

**Shallow subtidal sand:
Permeability, nutrient dynamics,
microphytobenthos and organic matter**

DISSERTATION

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Summary

Most coastal biogeochemical studies have focussed on intertidal sediments. To complement these, this study describes the temporal dynamics of a permeable shallow subtidal sandy sediment by measuring pore water nutrients, microphytobenthos and organic matter. This study was carried out in the List tidal basin in the northern Wadden Sea. Shallow subtidal sands comprise about half of the area of this large tidal basin.

This work is part of an EU - project (EVK – CT2002 – 0076) on the role of permeable sands in coastal exchange processes (COSA, “Coastal sands as biocatalytical filters”) and the task of this study was to elucidate key variables for remineralisation and primary production in permeable shallow subtidal sands near the island Sylt in the North Sea (Germany) over a two year period.

Permeability of the sediment is a key factor for sedimentary processes. Changes in sediment permeability and the potential forcing factors were measured monthly from March 2003 to April 2005. Permeability varied seasonally with highest values in winter and spring, and lowest values in summer and autumn and enabled advective pore water exchange all the time. Redundancy analysis (RDA) showed that the only significant and main influencing factor explaining sediment permeability was the mean average wind speed on the sampling day, suggesting that wave induced turbulence increase sediment permeability. The triplot of the RDA showed that permeabilities during autumn, especially in the year 2003, were influenced by the content of extrapolymeric substances (measured as EDTA-extractable carbohydrates) in the sediment. Permeability during the summer months in both years was also influenced by the amount of fine fraction in the sediment. The latter two factors were not statistically significant.

The results suggest that the shallow permeable subtidal sediment at the study site was influenced all the time by wind induced waves, leading to seasonal changes in the permeability. But it is probable that a combination of factors like changed consolidation of the sediment, diatoms and their extrapolymeric substances, and the trapping of fine particles in the sediment are contributing to the observed dynamics of permeability.

Temporal pore water nutrient and salinity changes were investigated between February 2003 and April 2005 at the same site. Si(OH)_4 and NH_4^+ pore water profiles showed low concentrations in the upper 4 - 6 cm of the sediment probably due to advection and assimilation by microphytobenthos. Concentrations increased below this layer. PO_4^{3-} concentrations always reached maximum values between 3 and 7 cm sediment depth, while NO_3^- and NO_2^-

reached maximum concentrations in the upper centimetres. The mean pore water concentrations in the upper 5 cm of the sediment showed similar dynamics for Si(OH)_4 , NH_4^+ and PO_4^{3-} in both years: lowest concentrations in spring and late summer / early autumn and two concentration peaks, one during summer and one during winter. A short peak of these nutrients occurred also during spring probably as a response to settling phytoplankton blooms. It is suggested that this pattern is the result of changing temperature, light conditions and organic matter loading in the sediment. In contrast NO_3^- followed the same dynamics as the overlying water column with low concentrations in summer and autumn and high concentrations in winter and spring. During winter and spring the nutrient dynamics at the sampling site were also influenced by inflowing water from below with low salinities, containing high concentrations of Si(OH)_4 and NH_4^+ . High NO_3^- concentrations in the inflowing water were observed during winter and spring 2004 / 2005.

Temporal dynamics of microphytobenthos biomass and organic matter were investigated between February 2003 and November 2004 at the same study site. Throughout the upper 6 - 10 cm a high standing stock of microphytobenthos was found, decreasing to low values at 15 cm. There was no apparent seasonality and biomass was high in comparison to the phytoplankton biomass of the overlying water column and reported biomass from other intertidal and subtidal sediment. In June 2004 microphytobenthos was sampled along a transect from the high water line down to a depth of 4 m below the low water level. Highest microphytobenthos biomass was found near the low water tide mark and in the shallow subtidal.

The organic matter content in these subtidal sediments was low but of high quality. Based on a carbon : chlorophyll *a* ratio of 40 about 50 % of the organic carbon was related to microphytobenthos in the upper 5 cm of the sediment. Organic matter not associated with live microphytobenthos correlated with benthic biomass suggesting a rapid turnover of benthic biomass. The C : N : P relationship was close to the Redfield ratio, indicating that the organic matter in the sediment was of a good quality.

The upper subtidal permeable sand is suggested to be an optimum habitat for microphytobenthos by combining reasonable light conditions with permanent advection of particulate matter, dissolved nutrients, O_2 and CO_2 .

Zusammenfassung

Die meisten biogeochemischen Untersuchungen entlang der Küsten beschäftigten sich bisher mit intertidalen Sedimenten. Um diese Studien zu ergänzen, ist Ziel dieser Arbeit, die zeitliche Dynamik u. a. von Nährstoffen im Porenwasser des Sediments, des Microphytobenthos und des organischen Materials in einem permeablen sandigen Sediment im flachen Sublitoral zu untersuchen. Die Untersuchung wurde im Lister Tidebecken im nordfriesischen Wattenmeer durchgeführt. Ungefähr die Hälfte der Fläche dieses großen Tidebeckens wird von flachem Sublitoral bedeckt.

Diese Arbeit ist Teil eines EU - Projektes (EVK – CT2002 – 0076), das die Rolle von permeablen Sänden bei Austauschprozessen in Küstengewässern untersucht (COSA, „Coastal sands as biocatalytical filters“). Ziel dieser Arbeit war es, die Schlüsselvariablen für Remineralisierungsprozesse und Primärproduktion in einem permeablen Sand im flachen Sublitoral in der Nähe der Insel Sylt in der Nordsee im Verlauf von zwei Jahren zu bestimmen.

Die Permeabilität des Sedimentes ist eine Schlüsselvariable bei im Sediment stattfindenden Prozessen. Von März 2003 bis April 2005 wurden monatlich die Änderungen der Sedimentpermeabilität und die möglichen Einflussfaktoren gemessen. Die Permeabilität änderte sich mit den Jahreszeiten und war im Winter und Frühling höher als im Sommer und Herbst. Advektiver Porenwassertransport war die gesamte Zeit möglich. Eine durchgeführte Redundanzanalyse (RDA) zeigte, dass der einzige signifikante Einflussfaktor für die Sedimentpermeabilität die mittlere Windgeschwindigkeit am Tag der Probenahme war. Das lässt vermuten, dass durch welleninduzierte Turbulenzen die Permeabilität des Sediments erhöht wird. Der Triplot der RDA zeigte, dass die Permeabilität im Herbst, besonders im Jahr 2003, durch den Gehalt von extrapolymere Substanzen im Sediment beeinflusst wurde. Im Sommer beider Jahre war die Permeabilität außerdem durch den Gehalt von Feinfraktion im Sediment beeinflusst. Die beiden letzteren Einflussfaktoren waren jedoch nicht signifikant.

Die Ergebnisse legen den Schluss nahe, dass das permeable Sediment im flachen Sublitoral an dieser Stelle permanent von windinduzierten Wellen beeinflusst wurde, was zu einer Saisonalität in der Permeabilität führte. Es ist jedoch wahrscheinlich eine Kombination aus verschiedenