwater sediments that affect bottom reflections. Mar. Geol., 13: 251–266.

Aller, R.C., 1994. Bioturbation and remineralisation of sedimentary organic matter: Effects of redox oscillation. Chem. Geol., 114: 331–345.

Andrushaitis, G., Andrushaitis, A., Bitenieks, Y., Priede, S. and Lenshs, E., 1992. Organic carbon balance of the Gulf of Riga. Proc. 17th CBO Conf., Norrköping 1990, Swed. Hydrol. Meteorol. Inst. Rep.

Balzer, W., 1984. Organic matter degradation and biogenic element cycling in a near shore sediment (Kiel Bight). Limnol. Oceanogr., 29: 1231–1246.

Berner, R.A., Ruttenberg, K.C., Ingall, E.D. and Rao, J.-L., 1993. The nature of phosphorus burial in modern marine sediments. In: R. Wollast et al. (Editors), Interactions of C, N, P and S Biogeochemical Cycles and Global Change. NATO ASI Ser., 14: 365–378.

Berner, R.A. and Rao, J.-L., 1994. Phosphorus in sediments of the Amazon river and estuary: Implications for the global flux of phosphorus to the sea. Geochim. Cosmochim. Acta, 58: 2333–2339.

Berzinsh, V., Berg, P.G. and Vidnere, E.E., 1988. Oxygen regime of the Gulf of Riga and the factors determining it (Rezhimoobrazuyschie faktory, gidrometeorologicheskie I gidrohimicheskie processi v moryach SSR). Gidrometeoizdat, Leninggrad, pp. 269–281 (in Russian).

Blomquist, S. and Abrahamsson, B., 1985. An improved Kajak-type gravity core sampler for soft bottom sediments. Schweiz. Z. Hydrol., 47: 81–84.

Canfield, D.E., 1989. Sulfate reduction and oxic respiration in marine sediments: Implications for organic carbon preservation in euxinic environments. Deep-Sea Res., 36: 121–138.

Canfield, D.E., 1994. Factors influencing organic carbon preservation in marine sediments. Chem. Geol., 114: 315–329.

Carman, R. and Jonsson, P., 1991. The distribution pattern of different forms of phosphorus in some surficial sediment types of the Baltic Sea. Chem. Geol., 90: 91–106.

Carman, R. and Rahm, L., in prep. Early diagenesis and chemical characteristics of interstitial water and sediments in the Baltic proper deep deposition bottoms.

Comans, R.N.J., Middelburg, J.J., Zonderhuis, J., Woittiez, J.R.W., De Lange, G.J., Das, H.A. and Van der Weijden, C.H., 1989. Mobilization of radiocaesium in pore water of lake sediments. Nature, 339: 367–369.

Copin-Montegut, C. and Copin-Montegut, G., 1983. Stoichi-

wide range. This is mainly dependant on alteration in redox conditions and adsorption capacity. Thus, at least with respect to early diagenesis, all changes in the total inorganic P pool determine of the changes of MOB-P. This is evidenced by the strong linear correlation between the total inorganic P amount and MOB-P (Fig. 7).

The amount of inorganic nitrogen (FIX-N and EX-N) depends to a great extent on the surface area of adsorbing species, but also on factors such as clay mineral composition, amount and prefixation.

An annual net sink on the accumulation bottoms of 678, 77 and 6.7 mmol/m^2 is estimated for C, N and P, respectively. For N and P this comprises about 9% and 40% of the total annual load (Yurkovskis et al., 1993).

The high correlation between both the physical and chemical measured parameters obtained in the present study will facilitate exploitation of additional sediment data from the Gulf of Riga. For example, the sediment carbon- and nutrient studies performed by the Estonian Geological Survey and the Latvian Geological Survey could be used, but also other physical and chemistry data from other studies with totally different aims, as long as they at least contain data on, for instance, WC and/or LOI content. By certain calculations one can receive good estimates of many selective carbon and nutrient fractions with small errors compared with analytically measured concentrations. This will pave a way to improve the accuracy of future nutrient transformation budgets and calculations of distribution- and annual sequestering amounts in the sediments. Proved strong correlations will also make future sediment analysis less complex since several tedious and time-consuming analyses could be excluded and still preserve good accuracy.

Acknowledgment

We would like to express our gratitude to Prof. R. Hallberg, Prof. L. Rahm, Dr. N. Holm and Prof. F. Wulff for constructive comments. This work was supported by the Swedish Environmental Protection Agency, Nordic Council of Ministers and Stockholm Marine Institute (SMF).

References

Aigars, A. and Andrushatis, J., 1993. Nutrient transport through the water–sediment interface in the Gulf of Riga, Baltic Sea. Latv. Zin. Akad. Vestis (Latvian Sci. Acad. News, Riga), 10(B): 73–78.

Akal, T., 1972. The relationship between the physical properties of underwater sediments that affect bottom reflections. Mar. Geol., 13: 251–266.

Aller, R.C., 1994. Bioturbation and remineralisation of sedimentary organic matter: Effects of redox oscillation. Chem. Geol., 114: 331–345.

Andrushaitis, G., Andrushaitis, A., Bitenieks, Y., Priede, S. and Lenshs, E., 1992. Organic carbon balance of the Gulf of Riga. Proc. 17th CBO Conf., Norrköping 1990, Swed. Hydrol. Meteorol. Inst. Rep.

Balzer, W., 1984. Organic matter degradation and biogenic element cycling in a near shore sediment (Kiel Bight). Limnol. Oceanogr., 29: 1231–1246.

Berner, R.A., Ruttenberg, K.C., Ingall, E.D. and Rao, J.-L., 1993. The nature of phosphorus burial in modern marine sediments. In: R. Wollast et al. (Editors), Interactions of C, N, P and S Biogeochemical Cycles and Global Change. NATO ASI Ser., 14: 365–378.

Berner, R.A. and Rao, J.-L., 1994. Phosphorus in sediments of the Amazon river and estuary: Implications for the global flux of phosphorus to the sea. Geochim. Cosmochim. Acta, 58: 2333–2339.

Berzinsh, V., Berg, P.G. and Vidnere, E.E., 1988. Oxygen regime of the Gulf of Riga and the factors determining it (Rezhimoobrazuyschie faktory, gidrometeorologicheskie I gidrohimicheskie processi v moryach SSR). Gidrometeoizdat, Leninggrad, pp. 269–281 (in Russian).

Blomquist, S. and Abrahamsson, B., 1985. An improved Kajak-type gravity core sampler for soft bottom sediments. Schweiz. Z. Hydrol., 47: 81–84.

Canfield, D.E., 1989. Sulfate reduction and oxic respiration in marine sediments: Implications for organic carbon preservation in euxinic environments. Deep-Sea Res., 36: 121–138.

Canfield, D.E., 1994. Factors influencing organic carbon preservation in marine sediments. Chem. Geol., 114: 315–329.

Carman, R. and Jonsson, P., 1991. The distribution pattern of different forms of phosphorus in some surficial sediment types of the Baltic Sea. Chem. Geol., 90: 91–106.

Carman, R. and Rahm, L., in prep. Early diagenesis and chemical characteristics of interstitial water and sediments in the Baltic proper deep deposition bottoms.

Comans, R.N.J., Middelburg, J.J., Zonderhuis, J., Woittiez, J.R.W., De Lange, G.J., Das, H.A. and Van der Weijden, C.H., 1989. Mobilization of radiocaesium in pore water of lake sediments. Nature, 339: 367–369.

Copin-Montegut, C. and Copin-Montegut, G., 1983. Stoichiometry of carbon, nitrogen and phosphorus in marine particulate matter. Deep-Sea Res., 30: 31–46.

Cowie, G.L. and Hedges, J.I., 1992. The role of anoxia in organic matter preservation in coastal sediments: relative stabilities of the major biochemicals under oxic and anoxic depositional conditions. Org. Geochem., 19: 229–234.

Cowie, G.L., Hedges, J.I., Prahl, F.G. and De Lange, G.J., 1995. Elemental and major biochemical changes across an oxidation front in a relict turbidite: An oxygen effect. Geochim. Cosmochim. Acta, 59: 33–46.

De Lange, G.J., 1992a. Distribution of exchangeable, fixed, organic and total nitrogen in imbedded turbiditic/pelagic sediments of the Madeira Abyssal Plain, eastern North Atlantic. Mar. Geol., 109: 95–114.

De Lange, G.J., 1992b. Distribution of various extracted phosphorus compounds in the imbedded turbiditic/pelagic sediments of the Madeira Abyssal Plain, eastern North Atlantic. Mar. Geol., 109: 115–139.

Elmgren, R., 1989. Man's impact on the ecosystem of the Baltic Sea: Energy flows today and at the turn of the century. Ambio, 18: 326–332.

Emelyanov, E.M., 1988. Biogenic sedimentation in the Baltic Sea and its consequences. In: B. Winterhalter (Editor), The Baltic Sea. Geol. Surv. Finl. Spec. Pap., 6: 127–135.

Froelich, P.N., Bender, M.L., Luedtke, N.A., Heath, G.R. and DeVries, T., 1982. The marine phosphorus cycle. Am. J. Sci., 282: 474–511.

Froelich, P.N., Arthur, M.A., Burnett, W.C., Deakin, M., Hensley, V., Jahnke, R., Kaul, L., Kim, K.-H., Roe, K., Soutar, A. and Vathakanon, C., 1988. Early diagenesis of organic matter in Peru continental margin sediments: Phosphorite precipitation. Mar. Geol., 80: 309–343.

Gächter, R., Meyer, J.S. and Mares, A., 1989. Contribution of bacteria to release and fixation in lake sediments. Limnol. Oceanogr., 33: 1542–1558.

Håkanson, L. and Jansson, M., 1983. Principles of Lake Sedimentology. Springer, Berlin, 316 pp.

Hartmann, M.P., Müller, P.J., Suess, E. and Van der Weijden, C.H., 1976. Chemistry of Late Quaternary sediments and their interstitial waters from the N.W. African continental margin. "Meteor" Forschungergebn., C 24: 1–67.

Heckey, R.E., Campbell, P. and Hendzel, L.L., 1993. The stoichiometry of carbon, nitrogen and phosphorus in particulate matter in lakes and oceans. Limnol. Oceanogr., 38: 709–724.

Hedges, J.I. and Stern, J.H., 1984. Carbon and nitrogen determinations of carbonate-containing solids. Limnol. Oceanogr., 29: 657–663.

Hendrikson, P., 1975. Auf- und Abbauprozesse partikulärer organischer Substanz anhand von Seston- und Sinkstoffanalysen. Thesis. Univ. Kiel, 160 pp.

Ingall, E.D. and Van Cappellen, P., 1990. Relation between sedimentation rate and burial of organic phosphorus and organic carbon in marine sediments. Geochim. Cosmochim. Acta, 54: 373–386.

Ingall, E.D., Schroeder, P.A. and Berner, R.A., 1990. The nature of organic phosphorus in marine sediments: New insights from ^{31}P NMR. Geochim. Cosmochim. Acta, 54: 2617–2620.

Ingall, E.D., Bustin, R.M. and Van Cappellen, P., 1993. Influence of water column anoxia on the burial and preservation of carbon and phosphorus in marine shales. Geochim. Cosmochim. Acta, 57: 303–316.

Ingall, D.E. and Jahnke, R., 1994. Evidence for enhanced phosphorus regeneration from marine sediments overlain by oxygen depleted water. Geochim. Cosmochim. Acta, 58: 2571–2575.

Iturriaga, R., 1979. Bacterial activity related to sedimenting particulate organic matter. Mar. Biol., 55: 157–169.

Jørgensen, B.B., 1983. Processes at the sediment–water interface. In: B. Bolin and R.B. Cook (Editors), The Major Biochemical Cycles and their Interactions. Wiley, New York, pp. 477–515.

Jahnke, R.A., 1990. Early diagenesis and recycling of biogenic debris at the seafloor, Santa Monica Basin, California. J. Mar. Res., 48: 413–436.

Juškevičs, V., Stiebriņš, O. and Baraškovs, V., 1993. Upper Pleistocene, Holocene Deposits and Bottom Sediments in the Gulf of Riga. Geol. Surv. Latvia, Riga.

Koop, K., Boynton, W.R., Wulff, F. and Carman, R., 1990. Sediment–water oxygen and nutrient exchanges along depth gradient in the Baltic Sea. Mar. Ecol. Progr. Ser., 63: 65–77.

Krom, M.D. and Berner, R.A., 1980. Adsorption of phosphate in anoxic marine sediments. Limnol. Oceanogr., 25: 797–806.

Krom, M.D. and Berner, R.A., 1981. The diagenesis of phosphorus in a near shore marine sediment. Geochim. Cosmochim. Acta, 45: 207–216.

Kuptzov, V.M., Seldina, B.B. and Ivanova, T.R., 1984. Rate of sedimentation of sediments of the Baltic Sea. In: Lissizin (Editor), Geological History and Geochemistry of the Baltic Sea. Nauka, Moscow, pp. 110–121 (in Russian).

Mach, D.L., Ramirez, A. and Holland, H.D., 1987. Organic phosphorus and carbon in marine sediments. Am. J. Sci., 278: 429–441.

Mackin, J.E. and Aller, R.C., 1984. Ammonium adsorption in marine sediments. Limnol. Oceanogr., 29: 250–257.

Murphy, I. and Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta, 27: 31–36.

Müller, P.J., 1977. C/N ratio in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. Geochim. Cosmochim. Acta, 41: 765–776.

Nommik, H., 1965. Ammonium fixation and other reactions involving a nonenzymaitic immobilization of mineral nitrogen I soil. Agronomy, 10: 200–260.

Parson, T.R., Maita, Y. and Lalli, C.M., 1984. A Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press, Sidney.

Pastors, A., 1967. Water and heat balance in the Gulf of Riga (Morskie zalivy kak priyomniki stochnykn vod). Zinätne, Riga, pp. 8–20 (in Russian).

Ramirez, A. and Rose, A.W., 1992. Analytical geochemistry of organic phosphorus and its correlation with organic carbon in marine and fluvial sediments and soils. Am. J. Sci., 292: 421–454.

Raudsep, J., Kask, J. and Väling, P., 1993. Distribution and Lithological Composition of Modern (Holocene) Marine Bottom Sediments in the Gulf of Riga (North of 58°N). Eston. Geol. Surv., Tallin.

Redfield, A.C., Ketchum, B.H. and Richards, F.A., 1963. The influence of organisms on the composition of seawater. In: M.N. Hill (Editor), The Sea. Wiley, New York, 2, pp. 26–77.

Rosenfeld, J.K., 1979. Ammonium adsorption in near shore anoxic sediments. Limnol. Oceanogr., 24: 356–364.

Ruttenberg, K.C. and Berner, R.A., 1993. Authigenic apatite formation and burial in sediments from non-upwelling continental margin environments. Geochim. Cosmochim. Acta, 57: 991–1007.

Sen-Gupta, R. and Koroleff, F., 1973. A quantitative study of nutrient fractions and stoichiometric model of the Baltic. Estuar. Coast. Mar. Sci., 1: 336–360.

Seibold, E., Exon, N., Hartman, M., Kögler, F.-C., Krumm, H., Lutze, G.F., Newton, R.S. and Werner, F., 1971. Marine geology of Kiel Bay. In: G. Müller (Editor), Sedimentology of Parts of Central Europe. Int. Sedimentol. Congr., Heidelberg, Guidebook, 8, pp. 209–235.

Shaffer, G., 1986. Phosphate pumps and shuttles in the Black Sea. Nature, 321: 515–517.

Shaffer, G., 1987. Redfield ratios, primary production, and organic carbon burial in the Baltic Sea. Deep-Sea Res., 34: 769–784.

Silva, J.A. and Bremner, J.M., 1966. Determination of isotope-ratio analysis of different forms of nitrogen in soils. 5. Fixed nitrogen. Soil Sci. Am. Proc., 30: 587–594.

Suess, E. and Müller, P.J., 1980. Productivity, sedimentation rate and sedimentary organic matter in the Oceans II—Elemental fractionation. In: Biogeochimie de la matière organique à l'interface eau–sediment marin. Colloq. Int. Centre Natl. Rech. Sci., 293: 17–26.

Williams, L.B. and Ferrel, R.E., 1991. Ammonium substitution in illite during maturation of organic matter. Clay Clay Miner., 39: 400–408.

Wulff, F. and Stigebrandt, A., 1989. A time-dependent budget model for nutrients in the Baltic Sea. Global Biogeochem. Cycles, 3: 63–78.

Yurkovskis, A., Wulff, F., Rahm, L., Andrushaitis, A. and Rodrigues-Medina, M., 1993. A nutrient budget of Gulf of Riga, Baltic Sea. Estuar. Coastal Shelf Sci., 37: 113–127.

Appendix

1.1 Chemical- and physical properties of sediments of the Gulf of Riga. WC, B.D. and LOI are in % of total weight, g/cm^3 and % of dry matter, respectively. All chemical fractions are in μmol/g of dry substance

Slice	Station	LOI	WC	B.D.	TOT-C	ORG-C	IN-C	TOT-N	EX-N	FIX-N	ORG-N	TOT-P	IN-P	MOB-P	AP-P	ORG-P
1	G1	7.3	71.7	1.19	3218	2576	642.5	218.6	10.9	7.4	200.3	37.9	29.8	19.6	10.2	8.0
2	G1	2.8	41.2	1.54	1637	878	758.3	74.3	3.6	9.3	61.4	16.1	11.0	2.4	8.6	5.1
3	G1	8.0	60.6	1.29	3147	2347	800	199.3	9.5	20.3	169.5	18.6	12.9	2.7	10.2	5.8
4	G1	10.7	67.8	1.21	3938	3127	810.8	256.4	11.0	22.0	223.5	25.7	13.8	3.5	10.3	11.9
5	G1	11.8	77.3	1.14	3338	2998	340	285	10.9	26.8	247.3	28.1	15.0	5.3	9.7	13.1
1	G1b	9.7	76.3	1.15	3987	3271	715.8	280.7	9.7	9.9	261.1	45.3	32.8	25.5	7.2	12.5
2	G1b	3.9	46.5	1.46	2171	1212	959.2	97.9	4.8	4.2	88.8	18.6	13.4	3.6	9.8	5.2
3	G1b	3.8	43.3	1.51	1808	1188	620	94.3	4.7	5.0	84.6	16.1	11.1	3.8	7.3	4.9
4	G1b	6.6	59.4	1.3	2441	1889	551.7	168.6	8.4	11.7	148.5	20.2	12.4	3.1	9.2	7.9
5	G1b	11.4	71	1.19	4238	3468	770	302.1	11.3	23.8	267.0	27.2	14.5	4.5	9.9	12.8
1	G2	17.4	90.3	1.05	5409	5268	141.7	515	9.4	24.5	481.0	90.5	59.3	52.0	7.3	31.2
2	G2	14.1	82.7	1.1	4162	3938	224.2	397.1	7.3	24.9	364.9	55.9	35.2	23.7	11.5	20.8
3	G2	13.4	81.8	1.11	3619	3465	154.2	362.1	10.5	26.5	325.2	41.7	24.1	13.6	10.5	17.6
4	G2	12.9	79.9	1.12	3516	3348	167.5	370.7	11.2	24.6	334.8	37.5	20.2	9.6	10.6	17.3
5	G2	12.0	77.5	1.14	3527	3290	236.7	334.3	10.1	25.6	298.5	35.5	20.5	9.3	11.2	15.0
1	G2b	16.3	87.8	1.07	4829	4693	136.7	464.3	4.6	29.1	430.6	73.7	66.9	61.8	5.0	6.9
2	G2b	14.2	81.6	1.11	4105	3863	242.5	400.7	10.3	26.9	363.5	43.6	27.1	23.0	4.2	16.4
3	G2b	13.8	80.9	1.11	3984	3783	201.7	400.7	11.4	30.2	359.1	33.1	22.2	12.4	9.8	10.9
4	G2b	12.8	79	1.13	3583	3401	181.7	370	10.7	29.5	329.8	30.2	20.4	10.3	10.1	9.8
5	G2b	12.1	77.3	1.14	3445	3256	189.2	358.6	10.8	28.1	319.6	28.0	19.3	9.5	9.8	8.7
1	G4	15.4	89	1.06	4062	3999	62.5	420.7	6.0	27.4	387.3	74.1	45.5	36.4	9.12	8.6
2	G4	14.6	86.1	1.08	3717	3666	50.8	389.3	6.6	28.9	353.8	69.8	43.3	33.2	10.1	26.5
3	G4	14.1	83.3	1.1	3645	3584	60.8	377.1	8.0	29.0	340.2	76.7	48.8	39.1	9.8	27.9
4	G4	13.8	81.8	1.11	3461	3388	72.5	367.9	9.4	29.1	329.4	74.5	48.3	38.3	10.0	26.3
5	G4	13.4	80.7	1.11	3463	3372	90.8	377.9	11.1	31.4	335.3	56.4	43.3	33.0	10.3	13.1
1	G4b	16.0	90.1	1.05	4313	4264	48.3	445	4.8	28.3	411.9	54.1	42.2	36.8	5.4	12.0
2	G4b	14.5	85.2	1.08	3688	3632	55.8	397.1	10.3	32.4	354.4	69.3	42.4	33.3	9.1	26.9
3	G4b	14.2	85	1.09	3509	3451	58.3	380	8.0	28.6	343.4	56.2	42.5	33.1	9.5	13.7
4	G4b	13.6	81.2	1.11	3440	3368	71.7	371.4	10.5	30.8	330.1	57.4	49.2	39.4	9.8	8.2
5	G4b	13.2	79.4	1.12	3475	3399	75.8	377.1	10.9	30.8	335.4	41.9	29.6	22.8	6.8	12.3
1	G5	14.7	87	1.07	4018	3950	68.3	427.9	7.1	40.8	380.0	50.2	43.6	32.7	11.0	6.6
2	G5	13.7	84	1.09	3490	3422	68.3	385.7	8.9	29.1	347.7	57.6	47.8	36.9	10.9	9.8
3	G5	12.7	80.6	1.12	3328	3250	77.5	368.6	10.0	27.4	331.1	49.2	37.2	25.4	11.8	12.0
4	G5	11.5	77.8	1.14	2885	2809	75.8	324.3	9.6	27.2	287.5	32.5	23.6	12.2	11.3	9.0
1	G5	11.9	78.3	1.13	3242	3142	100	361.4	10.6	29.0	321.9	31.7	23.3	12.0	11.3	8.4
1	G6	16.1	87.9	1.07	4688	4603	85	484.3	11.2	30.6	442.6	68.9	59.1	50.5	8.5	9.8

Slice	Station	LOI	WC	B.D.	TOT-C	ORG-C	IN-C	TOT-N	EX-N	FIX-N	ORG-N	TOT-P	IN-P	MOB-P	AP-P	ORG-P
2	G6	13.7	83.4	1.1	3537	3460	76.7	385.7	10.2	29.5	346.1	53.9	41.0	34.6	6.4	12.9
3	G6	13.3	81.3	1.11	3363	3290	73.3	382.9	11.1	31.5	340.3	5.2	28.9	18.2	10.7	6.3
4	G6	13.0	80.8	1.11	3404	3343	60.8	386.4	11.6	32.9	341.9	31.9	20.6	12.1	8.5	11.3
5	G6	12.5	80.2	1.12	3127	3061	65.8	370	11.0	32.5	326.5	29.5	19.4	9.4	10.0	10.1
1	G7	14.0	85.6	1.08	4123	4035	87.5	405.7	6.3	25.2	374.2	49.2	38.3	28.3	10.0	10.9
2	G7	12.9	82.8	1.1	3620	3542	78.3	342.9	5.9	26.2	310.7	47.0	37.8	27.9	9.9	9.2
3	G7	12.0	78.8	1.13	3373	3275	97.5	337.1	8.0	25.7	303.4	42.1	34.0	23.5	10.4	8.1
4	G7	11.6	78.5	1.13	3325	3226	99.2	335	10.1	25.2	299.7	45.5	33.4	22.7	10.7	12.1
5	G7	9.5	74.3	1.17	2608	2498	110.8	263.6	10.5	28.4	224.7	22.6	12.4	5.2	7.3	10.2
1	G8	16.9	88	1.07	4998	4911	87.5	520.7	11.3	29.8	479.6	72.5	47.8	35.7	12.1	24.8
2	G8	14.4	84.5	1.09	4081	3998	83.3	442.9	11.3	38.6	393.0	41.0	19.4	9.6	9.9	21.6
3	G8	13.4	82.2	1.1	3598	3500	97.5	392.1	10.9	31.6	349.6	30.3	16.4	6.8	9.6	14.0
4	G8	13.5	83.7	1.1	3502	3426	75.8	389.3	11.3	20.8	357.3	32.7	16.1	7.0	9.2	16.6
5	G8	12.3	81.7	1.11	3287	3172	115	352.1	11.2	26.3	314.7	34.1	17.2	6.4	10.8	16.9
1	G9	17.0	89	1.06	4979	4915	64.2	485.7	9.7	24.1	451.9	80.6	49.9	38.8	11.1	30.7
2	G9	14.6	85	1.09	3790	3732	58.3	380.7	6.9	22.3	351.5	78.5	43.1	35.3	7.8	35.4
3	G9	13.8	82.1	1.1	3527	3455	71.7	368.6	10.1	23.2	335.3	68.6	38.1	31.4	6.7	30.5
4	G9	13.5	80.6	1.12	3574	3496	78.3	379.3	10.7	25.1	343.5	50.6	30.5	17.5	13.0	20.1
5	G9	12.9	80	1.12	3391	3306	85	370.7	11.1	27.9	331.7	38.9	20.8	9.4	11.5	18.1
1	G10a	1.7	28.7	1.76	509	484	24.6	45.7	1.6	6.6	37.5	25.8	23.8	19.4	4.4	2.0
2	G10a	0.7	26.3	1.82	193	173	19	27.9	1.1	8.8	17.9	15.0	12.7	3.3	9.4	2.3
3	G10a	1.8	47.8	1.46	245	204	40.1	30.7	1.8	17.2	11.8	14.1	13.2	1.4	11.8	0.9
4	G10a	3.3	53.7	1.38	365	288	74.1	38.6	2.8	27.8	8.0	19.8	19.7	1.1	18.6	0.0
5	G10a	5.8	51.4	1.39	484	348	128	37.1	3.1	27.9	6.2	18.1	17.4	0.9	16.6	0.7
1	G11	13.6	87.4	1.07	3957	3774	182.5	374.3	5.5	18.9	349.9	54.1	34.5	23.6	10.9	19.6
2	G11	12.3	81	1.11	3489	3288	200.8	327.1	7.5	20.1	299.5	48.5	30.9	20.1	10.8	17.7
3	G11	11.9	77.8	1.14	3438	3190	248.3	324.3	7.0	18.4	298.9	48.5	31.2	19.6	11.6	17.3
4	G11	11.2	74.7	1.16	3297	2992	305	307.1	7.3	19.2	280.6	44.8	25.3	16.7	8.6	19.5
5	G11	10.4	73.7	1.17	2988	2704	283.3	288.6	11.2	20.6	256.8	36.9	21.2	10.8	10.4	15.7
1	G12	1.1	29.1	1.76	496	450	45.8	37.1	1.7	2.2	33.3	10.0	8.7	2.2	6.4	1.4
2	G12	0.8	25.4	1.84	270	220	50	20.7	2.2	1.2	17.3	9.0	7.9	1.4	6.4	1.2
3	G12	2.0	35.1	1.64	364	264	100	24.3	2.8	5.2	16.4	13.8	12.3	0.9	11.4	1.4
4	G12	3.0	40.1	1.56	241	208	32.5	28.6	3.4	10.4	14.8	15.4	14.1	1.9	12.2	1.3
5	G12	4.5	47.8	1.44	298	245	53.3	40	4.3	17.9	17.9	18.6	14.5	2.3	12.2	4.1
1	G14	17.0	88.9	1.06	5148	5048	100.8	477.1	4.5	22.4	450.3	71.6	43.9	35.8	8.1	27.7
2	G14	13.5	82.6	1.1	3589	3434	155	347.1	7.7	23.5	316.0	58.3	37.2	23.6	13.6	21.1
3	G14	13.0	80.6	1.12	3431	3317	114.2	335	8.6	22.3	304.1	52.7	33.4	20.2	13.2	19.3
4	G14	12.6	79	1.13	3288	3162	126.7	327.1	9.1	22.7	295.4	59.2	40.6	27.7	12.9	18.6
5	G14	12.9	78.2	1.13	3282	3166	115.8	327.9	7.4	23.6	296.8	63.6	41.5	30.7	10.8	22.1
1	G14a	12.2	84	1.09	3924	3627	261.2	367.1	5.4	26.6	335.1	51.3	39.3	28.9	10.4	12.0
2	G14a	11.3	80	1.12	3648	3388	229.8	355.7	9.2	17.0	329.5	37.7	25.7	14.4	11.3	12.0
3	G14a	11.0	78.1	1.14	3368	3228	125.3	347.9	9.2	29.6	309.1	34.0	20.7	10.2	10.5	13.3

4	G14a	11.0	77.9	1.14	3239	3095	128.3	329.3	7.8	29.1	292.4	35.6	22.1	10.2	11.9	13.5
5	G14a	11.3	78.7	1.13	3188	3041	130.9	337.11	2.9	30.2	294.0	35.2	22.2	10.3	11.9	13.0
1	G15	9.4	75.6	1.16	3228	2690	538.3	252.1	6.1	11.0	235.1	58.2	43.5	32.1	11.4	14.7
2	G15	7.3	62.3	1.27	2369	1878	491.7	184.3	6.0	6.5	171.8	56.0	49.6	37.3	12.3	6.4
3	G15	4.9	52.8	1.38	1785	1336	449.2	130	6.3	5.7	118.1	31.8	25.3	13.6	11.7	6.5
4	G15	2.5	33.3	1.67	986	693	293.3	62.1	3.9	1.5	56.8	25.6	21.4	8.2	13.2	4.2
5	G15	1.6	30.1	1.73	704	436	268.3	41.4	2.9	1.5	37.1	21.7	19.9	2.9	17.0	1.8
1	G16	13.0	81.6	1.11	4098	3791	307.5	371.4	11.2	17.8	342.4	49.8	31.8	20.4	11.3	18.1
2	G16	10.7	74.5	1.16	3173	2784	388.3	290	9.0	18.5	262.5	36.1	21.4	13.2	8.2	14.7
3	G16	10.7	71.1	1.19	3180	2868	311.7	316.4	11.2	20.5	284.7	33.1	19.9	9.0	11.0	13.1
4	G16	10.6	71.2	1.19	2920	2688	232.5	282.1	11.2	22.5	248.4	22.9	17.1	7.2	10.0	5.8
5	G16	10.0	67.7	1.22	2623	2466	157.5	255.7	10.3	22.2	223.3	23.4	16.1	4.9	11.3	7.3
1	G18	3.6	52.6	1.39	1583	987	595.8	86.4	1.8	2.2	82.4	30.3	17.6	13.7	3.9	12.8
2	G18	2.2	33.3	1.67	1205	600	605	56.4	1.8	0.5	54.2	16.1	13.9	3.6	10.2	2.2
3	G18	1.9	30.2	1.73	903	502	400.8	42.9	2.2	0.7	40.0	17.9	13.5	3.6	9.9	4.4
4	G18	3.1	29.5	1.73	673	428	245	45.7	3.8	8.0	33.9	17.7	16.4	4.6	11.8	1.3
5	G18	4.5	51.9	1.39	383	293	90	44.3	4.0	19.2	21.1	17.8	16.0	1.7	14.3	1.8
1	G21	1.3	30.3	1.73	440	423	16.5	46.4	2.2	8.1	36.1	7.8	6.0	2.5	3.5	1.8
2	G21	1.2	24.5	1.85	437	348	88.1	38.6	1.9	9.6	27.0	7.8	6.0	1.0	5.0	1.8
3	G21	2.2	30.7	1.72	946	489	446.8	52.1	1.6	14.8	35.8	13.0	11.5	0.7	10.8	1.5
4	G21	2.7	40.9	1.55	1268	483	763.5	38.6	1.4	26.1	11.1	17.5	17.0	0.9	16.1	0.5
5	G21	3.0	40.5	1.55	1393	514	852.3	39.3	1.6	23.0	14.7	17.5	16.8	0.5	16.4	0.7
1	G22	15.7	87.3	1.07	5398	4938	386.9	530.7	11.3	32.2	443.6	57.6	44.4	32.7	11.7	13.2
2	G22	12.5	83.6	1.1	4094	3807	251.5	431.4	9.1	29.2	392.9	34.0	19.0	8.3	10.8	15.0
3	G22	11.5	81	1.12	3552	3386	146.8	382.1	10.6	29.1	342.4	31.2	18.7	7.3	11.4	12.6
4	G22	11.3	80.2	1.12	3422	3258	145.6	367.1	9.7	28.6	328.3	31.4	19.4	9.0	10.4	12.0
5	G22	11.2	78.7	1.13	3503	3349	136.9	357.1	9.9	28.6	318.6	28.4	18.0	6.6	11.4	10.4
1	G120	16.1	89.1	1.06	4839	4743	81.1	467.1	7.1	36.0	423.9	68.5	59.6	53.7	5.9	8.9
2	G120	14.2	84.8	1.09	4219	4134	73	445	15.4	40.8	388.8	45.1	29.4	18.2	11.1	15.7
3	G120	13.1	83.7	1.1	3662	3488	150.6	398.6	14.4	31.4	352.8	35.7	21.6	11.6	10.1	14.1
4	G120	12.6	82	1.11	3435	3334	88.1	380.7	19.7	36.0	325.0	36.0	21.0	9.3	11.7	15.0
5	G120	12.8	81	1.11	3303	3226	66.9	370.7	19.5	35.8	315.3	33.9	19.7	8.6	11.1	14.2
6	G120	12.5	81.1	1.11	3208	3148	52.5	356.4	23.5	25.7	307.2	31.9	19.0	8.8	10.3	12.8
7	G120	12.0	80.4	1.12	3043	2984	51.3	342.1	20.6	28.7	292.8	30.3	17.4	7.2	10.2	12.9
8	G120	11.5	80.2	1.12	2974	2917	50.9	337.9	23.3	28.2	286.4	26.4	17.8	7.2	10.6	8.6
9	G120	11.3	79	1.13	2966	2884	72.4	336.4	15.6	37.6	283.2	29.7	17.2	6.3	10.9	12.5
10	G120	10.4	77.1	1.14	2802	2723	71	304.3	11.9	28.9	263.5	27.8	16.9	4.8	12.0	10.9
1	T2	13.2	83.5	1.1	4663	4176	422.2	387.1	11.6	28.9	346.7	49.3	22.2	11.2	11.0	27.1
2	T2	12.5	80.7	1.12	3988	3616	325.3	373.6	12.9	27.9	332.7	28.9	16.9	6.9	9.9	12.0
3	T2	12.3	78.3	1.13	3708	3460	217.8	361.4	15.6	31.2	314.6	26.0	15.9	11.7	4.2	10.2
4	T2	10.9	74.4	1.16	3444	3098	308.2	313.6	16.4	24.7	272.5	25.6	14.7	4.8	9.9	10.8
5	T2	8.7	69.1	1.21	2908	2432	435.3	245.7	7.0	23.5	215.2	22.8	14.2	4.1	10.1	8.7
1	T3	15.4	87.2	1.07	5076	4902	147.3	486.40	7.1	42.2	437.2	62.0	54.2	45.9	8.3	7.9

Slice	Station	LOI	WC	B.D.	TOT-C	ORG-C	IN-C	TOT-N	EX-N	FIX-N	ORG-N	TOT-P	IN-P	MOB-P	AP-P	ORG-P
2	T3	12.0	81.2	1.11	3619	3498	106.3	372.1	7.2	27.5	337.5	36.2	25.1	14.9	10.2	11.1
3	T3	10.8	6.6	1.15	3184	3052	118.2	324.3	11.5	30.0	282.8	29.7	18.8	7.2	11.6	11.0
4	T3	10.1	75.8	1.15	3027	2918	98.2	312.9	12.2	28.3	272.4	27.5	16.5	5.5	11.0	11.0
5	T3	9.4	74.1	1.17	2735	2602	120.8	275	9.9	29.1	236.0	26.6	15.74.1	11.6	11.0	
1	T5A	1.2	30.3	1.73	473	403	69.1	42.1	4.4	6.6	31.2	10.3	8.7	2.1	6.6	1.6
2	T5A	1.7	36.4	1.63	589	423	163	42.1	1.3	9.6	31.2	10.9	9.8	0.6	9.2	1.1
3	T5A	3.2	49.8	1.43	1111	525	567	43.6	1.0	21.5	21.1	17.6	16.6	0.5	16.2	1.0
4	T5A	4.0	51.4	1.4	1181	678	483	55.7	3.0	25.9	26.9	18.5	17.1	0.8	16.3	1.4
5	T5A	3.7	51.5	1.4	1148	555	571.1	50	4.2	26.0	19.8	18.1	17.0	0.6	16.4	1.1
1	T6	6.1	67.2	1.23	2194	2121	68.8	208.6	3.1	13.5	192.0	37.8	31.0	25.1	6.0	6.7
2	T6	2.1	39.7	1.57	693	668	24.5	72.9	1.7	8.7	62.5	8.8	7.1	1.7	5.4	1.7
3	T6	0.9	24.5	1.85	243	231	12.4	27.1	0.4	7.3	19.4	7.2	6.0	0.8	5.3	1.2
4	T6	1.2	23.8	1.86	1132	285	836.6	23.6	0.3	8.1	15.2	12.3	11.2	0.3	11.0	1.0
5	T6	1.7	29.9	1.74	2018	227	1760.8	20	0.3	12.6	7.1	14.3	13.8	1.1	12.7	0.5

Paper II

Toxicological and Environmental Chemistry, Vol. 60, pp. 245-259
Reprints available directly from the publisher
Photocopying permitted by license only

VERTICAL AND SPATIAL DISTRIBUTION OF BIOGENIC SILICA IN THE SEDIMENT OF THE GULF OF RIGA, BALTIC SEA

ROLF CARMAN[a] and JURIS AIGARS[a,b]

[a]*Department of Geology and Geochemistry, Stockholm University, S-106 91 Stockholm;* [b]*Institute of Aquatic Ecology, Latvian University, Salaspils, Latvia*

(Received 10 April 1996; Revised 2 September 1996)

The vertical and spatial concentration trends of biogenic silica (BSi) were investigated in a variety of sediment types from the Gulf of Riga. These trends were compared with the concentration of organic carbon to examine how variations in the mass sedimentation and the dissolution rate of BSi versus bacterially mediated oxidation of organic matter affect the distribution of BSi in different environments. The effects of important physical and biogeochemical factors on the distribution of BSi have also been examined.

The concentration of BSi in the surface sediment at accumulation bottoms ranges between 0.8-1.5 mmol/g with an average concentration of 1.1 mmol/g. This is about two times the concentration that has been reported in similar sediments in the open Baltic proper. Much lower concentrations were measured in erosion and transitional areas; on average around 0.2 and 0.6 mmol/g, respectively.

A comparison between recent sedimentation rate measurements (^{210}Pb) and concentrations of BSi within different accumulation bottoms suggests an approximate inverse relationship with each other. The importance of variation in the sedimentation rate on the surface BSi concentration is supported by the fact that higher C_{org}/BSi ratios are found in periphery accumulation zones close to transition areas (larger supply of carbon rich allochthonous material that dilutes settled amounts of BSi) than at accumulation bottoms in the central part of the Gulf. The C_{org}/BSi ratio in the sediment is always lower than in living siliceous algae which shows that the microbial degradation of organic carbon is always greater than the inorganic dissolution of BSi, irrespective of the assemblage of silica and non-silica species.

The general vertical concentration pattern at accumulation sites showed a decreased concentration with increased depth down to 2-6 cm below seafloor where the concentration gradually equalizes. The concentration in the equalizing zone is on average about 20% lower than in the uppermost centimeter. This implies that the main part of the BSi entering the accumulation bottoms is permanently buried and that a great amount of silica already has been released during halmyrolysis. The spatial and vertical BSi trends at sites in transitional and erosional areas reflects prevailing sedimentation conditions with a low concentration in sections with a dominance of sand and gravel (no deposition of fine material) and a higher concentration in the sections containing stiff glacial clay (former accumulation area).

The average annual burial amount of BSi in the Gulf has been estimated to be around 50 000 tons of which most is buried in accumulation bottoms outside the central muddy part of the Gulf. The buried amount is about 60% of the annual river load of silica.

Keywords: Biogenic silica; sediment; Baltic Sea; Gulf of Riga

INTRODUCTION

Silic acid regeneration from biogenic silica (BSi) is supposed to be a major pathway in the estuarine silicon cycle. Its dissolution rate is important in regulating the geochemistry in natural waters and adjusting the productivity in aquatic environments. Silic acid flux from the sediment to the overlaying water is regulated primarily by changes in temperature and salinity (e.g. Werner, 1977; Williams and Crerar, 1985) while variations of pH (Williams *et al.*, 1985), pressure (Fournier and Marshall, 1983) and oxygen condition (Yamada and D'Elia, 1984) normally play a minor role in common marine environments. However, it has been suggested that an increased dissolution of silica occurs during transition from oxidized to reduced condition when silica associated with iron(III) complexes are removed (Lewin, 1961). Although it is established that all major salts in sea water and variations in temperature strongly catalyze the silica dissolution, it should also be mentioned that Yamada and D'Elia (1984) have shown that the release rate accelerated very rapidly between 10 and 20‰ salinity and temperatures above 15 °C, but were less dependent beneath 15 °C and on change in salinity in the low and high ranges. Additionally, the silica solubility also depends on supply and host sediment composition, specific surface area, and solubility of certain silica polymorphs (e.g. Pattan *et al.*, 1992; Tribble *et al.*, 1995).

The surficial spatial distribution of BSi between different types of bottoms is determined largely by the mass accumulation rate (MAR) and differences in productivity of certain phytoplankton-based ecosystem, e.g. flagellates or diatoms. During enhanced diagenesis variations of environmental factors such as mineral composition, salinity and temperature may become increasingly important in regards to the concentration of BSi found.

The purpose of this study was to depict the vertical and spatial distribution of BSi and explore how physical and biogeochemical properties affect the concentration of BSi in different sediment environments of the Gulf of Riga.

Study area

The Gulf of Riga (Figure 1) represents a semi-enclosed basin and is a comparatively shallow region of the Baltic Sea. Its maximum and mean

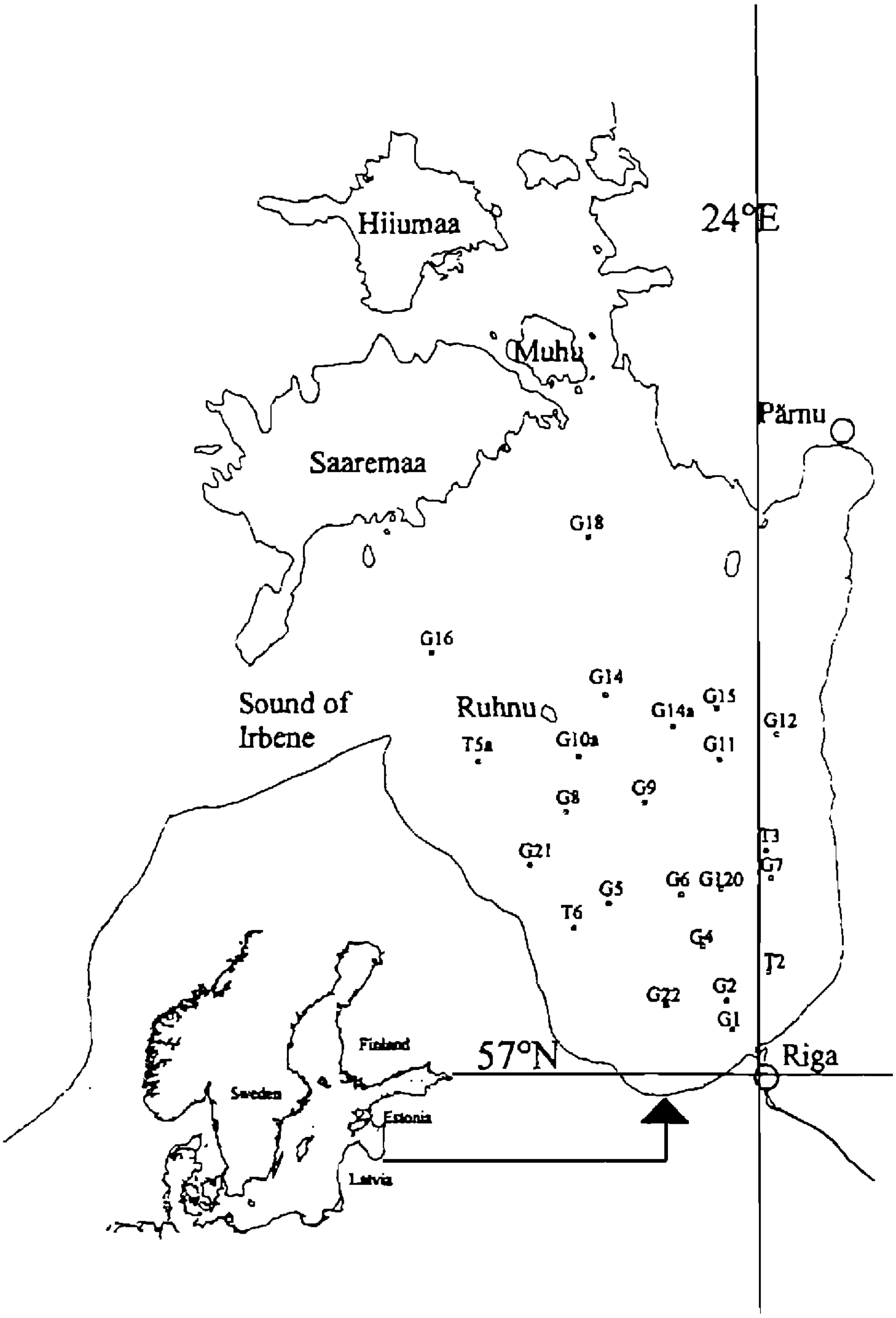


FIGURE 1 Map showing the location of the sampling sites in the Gulf of Riga.

depths are 62 and 20 m, respectively. The bottoms of the Gulf constitute a mosaic of different bottom types with only about 30% of its area containing bottoms with continuous deposition of fine material (Emelyanov, 1988; Juškevi s *et al.*, 1993; Raudsep *et al.*, 1993). The main river inputs are located in the southeastern part of the Gulf (e.g. river Daugava). Water exchange with the Baltic proper occurs via two shallow sills in the north and western part of the Gulf (Pastors, 1967). The salinity varies between 4 and 7‰ (Yurkovskis *et al.* 1993).

The Gulf of Riga is one of the most eutrophic areas of the Baltic Sea. The average sedimentation rate is about 290 g C m^{-2} yr^{-1} or about twice as much as an average for the entire Baltic proper. According to Yurkovskis *et al.* (1993), the primary production, in contrast to the usually nitrogen limited Baltic proper, is strongly limited with respect to phosphorus. However, it has been suggested that during certain periods in the southern Baltic proper (Wulff and Rahm, 1988) silica can not be excluded as a nutrient limiting agent for selective primary producers.

METHODS

Sediment cores were collected from the research ships "Antonia" and "Geofizikis" at a total of 23 sites in the summers of 1991 and 1993 (Table I and Figure 1). We used a modified version of a Kajak gravity corer equipped with an acrylic liner with an inside diameter of 80 mm (Blomquist and Abrahamsson, 1985). The cores were sliced on board the ship in one cm slices down to 5 cm, except at sites G5, G14a, G22, G120, T2 and T3 where the slicing depth was 10 cm. After slicing, the sediment samples where immediately put in a freezer. Measurements for the calculation of porosity (Berner, 1971) were done by freeze-drying the samples. Extraction of BSi was made according to the method originally described by DeMaster (1981) with modification according to Conley and Newberry (1989). Dissolved silica was measured calorimetrically according to the procedure described by Parsons *et al.* (1984). Organic carbon concentrations were measured by using the acid volatile procedure (Hedges and Stern, 1984). The loss on ignition (LOI, % d.w.) was measured by heating the freeze dried sediment at 500°C.

RESULTS AND DISCUSSION

Spatial Distribution of BSi

Of the 23 sampling cores examined (Figure 1 and Table I) 15 are sampled at bottoms characterized as deposition bottoms for continuous accumulation of fine material, i.e. sites G2, G4, G5, G6, G7, G8, G9, G11, G14, G14a, G16,

TABLE I The sampling site coordinates in the Gulf of Riga and a brief sediment description

Station	*Position (Decca)*	*Depth (m)*	*Temp. (°C)*	*Sediment description*	*Sampling date*
G1	N57°06′45″ E23°57′30″	27	2.2	sandy aleurite, light brown down to 2 cm	19.06.91
G2	N57°10′30″ E23°56′0″	40	2.1	aleuritic mud, light brown down to 1.5 cm	19.06.91
G4	N57°17′40″ E23°50′50″	42	3.2	mud, light brown down to 6.5 cm	18.06.91
G5	N57°23′18″ E23°28′30″	44	3	sandy-mud, light brown down to 4.5 cm	17.06.91
G6	N57°24′30″ E23°45′45″	44	1.9	mud, light brown down to 3 cm	18.06.91
G7	E57°26′30″ E24°07′10″	41	2	mud, light brown down to 4.5 cm	18.06.91
G8	N57°35′30″ E23°18′30″	44	3.1	mud, light brown down to 1.1 cm	17.06.91
G9	N57°36′45″ E23°37′0″	54	2.1	mud, light brown down to 4 cm	17.06.91
G10a	N57°42′6″ E23°21′6″	28	12.1	fine sand (2.5 cm) on stiff clay	30.07.93
G11	N57°42′0″ E23 55′0″	41	1.8	mud, light brown down to 5 cm	18.06.91
G12	N57°45′20″ E24°09′15″	27	3.5	sandy aleuriteon stiff clay light brown down 1.5 cm	18.06.91
G14	N57°50′7″ E23°28′0″	50	1.9	mud, light brown down to 3.2 cm	17.06.91
G14a	N57°46′5″ E23°44′0″	42	2.5	muddy aleurite, light brown down to 1.5 cm	30.07.93
G15	N57°48′8″ E23°54′45″	32	1.7	sandy aleurite, light brown down to 3 cm	18.06.91
G16	N57°56′35″ E22°46′15″	34	4	sandy mud, light brown down to 2 cm	17.06.91
G18	N58°11′45″ E23°24′30″	27	7.4	aleuritic sand	18.06.91
G21	N57°28′4″ E23°09′7″	36	2.6	fine sand (0.5 cm) on muddy sand	31.07.93
G22	N57°09′75″ E23°41′78″	38	2.6	mud, light brown down to 2 cm	31.07.93
G120	N57°25′0″ E23°55′0″	43	2.1	mud, light brown down to 2 cm	28.07.93
T2	N57°14′0″ 24°06′0″	35	4.2	aleruiteic mud on sandy mud, light brown down to 1.5 cm	28.07.93
T3	N57°30′0″ E24°06′0″	43	3.6	mud, light brown down to 2 cm	28.07.93
T5a	N57°42′0″ E22°57′4″	32	4.2	aleuritic sand on stiff clay	29.07.93
T6	N57°20′0″ E23°20′0″	45	2.4	sandy aleruite, light brown down to 1 cm	29.07.93

G22, G120, T2, and T3. The other sites are sampled at transitional bottoms (G1, G15, G18 and T6) and erosion or nondepositional bottoms (G10a, G12, G21 and T5). The results and discussions regarding the spatial distribution of

BSi originate from data from the uppermost level (i.e. 0-1 cm below seafloor; Table II).

As expected, the surficial (0-1 cm) sediments in depositional areas always contain greater concentrations than in transitional and erosional areas. Thus, in areas with infrequent or lack of sedimentation of fine material the concentration of BSi is low (100-600 μmol/g). The highest concentrations at accumulation bottoms (with an upper limit of around 1.5 mmol/g) are found at sites in the central muddy part of the Gulf (e.g. G6, G9, G120, G11, G22). This may be attributed to differences in sedimentation rates, productivity, halmyrolysis or diagenesis between the different site locations. However, a weak correlation between concentration of BSi, distance from the main nutrient source (e.g. river Daugava), small variations of parameters affecting the dissolution of BSi during halmyrolysis (salinity, temperature, water depth etc.), and surface sediment properties (mineral composition, oxygen condition, salinity and temperature) between accumulation sites suggest that the MAR largely determines the surficial concentration found at each site. This conclusion supports the fact that the two main environmental factors (salinity and temperature) that affect the dissolution of BSi almost always exhibit values outside the ranges where it has been shown to greatly alter its dissolution rate (Yamada and D'Elia, 1984), i.e. the salinity and temperature seldom exceed 10‰ and 15°C, respectively. Furthermore, the measured C_{org}/BSi ratios within different accumulation sites in the Gulf of Riga justify the importance of variation in MAR on the concentration of BSi. This is because the highest C_{org}/BSi ratios (>3.8) are found at sites close to the outflow of river Daugava (e.g. G1, G4, G22, G120, T2) and at accumulation sites close to transition areas in the northern part of the Gulf (G14, G14a, G15) while the lowest (<3.8) are found at sites in the central part of the Gulf (G5, G6, G8 and G9). Thus, accumulation bottoms adjacent to transition areas are supplied with a larger amount of allochthonous and resuspended material diluting settled amount of BSi. Additionally, recent sedimentation rate estimates (^{210}Pb) from a variety of sites in the Gulf of Riga (B. Larson, pers. com.) affirm that variations in the sedimentation rate are of great importance for the surface concentration of BSi. This is because the distribution of BSi in surficial accumulation sediments roughly appears to vary inversely with the estimated sedimentation rate. The large significant differences in the MAR for the sediment surface concentration of BSi has also been emphasized by Conley *et al.* (1986) and Pattan *et al.* (1992). Conley *et al.* (1986) suggest that the concentration of BSi in the sediment of Lake Michigan varies inversely with the sedimentation rate, mainly due to that enhanced portion of allochthonous material diluted by diatom frustules in sites near the coast. This was also concluded by Pattan *et al.* (1992) to be the case in the Indian Ocean sediments even though the authors also stressed the variations created in productivity and preservation of siliceous tests.

Much lower C_{org}/BSi ratios (Figure 2) are found in the topmost layer at sites in transitional and erosion areas which suggests that dissimilarities between the dissolution rate of BSi and the microbial breakdown of organic carbon are of significance during enhanced diagenesis if the bulk settled material during that time were not of completely different composition than found currently.

The average concentration of BSi found in present study (1.1 mmol/g or 3.1% d.w.) is about two times higher than what is reported to be an average value for the entire open Baltic Sea (Lisitzin, 1972; Emelyanov, 1988). This is most likely caused by higher diatom production in the Gulf of Riga than the average in the open Baltic Sea. Diversity in water depth between the Gulf of Riga and the open Baltic proper could also partly explain the differences since it is well known that the most labile part of BSi rapidly releases during

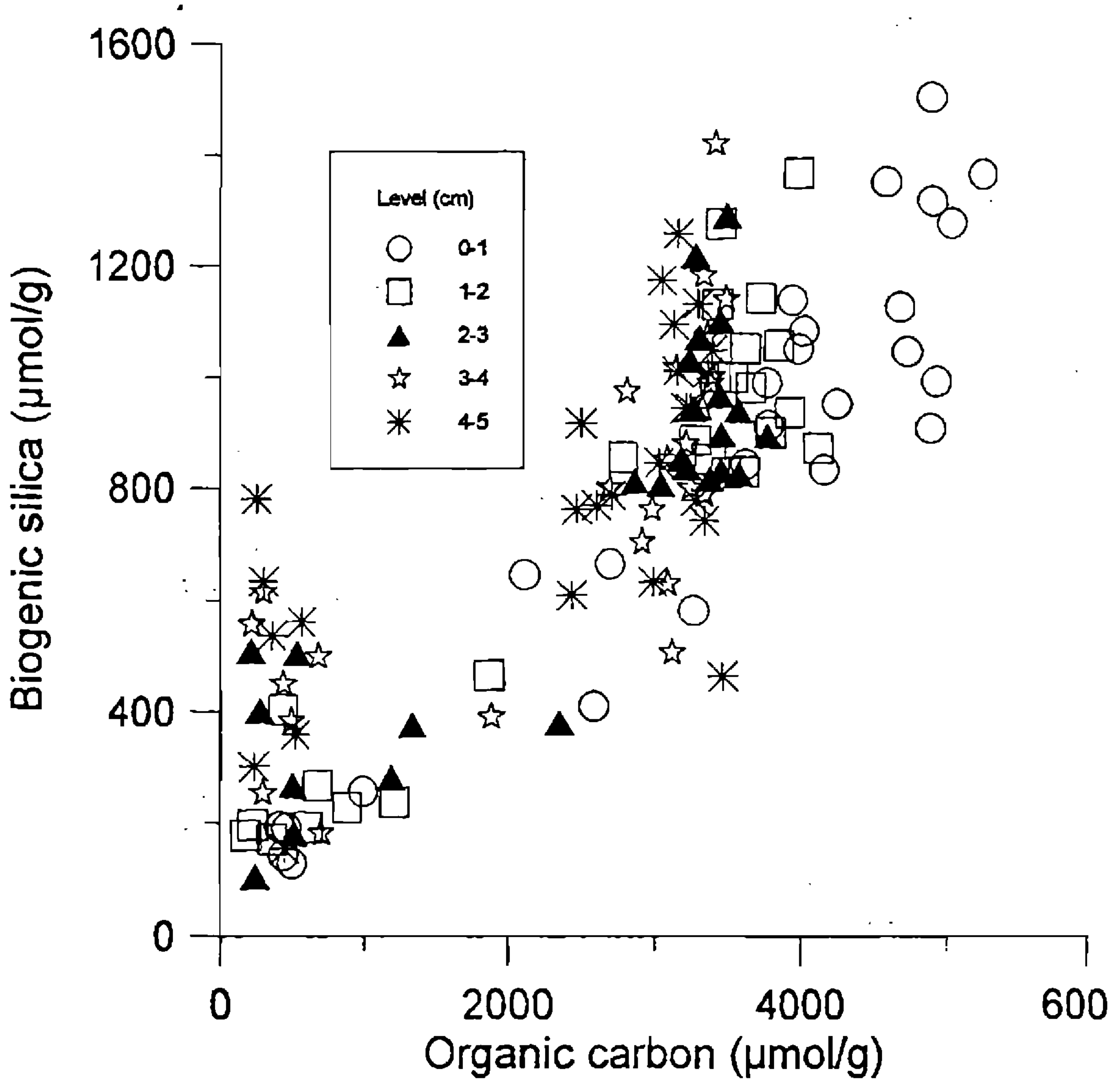


FIGURE 2 Relationship between the concentration of organic carbon and BSi.

halmyrolysis (Skjodal and Wassmann, 1986; DeMaster *et al.*, 1992; Thunell *et al.*, 1994). The concentration of BSi in the Baltic region is in the lower range compared to other marine environments (DeMaster, 1981).

Vertical Concentration Trends of BSi

The vertical concentration trend of BSi at all accumulation bottom sites, except site G14a, exhibits a sharp initial decrease (down to 2-6 cm below seafloor) followed by a leveling off of concentration (Table II). The uniform concentration occurred closer to the sediment-water interface at accumulation bottoms in the central muddy part of the Gulf (2-3 cm below seafloor) than at similar bottoms closer to transition areas. Thus, the differences between depth below seafloor and observed uniform concentrations of BSi between different accumulation bottom areas are most likely correlated to the MAR at each site, i.e. elapsed time between settling and final burial content is similar at all kinds of accumulation bottoms. Site G14a represents an exception from the general vertical pattern of BSi with almost an even concentration throughout the sediment profile. This may be attributed to intense bioturbation in that area. The vertical BSi concentration trends at transition bottoms exhibit an initial decrease followed by an increase below 2-3 cm below seafloor (except at site G15 where the concentration decreases with increasing depth below seafloor throughout the profile). The vertical concentration trend of BSi at erosion bottoms exhibits constant increasing concentration with increasing depth below seafloor.

The observed main vertical concentration trends at sites from accumulation areas reflect the kinetics of the diagenetic silica acid regeneration of deposited BSi. It also suggests that permanent silica storage occurs somewhere between 2-6 cm below seafloor or about 5-15 years after settling (according to recent ^{210}Pb measurements). The decrease in the BSi concentration normally ranges between 100-400 μmol/g (on average about 200 mol/g or 20% of surface concentration). Thus, it would appear the major parts of the BSi entering the sediment surface are permanently buried. The vertical BSi trends at sites in transitional and erosional areas reflect prevailing sedimentation conditions with low concentrations in sections with dominance of sand and gravel (no deposition of fine material) and higher concentrations in the sections containing finer material such as stiff glacial clay (indicating a former accumulation area).

The general vertical trends of the C_{org}/BSi ratio at all bottoms decrease with increased burial depth. The decrease of the ratio is especially pronounced at transition and erosion bottoms. The lowest ratios were found in the glacial

TABLE II Vertical organic carbon (ORG-C; μmol/g), biogenic silica (BSi; μmol/g) and loss on ignition (LOI; % d.s.) figures from the different sites

Site	*Slice*	*ORG-C*	*BSi*	*LOI*	*Site*	*Slice*	*ORG-C*	*BSi*	*LOI*
G1	1	2576	409	7,3	G9	1	4915	1318	17,0
	2	878	227	2,8		2	3732	1142	14,6
	3	2347	378	8,0		3	3455	1101	13,8
	4	3127	506	10,7		4	3496	1140	13,5
	5	2998	634	11,8		5	3306	1132	12,9
G2	1	5268	1366	17,4	G10a	1	484	129	1,7
	2	3938	937	14,1		2	173	177	0,7
	3	3465	896	13,4		3	204	509	1,8
	4	3348	789	12,9		4	288	614	3,3
	5	3290	778	12,0		5	348	537	5,8
G4	1	3999	1052	15,4	G11	1	3774	991	13,6
	2	3666	981	14,6		2	3288	886	12,3
	3	3584	826	14,1		3	3190	851	11,9
	4	3388	989	13,8		4	2992	761	11,2
	5	3372	1008	13,4		5	2704	787	10,4
G5	1	3950	1346	14,7	G12	1	450	191	1,1
	2	3422	1229	13,7		2	220	196	0,8
	3	3250	1082	12,7		3	264	402	2,0
	4	2809	1074	11,5		4	208	557	3,0
	5	3142	1078	11,9		5	245	781	4,5
	6	2796	1063	10,4	G14	1	5048	1278	17,0
	7	2186	963	10,6		2	3434	1130	13,5
	8	2078	954	10,6		3	3317	1072	13,0
	9	2103	957	10,3		4	3162	1016	12,6
	10	2133	1012	10,4		5	3166	1011	12,9
G6	1	4603	1352	16,1	G14a	1	3627	843	12,2
	2	3460	1276	13,7		2	3388	853	11,3
	3	3290	1218	13,3		3	3228	838	11,0
	4	3343	1184	13,0		4	3095	851	11,0
	5	3061	1174	12,5		5	3041	845	11,3
G7	1	4035	1083	14,0		6	3310	809	11,1
	2	3542	1000	12,9		7	3351	864	11,2
	3	3275	944	12,0		8	3313	868	11,0
	4	3226	880	11,6		9	2777	809	10,5
	5	2498	916	9,5		10	2068	630	8,9
G8	1	4911	1505	16,9	G15	1	2690	666	9,4
	2	3998	1368	14,4		2	1878	464	7,3
	3	3500	1290	13,4		3	1336	375	4,9
	4	3426	1421	13,5		4	693	182	2,5
	5	3172	1258	12,3		5	436	154	1,6
G16	1	3791	914	13,0	T2	1	4176	833	13,2
	2	2784	855	10,7		2	3616	729	12,5
	3	2868	813	10,7		3	3460	699	12,3
	4	2688	801	10,6		4	3098	630	10,9
	5	2466	761	10,0		5	2432	609	8,7
G18	1	987	257	3,6		6	2267	479	8,6
	2	600	192	2,2		7	2454	502	8,5
	3	502	181	1,9		8	2096	437	7,9
	4	428	450	3,1		9	2004	436	7,5
	5	293	634	4,5		10	1955	456	7,8

TABLE II *(Continued)*

Site	*Slice*	*ORG-C*	*BSi*	*LOI*	*Site*	*Slice*	*ORG-C*	*BSi*	*LOI*
G21	1	423	143	1,3	T3	1	4902	909	16,4
	2	348	170	1,2		2	3498	827	15,0
	3	489	267	2,2		3	3052	807	13,1
	4	483	383	2,7		4	2918	705	12,2
	5	514	359	3,0		5	2602	769	11,2
G22	1	4938	994	15,7		6	2575	699	10,1
	2	3807	901	12,5		7	2203	748	9,7
	3	3386	816	11,5		8	2083	743	9,7
	4	3258	801	11,3		9	2135	762	9,8
	5	3349	742	11,2		10	2014	685	9,3
	6	3220	684	10,3	T5a	1	403	193	1,2
	7	3146	763	10,6		2	423	403	1,7
	8	3098	762	10,6		3	525	506	3,2
	9	2746	686	9,9		4	678	500	4,0
	10	2654	647	9,6		5	555	562	3,8
G120	1	4743	1047	16,1	T6	1	2121	646	6,1
	2	4134	972	14,2		2	668	267	2,1
	3	3581	940	13,1		3	231	105	0,9
	4	3334	944	12,6		4	285	253	1,2
	5	3226	944	12,8		5	227	301	1,7
	6	3148	908	12,5					
	7	2984	932	12,0					
	8	2917	888	11,5					
	9	2884	862	11,3					
	10	2723	913	10,4					

clay part at erosion bottoms (down to 0.3). It shows that the diagenetic microbial degradation of the bulk organic carbon concentration (e.g. diatoms and flagellates) proceeds faster and different from the dissolution of BSi, independent of variations in the MAR and biogeochemical properties. Although a relatively high coefficient of determination is obtained by comparing all measured concentrations of C_{org} and BSi (Figure 2; $R^2 = 0.77$), it could clearly be seen that the ratios obtained from transition/erosion and from accumulation areas vary considerable both between these three bottom categories and also between sites located within accumulation areas ($R^2 = 0.32$). It thus confirms that the dissolution of BSi and degradation of C_{org} are separate and of different magnitude, irrespective of bottom environment. Fractionated separation, both during halmyrolysis and diagenesis, between BSi and organic carbon has also been emphasized by Martin *et al.* (1991) and DeMaster *et al.* (1992). Further, the obtained bulk sediment C_{org}/BSi ratios are always lower than the average in living diatoms (i.e. 7.7, Brzezinski, 1985) which additionally confirms that the breakdown of organic carbon proceeds faster than the dissolution of BSi, irrespective of variation in productivity and sedimentation rate between silicon and non-silicon carrying organisms.

The differences between dissolution rate of BSi and microbial degradation of organic carbon disallow one to be calculated form the other (Figure 2). Irrespective of bottom type and burial depth, a better coefficient of determination is obtained by comparing the concentration of BSi with the poorly defined chemical quantity loss on ignition (LOI) ($R^2 = 0.89$; Figure 3). The LOI content is normally used as a qualitative measure of the organic content of the sediment, despite the well known fact that chemically bound water and other void compounds normally evaporate to some extent during combustion. However, even though LOI does not represent a well defined quantity, it is a very commonly measured quantity in practically all kinds of sediment investigations (e.g. the large sediment investigations performed by Estonian and Latvian Geological Survey; Juškevi s *et al.*, 1993; Raudsep *et al.*, 1993) and could, thus, be used to estimate the concentration of BSi with precision. This will pave the way for the use of old sediment data which lacks measurements

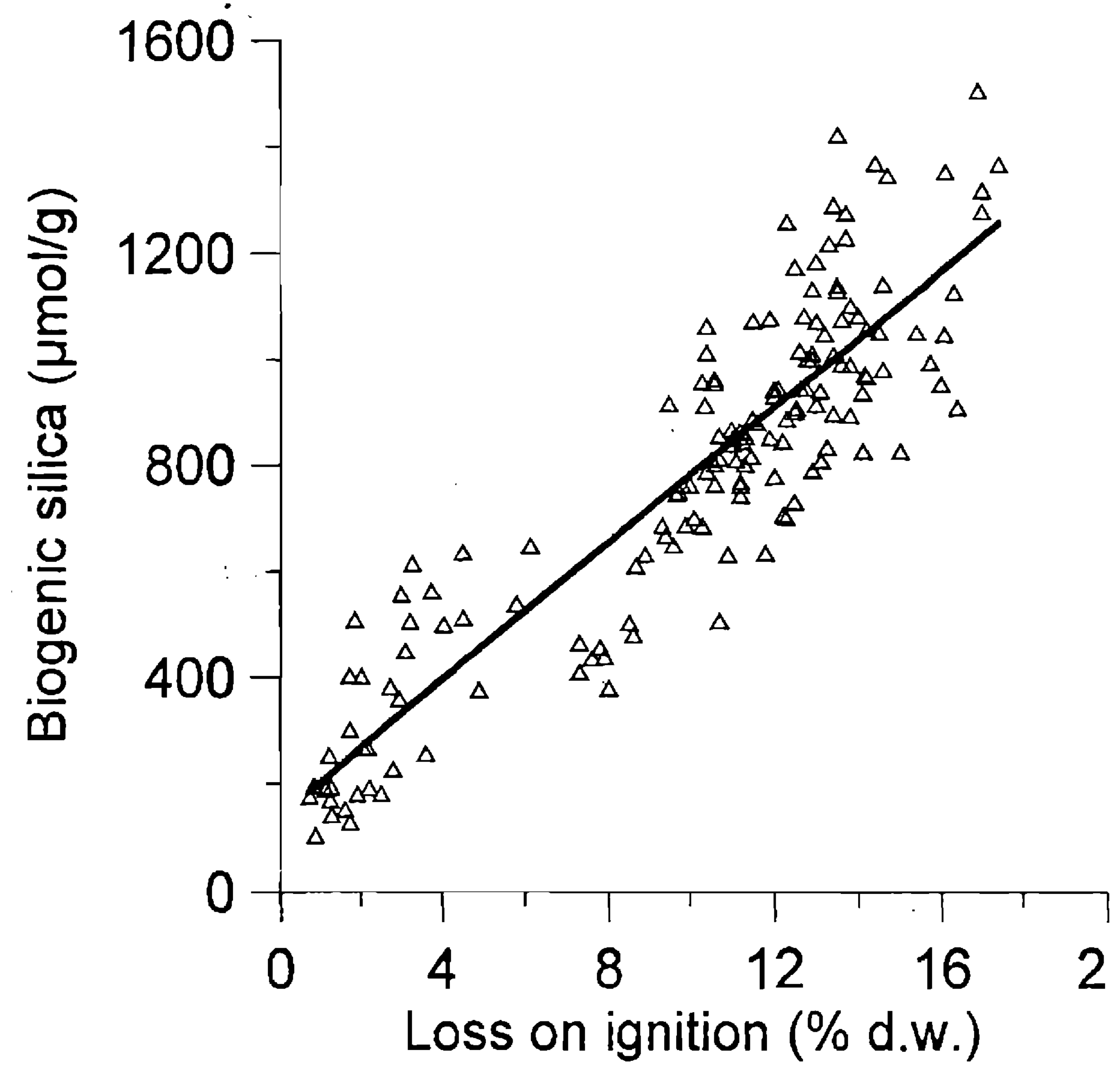


FIGURE 3 Relationship between the loss on ignition (LOI) and the concentration of BSi. The linear regression line drawn in the figure has a coefficient of determination (R^2) of 0.89.

of BSi, to improve the accuracy of future silica transformation budgets and calculations of distribution and annual burial amounts of the sediments.

Estimation of Annual Sequestering of BSi

As has been mentioned earlier, silica acid regeneration and flux from the sediment is governed mainly by variations in chemical composition and temperature of the solution. However, it has also been shown that the dissolution rate of BSi with respect to salinity and temperature are only of major significance in salinity ranges between 10 and 20‰ and temperatures above 15 °C (Yamada and D'Elia, 1984). If this is also true for the Gulf of Riga, variations in salinity and temperature between the different accumulation sites can be neglected since they normally are below 10‰ and 15 °C, respectively. Thus, the only remaining diagenetic factor that may affect the dissolution of BSi is when silica attached to ferric complexes releases simultaneously with the dissolution of solid ferric complexes during redox shifts. However, as has been stated earlier, BSi normally reaches uniform concentrations between 2–6 cm below seafloor, i.e. hardly ever above the transition zone between oxidized and reduced conditions (Aigars, unpublished data). Therefore, based on the general vertical concentration pattern with a uniform concentration somewhere between 2–6 cm below seafloor, an estimate of total annual sequestering of BSi can be made by calculating average amount (moles/area) of BSi from levels beneath the redox boundary layer.

We have subdivided the accumulation bottoms in the Gulf into two different categories. First, accumulation bottoms located in the central muddy part of the Gulf with C_{org}/BSi ratios below 3.8 and with a uniform concentration 2–3 cm below seafloor. Second, accumulation bottoms closer to transitional areas with a higher sedimentation rate, with C_{org}/BSi ratios larger than 3.8 and with a uniform concentration deeper than 5 cm depths below seafloor, i.e. average concentrations are taken only from sites where the slicing depth exceeds 5 cm (G14a, G22, T2 and T3). The sedimentation rate estimates done by Kuptzov *et al.* (1984) suggest a sedimentation rate of 2.2 mm/year (consolidated sediment) close to transitional areas and about one mm/year at accumulation bottoms in the central part of the Gulf. These sedimentation rates are comparable with recent estimates (^{210}Pb). From these figures the average sediment weight/m^2 (using bulk densities; Richards *et al.* 1974) is estimated at 0.65 and 0.23 kg for sediment adjacent to transition areas and accumulation bottoms in the central part of the Gulf, respectively. Based on an estimate of the total amount of fine grained sediment material deposited in the Gulf of Riga the mean long term accumulation rate is estimated at 0.285 kg m^{-2} yr^{-1}.

This agrees with the estimate above but on the low side compared with recent ^{210}Pb determinations. Nevertheless, based on a sedimentation rate of 0.65 and 0.23 kg m^{-2} yr^{-1} and a mean final burial concentration of BSi of 650 and 900 μmol g^{-1} for accumulation bottoms close to areas with high resuspension activity and accumulation bottoms in the central part of the Gulf, respectively, we can calculate that 423 and 207 mmol m^{-2} on average are finally buried in these two different types of accumulation environments. The total area of accumulation bottoms covers about 30% (5700 km^{-2}) of the total seafloor area and approximately half of this area represents accumulation bottoms adjacent to areas with high resuspension activity. Thus, the average total net sink of BSi is 50 300 ton yr^{-1} of which the main part (67%) is buried outside the central muddy part of the Gulf. It represents around 60% of the total annual average runoff of silica (estimated from the figures given by Andrushaitis *et al.* (1995) on average annual runoff values of water and silica). The remaining amount should thus be exported to the Baltic proper.

CONCLUSIONS

The highest concentration of BSi is found at accumulation bottoms in the central muddy part of the Gulf. The concentration at accumulation bottoms seems to vary inversely with the measured MAR (^{210}Pb). Inverse dependence between the MAR and the concentration of BSi agrees with lower C_{org}/BSi ratios measured in accumulation bottoms close to transition bottoms supplied with comparatively larger amounts of allochthonous material that dilute settled amounts of BSi. The vertical and spatial concentration trends at transition and erosion bottoms reflect roughly prevailing sedimentation conditions with low concentrations in areas with a dominance of sand and gravel and higher concentrations in areas with A greater abundance of clay material (former accumulation site). The relatively uniform temperature and salinity between different accumulation bottom areas exclude to a large extent diagenetic affected variations in silica acid regeneration from BSi.

The surface C_{org}/BSi ratio is always lower than the average ratio in living diatoms indicating that the microbial breakdown of organic carbon during halmyrolysis and diagenesis are always faster than the inorganic dissolution of BSi, irrespective of the ratio between phytoplankton-based communities.

Permanent burial of BSi seems to occur 2–6 cm below seafloor or about 5–15 year after settling (according to recent MAR measurements). A decrease in concentration of around 20% from surface down to the uniform concentrations suggests that a dominant part of the sediment BSi is permanently buried.

The average annual burial of BSi in the Gulf of Riga has been estimated to be around 50 000 tons of which a dominant part IS buried in accumulation bottoms outside the central muddy part of the Gulf.

Acknowledgement

This work was supported by the Swedish Environmental Protection Agency, Nordic Council of Ministers, and Stockholm Marine Institute (SMF).

References

A. Andrushaitis, Z. Seisuma, M. Legzdina and E. Lenshs (1995) "River load of eutrophying substances and heavy metals into the Gulf of Riga". In: E. Ojaveer, *Ecosystems of the Gulf of Riga between 1920 and 1990*, (Estonian Academy Publishers. Tallin,. Estonia), pp. 32-40.

R. A. Berner (1971) *Principles of chemical sedimentology*, (McGraw-Hill Book Company).

S. Blomquist and B. Abrahamsson (1985) "An improved Kajak-type gravity core sampler for soft bottom sediments". *Schweizerische Zeitschrift für Hydrologie*, **47**, 81-84.

M. A. Brzezinski (1985) "The Si:C:N ratio of marine diatoms: interspecific variability and effects of some environmental variables". *J. Phycol.*, **21**, 347-357.

D. Conley and T. L. Newberry (1989) "Extraction of sediments for biogenic silica", *Horn Point Env. Lab., Centre for Env. and Estuarine Studies*, Univ. of Maryland, Cambridge, USA.

D. Conley, C. L. Schelske, B. G. Dempsey, C. D. Campbell and T. L. Newberry (1986) "Distribution of biogenic silica in the surficial sediments of Lake Michigan". *Can. J. Earth Sci.*, **23**, 1442-1449.

D. J. DeMaster (1981) "The supply and accumulation of silica in the marine environment". *Geochim. Cosmochim. Acta*, **45**, 1715-1732.

D. J. DeMaster, R. B. Dunbar, L. I. Gordon, A. R. Leventer, J. M. Morrison, D. M. Nelson, C. A. Nittrouer and W. O. Smith Jr. (1992) "Cycling and accumulation of biogenic silica and organic matter in high-latitude environments:" *The Ross Sea. Oceanography*, **5**, 146-153.

E. M. Emelyanov (1988) "Biogenic sedimentation in the Baltic Sea and its consequences". In: B. Winterhalter (editor), *The Baltic Sea. Geol.*, Survey Finland, Special Paper, **6**, 127-135.

R. O. Fournier and W. L. Marshall (1983) "Calculation of amorphous silica solubilities at 25 °C and 300 °C and apparent cation hydration numbers in aqueous salt solutions using the concept of effective density of water". *Geochim. Cosmochim. Acta*, **47**, 587-596.

J. I. Hedges and J. H. Stern (1984) "Carbon and nitrogen determinations of carbonate-containing solids". *Limnol. Oceanogr.*, **29**, 657-663.

V. Juškevi s, O. Stiebri š and V. Baraškovs (1993) "Upper Pleistocene, Holocene deposits and bottom sediments in the Gulf of Riga". *Geological Survey of Latvia, Riga.*

V. M. Kuptzov, B. B. Seldina and T. R. Ivanova (1984) "Rate of sedimentation of sediments of the Baltic Sea". In: Lissizin (editor), *Geological history and geochemistry of the Baltic Sea. Publ.*, "Nauka", Moscow, 1984. (in Russian), pp. 110-121.

A. P. Lisitzin (1972) "Sedimentation in the world ocean", (ed. K. S. Rodolfo), *Soc. Econ.Paleo. Min. Spec. Publ.*, **17**.

J. C. Lewin (1961) "The dissolution of silica from diatom walls". *Geochim Cosmochim. Acta*, **21**, 182-198.

W. R. Martin, M. Bender, M. Leinen and J. Orchardo (1991) "Benthic organic carbon degradation and biogenic silica dissolution in the central equatorial Pacific". *Deep-Sea Res.*, **38**, 1481-1516.

T. R. Parson, Y. Maita and C. M. Lalli (1984) *A manual of chemical and biological methods for seawater analysis*. (Pergamon Press, Sidney).

A. Pastors (1967) "Water and heat balance in the Gulf of Riga". *Morskie zalivy kak priyomniki stochnykn vod. Riga, Zinātne* (in Russian), 8-20.

J. N. Pattan, S. M. Gupta, A. V. Mudholkar and G. Parthiban (1992) "Biogenic silica in space and time in sediments of central Indian Ocean". *Indian J. of Mar. Sci.*, **21**, 116-120.

J. Raudsep, J. Kask and P. Vāling (1993) "Distribution and lithological composition of modern (Holocene) marine bottom sediments in the Gulf of Riga (north of 58°N)". *Estonian Geological Survey*, Tallin.

A. F. Richards, T. J. Hirst and J. M. Parks (1974) "Bulk density-water content relationship in marine silts and clays". *J. Sed. Petrol*, **44**, 1004-1009.

H. R. Skjoldal and P. Wassmann (1986) "Sedimentation of particulate organic matter and silicum during spring and summer in Lindåspollene", *Western Norway. Mar. Ecol. Prog. Ser.*, **30**, 49-63

R. C. Thunell, C. J. Pride, E. Tappa and F. E. Muller-Karger (1994) "Biogenic silica fluxes and accumulation rates in the Gulf of California". *Geology*, **22**, 303-306.

J. S. Tribble, R. S. Arvidson, M. Lane III and F. T. Mackenzie (1995) "Crystal chemistry, and thermodynamic and kinetic properties of calcite, dolomite, apatite, and biogenic silica: application to petrologic problems". *Sedimentary Geology*, **95**, 11-37.

D. Werner (1977) "Silicate metabolism". In. Werner, D. (Ed). "The biology of diatoms". *Botanical monographs*, (University of California Press, Berkeley and Los Angeles), **13**, p. 110-149.

L. A. Williams, G. A. Parks and D. A. Crerar (1985) "Silica diagenesis, I. Solubility controls". *J. of Sed. Petrol*, **55**, 301-311.

L. A. Williams and D. A. Crerar (1985) "Silica diagenesis, II. General mechanisms". *J. of Sed. Petrol.* **55**, 312-321.

F. Wulff and L. Rahm (1988) "Long-term, seasonal and spatial variations of nitrogen, phosphorus and silicate in the Baltic: An overview". *Marine Environ. Res.*, **26**, 19-37.

S. S. Yamada and F. D'Elia (1984) "Silicic acid regeneration from estuarine sediment cores". *Mar. Ecol. Prog. Ser.*, **18**, 113-118.

A. Yurkovskis, F. Wulff, L. Rahm, A. Andrushaitis and M. Rodrigues-Medina (1993) "A nutrient budget of Gulf of Riga, Baltic Sea". *Estuarine, Coastal and Shelf Sci.* **3**, 113-127.

Paper III

Estuarine, Coastal and Shelf Science (1998) **46**, 713–722

Spatial Estimation of Nutrient Distributions in the Gulf of Riga Sediments using Cokriging

Å. Danielsson[a], **R. Carman**[b], **L. Rahm**[a] **and J. Aigars**[b,c]

[a]*Department of Water and Environmental Studies, Linköping University, S-581 83, Linköping, Sweden*
[b]*Department of Geology and Geochemistry, University of Stockholm, S-106 91, Stockholm, Sweden*
[c]*Department of Aquatic Ecology, Latvia University, Salaspils, Latvia*

Received 10 March 1997 and accepted in revised form 26 September 1997

Basinwide mass budgets and models are important tools in coastal zone analysis. Sediments play an important role, as storage, in the nutrient dynamics of these relatively shallow regions. Due to economic and practical reasons, sediment sampling is often made rather sparsely and irregularly. Most interpolation methods are therefore not suitable, as they demand a great deal of data sampled on a regular grid. Cokriging is a method that, at least in some part, overcomes these drawbacks. From a monitoring point of view it is a favourable method, as it incorporates information from additional variables, that may be more economical and more frequently sampled.

Estimates of spatial distribution and total amounts were carried out for organic carbon, nitrogen and phosphorus in the Gulf of Riga surficial sediments. Loss on ignition was included as a covariable. Using known deposition rates on the accumulation bottoms, the mean sink values of these substances were estimated and compared with previous model results. For this study, the resulting total amounts were 1 100 000, 129 000 and 14 000 tons for carbon, nitrogen and phosphorus, respectively. This leads to an annual accumulation of 5 g C m^{-2}.

Keywords: nutrients; cokriging; spatial distribution; surficial sediments; deposition

Introduction

Sediments are important in environmental studies of the coastal zone. They act as sinks and sources for both degraded/transformed organic matter and pollutants. As an example, Shaffer and Rönner (1984) showed that 80–90% of the denitrification process (which is assumed to represent the major nitrogen sink in the Baltic proper) originates from the sediments. Wulff *et al.* (1986) found that approximately 23% of the annual gross nitrogen assimilation in the Baltic proper entered the sediments. Half of it was denitrified and half was recycled. Only a minor portion was sequestered.

In most monitoring programmes, sediment samples are taken irregularly and sparsely over a chosen area, often without a well-defined sampling strategy/design. Sandén and Danielsson (1995) showed that the most commonly used hydrographic stations in the Baltic Sea cannot be seen as representative for their subbasin. Their investigation was concerned with the conditions in the water mass, but the situation is similar for the sediments, where the sampling generally is limited to only a few bottom types.

Sediment sampling is usually restricted to soft (accumulation) bottoms, where it is possible to use some kind of gravity sampler. The use of grab samplers allows sampling at other bottom types, but the vertical resolution deteriorates. Transport and erosion bottoms (Håkansson & Jansson, 1983) are examples of undersampled regions for measurement of reliable vertical concentration profiles. Consequently, sampling often results in a skewed picture of reality. It would be helpful for monitoring programmes if additional information could be embraced to improve the estimates. By doing so, a more thorough picture of nutrient conditions can be obtained. These additional variables are especially interesting if measured more frequently in a spatial sense. Physical variables (e.g. water depth), hydrographic observations (e.g. salinity) or sediment characteristics (e.g. loss on ignition) could all be included in the analysis. In addition to having high sampling frequency, they are often closely coupled to element concentrations in sediments, and are significantly less expensive to obtain.

Most marine studies concerning modelling and budget calculations are built upon sparse data sets. Total amounts are estimated for entire basins using the mean concentration from just a few stations (e.g. Carman & Wulff, 1989) or some sort of interpolation routine, with no consideration taken to spatial dependence (e.g. Wulff & Rahm, 1988).

0272–7714/98/050713+10 $25.00/0/ec970295

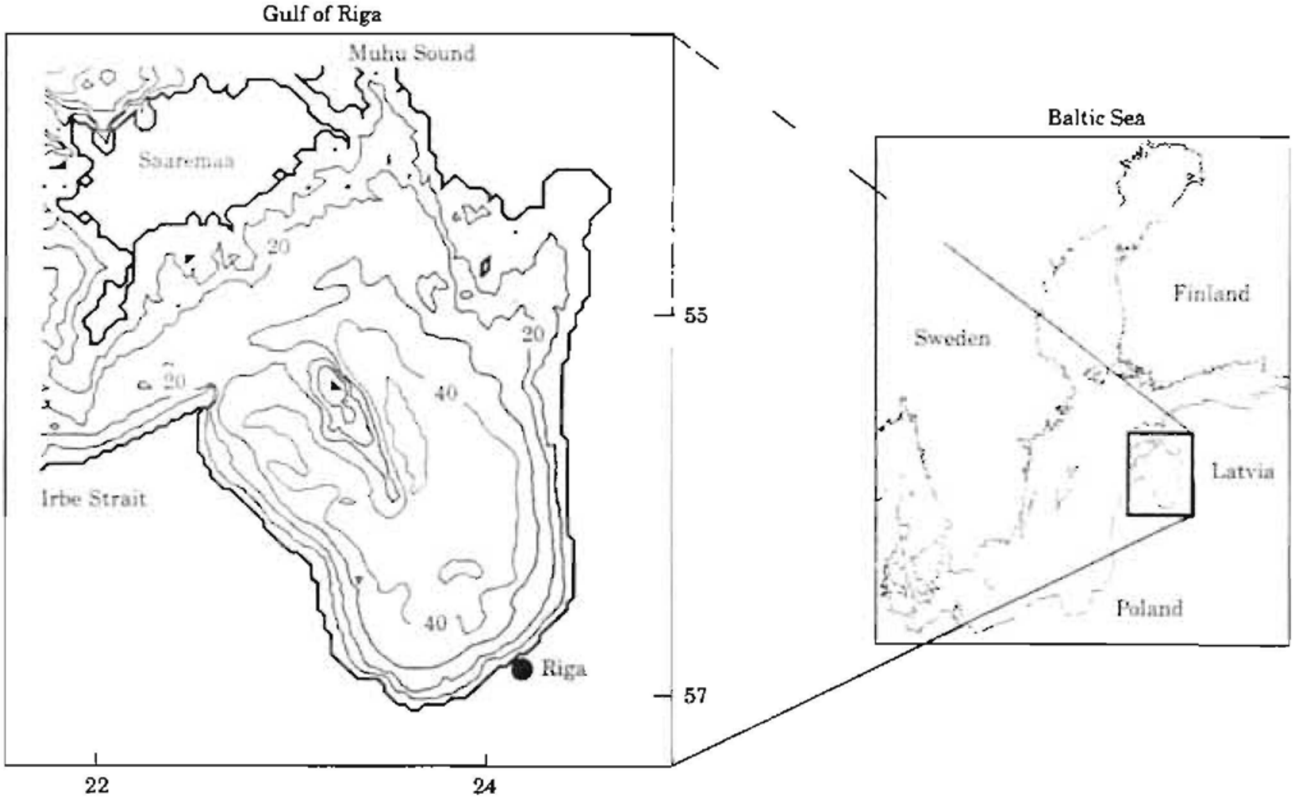


FIGURE 1. The Baltic Sea with the Gulf of Riga. Isolines indicate depth in metres.

Another common weakness in most interpolation methods, with the exception of kriging, is the lack of uncertainty calculations, making it difficult to judge the value of the outcome. To overcome this problem, an attempt to interpolate the concentration of organic phosphorus in sediments using a geostatistical method, cokriging, has been reported by Danielsson (1994).

The aims of this study are to estimate the surficial spatial distribution and standard deviation for organic carbon, nitrogen and phosphorus in the Gulf of Riga sediments, and to calculate the net sink for each respective substance. By combining these estimates with existing nutrient budget calculations, ' new ' information about processes involved is obtained. These sinks are compared to previous estimates, based on only a few observations. The real advantage of cokriging, compared to other interpolation routines, including other kriging techniques, is the inclusion of covariables. This means that one may improve estimates with additional information from variables that are easier and cheaper to measure. When calculating the total amount of each substance being accumulated in the sediments, the entire concentration fields are used instead of, as usually, only the mean concentration of a few stations.

Gulf of Riga and data material

Physics and hydrogeochemistry of the Gulf

The Gulf of Riga is located on the eastern side of the Baltic Sea (Figure 1). This basin is rather shallow (area = 18 000 km^2, volume = 406 km^3), with a maximum and mean depth of 51 and 23 m, respectively. The islands of Muhu Sound and Archipelago and the large island of Saarema separate it from the Baltic proper. There are two sounds, the northern Sound of Muhu (mean depth of 5 m) and the southern Sound of Irbene (maximum depth of 35 m and a mean width of 30 km). The water exchange is rather limited. Petrov (1979) estimated the annual water exchange to approximately 360 km^3, i.e. a residence time of almost 1 year. This exchange occurs mainly through the souhern sound and primarily during wintertime (Pastors, 1967).

There is a large seasonal variation for most physical and geochemical variables in the Gulf. During autumn and winter the Gulf is well mixed and homohaline (4–7), except at the Sound of Irbene and close to the river mouths (Berzinsh, 1980). A residual circulation exists, southwards along the west coast and northwards on the eastern side of the Gulf (Yurkovskis *et al.*, 1993). During summer there is a strong thermal stratification, which later is mixed by the autumn winds. Oxygen concentrations near the bottom increase during winter and spring to decrease in summer. This is mainly an effect of the degradation of deposited organic matter and a thermal control of turbulent vertical mixing (Berzinsh, 1980).

According to the classification of Vollenweider (1968), the Gulf is categorized as eutrophic. The major inputs, to the Gulf, come from rivers, coastal municipalities and diffuse sources, e.g. the atmosphere (Yurkovskis *et al.*, 1993). The drainage covers an area of 135 700 km^2, where the major part is forested (38%) and only 0·1% is classified as urban areas (Sweitzer *et al.*, 1996). The two main rivers are the Daugava and Lielupe. Grimvall *et al.* (1991) calculated the total river load for 1989 to be 71 300 tons of inorganic nitrogen and 1850 tons of total phosphorus. In the same year, the dominating point source, the city of Riga (population of ~910 000), contributed with approximately 4600 tons of total nitrogen and 690 tons of total phosphorus (Yurkovskis *et al.*, 1993). The annual atmospheric deposition is about 16 000 tons of inorganic nitrogen and 300 tons of organic phosphorus (Yurkovskis *et al.*, 1993). The nitrogen load (approximately 0·36 mol m^{-2} year^{-1}) will be significant for this limited area. It may be compared with the corresponding loads to the Baltic Sea and Chesapeake Bay of 0·22 and 0·94 mol m^{-2} year^{-1}, respectively (Nixon *et al.*, 1996). For phosphorus the load (5 mmol m^{-2} year^{-1}) is close to one of the entire Baltic Sea (4 mmol m^{-2} year^{-1}), but well below that of Chesapeake Bay (41 mmol m^{-2} year^{-1}).

The Gulf has a high N:P ratio (20:1 wintertime and 50:1 during productive seasons) suggesting phosphorus is the limiting nutrient for primary production. Yurkovskis *et al.* (1993) also showed that the Gulf has a large internal sink (of sedimentation and denitrification) for inorganic nitrogen, >75% of the total load. They found hardly any deposition of total phosphorus, probably a result of export as particulate matter to the Baltic proper. Together, the riverborn and point loads of inorganic nitrogen to the Gulf represents over 30% of the total load to the Baltic proper (Rosenberg *et al.*, 1990).

Dahlberg *et al.* (1995) set up a prediction model concerning the turnover of phosphorus and nitrogen. Their model showed that a reduction of phosphorus input to the Gulf would result in an increased net export of nitrogen to the Baltic proper. This would result in an increase of the Baltic eutrophication, although the conditions in the Gulf would improve. On the other hand, a moderate reduction in the nitrogen load would not change the conditions in the Gulf significantly. This shows that a proper estimate of the fate of nutrient loads to the Gulf is not only of local interest, but also of regional importance.

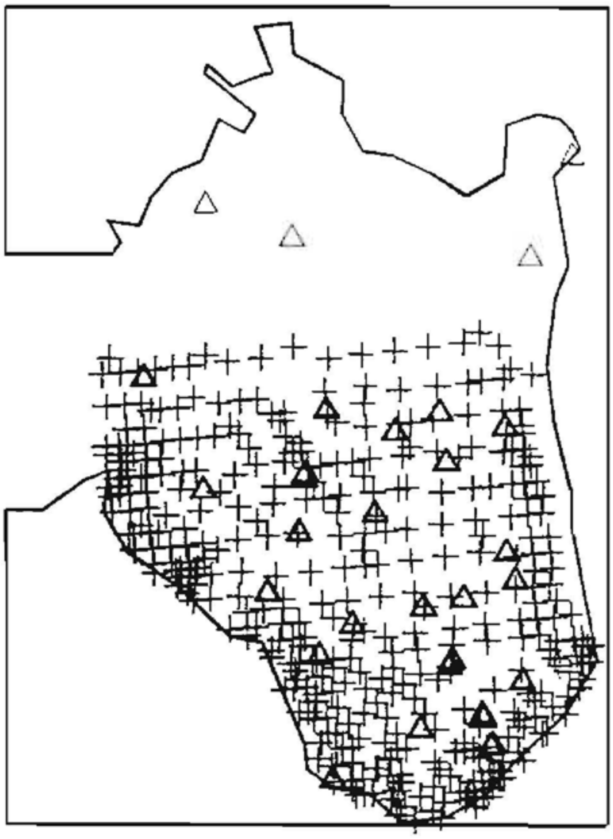


FIGURE 2. The Gulf of Riga showing the positions of the sampling stations. (+) denote digitized stations from maps and (△) the sampled stations. No samples in the northern part, as this area is Estonian territory.

Data

Thirty-one sediment cores were sampled in the summers of 1991 and 1993 by Latvian ships (Figure 2). Twenty-six of these cores were divided into five layers (0–1, 1–2, . . ., 4–5 cm below sediment surface), while the other five consisted only of one layer. In addition, data from 386 locations with loss on ignition data was available. These data were extracted from maps obtained from the Nordic Council of Minister's project ‘ Gulf of Riga ’. There is a lack of data in the northern part of the Gulf as this is Estonian territory. In these maps values were given for the top 2 cm and therefore this interval was chosen for the present study. Those cores, with 1 cm layers, were weighted to account for the top 2 cm, using weights considering the amount of organic substance in the sediment for each of the two layers.

TABLE 1. Descriptive statistics

Variable	Mean/Median	SD	*n*
C_{org}	29·79/41·71	20·48	31
N_{org}	3·19/4·42	2·28	31
P_{org}	0·38/0·31	0·29	31
LoI	4·65/2·58	4·73	31+386

Mean/median are given in mg g^{-1}, except for LoI which is given in percent, all of them dry weight.
n denotes the number of observations. Note that LoI includes the 31 stations as well as the 386 digitized. SD, standard deviation.

The inorganic concentrations of carbon, nitrogen and phosphorus were estimated by standard methods (Hedges & Stern, 1984; Mackin & Aller, 1984; Froelich *et al.*, 1988). Organic carbon (C_{org}), nitrogen (N_{org}) and phosphorus (P_{org}) were calculated by difference to their total amounts (Hedges & Stern, 1984; Froelich *et al.*, 1988). The water content (WC) was measured by drying the sediment at 80 °C to constant weight. LoI was measured after heating the sediment samples to 500 °C during 2 h. For a closer description of the chemical analysis see Carman *et al.* (1996). Descriptive statistics for each of the variables are shown in Table 1.

Methods

Spatial interpolation

Cokriging was used for spatial interpolation. It is an interpolation method derived from kriging, which is an optimal, in the sense of being a best linear unbiased estimator, interpolation method (see e.g. Cressie, 1993). In cokriging, additional information from other variables, so called covariables, are incorporated into the analysis.

There are two situations when cokriging usually provides better estimates than most other interpolation methods—the undersampled and the isotropic case. In the first case (Myers, 1982) the primary variable is measured sparsely and additional, highly correlated, data are sampled also at additional locations. By including these stations the area is spatially better covered and more information is gained. Isotropic means that more than one variable is measured at every spatial location. The latter situation is common in for example sediment samples, where more than one variable is usually analysed for each core. Yates and Warrick (1987) showed that if the correlation coefficient between a primary variable and the covariable exceeds 0·5 the inclusion of the covariable is favourable, and cokriging performs better than kriging.

The concentrations $Z(s)$, can be described by the model:

$$Z(s)=\mu+\sum_{i=1}^{n}\delta_i(s) \qquad (1)$$

where s denotes the spatial location of the sample, υ is a vector containing the unknown large scale variations, $\delta_i(s)$ denotes the small scale fluctuation for variable i and n is the number of observations. As seen above, μ is independent of s, i.e. the model does not account for any major spatial trends, so-called drifts. Instead it assumes one overall concentration, except for some smaller deviations dependent on the spatial location.

The aim for cokriging is to estimate the concentration at some locations where no observations exist. For this, a weighted linear estimator (Cressie, 1993) is used:

$$Z_i(\mathbf{s}_0)=\sum_{k=1}^{M}\mathbf{u}_k Z_i(s)+\sum_{l=1}^{P}\mathbf{v}_l Z_j(s) \qquad (2)$$

with conditional weights

$$\sum_{k=1}^{M}\mathbf{u}_k=1 \quad \sum_{l=1}^{P}\mathbf{v}_l=0 \qquad (3)$$

to make it unbiased, i.e. ordinary cokriging with two non-biased constraints (Marcotte, 1991). Z_i and Z_j are observed concentrations of variable i respective j. $\mathbf{s}_0$ denotes a vector of geographical positions for the estimates. **u** and **v** are the vectors of the kriging weights for each respective variable.

According the regionalization theory, two observations are assumed to have less correlation if far from each other than two closely positioned observations. This means stations geographically close to the estimation location should be given higher weights than those further away (Cressie, 1993). To decide the weights, cross-variogram functions are used. These functions describe the spatial correlation structure between different variables. The cross-variograms (and variograms when $i=j$, i.e. the correlation structure within one variable) are calculated according to (Cressie, 1993):

$$\gamma(h)_{ij}=\left\{\frac{1}{2N(h)}\sum_{p=1}^{N}[Z_i(s_p+h)-Z_i(s_p)][Z_j(s_p+h)-Z_j(s_p)]\right. \qquad (4)$$

where the h (called the lag) is the Euclidean distance between two stations. $N(h)$ is the total number of pairs at lag h (see McBratney and Webster, 1986).

To each set of cross-variograms, calculated according to Equation 4, a function was adopted, using cross-validation (Hjorth, 1994). The function chosen, was the one that best described the features of the cross-variogram *vs* lag. A spherical function (see Cressie (1993) for an overview of alternative functions) was chosen as the most suitable for all combinations,

$$\gamma(h)_{ij} = \begin{cases} 0 & h=0 \\ C_0+C_s\{(3/2)(h/a)-(1/2)(h/a)^3\} & 0<h<a \\ C_0+C_s & h\geq a \end{cases} \quad (5)$$

The nugget, C_0, is the value of the function when the lag approaches zero. This property is caused by either measurement error or where small scale variations are apparent at shorter distances than the shortest distance between measurement points. The parameter a, called the range, is the lag where a correlation is no longer apparent. The corresponding value on the variogram, C_s, is called the sill.

One of the greatest advantages of kriging as an interpolation method, is that it provides a variance estimate for each value. It can for example be used to see where the estimates are rather uncertain and thereby where extra sampling effort should be put. The cokriging variances are calculated, according to Marcotte (1991):

$$\sigma_c^2=\sigma^2-\mathrm{diag}[K_0^T{*}\tau] \quad (6)$$

where σ^2 is a vector containing the observation variances (one for each variable), K_0 is a matrix consisting of the covariances between the variables and τ is the cokriging weights matrix.

Cokriging does not account for trends. Median polish (see e.g. Cressie, 1993) was used to examine the material for drift and anisotropy, i.e. overall spatial trend and spatial trends depending on direction. No signs of any trend appeared in the present data set and no further consideration was taken.

It should also be mentioned that the data used are standardized. The reason for using standardized data and then transforming them back to original scale after cokriging, is that no variable should be given higher influence just because it had much higher concentrations.

Total amount calculations

Total amounts are often interesting information in modelling as they serve as inputs or storages. Often, mean concentrations, for only a few stations, are multiplied by the mean sediment weight and the total area to get the total amount. In this paper, the aim was to use more of the information given when estimating the total amounts to improve the accuracy and resolution.

To achieve the total amount per area unit, the concentration in each grid node obtained from the cokriging procedure, was multiplied by the dry sediment weight at each spatial location. Then to estimate the total amount these values are integrated over the accumulation bottoms. There are two reasons for why only this sediment type was used. First, the study should be comparable with previous sediment studies, where only accumulation sediments have been under consideration. Secondly, the content is only deposited on accumulation sediments, although looking at the top 2 cm does not give the true accumulation rate.

For each position, where the concentration is estimated, the sediment weight is needed. This mass content is calculated as bulk density minus water content. Bulk density is the sediment-water mixture weight per volume unit. According to Håkansson and Jansson (1983), bulk density is parameterized by:

$$\text{Bulk Density} = \frac{260}{100+1{\cdot}6*(\text{Water Content}+\text{Loss on Ignition})} \quad (7)$$

Bulk density could not be calculated in the cokriging locations, due to lack of water content estimates. Therefore, a relationship between bulk density and organic carbon, which has been observed in different environments (see e.g. Håkansson & Jansson, 1983) was used. To estimate this relation, simple linear regression was adopted, with the natural logarithm on bulk density minus water content as the dependent variable, and organic carbon as the independent one. The regression equation was determined from the 31 sampled stations, where data on both bulk density and organic carbon exists. The regression model, in exponential forms:

$$(\text{Bulk Density}-\text{Water Content}\times\text{Water Density}) = e^{-(A+B\times C_{org}+\varepsilon)} \quad (8)$$

where A is the intercept, B the slope from the regression analysis and ε the random component.

Results

The results are divided into two parts: spatial distributions of organic C, N and P; and calculation of total amounts. The first gives a description of the

Table 2. Pearson bivariate correlation coefficients

Variable	N_{org}	P_{org}	LoI
C_{org}	0·99	0·88	0·98
N_{org}		0·88	0·97
P_{org}			0·86

concentration and variance fields. The total amount, for respective substance, is compared with previous studies from the same area. They will probably give an overestimation of the sequestering as it is based on surficial sediments with only partly degraded organic matter. With a calculated time span of 1–3 decades, the degradation process will probably have reached the final stages for only the deeper parts of the investigated sediment layer. Using some additional data from the deeper sediments, it was seen that the concentration of carbon decreases about 35–50% from the surface layer (0–2 cm) to the bottom layer (9–10 cm). Nitrogen shows a similar behaviour. Phosphorus, on the other hand, shows a 50% lower concentration in the lower layer, but there bulk density is higher, i.e. from 1·08 g cm^{-3} in the surface layer to 1·19 g cm^{-3} in the bottom layer. This means that the total amounts become almost the same for both layers.

Concentration fields

Cokriging was used for estimating the spatial distribution. To see if the covariable (LoI) was suitable (correlation coefficient >0·5) the correlation coefficients between the organic substances and the covariable were calculated (Table 2). As seen, the correlation between LoI and each of the three substances was high and LoI was seen as an appropriate covariable. For each substance the concentration was estimated according to Equation 2, with LoI as covariable:

$$
\begin{aligned}
C_{org}(s_0) &= \sum_{k=1}^{M} u_k\, C_{org}(s) + \sum_{l=1}^{P} v_l\, \mathrm{LoI}(s) \\
N_{org}(s_0) &= \sum_{k=1}^{M} u_k\, N_{org}(s) + \sum_{l=1}^{P} v_l\, \mathrm{LoI}(s) \qquad (9) \\
P_{org}(s_0) &= \sum_{k=1}^{M} u_k\, P_{org}(s) + \sum_{l=1}^{P} v_l\, \mathrm{LoI}(s)
\end{aligned}
$$

To determine the weights (u_i and v_j) the cross-variogram functions were estimated, using Equation 5. The characteristics of the various cross-variogram functions are presented in Table 3. It may seem unrealistic to have nugget values of zero for all variograms, but due to a lack of data, it was difficult to get a good picture of the nugget effect—except for LoI. Therefore, the nugget was assumed to be zero. As seen, the correlation lengths were rather similar for all variables, although a bit lower for LoI.

Table 3. Cross-variogram functions after standardization

Variable	Nugget (c_0)	Sill (c_s)	Range (a)
C_{org}	0	0·950	20 000
N_{org}	0	0·951	35 000
P_{org}	0	1·041	30 000
LoI	0	1·050	15 000
C_{org}/LoI	0	0·413	30 000
N_{org}/LoI	0	0·458	37 000
P_{org}/LoI	0	0·359	35 000

Estimates were calculated for each node in a grid net (each square of size 10 000 m × 10 000 m) covering the Gulf. This grid size was decided according to the results from the correlation lengths. Using a larger grid would, i.e. larger than the range, give zero weights for stations at longer distances. A smaller grid would be more time consuming without substantially changing the concentration field and would probably lead to a lack of stations for some estimates.

Using linear interpolation on the estimates, the concentration field for the respective substances was received [see Figures 3(a), 4(a) and 5(a)]. The northernmost parts of the Gulf are left out in the calculations, due to lack of observations. The southernmost bottoms mainly consist of erosion bottoms with very low concentrations. All three concentration fields show similar patterns, with higher concentrations in a belt of accumulation bottoms. The island of Ruhnu and the erosion bottoms surrounding it cause the low concentration in the middle of the basin. There is also a possibility that the closeness of the river mouth of Daugava may be the cause of high organic content in the south-east of the Gulf. However, the direct reason for most of the patterns are due to the sediment type and thus the sedimentation conditions.

Figures 3(b), 4(b) and 5(b) give the cokriging standard deviations for the concentration estimates. High standard deviation can be explained by both the large variations within the data set and the sparse data available. In the middle of the basin there is lower than mean standard deviation. This is mostly due to smaller variations in sediment type. This is favourable for the next step—the calculation of total amounts in the accumulation bottoms.

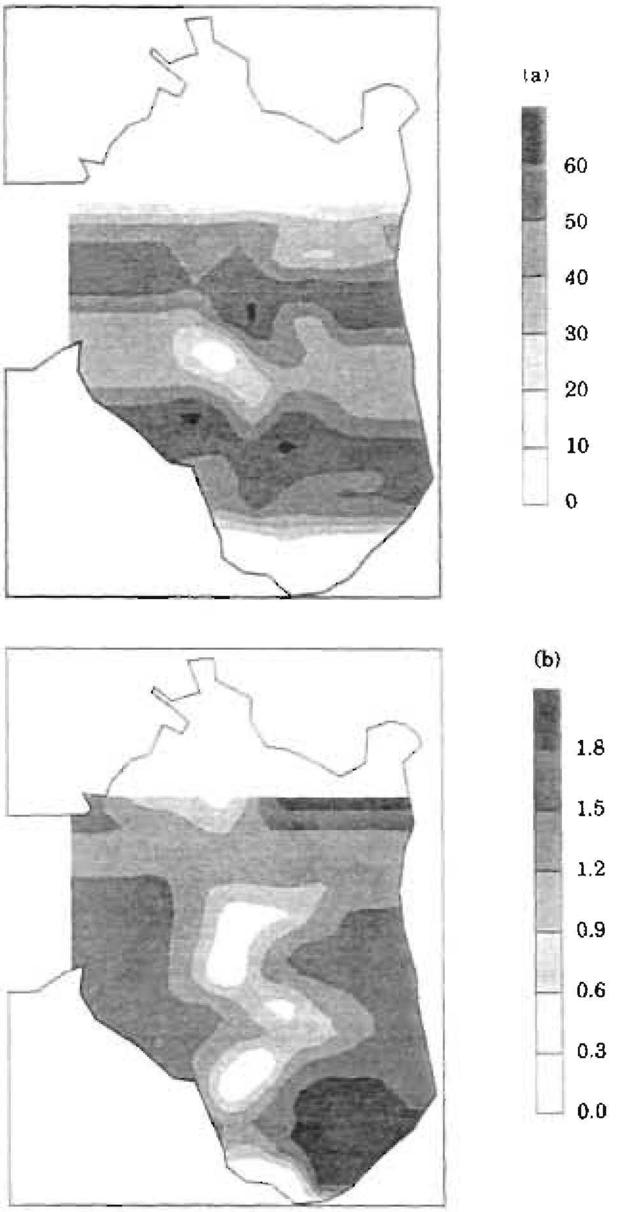


FIGURE 3. Map showing the spatial distribution of the organic carbon (a) concentration (mg g^{-1}) and (b) standard deviation.

Total amounts

The total amount for each of the three substances was calculated according to the method previously described. Linear regression analysis, to estimate the sediment weight, resulted in:

$$(\text{Bulk Density} - \text{Water Content} \times \text{Water Density}) = e^{-(0{\cdot}598 - 0{\cdot}052 \times C_{org})} \quad (10)$$

In Figure 6, the curve fitting is shown. The fitting was successful, with an R^2-value of 0·97.

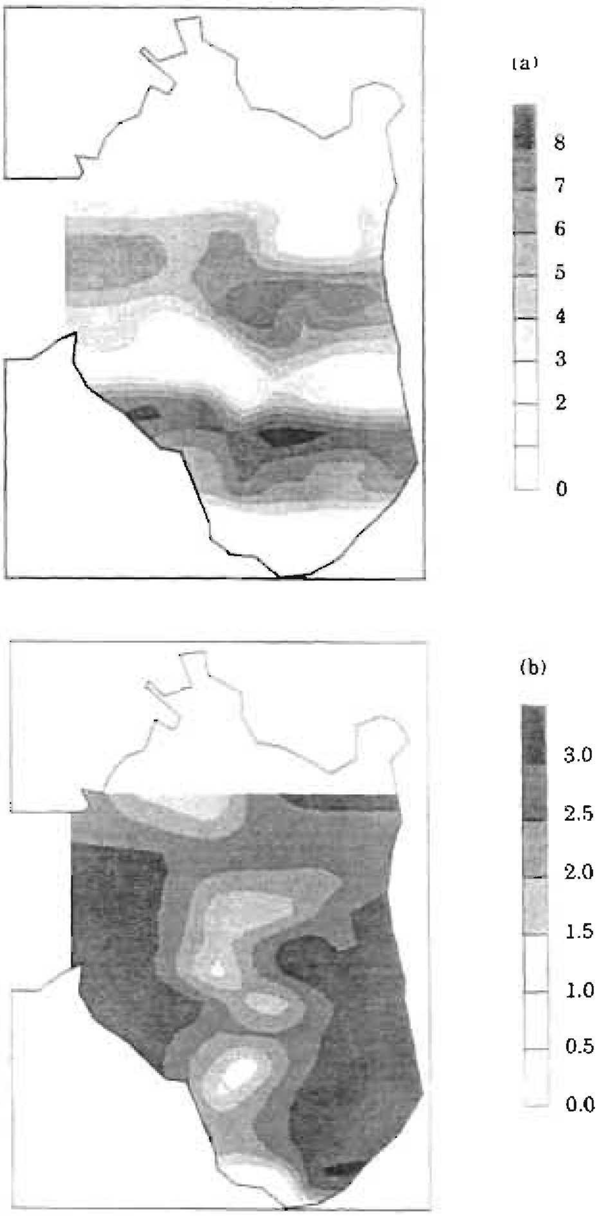


FIGURE 4. Map showing the spatial distribution of the organic nitrogen (a) concentration (mg g^{-1}) and (b) the standard deviation.

When integrating over the area with accumulation bottoms, the total amount in the upper 2 cm for each substance was established: organic carbon, 1 100 000 tons; organic nitrogen, 129 000 tons; organic phosphorus, 14 000 tons.

Discussion

The outcome from this study was compared with previous studies concerning the nutrient situation in

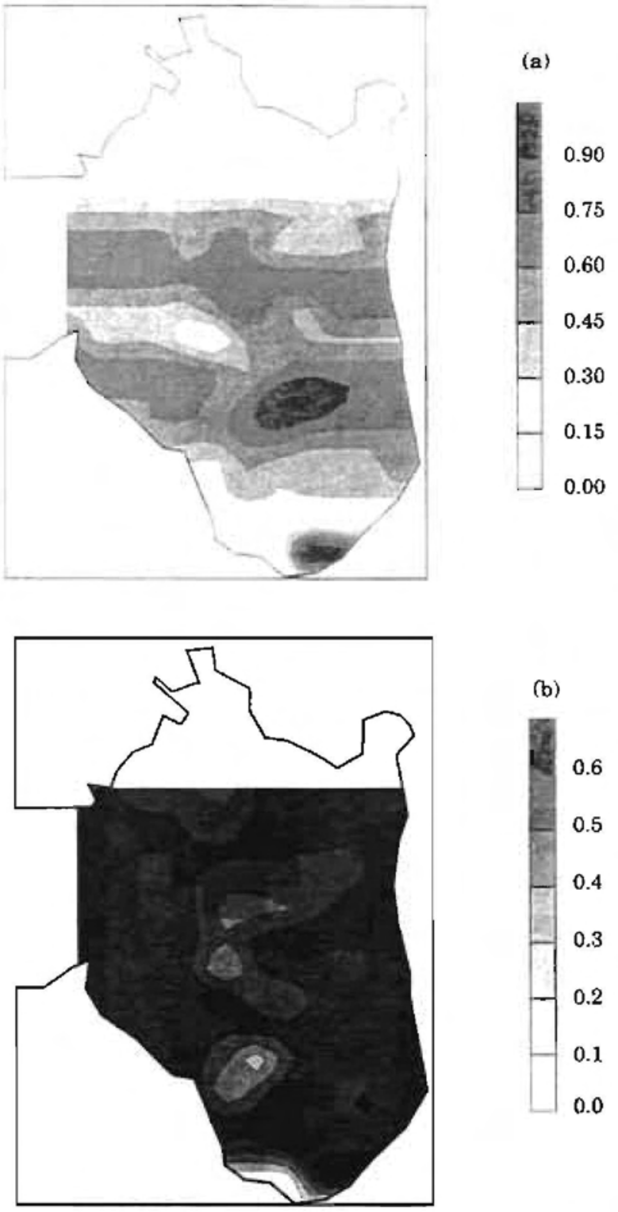


FIGURE 5. Map showing the spatial distribution of the organic phosphorus (a) concentration (mg g^{-1}) and (b) the standard deviation.

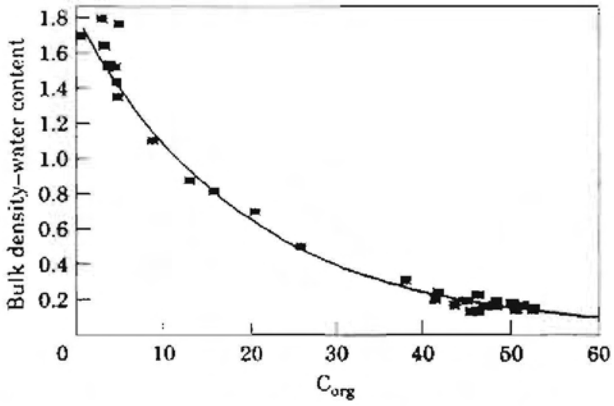


FIGURE 6. Organic carbon concentration *vs* bulk density minus water content.

TABLE 4. Comparison between storage estimates

Time/ sediment thickness	Carbon (tons)	Nitrogen (tons)	Phosphorus (tons)
Sink 10 years[a]	5 950 000	680 000	—
Storage (2 cm)[b]	860 000	115 000	22 000
Our estimate (2 cm)	1 100 000	129 000	14 000

[a] Yurkovskis *et al.* (1993), note that it is based solely on the annual inorganic nitrogen sink.

[b] Carman *et al.* (1996), based on average estimates of concentration and sediment rate.

the Gulf of Riga, i.e. Yurkovskis *et al.* (1993) and Carman *et al.* (1996)—see Table 4.

To achieve an estimate of the annual deposition the sediment rate was needed. Kuptzov *et al.* (1984) estimates the average annual sedimentation rate in the Gulf to 1–2 mm year^{-1}. Their value represents consolidated sediments (i.e. 7–10 cm below seafloor) and thus an assumed deposition velocity of 2 mm year^{-1} is, probably, an underestimate of the annual deposition rate. Further Perttilä *et al.* (1995) calculated a sedimentation rate of 1·6 mm year^{-1} in the surficial sediments of the Gulf of Finland. It was based on budget estimated total phosphorus sedimentation and dry matter content. Since the Gulf of Finland, in several aspects, is similar to the Gulf of Riga their estimates support the assumption of a sediment rate of roughly 2 mm year^{-1}. With this assumption, the annual area-weighted estimates become 110 000, 13 000 and 1400 tons for organic carbon, nitrogen and phosphorus, respectively.

Carman *et al.* (1996) report a net storage of 860 000, 115 000 and 22 000 tons for organic carbon, nitrogen and phosphorus, respectively, in the upper 2 cm of the Gulf (Table 4). Their estimates are based on six stations on accumulation bottoms. The estimates in this study, which are similar to those given by Carman *et al.* (1996), are based on all available nutrient data (31 stations) and a frequently measured (386 stations) covariable, LoI. This makes a substantial improvement in marine system analysis as the well-used concept of 'representative stations' is avoided. Also Yurkovskis *et al.* (1993) results are compared with the present analysis in Table 4. They report substantially higher annual net sinks of both carbon and nitrogen (see Table 4), but their sinks also

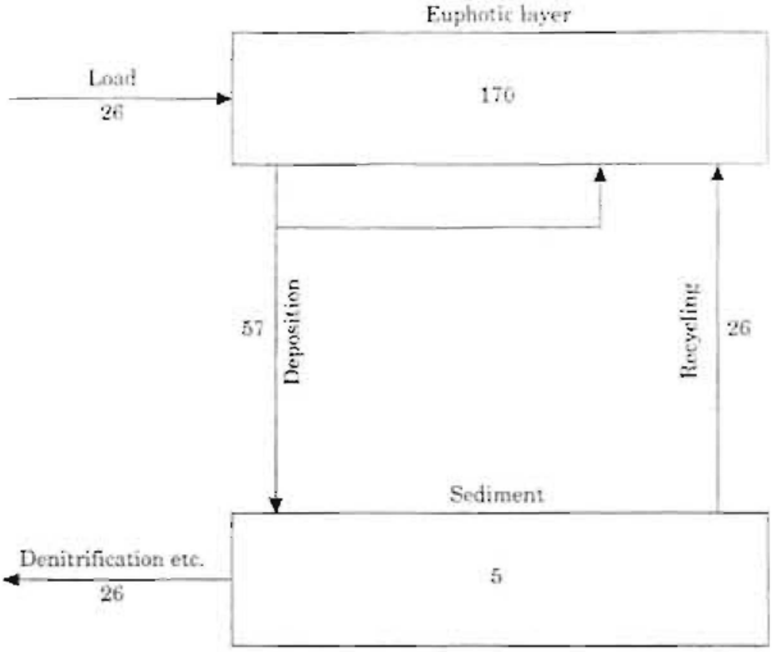


FIGURE 7. The organic carbon cycle of the Gulf of Riga. The arrows indicate the carbon fluxes (g C m^{-2} year^{-1}).

include processes like denitrification and export of organic matter to the Baltic proper.

To broaden the outlook, a simple steady-state model of the nutrient fluxes in the Gulf of Riga was formed (see Figure 7). Elmgren (1984) estimated, for the Gulf of Riga, the total annual primary production and allochthonous supply to 170 g C m^{-2} year^{-1} and the gross deposition to 57 g C m^{-2} year^{-1}. Together with the net sink estimated by Yurkovskis *et al.* (1993) of 31 g C m^{-2} year^{-1}, based on a Redfield ratio (by atoms) of C:N to 10·2:1, the present estimate of net deposition in the sediments gives a recycled flux of 26 g C m^{-2} year^{-1} from the sediments. The permanently buried part of the net deposition (present estimate) mounts to 5 g C m^{-2} year^{-1} [3% of the total primary production given by Elmgren (1984)]. The rest (26 g C m^{-2} year^{-1}) is probably lost in the degradation and recycling process.

In comparison, Wulff *et al.* (1986) claim the more permanent storage in the Baltic proper upper sediments to be 3% of the total production for this area. This storage is modest compared to the amounts cycling in the water mass. Still, it is the only internal, more permanent storage, representing a fifth of the annual load. In Gulf of Riga, the present estimates of annual amounts sequestered in the sediments compared to their respective loads mount to 14 and 22% for nitrogen and phosphorus, respectively. The present model is in all respects comparable to the corresponding Baltic proper model by Wulff *et al.* (1986).

To improve the estimates, additional sampling in areas with high uncertainty would be helpful. That would also put the cross-variogram functions (e.g. the nugget effect) on firmer ground, which would be valuable in future sampling programmes. A function describing the spatial correlation also indicates how close the sampling needs to be; it may not be necessary to take samples at short distances, as they will give equal information. Vauclin *et al.* (1986); McBratney and Webster (1983) as well as Trangmar *et al.* (1986) have shown that regular sampling, in a geometric scheme, would be preferable in monitoring. Yfantis *et al.* (1987) insist on a triangular grid net for best results.

To summarize, sediment data are often infrequently spatially sampled and their spatial distribution is usually far from optimal with regard to bottom characteristics. Evidently, the use of cokriging to get spatial distributions is practical as it is based on information about the sample characteristics and additional variables to improve the estimates. It also has the advantage of giving a measure of the uncertainty, something that is still generally lacking in most marine studies. The extensive agreement between the present total amount calculations and those previously reported, based on more conventional methods, corroborate this conclusion. Furthermore, the distribution of variance over the sampling area is essential in any improvement of the sampling strategy. This leaves ample scope for future improvements of the monitoring programmes and improvements of the geostatistical methods used.

Acknowledgements

We would like to thank Dr B. Larsen, Geological Survey of Denmark, for providing us with data and maps. We would also like to pay our gratitude to two anonymous referees for their valuable comments. The work was financially supported by the Swedish Environmental Protection Agency and the Swedish Natural Science Research Council.

References

Berzinsh, V. 1980 Interannual and seasonal changes of water salinity in the Gulf of Riga. *Rybokhozyaist vennye issledovaniya* (BaltNIIRKH), Riga Avots **15**, 3–12.

Carman, R. & Wulff, F. 1989 Adsorption capacity of phosphorus in Baltic Sea sediments. *Estuarine, Coastal and Shelf Science* **29**, 447–456.

Carman, R., Aigars, J. & Larsen, B. 1996 Carbon- and nutrient geochemistry of the surface sediments of the Gulf of Riga, Baltic Sea. *Marine Geology* **134**, 57–76.

Cressie, N. 1993 *Statistics for Spatial Data*. John Wiley & Sons, New York, pp. 900.

Dahlberg, K., Hallin, A.-K. & Wulff, F. 1995 Phosphorus versus nitrogen abatement in the Gulf of Riga—a nutrient budget model approach. In *International Congress on Modelling and Simulation Proceedings*, Vol. 3 (Bining, P., Bridgman, H. & Williams, B., eds). *Water Resources and Ecology*, 113–118.

Danielsson, Å. 1994 Cokriging for interpolating 3-dimensional data. *Conference Proceedings: Nordic Seminar—Spatial and Temporal Variability and Interdependencies Among Hydrological Processes* (Helsinki, Finland 1994). *Report* No. 36.

Elmgren, R. 1984 Trophic dynamics in the enclosed, brackish Baltic Sea. *Réun. Cons. Int. Explor. Mer.* **183**, 152–169.

Froelich, P. N., Arthur, M. A., Burnett, W. C., Deakin, M., Hensley, V., Jahnke, R., Kaul, L., Kim, K.-H., Roe, Soutar, A. & Vathakanon, C. 1988 Early diagenesis of organic matter in Peru continental margin sediments: Phosphorite precipitation. *Marine Geology* **80**, 309–343.

Grimvall, A., Stålnacke, P., Sundblad, K., Niemirycz, E., Pitkänen, H. & Bruhn, A. 1991 Trend analysis of nutrient concentrations in Baltic Sea rivers. *Conference Proceedings: 3rd International Conference on System Analysis Approach to Environment. Energy and Natural Resource Management in the Baltic Region* (Copenhagen, Denmark 1991).

Håkansson, L. & Jansson, M. 1983 *Lake sedimentology*. Springer, Berlin, pp. 316.

Hedges, J. I. & Stern, J. H. 1984 Carbon and nitrogen determinations of carbonate-containing solids. *Limnology and Oceanography* **29**, 657–663.

Hjorth, U. 1994 *Computer Intensive Statistical Methods—Validation, Model Selection and Bootstrap*. Chapman & Hall, London, pp. 263.

Kuptzov, V. M., Seldina, B. B. & Ivanova, T. R. 1984 Rate of sedimentation of sediments of the Baltic Sea. In *Geological History and Geochemistry of the Baltic Sea* (Lisitzin, A., ed.). Nauka, Moscow, pp. 110–121.

Mackin, J. E. & Aller, R. C. 1984 Ammonium adsorption in marine sediments. *Limnology and Oceanography* **29**, 250–257.

Marcotte, D. 1991 Cokriging with MatLab. *Computers and Geosciences* **17**, 1265–1280.

McBratney, A. & Webster, R. 1983 Optimal interpolation and isarithmic mapping of soil properties: V. Co-regionalization and multiple sampling strategy. *Journal of Soil Science* **34**, 137–162.

McBratney, A. & Webster, R. 1986 Choosing functions for semi-variograms for soil properties and fitting them to sampling estimates. *Journal of Soil Science* **37**, 617–639.

Myers, D. E. 1982 Matrix formulation of cokriging. *Mathematical Geology* **14**, 249–257.

Nixon, S. W., Ammerman, J. W., Atkinson, L. P., Berounsky, V. M., Billen, G., Boicourt, W. C., Boynton, W. R., Church, T. M., Ditoro, D. M., Elmgren, R., Garber, J. H., Giblin, A. E., Jahnke, R. A., Owens, N. J. P., Pilson, M. E. Q. & Seitzinger, S. P. 1996 The rate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. *Biogeochemistry* **35**, 141–180.

Pastors, A. 1967 Water and heat balance in the Gulf of Riga. *Morski-Zalivy Kak Priyomniki Stochnykn Vod*, Riga, Zinātne 8–20.

Pertillä, M., Niemistö, L. & Mäkelä, K. 1995 Distribution, development and total amounts of nutrients in the Gulf of Finland. *Estuarine, Coastal and Shelf Science* **41**, 345–360.

Petrov, B. 1979 Water Balance and Water exchange between the Gulf of Riga and the Baltic proper. *Spornik Rabot Rizhskij Gidrometrologicheskoj Observatorii* **18**, 20–40.

Rosenberg, R., Elmgren, R., Fleischer, S., Jonsson, P., Persson, G. & Dahlin, H. 1990 Marine eutrophication case studies in Sweden. *Ambio* **19**, 102–108.

Sandén, P. & Danielsson, Å. 1995 Spatial properties of nutrient concentrations in the Baltic Sea. *Environmental Monitoring and Assessment* **34**, 289–307.

Shaffer, G. & Rönner, U. 1984 Denitrification in the Baltic proper deep-water. *Deep-sea Research* **31**, 197–220.

Sweitzer, J., Langaas, S. & Folke, C. 1996 Land cover and population density in the Baltic Sea drainage basin: a GIS database. *Ambio* **25** (3), 191–198.

Trangmar, B., Yost, R. & Uehara, G. 1986 Spatial dependence and interpolation of soil properties in West Sumatra, Indonesia: II. Coregionalization and cokriging. *Soil Science Society of American Journal* **50**, 1396–1400.

Vauclin, M., Vieira, S., Vachaud, G. & Nielsen, D. 1986 The use of cokriging with limited field soil observations. *Soil Science Society of American Journal* **47**, 175–184.

Vollenweider, R. A. 1968 Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorus as focus in eutrophication. *Organization for Economic Cooperative Development. Technical Report* DAS/CSI/68.27, Paris, 182 pp.

Wulff, F., Ærtebjerg, G., Nicolaus, G., Niemi, Å., Ciszevski, P., Schulz, S. & Kaiser, W. 1986 The changing pelagic ecosystem of the Baltic Sea. *Ophelia* Suppl. **4**, 299–319.

Wulff, F. & Rahm, L. 1988 Long-term seasonal and spatial variations of nitrogen, phosphorus and silicate in the Baltic: An Overview. *Marine Environmental Research* **26**, 19–37.

Yates, S. & Warrick, A. 1987 Estimating soil water content using cokriging. *Soil Science Society of American Journal* **51**, 23–30.

Yfantis, E., Flatman, G. & Behar, J. 1987 Efficiency of kriging estimation for square, triangular and hexagonal grids. *Mathematical Geology* **19** (3), 183–205.

Yurkovskis, A., Wulff, F., Rahm, L., Andruzaitis, A. & Rodriguez-Medina, M. 1993 A nutrient budget of the Gulf of Riga, Baltic Sea. *Estuarine, Coastal and Shelf Science* **37**, 113–127.

Paper IV

ELSEVIER SCIENCE Ltd. [DTD 4.1.0]
JOURNAL CHEM ARTICLE No. 3262
PAGES 1-8 DISPATCH 4 May 2000
CHEM 3262 A
PROD. TYPE: FROM DISK

CHEMOSPHERE

PERGAMON

Chemosphere 000 (2000) 000–000

Seasonal and spatial variations of carbon and nitrogen distribution in the surface sediments of the Gulf of Riga, Baltic Sea

Juris Aigars [a,b] , Rolf Carman [a]

[a] *Department of Geology and Geochemistry, Stockholm University, 106 91 Stockholm, Sweden*
[b] *Institute of Aquatic Ecology, Latvian University, LV-2163 Salaspils, Latvia*

Received 30 August 1999; accepted 4 April 2000

Abstract

The variations in concentrations of carbon and nitrogen in surface sediments of the Gulf of Riga were investigated between December 1993 and January 1995. The sediment samples were taken nine times during this period at two sampling sites. One sampling site, G5, exhibited high abundance of burrowing amphipods, whereas at the second site, T3, the number of macrozoobenthic organisms was comparatively small.

Similar vertical profiles of mean sediment dry-weight concentrations of total carbon (TC) and total nitrogen (TN) were obtained at both sites G5 and T3. However, during autumn–winter considerable differences of TC and TN concentrations in surface sediments (0–2 cm) between sites were observed. This was probably the effect of differences in the bioturbation level. During summer, when decline in numbers of amphipods were recorded, the vertical profiles of TC and TN at site G5 were similar to those at site T3.

Significant differences between months were detected for TN at site T3 reflecting sedimentation of spring and autumn blooms in April and late October–early November, respectively. This was supported also by lower atomic C/N ratios in surface sediments during corresponding sampling events. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Carbon; Nitrogen; Sediments; Baltic sea; Gulf of Riga

---

1. Introduction

The fraction of the organic matter produced during primary production reaching the sea bottom is generally related to water-column depth and varies from 10% to 80% in coastal and estuarine sediments (Suess and Müller, 1980; Suess, 1980). Subsequent remineralisation of organic material in the sediments and release of dissolved nutrients into the overlying water column can supply a significant portion of the nutrient requirements for primary producers in shallow coastal areas (Zeitzschel, 1980; Klump and Martens, 1987). However, sediments act not only as a source of nutrients but also as a sink.

The sedimentation rate and quality of organic matter influence to different degrees the abundance of macrobenthic organisms (Cederwall and Elmgren, 1980) and microbial activity (Graf, 1987), and can change the preservation of organic material in sediments due to altered redox conditions (e.g., Jonsson et al., 1990).

Many workers have examined the effects of organic matter addition on the sediment nutrient recycling processes (e.g., Garber, 1984; Banta, 1992; Caffrey et al., 1993). The previous studies indicated a wide range of the

---

*Corresponding author. Tel.: +1-46-8-164-738; fax: +1-46-8-674-7855.

E-mail address: rolf.carman@geo.su.se (R. Carman).

PII: S0045-6535(00)00150-8

half-life of added organic particles, most likely due to the different materials used for additions. For instance, Garber (1984) used lyophilised algae culture and seston whereas Enoksson (1993) used untreated algae culture, and both estimated that the half-life of added particulate phosphorus and nitrogen is approximately four weeks. In contrast, Conley and Johnstone (1995) used additions of freshly harvested algae cells and estimated that only 19% of added nitrogen and 15% of added phosphorus was released in inorganic form from the sediments during the 27-day experiment. Thus, remineralisation can vary according to sediment type, temperature, and quality and quantity of added material (e.g., Garber, 1984; Kelly and Nixon, 1984; Conley and Johnstone, 1995).

The phytoplankton blooms in the Baltic sea undergo remarkable seasonality (Smetacek, 1980) and can form, grow, and senesce in as little as 1–2 weeks (Smetacek et al., 1978). The settling of phytoplankton blooms considerably exceeds average sedimentation rates of the phytoplankton growth period (Smetacek, 1980). Therefore, the signal of bloom deposition in the sediments of shallow and productive areas can be expected.

The aim of this study was to deduce whether nutrient distribution in surface sediments reflects naturally occurring succession of sedimentation events, seasonal changes in physico-chemical parameters of the overlying water column, and intensity of bioturbation in the shallow and eutrophicated Gulf of Riga.

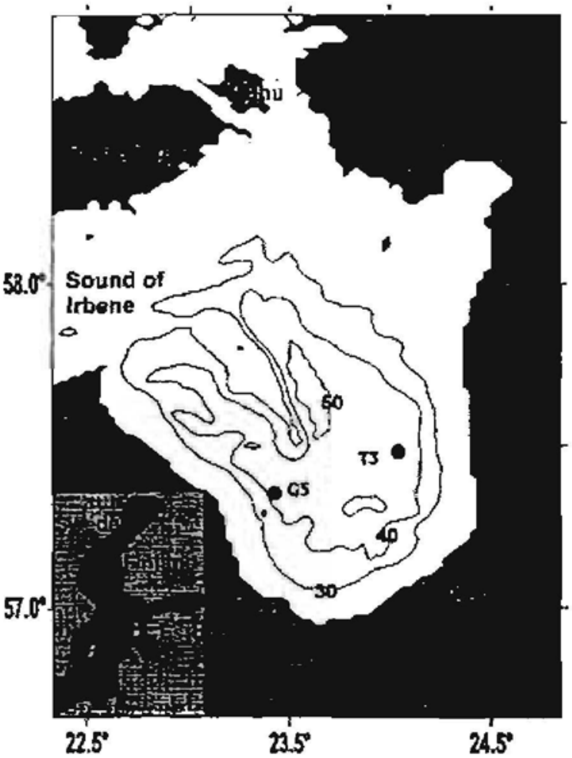


Fig. 1. Map showing the sampling locations (G5 and T3) in the Gulf of Riga. The depth isolines of 30, 40 and 50 m are marked, respectively.

2. Description of the study site

The Gulf of Riga is, compared with other sub-basins of the Baltic sea, quite shallow with maximum and average depths of 62 and 20 m, respectively (Yurkovskis et al., 1993). The water mass is normally mixed completely once a year (during winter). A strong thermocline develops quickly after this mixing at around 30 m of depth and lasts until the next complete mixing of the water mass (Berzinsh, 1995).

The average annual primary production is 290 g C m^{-2} yr^{-1}, which is among the highest values in Baltic sea (Wassmann and Andrushaitis, 1993).

Sediment bottoms with continuous deposition of fine material (<0.006 mm) are situated 40–50 m deep. These bottoms cover around 28% of the total area of the Gulf of Riga (Carman et al., 1996). Generally, the surface sediments are oxidised throughout the year and are, therefore, normally exposed to a certain degree of bioturbation.

Based on previous investigations (Carman et al., 1996), two sampling sites (G5 and T3) from two different deposition bottom areas were chosen (Fig. 1). Site T3, which is located in the eastern part of the Gulf, is mainly influenced by the major rivers' input in the south and southeast (Berzinsh, 1995). Site G5, on the other hand, which is located in the southwestern part of the Gulf, is strongly influenced by the saline water inflow from the adjacent Baltic proper through the Sound of Irbene (Berzinsh, 1995). The Gulf of Riga is usually thermally stratified from April/May through September/October. According to echo-sounding recordings (not shown) both sampling areas are fairly flat. Some general parameters regarding the sampling sites are summarised in Table 1.

3. Materials and methods

Sediment cores were collected nine times from December 1993 to January 1995. Use of a global positioning system (GPS) system allowed repeated sampling within an area of 100 m^2. Since remarkably homogeneous results were obtained in December 1993 (Fig. 5), when four parallel cores were sampled, duplicate-triplicate sediment cores for chemical analysis were collected during the rest of sampling times. We used a modified Kajak gravity corer equipped with an acrylic liner with an inside diameter of 80 mm (Blomqvist and Abrahamsson, 1985). Sub-samples from the uppermost 10 cm

Table 1
Position and brief description of sampling sites

Parameter	Sites	
	T3	G5
Position	N57°30′0″ E24°06′0″	N57°23′18″ E23°28′30″
Water depth (m)	43	44
Water content (%) in 0–1 cm	89	87
Accumulation rates[a]		
Dry matter (g m^{-2} yr^{-1})	2000	1000
(mm yr^{-1} (0–2 cm))	(14)	(6)
Primary production (g C m^{-2})[b]	400–500	300–400
Dominating macrofauna species annual mean abundance (ind. m^{-2})[c]		
P. femorata	40	378
Marenzelleria viridis	108	62

[a] Larsen (1995).

[b] Wassmann and Andrushaitis (1993).

[c] Cederwall and Jermakovs (1999).

were sliced in centimetre sections. They were dried to a constant weight at 80°C and afterwards ground to a fine powder in an agate mortar for future analysis.

Bottom-water temperatures were measured in situ and the oxygen concentrations were measured by Winkler titration (Parson et al., 1984). The redox potential was also measured in situ by moving a platinum electrode vertically through the additional sediment core.

Total carbon (TC) and total nitrogen (TN) were measured using a Leco elemental analyser (the mean standard deviation (S.D.) of standard substances analysed through the whole sample measurement period constitutes 1.2% of the standard substances pre-set value). Inorganic carbon (IN-C) was measured using the same elemental analyser by analysing samples ignited in an oven (2 h at 550°C) before analysis (Hedges and Stern, 1984). Organic carbon (OC) was obtained as the difference between the total and IN-C values. Exchangeable nitrogen (EX-N) was measured according to Mackin and Aller (1984) as a sum of pore water and adsorbed ammonia leached in 2 M KCl. The wet extracts of NH_4^+ were measured according to Parson et al. (1984).

Statistical analyses of data were done using one-way ANOVA test. Heterogeneity of variances was also tested.

4. Results and discussion

The bottom-water temperature and the oxygen concentration just above the sediment surface generally agree well with the long-term trends reported by Berzinsh (1995) (see Figs. 2 and 3). However, the temperatures at both sites deviate from the long-term average values and exhibit considerable higher values from the end of May to the end of August. The variability of the temperature time series in the near-bottom layer is not

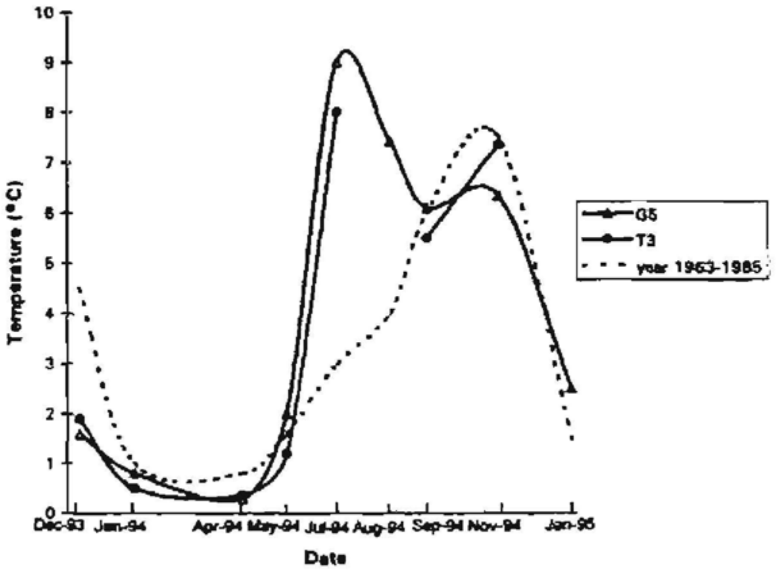


Fig. 2. Seasonal variations of temperature of the bottom water from December 1993 to January 1995. The long-term average of bottom-water temperature is presented by a dashed line (Berzinsh, 1995).

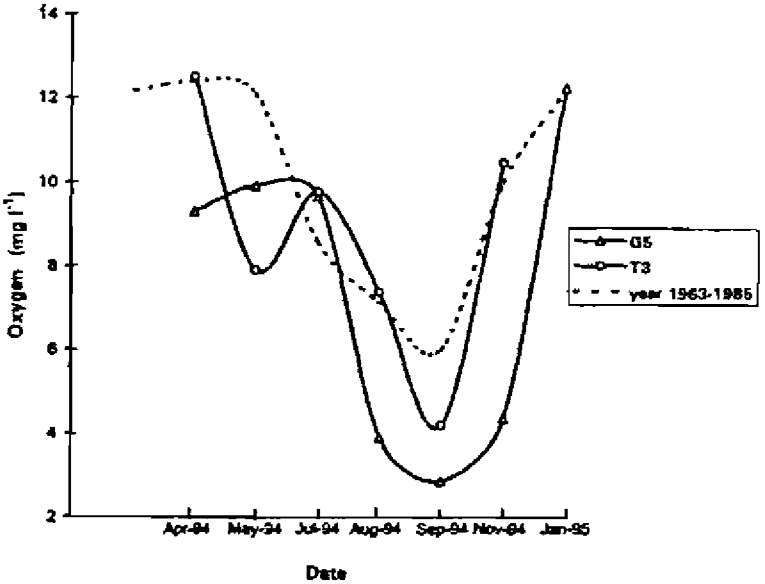


Fig. 3. Seasonal variations of oxygen concentration in the bottom water (1 m above sediments). The long-term average bottom-water oxygen is presented by a dashed line (Berzinsh, 1995).

available from the literature. However, the deviation in the entire water column from the long-term observations between 1963 and 1990 by Berzinsh (1995) was ±3°C and ±1.5°C in spring and summer, respectively. Therefore, deviations observed during summer time in this study seem to be rather extreme (Fig. 2). Furthermore, the oxygen concentrations (Fig. 3) were somewhat lower during August–November at site G5 and during September at site T3 than the measured long-term average values. The deviations of temperature and subsequently

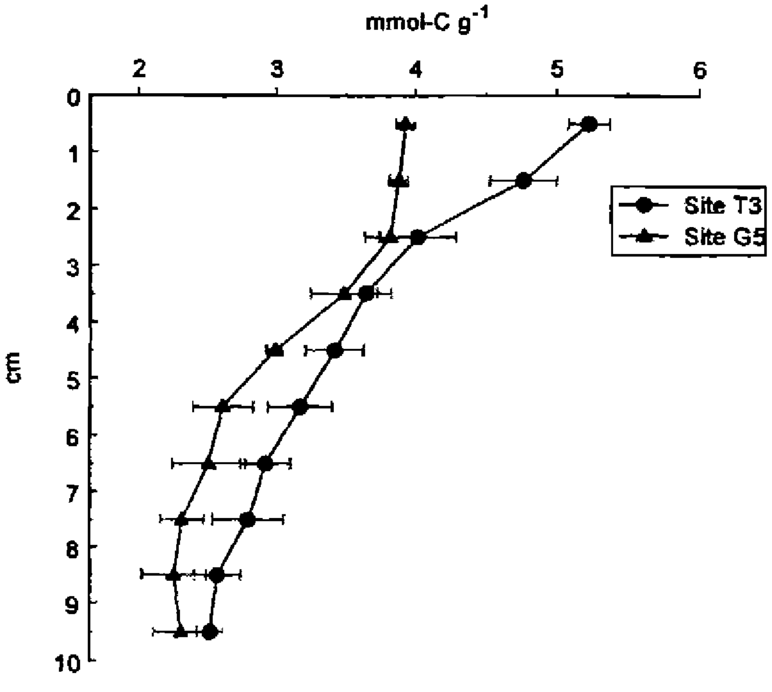


Fig. 4. Vertical profile of sediment TC concentrations in December 1993. Horizontal bars represent mean standard deviation.

O_2 most probably were caused by a strong storm event in late June.

Although the chemical analyses of the sediments have been performed down to 10 cm depths, we will mostly focus our discussion on the alterations in the uppermost 5 cm of the sediment column. This is because below 5 cm depths only limited alterations were seen during the sampling period. The organic carbon (not shown) comprised 96–99% of TC content throughout the experiment time.

Similar vertical profiles of mean sediment dry-weight concentrations of TC and TN were obtained at both sites G5 and T3. However, during autumn–early spring considerable differences of TC and TN concentrations in surface sediments (0–2 cm) between sites were observed (e.g., Fig. 4). An investigation performed by Krezoski et al. (1984) established that burrowing amphipods in Lake Michigan redistribute surficial sediments to a depth of about 1.5 cm. More recent work in the Baltic Proper by Hill and Elmgren (1987) showed that 80–90% of the amphipods *Pontoporeia affinis* and *Pontoporeia femorata* concentrate between 0 and 5 cm although they feed in more surficial depths (Lopez and Elmgren, 1989). Therefore, it seems very likely that uniformity of TC and TN concentrations in the 0–2 cm sediment layer during autumn–spring at site G5 was due to bioturbation. The drastic decline in numbers and biomass of *P. femorata* and *Monoporeia affinis* in May (1 $g_{wet\ weight}$ m^{-2}) compared to winter–early spring (on average 4.4 $g_{wet\ weight}$ m^{-2}) (Cederwall and Jermakovs, 1999) probably together with input of fresh organic material resulted in development of more a pronounced vertical gradient during summer. In contrast to site G5, considerable vertical gradient was observed during most of the year at site T3 (Figs. 5 and 6) probably due to much lower amphipod abundance (Table 1). The disruption of this gradient in November 1994 might be due to significant increase in amphipod numbers, i.e., 164 individuals (ind.) m^{-2} in November compared to 75 ind. m^{-2} on average of *P. femorata* and *M. affinis* (Cederwall and Jermakovs, 1999). We do not have biological data from January 1994, therefore it is not possible to conclude whether fairly similar concentrations of TC and TN in 0–1 cm and 1–2 cm are due to bioturbation at site T3.

Large spring and autumn blooms are often found in regions of remarkable seasonality. These blooms can

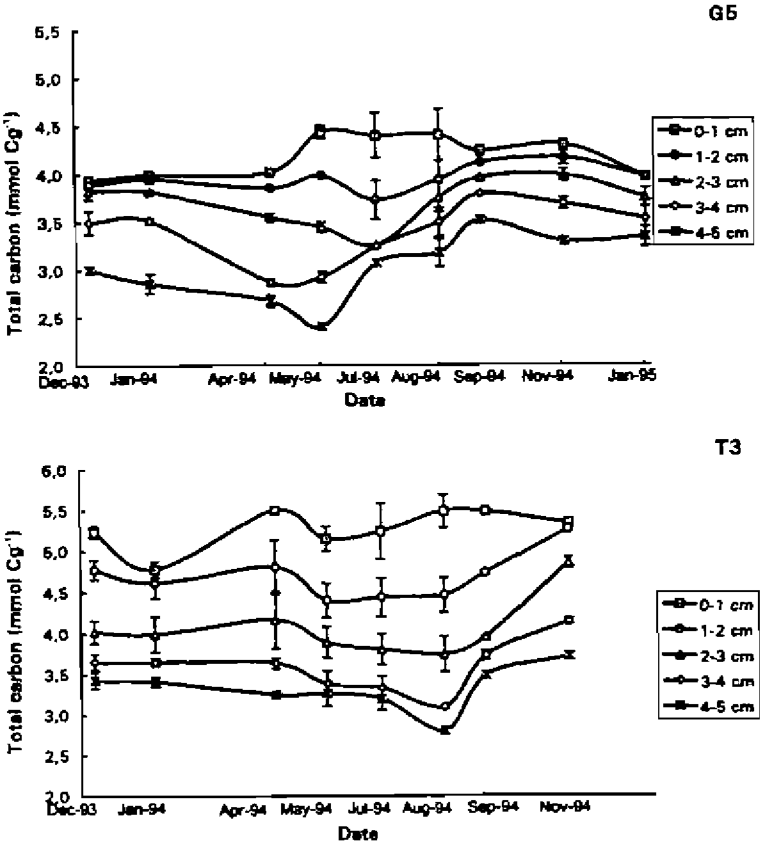


Fig. 5. Seasonal variations of TC concentrations in the surface sediments at sites G5 and T3. Vertical bars represent mean standard deviation.

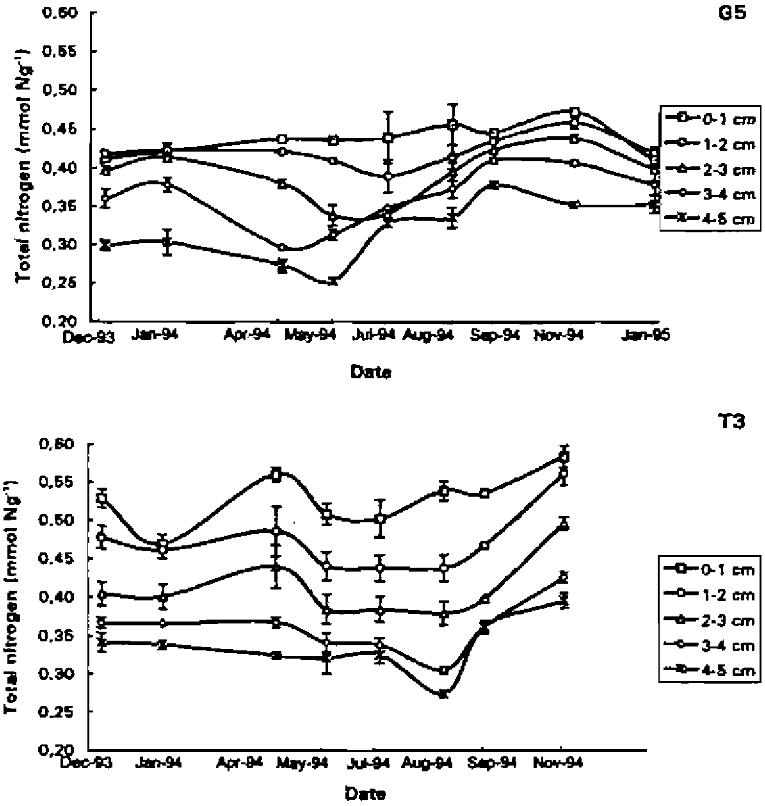


Fig. 6. Seasonal variations of TN concentrations in the surface sediments at sites G5 and T3. Vertical bars represent mean standard deviation.

form and senesce in as little as 1–2 weeks (Smetacek, 1985). In comparatively shallow ecosystems, the bulk of this material may reach the sediments due to low grazing pressure of zooplankton (Smetacek, 1980). However, significant differences (ANOVA, $P < 0.01$) between months were obtained only for TN (0–1 cm) at site T3. A post-hoc test (Tukey HSD test) following a one-way ANOVA revealed that TN concentrations (Fig. 6) in April and November were significantly different ($P < 0.01$) from January values. Non-significant increase of TC concentration (Fig. 5) was measured during May–August at site G5 and April at site T3. Although large variations can occur in bloom timing (Smetacek, 1985), the pattern of sedimentation is alike each year (Smetacek, 1980), i.e., sedimentation of spring and autumn blooms in Kiel Bight, Baltic sea occur mostly in March–April and October–November, respectively. Although, to our knowledge, there is no published information on a seasonal sedimentation pattern in the Gulf of Riga, it is reasonable to assume that seasonality of the pelagic system is similar to that of Kiel Bight reported by Smetacek (1980). Therefore, it seems very likely that the observed significant increase of TN concentration (Fig. 6) in April and November at site T3 reflect sedimentation of spring and autumn blooms, respectively. Moreover, the observed lowest C/N atomic ratios in April (9.1 [S.D. = 0.02] and 9.6 [S.D. = 0.2] for sites G5 and T3, respectively) and November (9.0 [S.D. = 0.1] and 9.1 [S.D. = 0.3] for sites G5 and T3, respectively) may support the assumption that the major bulk of settled particles originate from primary producers during these months.

A non-significant increase of TC in 0–1 cm at site G5 during May–August may indicate deposition of particulate organic material. However, elevated atomic C/N ratios in sediments (10.2–10.4 [S.D. = 0.4]) suggest that there is a source of deposited material other than the pelagic system. Most likely this material originates from macrophytes or from material delivered by rivers.

The elevated concentrations of TC in 0–1 cm prevailed from May through August. Without additional sedimentation data or refractority estimates of deposited material it is not possible to conclude whether deposition of particulate material occurred once in May and persisted at sediment surface due to its refractory nature and limited bioturbation or was deposited regularly throughout the period.

CHEM 3262

Only one replicate was analysed for EX-N. The concentration of EX-N was very low throughout the whole year in comparison with the TN (1–5% of the total amount). The highest concentrations of EX-N were measured during summer to early autumn, with the maximum occurring in September at site G5. The vertical gradient was very weak at site G5 throughout the year whereas a strong difference between the surface and deeper layers developed at site T3 during summer.

5. Conclusions

There is significant evidence that burrowing amphipods in the Gulf of Riga affect the concentration pattern of carbon and nitrogen in surface sediments down to 2–3 cm below the sediment surface.

Significant increase of TN concentration at site T3 in April and November most likely indicates deposition of spring and autumn blooms, respectively. However, TC concentrations at both sites and TN concentration at site G5 did not exhibit a significant increase. This might be due to several reasons, e.g., low bloom sedimentation, bioturbation, high accumulation rates. However, we need additional data for a more solid conclusion.

References

Banta, G.T., 1992. Decomposition and nitrogen cycling in coastal marine sediments – controls by temperature, organic matter inputs, and benthic macrofauna. Ph.D. thesis, University of Boston.

Berzinsh, V., 1995. Hydrology. In: Ojaveer, E. (Ed.), Ecosystem of the Gulf of Riga between 1920 and 1990. Estonian Academy Publishers, Tallin, pp. 7–32.

Blomqvist, S., Abrahamsson, B., 1985. An improved Kajak-type gravity core sampler for soft bottom sediments. Schweiz. Z. Hydrol. 47, 81–84.

Caffrey, J.M., Sloth, N.P., Kasper, H.F., Blackburn, T.H., 1993. Effect of organic loading on nitrification and denitrification in a marine sediment microcosm. FEMS Microbiol. Ecol. 12, 159–167.

Carman, R., Aigars, J., Larssen, B., 1996. Carbon and nutrient geochemistry of the surface sediments of the Gulf of Riga, Baltic sea. Mar. Geol. 134, 57–76.

Cederwall, H., Elmgren, R., 1980. Biomass increase of benthic macro fauna demonstrates eutrophication of the Baltic sea. Ophelia (Suppl. 1), 287–304.

Cederwall, H., Jermakovs, V., 1999. Growth and production of three macrozoobenthic species in the Gulf of Riga, including comparisons with other areas. Hydrobiologia 393, 201–210.

Conley, J.D., Johnstone, R.W., 1995. Biogeochemistry of N, P and Si in Baltic sea sediments: response to a simulated deposition of a spring diatom bloom. Mar. Ecol. Prog. Ser. 122, 265–276.

Enoksson, V., 1993. Nutrient recycling by coastal sediments: effects of added organic material. Mar. Ecol. Prog. Ser. 92, 245–254.

Garber, J.H., 1984. Laboratory study of nitrogen and phosphorus remineralization during decomposition of coastal plankton and seston. Estuar. Coast. Shelf Sci. 18, 685–702.

Graf, G., 1987. Benthic energy flow during a simulated autumn bloom sedimentation. Mar. Ecol. Prog. Ser. 39, 23–29.

Hedges, J.I., Stern, J.H., 1984. Carbon and nitrogen determinations of carbonate-containing solids. Limnol. Oceanogr. 29, 657–663.

Hill, C., Elmgren, R., 1987. Vertical distribution in the sediment in the cooccurring amphipods *Pontoporeia affinis* and *P. femorata*. Oikos 49, 221–229.

Jonsson, P., Carman, R., Wulff, F., 1990. Laminated sediments in the Baltic – a tool for evaluating nutrient mass balances. Ambio 19, 152–158.

Kelly, J.R., Nixon, S.W., 1984. Experimental studies of the effect of organic deposition on the metabolism of a coastal marine bottom community. Mar. Ecol. Prog. Ser. 17, 157–169.

Klump, J.V., Martens, C.S., 1987. Biogeochemical cycling in an organic-rich coastal marine basin. 5. Sedimentary nitrogen and phosphorus budgets based upon kinetic models, mass balances, and the stoichiometry of nutrient regeneration. Geochim. Cosmochim. Acta 51, 1161–1173.

Krezoski, J.R., Robbins, J.A., White, D.S., 1984. Dual radio tracer measurement of zoobenthos-mediated solute and particle transport in freshwater sediments. J. Geophys. Res. 89, 7937–7947.

Larsen, B., 1995. Evaluation of sediment pollution data: examples from the Gulf of Riga – status August 1995. Publications on Chemistry XXIII, Extended abstracts of the Symposium Environmental Analyses, Department of Chemistry, University of Tartu, pp. 81–92.

Lopez, G., Elmgren, R., 1989. Feeding depths and organic carbon absorption for the deposit-feeding benthic amphipods *Pontoporeia affinis* and *Pontoporeia femorata*. Limnol. Oceanogr. 34, 982–991.

Mackin, J.E., Aller, R.C., 1984. Ammonium adsorption in marine sediments. Limnol. Oceanogr. 29, 250–257.

Parson, T.R., Maita, Y., Lalli, C.M., 1984. Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon, Sidney.

Smetacek, V., 1980. Annual cycle of sedimentation in relation to plankton ecology in western Kiel Bight. Ophelia (Suppl. 1), 65–76.

Smetacek, V., 1985. The annual cycle of Kiel Bight plankton: a long term analysis. Estuaries 8, 145–157.

Smetacek, V., von Brockel, K., Zeitschel, B., Zenk, W., 1978. Sedimentation of particulate matter during a phytoplankton spring bloom in relation to the hydrographical regime. Mar. Biol. 47, 211–226.

Suess, E., 1980. Particulate organic carbon flux in the oceans – surface productivity and oxygen utilization. Nature 288, 260–263.

Suess, E., Müller, P.J., 1980. Productivity, sedimentation rate and sedimentary organic matter in the oceans. II. Elemental fractionation. In: Biogeochimie de la matiere organique a interface eau-sediment marin. CNRS, Paris, pp. 17–26.

CHEM 3262

Wassmann, P., Andrushaitis, A., 1993. Övergjödsling av Östersjoen og Rigabukten. Naturen 5, 205–213 (in Norwegian).

Yurkovskis, A., Wulff, F., Rahm, L., Andruzaitis, A., Rodriquez-Medina, M., 1993. A nutrient budget of the Gulf of Riga, Baltic Sea. Estuar. Coast. Shelf Sci. 37, 113–127.

Zeitzschel, B., 1980. Sediment–water interactions in nutrient dynamics. In: Tenore, K.R., Coull, B.C. (Eds.), Marine Benthic Dynamics. University of South Carolina, USA, pp. 195–218.

Paper V

Redox-dependent seasonal variations of the phosphorus geochemistry in the surface sediments of the Gulf of Riga.

Juris Aigars[1,2]

1. Institute of Aquatic Ecology, Latvian University, 21 63 Salaspils, Latvia.
2. Department of Geology and Geochemistry, Stockholm University, 106 91 Stockholm, Sweden

Abstract

The redox-dependent variations in concentrations of phosphorus at two different accumulation bottom areas were investigated in the Gulf of Riga (Baltic Sea) between December 1993 and January 1995. The sediment samples from 9 sampling occasions were analyzed for phosphorus forms and redox potential.

The average concentrations of total phosphorus measured in 0-1 cm (65 and 89 µmol P g^{-1} for sites G5 and T3, respectively) were among the highest reported from the entire Baltic Sea. Redox dependent "mobile" phosphorus contributed more than 50 % of total in the uppermost oxidised centimetre, whereas in reduced layers 16-18 % throughout the year.

A significant differences (ANOVA, $P<0.01$) among moths of inorganic phosphorus concentration at 0-1 cm were observed at site G5 due to temporary accumulation of mobile phosphorus mediated by redox-dependent bacteria activity during summer. On the contrary no accumulation was observed at T3 most likely as a result of low redox potential caused by high accumulation rates and low bioturbation.

Although water above sediments remained oxic throughout the investigation period, the redox potential at site T3 was close to redoxcline (i.e. + 230 mV) during summer. Further increase of eutrophication might lead to development of anoxic conditions at sediment-water interface and that in turn will result in rapid release of redox dependent phosphorus stored in surface sediments. The availability of excess phosphorus will further enhance eutrophication in partly phosphorus limited Gulf of Riga.

Key words: phosphorus, redox-dependent variations, sediments

Introduction.

In shallow marine ecosystems a large proportion of sedimenting particular organic matter reaches sea bottom. It could vary from 10-50 % in coastal to 50-80 % in near shore and estuarine sediments (*Suess and Muller*, 1980; *Suess*, 1980). The subsequent microbial organic matter remineralization and nutrient release from the sediment-water interface can supply a significant portion of nutrient requirements for the primary producers in the overlying water column (*Pamatmat*, 1977; *Hinga et al*., 1979; *Zeitzschel*, 1980; *Nixon*, 1981). However, sediments act not only as a source of nutrients but also as a sink. Therefore an attempt to assess or model the nutrient dynamics of marine ecosystem should include an examination of sediment-water interactions.

Sedimentation of fresh particulate organic material mostly is limited to plankton growth season (March-November) while in winter bulk of settling material is of resuspension origin (*Smetacek*, 1980). Large spring and autumn bloom sedimentations are often found in regions characterised by marked seasonality such as in the Baltic Sea. Although, sedimentation rates are lowest during summer the occasional events of summer bloom sedimentation have been observed. Moreover particulate organic material settling during summer stratification have highest organic carbon content of the year (*Smetacek*, 1980). Large variations can occur in bloom sedimentation timing and quantity, e. g. Olesen and Lundsgaard (1995) have shown that rapid mass sedimentation following the phytoplankton bloom in spring can contribute less than 10 % of the total flux during the stratified period.

Pulsed inputs of organic material can have profound impact on sediment-water fluxes (*Enoksson*, 1993; *Conley and Johnston*, 1995), benthos (*Cederwall and Elmgren*, 1980), underlying sediment chemistry (*Graf et al*., 1984), and may increase microbial activity (*Graf*, 1987).

However, the previous experiments mostly focused on comparatively short term effects of spring bloom simulation. Moreover, due to differences in material used they demonstrated rather controversial results. I.e. numerous authors estimated half life of added algae material to be around 4 weeks (e. g. *Garber*, 1984; *Enoksson*, 1993). Although Garber (1984) used lyophilized algae culture and seston whereas Enoksson (1993) used untreated algae culture their estimation of half life of added particulate P and N generally agree well. Except Garber (1984) demonstrated that large proportion of P (20-25 %) from freeze-dried organic material was released to solution within first 7 h as DIP. On the contrary to that experiment performed by Conley and Johnstone (1995), using fresh algae cells, estimated that only 19 % of added nitrogen and 15 % of added phosphorus was released during 27 days as dissolved inorganic fractions. Furthermore Baccini (1985) reported preservation of added organic phosphorus in uppermost sediments and likewise Sondergaard (1989) showed an equilibrium state for phosphorus in the uppermost oxidized sediments with net release from deeper reduced sediments.

The aim of this study was to deduce whether sediments of semi-enclosed Gulf of Riga may act as temporary nutrient trap during phytoplankton growth season. Specifically, the study aims to characterize the changes in sediment phosphorus chemistry in correlation with oxygen dynamics and bioturbation.

Study area

Compared to others sub-basins of the Baltic Sea the Gulf of Riga is quite shallow with maximum and average depths of 62 and 20 m, respectively (*Yurkovskis et al.*, 1993). The water mass is normally mixed completely once a year during winter. A strong thermocline develops quickly after the mixing of the water mass (*Berzinsh*, 1995). The average annual primary production, 290 g C $m^{-2}yr^{-1}$, is among highest values reported for Baltic Sea (*Wassmann and Andrushaitis*, 1993). Sediment bottoms with continuous deposition of fine material are situated at 40-50 m depth, and comprise ca. 28 % of total area of the Gulf of Riga (*Carman et al.*, 1996). The bottom water is oxygenated throughout the year (*Berzinsh*, 1995).

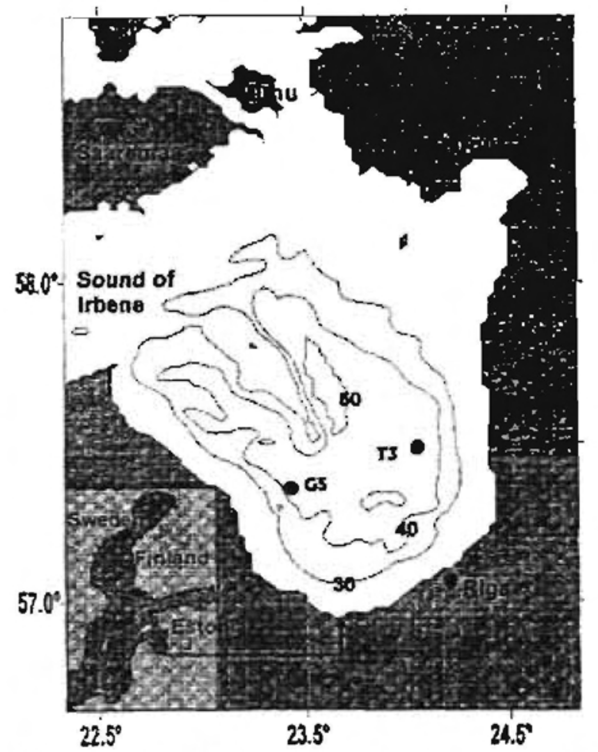


Figure 1. Map showing the sampling locations in the Gulf of Riga

In a previous investigation (*Carman et al.*, 1996) 23 sampling sites were analyzed for wide range of parameters. From those two sampling sites (G5 and T3) were chosen for present study (Figure 1).

Site T3, located in the eastern part of the Gulf, is strongly influenced by the major rivers input in south and south-east (*Berzinsh*, 1995). Site G5, on the other hand, is strongly influenced by the saline water inflow through Sound of Irbene (*Berzinsh*, 1995). According to echo sounding recordings (not shown) both sites are situated on fairly flat bottoms. Some general parameters regarding the sampling sites are summarized in Table 1.

Table 1. Position and brief description of sampling sites.

Parameter	Site T3	Site G5
Position	N57°30.0' E24°06.0'	N57°23.0' E23°28.0'
Sediment type*	mud	mud
Water content (%) in (0-1 cm)	89	87
Water depth (m)	43	44
Primary production (g Cm^{-2})**	400-500	300-400
Dominating macrofauna specie+	*Marenceleria viridis*	*Pontoporia femorata*

*Carman et al. 1996

**Wassmann and Andrushaitis 1993

+Cederwall and Jermakov, pers. comm.

Materials and methods

Since first sampling in December 1993 (five cores sampled) showed remarkably small spatial dispersion only duplicate - triplicate sediment cores were collected at each deposition area 9 times from December 1993 to January 1995. A modified Kajak gravity corer equipped with an acrylic liner with an inside diameter of 80 mm (*Blomqvist and Abrahamsson*, 1985) was used. Sub-samples from the uppermost 10 cm were sliced in centimetre sections immediately after sampling. They were dried to constant weight at +80 °C and afterwards ground to fine powder in an agate mortar.

Bottom water, sampled by batometer 1-2 m above sea floor, temperatures and oxygen concentrations by Winkler titration (*Parson et al.*, 1984) were measured on ship just after sampling. The redox potential was measured *in situ* by moving of a platinum electrode vertically through the additional sediment core.

Total phosphorus (TP), after heating the sediment sample for 2 h under 550 °C, and inorganic phosphorus (IP) was extracted by 1 M HCl (*Froelich et al.*, 1988). Redox dependent or mobile phosphorus (MP) was extracted by H_2S treatment (*Carman and Jonsson*, 1991) without pre-treatment with other chemicals. Apatite phosphorus (AP) was obtained from the difference between IP and MP while the concentration of organic phosphorus (OP) was obtained as a difference between TP and IP. All wet extracts of P were measured according standard molybdenum blue spectrophotometric technique (*Murphy and Riley,* 1962).

Statistical analysis were performed using one way ANOVA test. Heterogeneity of variances was tested also.

Results

Due to limited alterations of phosphorus concentrations below five centimeters, the discussion will be focused only on uppermost five centimeters.

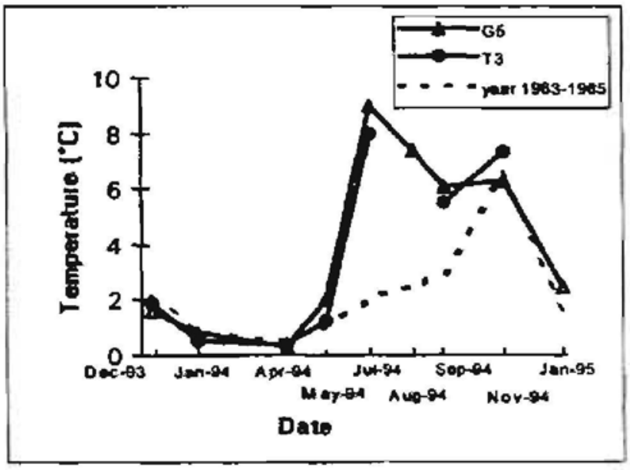


Figure 2. Seasonal variations of temperature of the bottom water. Berzins et al., (1987) data set represent long term average of bottom water temperature.

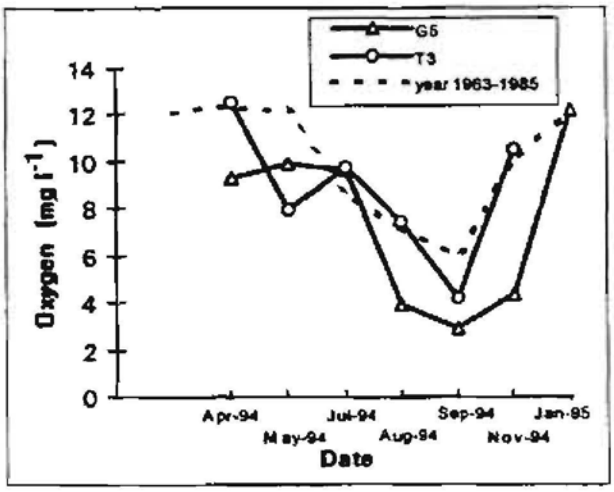


Figure 3. Seasonal variations of oxygen concentration of the bottom water. Berzins et al., (1987) data set represent long term average bottom water oxygen concentration.

Oxygen, temperature and redox potential.

The bottom water temperature (Fig. 2) and the concentration of oxygen (Fig.3) just above the sediment surface generally agree well with the long time average measurements reported by Berzinsh (1995). However, the temperature at both sites was up to 6 °C higher and the concentration of oxygen up to 3 mg l^{-1} lower during summer than long-term average measurements reported by Berzinsh (1995) between 1963 and 1985. Obviously introduction of higher than long-term average temperature in near-bottom water by stormy weather during late June enhanced activity of benthos community what resulted in high oxygen demand at sediment-water interface.

At both sites the sediment surface (0-1 cm) was oxic during most time of the year (Fig. 4). Although the redox potential at site T3 was close to the redoxcline (e.g. *Mortimer*, 1942) from May through summer, it was below +230 mV only in November. The redox potential at site G5 reached anoxic conditions in September in uppermost centimetre. At both sites the redox potential beneath the second centimetre always exhibited values below +230 mV. Further down in sediments the redox potential was always between +100 and -100 mV.

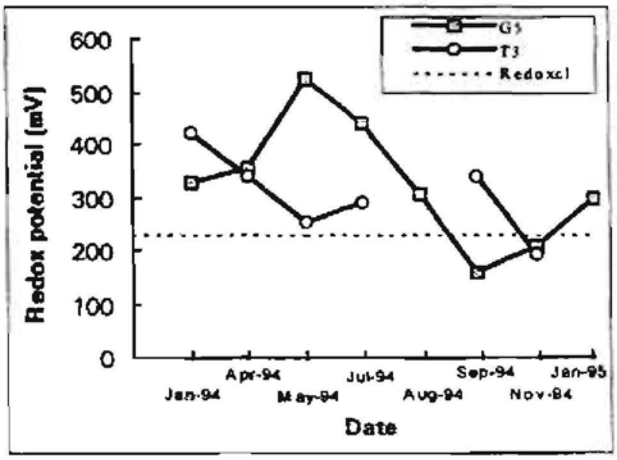


Figure 4. Seasonal variations of redox potential of uppermost sediment centimetre. Redoxcline is at 230 mV (see for instance Mortimer, 1942).

Phosphorus forms.

Inorganic phosphorus (IP) (Fig. 5) comprised on average more than 80 % of the total phosphorus what is similar to other areas in the Baltic Sea (e.g., *Carman and Jonsson*, 1991). Mobile phosphorus (MP) comprised on average more than 70 % and below 20 % of the extracted IP in 0-1 cm and below 5-6 cm, respectively.

Significant differences (ANOVA; P=0.007 and P=0.006) between months were obtained at site G5 for IP at 0-1 and 1-2 cm, respectively. A *post-hoc* Tukey (HSD) test following a one-way ANOVA for IP at 0-1 cm revealed that July was different from December, January and April, while for IP at 1-2 cm revealed that July is significantly different from April, May, August, January.

No significant differences (ANOVA; P>0.05) among months were detected for IP levels at site T3.

Organic phosphorus (OP) concentrations (not shown) were low compared to IP throughout the year.

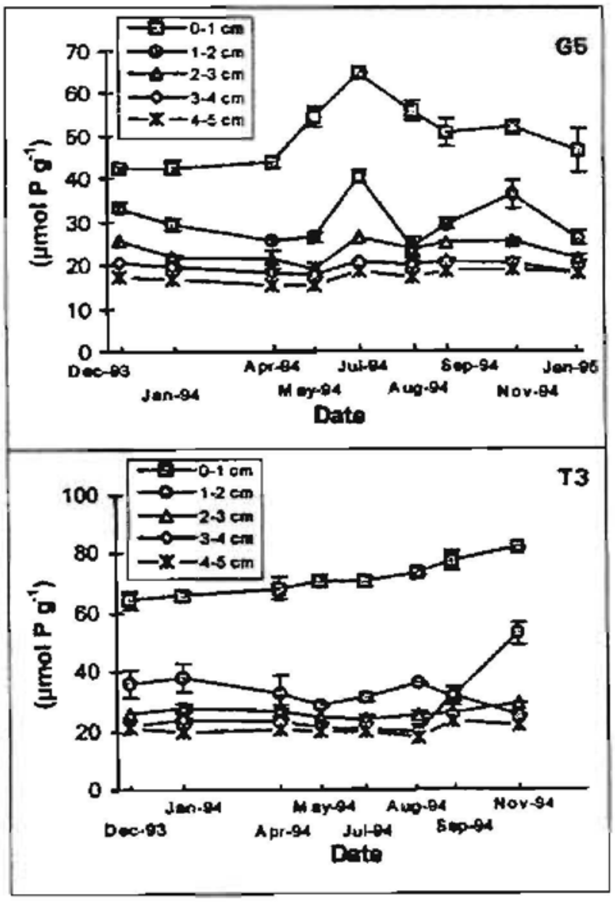


Figure 5. Seasonal variations of inorganic phosphorus in the surface sediments of the Gulf of Riga. Vertical bars show mean standard deviation.

Discussion.

The TP concentrations measured in this study were among the highest reported from other Baltic Sea areas (e. g. *Nedwell et al.*, 1983; *Koop et al.*, 1990; *Conley et al.*, 1997) and exceeded the values from deep basins in Baltic Sea with reduced sediments reported by Carman and Rahm (1997). As with other areas in the Baltic, oxidised sediments in the Gulf of Riga have much higher IP concentrations than reduced sediments (*Carman and Jonsson*, 1991). This is due to accumulation of large amounts of redox dependent "mobile" phosphorus in oxidised surface sediments.

Significant difference (ANOVA; P<0.001) in concentrations of TP in the uppermost centimetre between sites G5 and T3 was detected due to the large MP pool at site T3. The enrichment of MP in 0-1 cm at site T3 compared to site G5 may be due to differences in overlying water productivity as reported by Wassmann and Andrushaitis, (1993). However, the particulate material deposited at sites T3 and G5 largely is of different origin since site T3 is influenced by major rivers inflow in south and site G5 is influenced by water inflow from Baltic Proper (*Berzins*, 1995). Therefore, the particulate material deposited at site T3 might be enriched with phosphorus comparing to site G5.

Temporal increase of IP at site G5 (Fig. 5) was due to accumulation of MP. A possible explanation for accumulation of MP as suggested by Einsele (1936) is that phosphorus flux through the sediment-water interface is controlled by adsorption of phosphate on iron (III) complexes during oxic conditions with subsequent release under reduced due to dissolution of these complexes. This approach has been used by numerous investigators (e. g. *Balzer et al.*, 1983; *Balzer*, 1984; *Berkheiser et al.*, 1980; *Krom and Berner*, 1981; *Boström et al.*, 1988).

According to Einsele's theory, the release of iron-bound P will occur when redox potential in sediments shifts below +230 mV. However, in this study (at site G5) the redox potential decreased to this value in the uppermost centimeter only in September (Fig. 4) when temporary accumulated MP already had been released. Furthermore, investigation by Jensen et al. (1995), which is similar to this study, did not demonstrate positive correlation between concentrations of FeOOH and accumulation of iron bound reactive phosphorus. This clearly suggests mechanisms other than sorption-desorption on iron oxyhydroxides controls concentration of redox dependent phosphorus in sediments. These observations are consistent with the uptake of phosphorus by bacteria from organic substrate under oxidised conditions, which has been suggested in many studies (e.g., *Shapiro*, 1967; *Osborn and Nicholls*, 1978; *Fenchel and Blackburn*, 1979; *Fleischer*, 1986; *Carlton and Wetzel*, 1988; *Gächter et al.*, 1988). It is suggested that bacteria uptake and store phosphorus as polyphosphate granules during favourable oxygen conditions for metabolic processes to generate energy under low oxygen conditions (*Marais etal.*, 1983; *Florentz et al.*, 1984). Consistent with this idea is that in this study the increase of IP concentrations from May through July followed by decrease in IP levels during August-September correlates with oxygen concentrations at site G5 (Figures 5 and 3, respectively). Ingall and Jahnke, (1994; 1997) discuss the significance of short-term redox sensitive cycling of phosphate by bacteria in sea sediments also. Consistent to the idea that phosphorus content in sediments is controlled by oxygen sensitive biota, laboratory experiments reveal that biota in oxic layer uptake and store radiotracer labeled phosphorus delivered as organic material but fluxes of dissolved inorganic phosphorus out of sediments originates from deeper sediment layers with reduced conditions (*Baccini*, 1985). Sondergaard (1989) presented evidence of similar processes from field studies also.

In contrast to the location G5, at T3 the redox potential (Fig. 4) indicated O_2 deficiency in 0-1 cm already in May when water column was still well oxygenated. This may be due to of differences in the abundance of macrofauna (Table 1). The high bioturbation provided better delivery of oxygen into the sediments at site G5 than at site T3 where delivery of oxygen was mostly via diffusion. However, as shown in previous investigations oxygen consumption increase with addition of fresh material (*Jensen et al.*, 1990; *Enoksson*, 1993). Therefore, high sedimentation rates at site T3 (*Larsen*, 1995) may result in low redox potential compared to site G5. Thus it seems hypoxic/anoxic conditions developed in spring at site T3 due to coupling of high sedimentation rates and low bioturbation.

The increase of IP concentration in the second centimeter during November at site T3 correlates with increase in numbers of benthic macrofauna (*Cederwall and Jermakovs*, 1999). Thus observed increase of concentration probably was due to bioturbation.

Although several bacteria and protozoan species can uptake and store excess phosphorus, this process will little influence permanent burial of phosphorus in sediments. However, Gächter and Meyer, (1993) have pointed out that during phosphorus cycling by bacteria, some of it is transformed into refractory organic phosphorus compounds, which cannot be recycled during successive production. Such organic phosphorus compounds have been detected in marine organic matter (*Ingall et al.*, 1990, 1993). Thus, the oxic sediments may increase burial efficiency of nonmetabolizable P-rich organic phases. Although the bottom waters of the Gulf of Riga was never exposed to even short term anoxia (*Berzins*, 1995), this study indicated that oxic conditions mostly are limited to 0-1 cm. Moreover, high sedimentation rates and low bioturbation may result in consumption rates of oxygen, which exceeds its delivery. This in turn results in suboxic conditions at sediment surface. The poor oxygen conditions in surface sediments of the Gulf of Riga probably limits the development of resistant P-rich organic compounds. This suggests that under more favorable oxygen conditions burial efficiency of phosphorus should increase. In contrast, the increase of eutrophication may result in reduced conditions at sediment surface and cause release of mobile redox dependent phosphorus fraction stored there. Although the Gulf of Riga is basically N limited, it is phosphorus co-limitation (*Tamminen and Seppala*, 1999; *Seppala et al.*, 1999). Therefore, additional phosphorus input from sediments might cause further enhancement of eutrophication.

Summary and conclusions.

Under favorable oxygen content and particulate material conditions conditions sediments can temporary accumulate large amounts of redox dependent phosphorus. Most probably the controlling factor of this process is the capacity of some bacteria species to assimilate and store excess amounts of phosphorus. The phosphorus assimilated and stored by bacteria is used in metabolic processes when oxygen conditions become less favorable. The presence of benthic macrozoofauna can indirectly influence this process by aerating surface layer of sediments.

Acknowledgments

I would like to thank staff of Institute of Aquatic Ecology for support during field work. I also would like to thank Daniel J. Conley and Rolf Carman for valuable comments on this paper.

References

Baccini P (1985) Phosphate interactions at the sediment-water interface. In: W. Stumm (ed.), Chemical processes in lakes (pp 189-205). Wiley-Interscience, New York.

Balzer W, Grasshoff K, Dieckmann P, Haardt H, Petersohn U (1983) Redox-turnover at the sediment/water interface studied in large bell jar system. Oceanologica Acta. 6: 337-344

Balzer W (1984) Organic matter degradation and biogenic element cycling in a near shore sediment (Kiel Bight). Limnology and Oceanography. 29: 1231-1246

Berkheiser VE, Street JJ, Rao PSC and Yan TL (1980) Partitioning of inorganic orthophosphate in soil-water systems. CRC Crit. Rev. Envir. Control. 10: 179-224

Berzins V (1995) Hydrology. In: E. Ojaveer (eds.), Ecosystem of the Gulf of Riga between 1920 and 1990, Estonian Academy Publishers, Tallin. p. 7-32.

Blomqvist S and Abrahamsson B (1985) An improved Kajak-type gravity core sampler for soft bottom sediments. Schweiz. Z. Hydrol. 47: 81-84

Boström B, Andersen JM. Fleischer S, Jansson M (1988) Exchange of phosphorus across the sediment-water interface. Hydrobiologia. 170: 229-244

Carlton RG and Wetzel RG (1988) Phosphorus flux from lake sediments: Effect of epipelic algal oxygen production. Limnology and Oceanography. 33: 562-570

Carman R and Jonsson P (1991) The distribution pattern of different forms of phosphorus in some surfical sediment types of the Baltic Sea. Chem. Geol. 90: 91-106

Carman R, Aigars J and Larssen B (1996) Carbon- and nutrient geochemistry of the surface sediments of the Gulf of Riga, Baltic Sea. Marine Geology. 134: 57-76

Carman R and Rahm L (1997) Early diagenesis and chemical characteristics of interstitial water and sediments in the deep deposition bottoms of the Baltic proper. Journal of Sea Research. 37: 25-47

Carman R and Wulff F (1989) Adsorption capacity of phosphorus in Baltic Sea sediments. Est. Coast. Shelf Sci. 29: 447-456

Cederwall H and Elmgren R (1980) Biomass increase of benthic macrofauna demonstrates eutrophication of the Baltic Sea. Ophelia Suppl. 1: 287-304

Cederwall H and Jermakovs V (1999) Growth and production of three macrozoobenthic species in the Gulf of Riga, including comparisons with other areas. Hydrobiologia, 393: 201-210.

Conley JD and Johnstone RW (1995) Biogeochemistry of N, P and Si in Baltic Sea sediments: response to a simulated deposition of a spring diatom bloom. Marine Ecology Progress Series. 122: 265-276

Conley DJ, Stockenberg A, Carman R, Johnstone RW, Rahm L, Wulff F (1997) Sediment-water nutrient fluxes in the Gulf of Finland, Baltic Sea. Estuarine, Coastal and Shelf Science. 45: 591-598

Einsele W (1936) Uber die Beziehungen des Eisenkreislaufs zum Phosphatkreislauf im eutrofen See. Arch. Hydrobiol. 29: 664-686.

Enoksson V (1993) Nutrient recycling by coastal sediments: effects of added algal material. Marine Ecology Progress Series. 92: 245-254

Fenchel T and Blackburn TH (1979) Bacterial and mineral cycling (pp. 225). Academic Press, London.

Fleischer S (1986) Aerobic uptake of Fe (III) - precipitated phosphorus by microorganisms. Arch. Hydrobiol. 197: 267-277

Florentz M, Granger P and Hartemann P (1984) Use of ^{31}P nuclear magnetic resonance and electron microscopy to study phosphorus metabolism of microorganisms from waste-water. Appl. Envir. Microbiology. 47: 519-525

Froelich PN, Arthur MA, Burnett WC, Deakin M, Hensley V, Jahnke R, Kaul L, Kim KH, Roe K, Soutar A, and Vathakanon C (1988) Early diagenesis of organic matter in Peru continental margin sediments: Phosphorite precipitation. Marine Geology. 80: 309-343

Garber JH (1984) Laboratory study of nitrogen and phosphorus remineralization during the decomposition of coastal plankton and seston. Estuarine Coastal Shelf Science. 18: 685-702

Graf G, Bengtsson W, Faubel L, Meyer-Reil L, Schulz R, Theede H, Thiel H (1984) The importance of the spring phytoplankton bloom for the benthic system of Kiel Bight. Rapp. P-v Reun. Cons. Int. Export Mer. 183: 136-143

Graf G (1987) Benthic energy flow during a simulated autumn bloom sedimentation. Mar. Ecol. Prog. Ser. 39: 23-29

Gächter R, Meyer JS and Mares A (1988) Contribution of bacteria to release and fixation of phosphorus in lake sediments. Limnology and Oceanography. 33: 1542-1558

Gächter R and Meyer JS (1993) The role of microorganisms in mobilization and fixation of phosphorus in sediments. Hydrobiologia. 253: 103-121

Hinga KR, Sieburth JMcN, Heath GR (1979) The supply and use of organic material at the deep-sea floor, J. Mar. Res. 37: 557-579

Ingall ED, Schroeder PA, Berner RA (1990) the nature of organic phosphorus in marine sediments: New insights from ^{31}P NMR. Geochim. Cosmochim. Acta. 54: 2617-2620

Ingall ED, Duchamp JC, Zilm KW (1993) ^{31}P and ^{13}C NMR characterization of organic phosphorus and carbon during aerobic decomposition of marine plankton. Am. Chem. Soc., Abstr. Pap. 205, 187-190

Ingall E and Jahnke R (1994) Evidence for enhanced phosphorus regeneration from marine sediments overlain by oxygen depleted waters. Geochimica et Cosmochimica Acta. 58: 2571-2575

Ingall E and Jahnke R (1997) Influence of water-column anoxia on the elemental fractionation of carbon and phosphorus during sediment diagenesis. Marine Geology. 139: 219-229

Jensen MH, Lomstein E, Sorensen J (1990) Benthic NH_4^+ and NO_3^- flux following sedimentation of a spring phytoplankton bloom in Aarhus Bight, Denmark. Mar. Ecol. Prog. Ser. 61: 87-96

Jensen HS, Mortensen PB, Andersen FO, Rasmussen E, Jensen A (1995) Phosphorus cycling in a coastal marine sediment, Aarhus Bay, Denmark. Limnol. Oceanogr. 40: 908-917

Kerrn-Jespersen JP and Henze M (1993) Biological phosphorus uptake under anoxic and aerobic conditions. Water Res. 27: 617-624

Koop K, Boynton WR, Wulff F, Carman R (1990) Sediment-water oxygen and nutrient exchanges along a depth gradient in the Baltic Sea. Marine Ecology Progress Series. 63: 65-77.

Krom MD and Berner RA (1981) The diagenesis of phosphorus in a nearshore marine sediment. Geochimica et Cosmochimica Acta. 45: 207-216

Larsen, B. (1995) Evaluation of sediment pollution data: examples from the Gulf of Riga-status August 1995. Publications on Chemistry XXIII, Extended abstracts of the Symposium Environmental Analyses, University of Tartu, Department of Chemistry. 81-92.

Marais GVR, Loewenthal RE, and Siebritz IP (1983) Observations supporting phosphate removal by biological excess uptake - a review. Wat. Sci. Tech. 15: 15-41

Mortimer CH (1942) The exchange of dissolved substances between mud and water in lakes. 3-4. Journal of Ecology. 30: 147-201

Murphy I and Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 27: 31-36

Nedwell DB, Hall SE, Andersson A, Hagstro ÅF, Linstrom EB (1983) Seasonal changes in the distribution and exchange of inorganic nitrogen between sediment and water in the Northern Baltic (Gulf of Bothnia). Estuarine, Coastal and Shelf Science. 17: 169-179

Nixon SW (1981) Remineralization and nutrient cycling in coastal marine ecosystems. In: Neilson, B.J., Cronin, L.E. (ed) Estuaries and nutrients. Humana Press, Clifton, NJ, p. 111-138

Olesen M and Lundsgaard C (1995) Seasonal sedimentation of autochthonous material from the euphotic zone of a coastal system. Est. Coast. And Shelf Sci. 41: 475-490

Osborn DW and Nichols HA (1978) Optimisation of the activated sludge process for the biological removal of phosphorus. Prog. Wat. Tech. 10: 261-277

Pamatmat MM (1977) Benthic community metabolism: a review and assessment of present status and outlook. In: Coull BC (Ed) Ecology of marine benthos (pp. 89-111). Columbia: Univ. South. Carolina Press.

Parson TR, Maita Y and Lalli CM (1984) A Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press, Sidney.

Seppala J, Tamminen T, Kaitala S (2000) Experimental evaluation of nutrient limitation of phytoplankton communities in the Gulf of Riga. J. of Marine Systems. 628: xx-xx

Shapiro J (1967) Induced rapid release and uptake of phosphate by microorganisms. Science. 155: 1269-1271

Sondergaard M (1989) Phosphorus release from hypertrophic lake sediment: Experiments with intact sediment cores in a continuous flow system. Arch. Hydrobiol. 116: 45-59.

Smetacek V (1980) Annual cycle of sedimentation in relation to plankton ecology in western Kiel Bight. Ophelia, Suppl. 1: 65-76

Suess E (1980) Particulate organic carbon flux in the oceans - surface productivity and oxygen utilisation. Nature (London). 288: 260-263

Suess E and Muller PJ (1980) Productivity, sedimentation rate and sedimentary organic matter in the oceans. II. Elemental fractionation. In: *Biogeochimie de la matiere organique a l'interface eau-sediment marin.* (pp. 17-26). CNRS, Paris.

Tamminen T and Seppala J (2000) Nutrient pools, transformations, raios, and limitation in the Gulf of Riga, the Baltic Sea, during four successional stages. J. of Marine Systems. 627: xx-xx

Van Veen HW, Abee T, Kortstee GJJ, Konings WN, Zehnder AJB (1993) Characterization of two phosphate transport systems in *Acinetobacter johnsonii* 210A. J. Bacteriol. 175: 200-206

Wassmann P og Andrushaitis A (1993) Overgjodsling av Ostersjoen og Rigabukten. Naturen, Nr. 5: 205-213

Yurkovskis A, Wulff F, Rahm L, Andrushaitis A. and Rodrigues-Medina M (1993) A nutrient budget of Gulf of Riga, Baltic Sea. Estuarine, Coastal and Shelf Science. 37: 113-127

Zeitzschel B (1980) Sediment-water interactions in nutrient dynamics. In: Tenore KR and Coull BC (Ed) Marine benthic dynamics (pp. 195-218). Univ. South Carolina

Paper VI

Sediment-water phosphorus fluxes in the Gulf of Riga, Baltic Sea: seasonal approach.

Juris Aigars[1,2] and Rolf Carman[1]
1. Department of Geology and Geochemistry, Stockholm University, S-106 91, Stockholm, Sweden
2. Institute of Aquatic Ecology, Latvian University, LV-2163, Salaspils, Latvia.

Abstract

The flux experiment has been performed in March, July and September in order to simulate the response of sediments to deposition of particulate material in the period between spring and autumn algae blooms. Fluxes of DIP, NH_4^+ and NO_3^- + NO_2^- were measured after daily seston additions under various environmental conditions.

The deposition of two different amounts of seston normalized to phosphorus content (50 and 280 µmol-P $m^{-2}d^{-1}$) was simulated during March experiment. Generally fluxes of dissolved nutrients were small and no clear differences between treatments were observed most probably due to quality of added material.

The summer stratification induced depletion of O_2 concentration down to 4 mg dm^{-3} was simulated during July experiment. The enhanced release of DIP and NH_4^+ from sediment-water interface was observed after decrease of O_2 concentration. In contrast, sub-surface sediments accumulated part of DIP and NH_4^+ released from sediment-water interface shortly after O_2 concentration decrease most probably due to abiotic binding. Generally fluxes of NO_3^- and NO_2^- were directed into the sediments.

The higher than average pulse sedimentation event was simulated during September experiment. The sediments overlying water was kept well aerated throughout experiment. The pulse addition of seston resulted in large release of DIP and NH_4^+ from sediment-water interface most likely due to depletion of O_2 at sediment-water interface. Similarly to July experiment an uptake of DIP and NH_4^+ in sub-surface sediments was observed.

Key words: phosphorus, nitrogen, fluxes

Introduction

In coastal areas with shallow water depths between 10-50 % of the particulate material produced in the water column reach the sediment surface (Suess and Müller 1980, Suess 1980). At the sediment surface the decomposition of the settled organic material continues using various electron acceptors, e.g. oxygen, nitrogen, iron, sulphur. Thus, sediments react upon the increased deposition of organic material by increasing, firstly, the oxygen demand and with subsequent recycling of nutrients back to the water (see for instance Stumm and Morgan, 1981). For example, Garber (1984a) and Kelly and Nixon (1984) demonstrated that additions of phytoplankton to the sediment surface results in a rapid release of ammonium from the sediments. More recently Enoksson (1993) and Conley and Johnstone (1995) obtained the same pattern for ammonium as well as for phosphorus in different areas of the Baltic Sea. Moreover, it was discussed by Garber (1984b) that about 28 % (range 22-52 %) of the phosphorus stored in algae is liberated within 7 h after it has died. However, on the other hand Smetacek (1980) has shown that relatively intact cells can reach the sediments during spring and autumn blooms. These blooms can form, grow and senesce in as little as 1 to 2 week time (Smetacek et al., 1978). The organic particles settled after the spring phytoplankton bloom have a high nutritional content and can form the bulk of the annual food supply to the benthos (Gardner et al., 1985). However, the rapid mass sedimentation following the spring phytoplankton bloom may contribute for less than 10 % of the total flux during the stratified period (e.g., Olesen and Lundsgaard 1995). Although the summer sedimentation is relatively small (compared to the spring bloom) due to high zooplankton grazing activity the amorphous particles that reach the sediments have high organic carbon content (Smetacek 1980). This indicates that the particles settled to the sea floor are undiluted by mineral particles. Therefore, although the sedimentation rate per day is lower in summer than in spring, the summer sedimentation may give higher overall effect on sediment-water nutrient interaction.

The semi-enclosed Gulf of Riga (Figure 1) is known to be one of the most eutrophicated regions in the Baltic Sea (Wassmann and Andrushaitis, 1993). The annual freshwater run-off is on average 30.7 km^3. This is almost 10 % of the water volume of Gulf of Riga (420 km^3) (Yurkovskis et al. 1993). In order to assess the nutrient dynamic in such marine basin it is important to achieve direct measurements of biogeochemical processes that control the sediment-water interactions. Hence, this

Table 1. Station locations and characteristics.

Site	Latitude	Longitude	Depth (m)	Sediment type	Accumulation rates dry matter $g\ m^{-2}y^{-1}$ *
G5	57°20'0"	23°30'0"	44	mud	1000
T3	57°30'0"	24°06'0"	43	mud	2000

* Data derived from Larsen (1995).

study approach this issue by an experimental simulation of the deposition of particulate material in the period between spring and autumn blooms using natural samples of seston. Specifically, we aimed to characterise changes of phosphorus and to some degree nitrogen sediment chemistry, in order to quantify the fluxes of N and P under reduced oxygen concentrations and enhanced sedimentation of organic material.

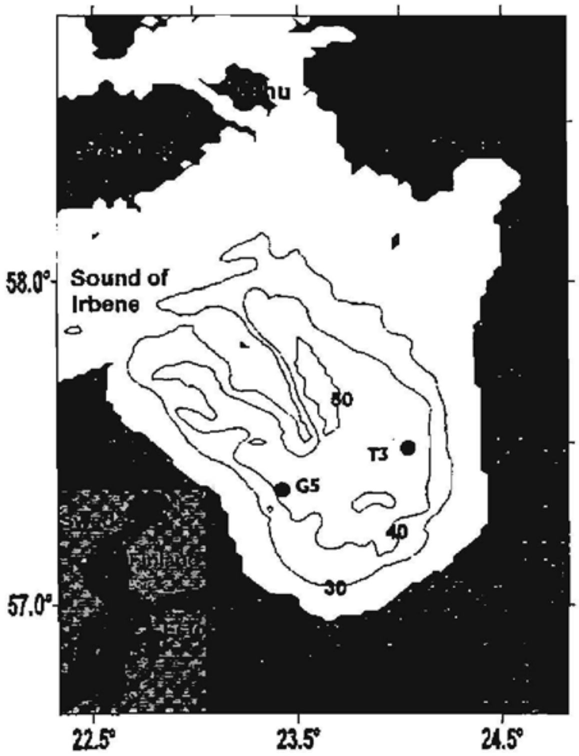


Figure 1. Map showing the sampling locations (G5 and T3) in the Gulf of Riga. The depth isolines of 30, 40, 50 m meters are marked, respectively.

Materials and methods

Sampling

Based on previous investigations (Carman et al., 1996) two sampling sites (Figure 1 and Table 1) were chosen. These sites represent two different deposition bottom regions regarding accumulation rate and geographical position in the Gulf of Riga. Sediments were sampled three times during 1998 i.e., in March, July and September. We used a modified Kajak corer (Blomquist and Abrahamsson, 1985) equipped with an acrylic liner with an inside diameter of 8 cm. At site T3 no samples were taken in September due to bad weather conditions. Altogether nine sediment cores were sampled during each sampling occasion. Three of these cores were immediately sectioned in 1 cm sections and transferred to 50 ml centrifuge tubes for centrifugation. The obtained pore water was filtered through Whatman GF/F filters (0.47 µm) and subsequently used for ammonia and orthophosphate analysis. The sediment pore water data reported are the mean value of these three cores. Further, one core was used to measure the vertical redox potential profile using a platinum electrode and one core was sectioned in 1 cm sections and stored in a freezer for later bulk analysis of different phosphorus fractions. The remaining four intact sediment cores were used in the flux experiment.

Seston (sinking dead plankton plus detritus) was collected below the euphotic zone using plankton net. Prior to use the seston was stored in suspension (sea water) in a refrigerator.

Experimental design for the flux measurements

Intact undisturbed sediment cores (n = 4) with about 1 l overlying seawater together with similar columns (n = 2) with unfiltered ambient bottom water were incubated in a dark room at *in situ* temperatures. The additions of seston normalized to phosphorus content were carried out daily. The particulate phosphorus was measured regularly throughout the experiment, while the total carbon and nitrogen of the seston was measured only during the summer experiment. The C:N:P ratio were at that time 241:37:1 (by atoms), i.e., depleted in phosphorus compared to Redfield ratio. Before the flux experiment began the system was allowed to stabilize for at least 24h. The first flux measurements (PO_4^{3-}, NH_4^+, NO_3^- + NO_2^-) were performed before the spring bloom occurred in the gulf. Since no actual sedimentation rates in the Gulf of Riga were measured during

Table 2. Bottom water nutrient and oxygen concentrations.

Sampling time	Site	Temp. (^{0}C)	O_2 (mg dm^{-3})	PO_4^{3-} (µmol dm^{-3})	NH_4^+ (µmol dm^{-3})	$NO_3^-+NO_2^-$ (µmol dm^{-3})
March 1998	G5	0.5	12.4	1.16	1.74	10.9
	T3	0.7	12.7	1.9	1.26	13.3
July 1998	G5	4.1	9.3	0.04	16.5	4.7
	T3	2.5	8.1	0.25	6.2	8
September 1998	G5	2.4	5.4	2.1	6.5	11.5

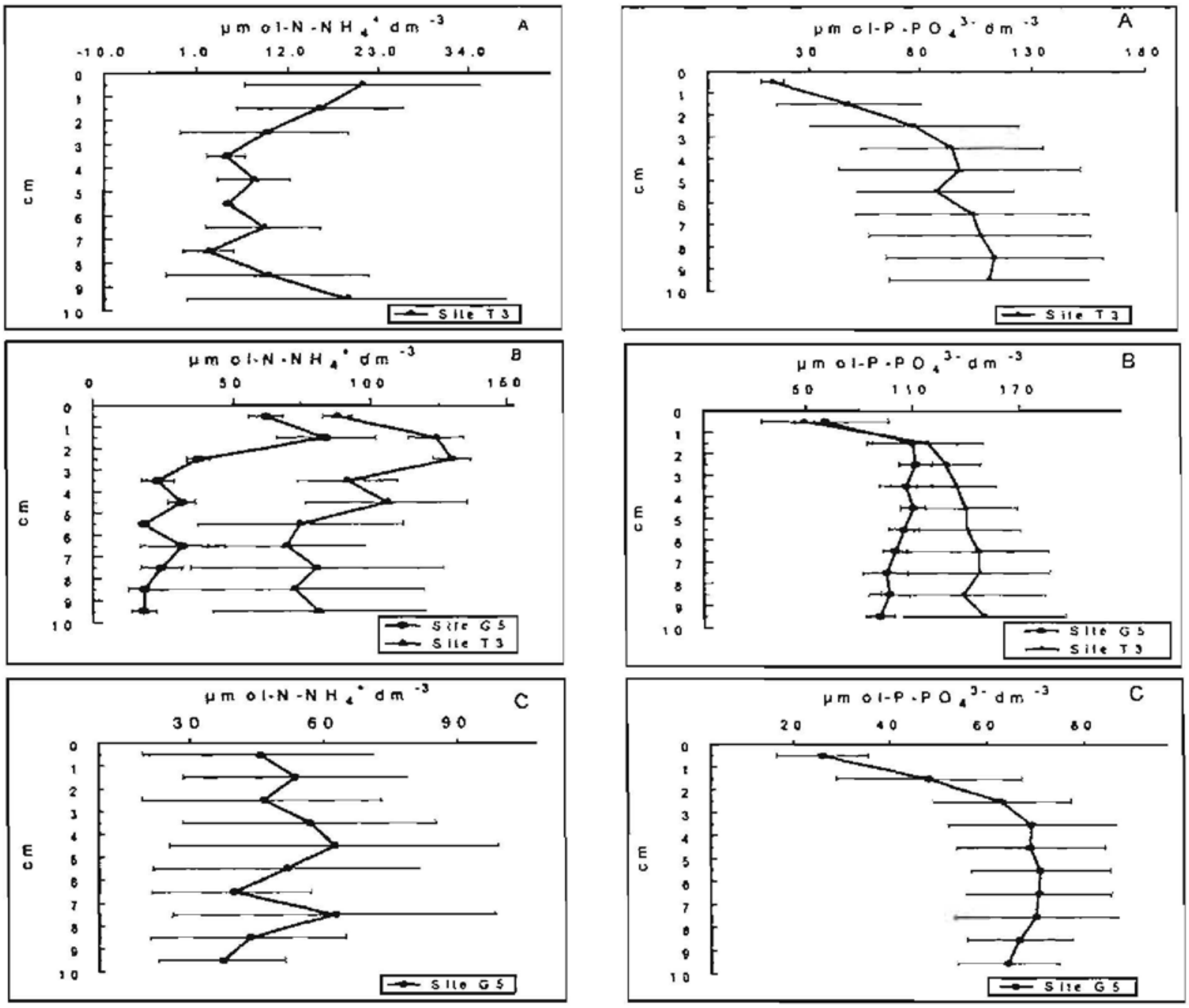


Figure 2. Average pore water profiles from three cores of ammonia and phosphate. A - sampled in March, B - sampled in July, C - sampled in September. Horizontal bars represent one standard deviation.

winter-early spring addition of 50 and 280 µmol m^{-2} of particulate phosphorus was carried out daily which are in a range of lowest and average sedimentation rates during spring-autumn (Reigstad et al. 1999). The supernatant water was maintained well aerated throughout the incubation period.

The second treatment was conducted in July 1998. The input of seston (650 µmol-P m^{-2}d^{-1}) was kept constant in the range of maximal sedimentation rate of particulate phosphorus reported for the Gulf of Riga (Reigstad et al. 1999). The concentration of oxygen was lowered from 11 mg dm^{-3} to 4 mg dm^{-3} which is the lowest average ambient concentration observed previously (Berzinsh, 1995).

The third treatment was conducted in September 1998 with the aim to simulate a higher than average impulse sedimentation i.e., impulse addition of 440 µmol-P m^{-2}d^{-1} while before and after pulse addition was kept at 180 µmol-P m^{-2}d^{-1} which is in range of autumn average sedimentation rate (Reigstad et al. 1999). As during the spring experiment the supernatant water was maintained well aerated throughout the incubation period.

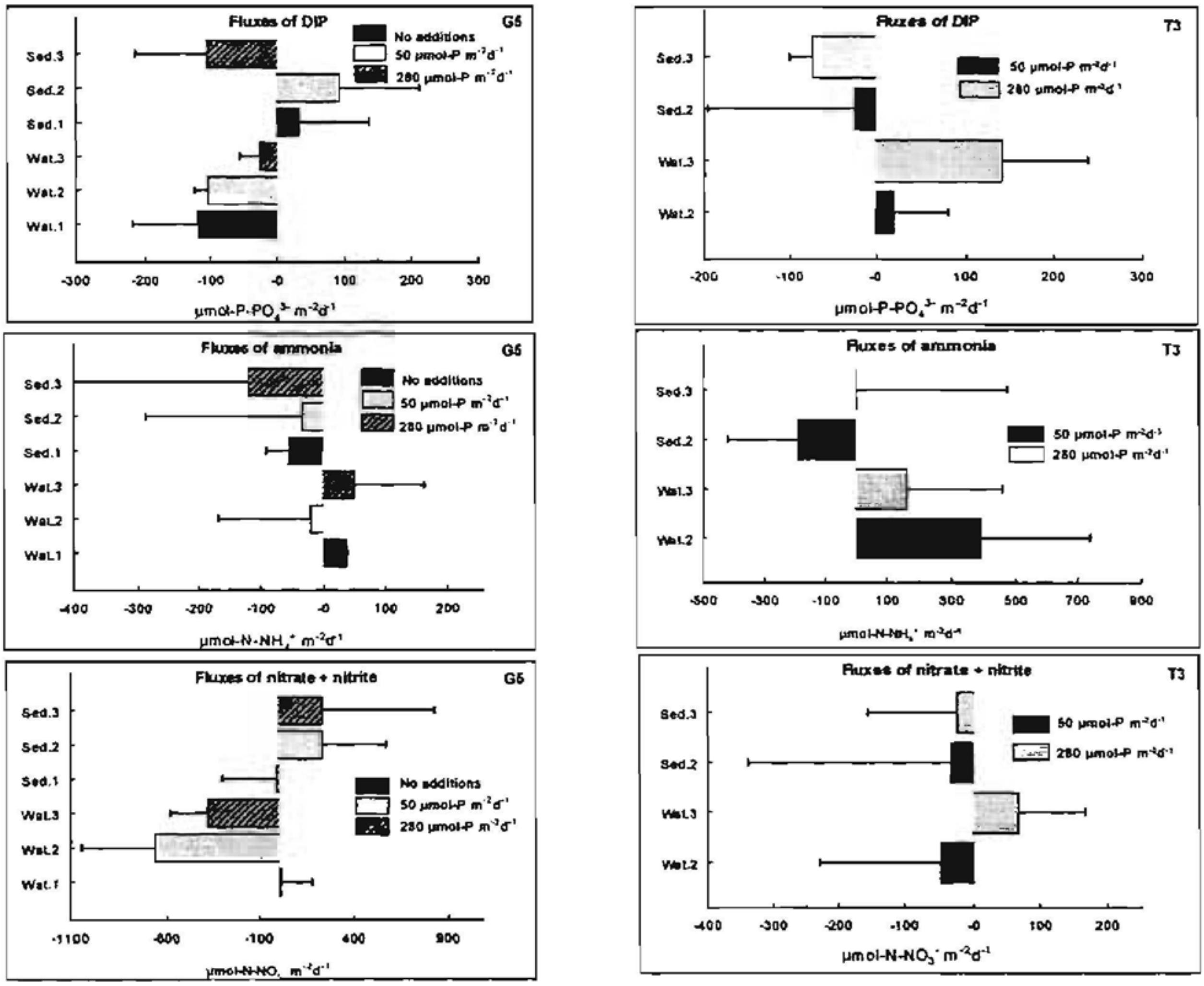


Figure 3. Average values (± one standard deviation) of sediment-water fluxes for DIP, NH_4^+, NO_3^- + NO_2^- during March 1998. Wat. - represents fluxes in columns without sediment and Sed. - represents fluxes in columns with sediments after values from columns without sediments were substituted. Numerical indexes indicate treatment additionally explained in figure legend. Positive values denote fluxes out of sediments into the overlying water and negative values fluxes into sediments.

Analytical determinations

Total concentration of phosphorus (TP) and inorganic phosphorus (IP) in the sediment were determined by extraction with 1 M HCl before and after combustion according to Froelich et al. (1988). All wet extracts of P were measured using standard spectrophotometric technique (e.g., Murphy and Riley, 1962). Ammonium (NH_4^+) and dissolved inorganic phosphorus (DIP) concentration in all water samples collected from the core incubations as well as the pore water was immediately determined using common standard methods (e.g., Parsons et al. 1984). Samples for nitrate + nitrite (NO_3^- + NO_2^-) were analyzed using cadmium reduction (Parsons et al. 1984). The analysis of the total P concentrations of the added particulate seston was accomplished by digestion in acid persulfate (Koroleff, 1976). Total carbon and total nitrogen was measured on LECO element analyzer

Results

Sediment cores and supernatant water

Due to technical problems at site G5 during the spring sampling event no sediment cores for pore water and sediment analysis were collected. Moreover, due to stormy weather conditions it was impossible to take any samples at all at site T3 during the autumn sampling event.

The concentrations of TP and IP from the uppermost sediment section (0-1 cm) were on average 56 and 44 µmol-P g^{-1} dry weight, respectively. This value was considerably higher than those from the second slice below sediment surface (1-2 cm) where the concentration on average were 36,7 and 26 µmol-P g^{-1} dry weight for TP and IP, respectively.

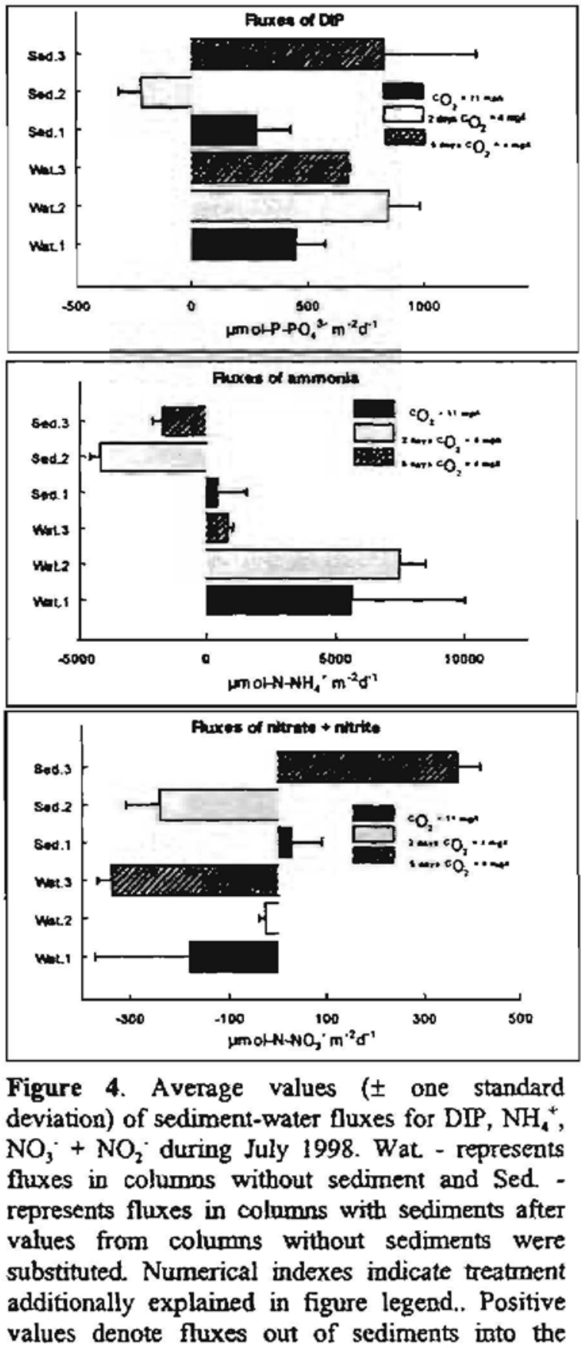


Figure 4. Average values (± one standard deviation) of sediment-water fluxes for DIP, NH_4^+, NO_3^- + NO_2^- during July 1998. Wat. - represents fluxes in columns without sediment and Sed. - represents fluxes in columns with sediments after values from columns without sediments were substituted. Numerical indexes indicate treatment additionally explained in figure legend.. Positive values denote fluxes out of sediments into the overlying water and negative values fluxes into sediments.

At site G5 the redox potential of the uppermost centimetre was 10 and 32 mV during July and September, respectively. At site T3 it was 347 and 364 mV during March and July, respectively. Stable negative redox values were reached already beneath third centimetre below sea floor (-120 and - 90 mV for sites G5 and T3, respectively).

The water content ranged from around 90 % in the uppermost part of the sediments to around 75 % between 9 and 10 cm below sea floor.

The overlying water temperatures and the concentrations of O_2, PO_4^{3-}, NH_4^+, NO_3^-+NO_2^- are compiled in Table 2. Temperature and ammonium concentration exhibit general increasing tendency between spring and autumn. However, PO_4^{3-} and NO_3^-+NO_2^- exhibit lowest concentrations during July.

Pore water profiles

Similar pore water profiles of NH_4^+ and DIP were obtained for both site G5 and T3 (Figure 2). The common feature for both sites is development of subsurface maximum of NH_4^+ at 1-2 cm and 1-3 cm for sites G5 and T3, respectively.

Sediment-water fluxes

Generally the sediment-water fluxes of all measured parameters during March were low and unidirectional. Mostly, no clear response to added organic matter could be seen (Figure 3). However, at site G5 significant differences (ANOVA, $P<0.01$) between 50 and 280 µmol-P m^{-2}d^{-1} treatments where detected for the DIP fluxes.

During initial stage of the July experiment at site G5 all fluxes in the columns with sediments were directed out from sediments even though the supernatant water was well aerated (Figure 4). When the concentration of O_2 in the supernatant water was adjusted to 4 mg dm^{-3} the fluxes of all measured parameters changed significantly (ANOVA, $P<0.01$) and were directed into the sediments. The DIP and NO_3^- + NO_2^- fluxes were directed out from the sediment after low oxygen level (4 mg-O_2 dm^{-3}) was maintained for 5 days. Although they were higher than under well-aerated conditions the difference between treatments was statistically significant (ANOVA, $P<0.01$) only for NO_3^- + NO_2^- fluxes. In contrast, fluxes of NH_4^+ were still directed into the sediments. The July experiment at site T3 were not completed because of experiment failure due to breakdown of the peristaltic pump. However, results from initial stage of experiment are presented in Table 3.

During the September flux measurement the fluxes of DIP and NH_4^+ were, comparing to measured summer values, small during the initial stage of organic matter treatment, i.e. addition of 180 µmol-P m^{-2}d^{-1}, (Figure 5). In contrast, fluxes of NO_3^- + NO_2^- were significantly higher in columns with sediments. After a pulse addition of seston (440 µmol-P m^{-2}d^{-1}) a significant changes in the flux of all measured parameters could be observed (NH_4^+ and NO_3^- + NO_2^- (ANOVA, $P<0.01$); DIP (ANOVA, $P=0.02$)). During this stage all these fluxes were directed into the sediments. After return to initial seston addition a significant (ANOVA, $P<0.01$) change in the DIP and NH_4^+ fluxes rate could be observed after 48 h. The flux were now directed out of the sediment. However, the fluxes of NO_3^- + NO_2^- remained unchanged i.e., directed into the sediments.

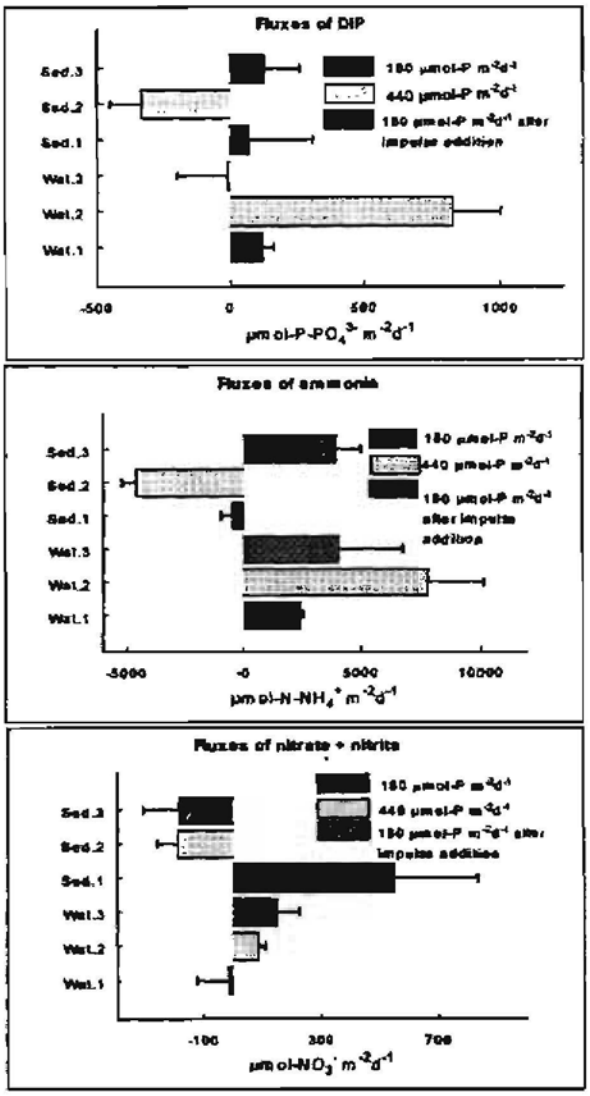


Figure 5. Average values (± one standard deviation) of sediment-water fluxes for DIP, NH_4^+, NO_3^- + NO_2^- during September 1998. Wat. - represents fluxes in columns without sediment and Sed. - represents fluxes in columns with sediments after values from columns without sediments were substituted. Numerical indexes indicate treatment additionally explained in figure legend. Positive values denote fluxes out of sediments into the overlying water and negative values fluxes into sediments.

Discussion

It has been argued in many investigations that the sediments of the Baltic Sea plays an important role in the cycling of nutrients (e.g. Nehring et al., 1984; Shaffer and Rönner, 1984; Larsson et al., 1985; Rönner, 1985; Wulff and Stigebrandt, 1989; Koop et al., 1990; Carman et al., 1996). For nutrient as well as for many other components the biogeochemical condition of the sediment-water system regulates the fluxes of nutrients through the sediment-water interface. For both nitrogen and phosphorus the oxygen condition (redox environment) is a key parameter in this flux between sediment and overlaying water.

The Gulf of Riga has during the last centuries received an increasing amount of nutrients, which in turn has resulted in increasing algae blooms and benthic fauna communities (Cederwall et al., 1999). However, due to limited water depths and a holomictic mixing of the water mass each year only the deeper parts of the Gulf will be occasionally depleted in oxygen (Berzinsh et al., 1988; Yurkovskis et al., 1993). Anyhow, it is still an open question how the sediment-water interaction processes have responded to these altered conditions in the Gulf and what will happen if the supply of organic material to the sediment surface will increase even more.

Measured pore water profiles from the two stations exhibit a normal pattern for soft bottom sediments in the Baltic Sea (e.g., Carman and Rahm, 1997; Conley et al., 1997). The pore water subsurface maximum observed in summer for NH_4^+ (Fig. 2) is most likely an effect of the supply of organic material during that time of sampling and not an effect of altered temperature in the bottom water since it were almost constant (around 3°C) during summer. Moreover, a similar peak were observed by Conley and Johnstone (1995) when they added organic material in their lab experiment and similar modifications of porewater nutrient concentrations following the deposition of diatom blooms have been occasionally observed also in nature (Nedwell et al. 1983, Jensen et al. 1990). However, Conley and Johnstone (1995) showed that changes in pore water concentrations require deposition of large amount of organic matter combined with altered redox condition.

After addition of an estimated daily deposition of organic material (Reigstad et al., 1999) the sediment-water fluxes of phosphorus as well as for nitrogen (both sites) were among the highest ever reported for the Baltic Sea (Table 3). However, the rates are comparable with fluxes from similar environments (Nixon, 1981; Boynton and Kemp, 1985; Boyton et al., 1990). As in similar environments, the alteration from oxic to hypohic/anoxic conditions is the main reason for such huge rates of nutrients out of the sediment. Change in redox conditions in the bottom water is mainly a result of alteration in the supply of organic material to sediments and it will, in turn, affect the rates and pathways of settled organic matter remineralization within the sediments (e.g. Graf et al. 1982; 1983; Conley and Johnstone, 1995). During winter, when the primary production is negligible, the contribution of resuspended sediment to settling material is expected to be highest. Therefore, although sedimentation rates in coastal and near-shore areas could be high even during winter, the deposited material normally has a low impact on the sediment-water fluxes of nutrients because the particulate material deposited

Table 3. Characteristics and flux rates from different Baltic Sea regions.

Location	Sampling Scheme	Type	Sediment characteristics[a]		Depth (m)	Temp. (°C)	Fluxes (µmol m^{-2} h^{-1})			Comments	Source
			% Org. C	Φ			N-NH$_4$	N-NO$_3$ + N-NO$_2$	P-PO$_4$		
Kiel Bight W Germany	Annual	Silt/sand	1.0-2.25[b]	37	20	2-18	5.6-27.8 (110)[c]	5.6-10.0	0.7-2.6	Occasional periods of anoxia encountered during summer	Balzer (1984)
Gulf of Bothnia	Apr/Jul	Soft silt	-	-	22	0-15	0.2-20 (40.0)[c]	2.8-8.5	-	NH$_4$ fluxes enhanced by presence of organic detritus on sediment surface	Nedwell et al. (1983)
Laholm Bay, W Sweden	Sept.	Silt	3.4	80	20	9	50 (200)[c]	0 to -5 (-20 to -30)[c]	0 to -5 (0-10)[c]	Organic - rich sediments	Enoksson (1987)
ASKÖ transect, Baltic proper	July	Sand/silt	0.5	71	47	4.1	13 (18)[d]	-2.2 (-1.0)[d]	-0.5 (12.6)[d]	Sediments well mixed	Koop et al. (1990)
	July	Silt	5.9	81	82	4.8	4 (24)[d]	-8.7 (-9.0)[d]	0.1 (21.7)[d]	Sediments partly mixed	Koop et al. (1990)
	July	Silt	6.7	91	130	4.9	13 (33)[d]	-14.3 (-10.0)[d]	0.2 (3.7)[d]	Sediments are laminated	Koop et al. (1990)
Gulf of Finland	July	-	3.4-7.8[e]	87-94[e]	35-85	-	9.37-34.7	-6.33 - 12.5[f] (0.1-2.45)	0-41		Conley et al. (1997)
Gulf of Riga	March	Mud	5[e,g] (6.3)		44[h] (43)	0.5[h] (0.7)	1.32[h] (13.7)	-7.6[h] (- 7.9)	-0.3[h] (- 4)	Large accumulation rate, sharp gradient between oxic and reduced sediments	This study
	July	Mud	5[e,g] (6.3)		44[h] (43)	4.1[h] (2.5)	-29.3[h] 141[k] (-86)	-3.3[h] -11[k] (38.5)	15.5[h] 26.4[k] (-27.8)	Large accumulation rate, sharp gradient between oxic and reduced sediments	This study
	Sept.	Mud	5[e,g] (6.3)		44[h] (43)	2.4[h]	125[h]	-117.4[h]	19[h]	Large accumulation rate, sharp gradient between oxic and reduced sediments	This study

[a] % Organic C and Φ represent percent organic carbon and porosity, respectively, in the upper 2 to 10 cm of the sediment column

[b] Range in the surface 2 mm. Entry in parenthesis is average for sediments below 3 cm.

[c] Flux recorded during anoxic period in summer.

[d] Fluxes recorded during hypoxic/anoxic periods.

[e] In the upper 1 cm of the sediment column.

[f] Only N-NO$_3$. N-NO$_2$ fluxes are given in brackets.

[g] From Aigars and Carman (2000) for site G5. Value in brackets is for site T3.

[h] For site G5. Value in brackets is for site T3.

[K] Recorded during low oxygen conditions.

during winter usually has low degradable organic carbon content. In contrast, the organic degradable carbon content in the settling particles during summer is high (e.g., Smetacek, 1980). Therefore, most likely the high fluxes measured in July and September were due to the high quality of deposited organic material during that time.

For fluxes of phosphorus between the sediment- water interface the oxygen condition/redox milieu has been widely accepted as a key factor in controlling phosphorus content in the sediments. Thus, it is observed in all flux experiments that DIP is released from sediments when oxygen approaches zero in the supernatant water. For instance, Koop et al. (1990) and Conley et al. (1997) showed enhanced DIP release from sediments when the concentration of oxygen in overlying water decrease below 1 g O_2 m^{-3} and the sediment surface exhibited reduced conditions. Furthermore, Conley and Johnstone (1995) discussed that although the water column remains well aerated a large addition of organic matter may cause oxygen deficiency at sediment surface because oxygen consumption at the sediment-water interface exceeds the delivery. Hence, it will induce anaerobic conditions to persist at the sediment-water interface and subsequently it will induce higher DIP fluxes than during oxic conditions (e.g., Krom and Berner, 1980). Generally our data (see Fig. 4 and Fig. 5) comply with above-mentioned investigations. However, the sub-surface sediments accumulated DIP and NH_4^+ shortly after oxygen concentration has been set to 4 mg dm^{-3} (Fig. 4) and after enhanced pulse addition of particulate material (Fig. 5). This is similar to the uptake of DIP observed by Enoksson (1993) shortly after algae additions and supported by modified nutrient pore water concentrations reported by Conley and Johnstone (1995). Most likely this is a result of an abiotic sorption of DIP and NH_4^+ due to altered by enhanced pore water concentrations kinetic equilibrium (e.g., Krom and Berner, 1980).

The spring phytoplankton bloom settling is normally accepted as the major input of fresh organic material to sediments. However, exception from that is reported, for instance, Olesen and Lundsgaard (1995) indicated that rapid mass sedimentation following spring phytoplankton bloom sedimentation might comprise less than 10 % of the total flux during the stratified period. Furthermore, the peaks in sedimentation rates due to sedimentation of summer phytoplankton blooms or resuspension events were observed during seasonal study of Smetacek (1980) in the Kiel Bight (Baltic proper). Similar sedimentation event of phytoplankton and resuspended organic material has also been observed in the Gulf of Riga (Floderus et al., 1999). The deposition of summer phytoplankton bloom is expected to give similar effect as deposition of spring phytoplankton bloom. During our experiment, simulation of such events (Fig. 5) resulted in significant increase of DIP and NH_4^+ release rates from sediment surface. However, significant changes in flux rates were observed only when two or three times the normal sedimentation of organic material was added causing oxygen deficiency at the sediment water interface.

The nutrient fluxes measured in July under simulated low oxygen conditions are similar to the fluxes observed in September under natural low oxygen conditions except for nitrate (Table 3). The nitrate concentration in near bottom water was more than two times lower (Table 2) during July than during September. This may partly explain the differences in flux rates. However, a more likely explanation is that during September the oxic layer was thinner than during July. Therefore, the oxic-anoxic interface was situated closer to the sediment surface in September and, thus, increased the denitrification efficiency during that period compared to that in July.

Although the Gulf of Riga normally develops a thermocline during summer the near-bottom water can be subjected to outside influences such as bottom water currents. This could, for instance, be seen from the temperature and nutrient concentration measurements at site G5 (Table 2). Obviously warmer and more saline surface water from the Baltic proper was introduced into the near bottom water layer of site G5 in July. It is reasonable to believe that the observed differences in the flux rates (Table 3) between site G5 and T3 during that time (July) were caused by this event.

In current study the decrease of the orthophosphate concentration in near bottom water between March and July (Table 2) reveal that during well oxygenated conditions, except at site G5 during July, fluxes of P-PO_4 is directed into the sediments (Table 3). The effective burial of phosphorus during grazing periods could be a result of the findings by Gächter and Mares (1985) and Hupfer et al. (1995) who presented evidence that sinking seston accumulate soluble reactive phosphorus from the water column. The increase of P-PO_4 concentration in near bottom water (Table 2) and positive P-PO_4 flux (Table 3) out of the sediment during September indicate that net release of P-PO_4 occurs late summer - autumn during periods when the oxygen concentration in near bottom water decreases substantially.

Some earlier investigations (e.g., Enoksson, 1993) indicated that significant amount of added particulate material could be utilized from the sediment as dissolved organic nitrogen (DON) and possibly also as dissolved organic phosphorus (DOP). Further, many authors (e.g. Kemp et al. 1990, Enoksson 1993) point out the importance of denitrification in the release of remineralized nitrogen. Another possible source for the observed increased release of NH_4^+ during low oxygen conditions could be a cat-ion exchange between potassium and ammonium in certain clay minerals (e.g., Müller, 1997). Thus, since DON, DOP and denitrification rates were not measured in this investigation we have avoided to perform a budget calculations since it could result in severe underestimation.

Conclusions

Present investigation shows clearly that even small alteration in the primary production in the Gulf of Riga will affect the sediment-water interaction properties largely. During summer stratification may develop large areas of anoxic or sub-oxic bottoms with absence of macro fauna. This will in turn hamper the bioturbation on certain areas even more than it is today and the oxygen supply to the superficial parts of the sediments will to a greater degree than today be hampered. It will not only induce a higher release of dissolved nutrients due to a higher degradation amount induced by enhanced settling of primary produced organic material but it will also decrease the storage capacity for phosphorus and decrease the possibility for denitrification and increase the ammonium flux towards photic zone. Hence, the eutrophication situation in the Gulf will accelerate largely due to changed internal sediment processes. For phosphorus it could be referred as the "phosphate pump" (Shaffer, 1986) but it could also be applied for the nitrogen cycle i.e., the ammonium release from the sediment will increase in similar fashion as for phosphorus.

The extinction of bottom biota will most likely also affect the fishery industry since the fish that lives close to the bottoms will have less food sources.

Additional consequence of increased eutrophication may be decrease of recreation value of Gulf of Riga due to visual effect of algae rich nearshore waters and decaying biomass on shores.

References

Banta, G.T. (1992) Decomposition and nitrogen cycling in coastal marine sediments - controls by temperature, organic matter inputs, and benthic macrofauna. PhD dissertation, Boston University

Berzinsh, V. (1995) Hydrological regime. In: E. Ojaveer (ed.) Ecosystem of the Gulf of Riga between 1920 and 1990. Estonia Academy Publishers, Tallinn. p. 7-31.

Blomqvist, S. and Abrahamsson, B. (1985) An improved Kajak-type gravity core sampler for soft bottom sediments. Schweiz. Z. Hydrol. 47: 81-84

Carman, R., Aigars, J. and Larsen, B. (1996) Carbon and nutrient geochemistry of the surface sediments of the Gulf of Riga, Baltic Sea. Marine Geology, 134: 57-76.

Conley, D.J. and Johnstone, R.W. (1995) Biogeochemistry of N, P and Si in Baltic Sea sediments: response to a simulated deposition of a spring diatom bloom. Mar. Ecol. Prog. Ser. 122: 265-276

Enoksson, V. (1993) Nutrient recycling by coastal sediments: effects of added algal material. Mar. Ecol. Prog. Ser. 92: 245-254

Froelich, P.N., Arthur, M.A., Burnett, W.C., Deakin, M., Hensley, V., Jahnke, R., Kaul, L., Kim, K.H., Roe, K., Soutar, A., and Vathakanon, C. (1988) Early diagenesis of organic matter in Peru continental margin sediments: Phosphorite precipitation. Marine Geology. 80: 309-343.

Floderus, S., Saarso, M., Kouts, T., Bäckström, L.G. and Jämlich, S. (1995) Aggregate resuspension and transport in the Gulf-of-Riga bottom pelagic. In (Wassmann, P. Ed.) Pelagical eutrophication and sedimentation. Status report on March 1995. Nordic Council of Ministers, Gulf of Riga project.

Garber, J.H. (1984a) ^{15}N tracer study of the short-term fate of particulate organic nitrogen at the surface of coastal marine sediments. Mar. Ecol. Prog. Ser. 16: 89-104

Garber, J.H. (1984b) Laboratory study of nitrogen and phosphorus remineralization during the decomposition of coastal plankton and seston. Est. Coast. Shelf Sci. 18: 685-702

Gardner, W.S., Nalepa, T.F., Frez, W.A., Chichoki, E.A., Landrum, P.F. (1985) Seasonal patterns in lipid content of Lake Michigan macroinvertebrates. Can. J. Fish. Aquat. Sci. 42: 1827-1832

Gerlach, S.A. and Schrage, M. (1971) Life cycles in marine meiobenthos. Experiments at various temperatures with *Monhystera disjuncta* and *Theristus pertenius* (Nematoda). Marine Biology. 9: 274-280

Graf, G., Bengtsson, W., Diesner, U., Schulz, R., Theede, H. (1982) Benthic response to sedimentation of a spring phytoplankton bloom: process and budget. Marine Biology. 67: 201-208

Graf, G., Schulz, R., Peinert, R., Meyer-Reil, L.-A. (1983) Benthic response to sedimentation events during autumn to spring at a shallow-water station in the Western Kiel Bight. Marine Biology. 77: 235-246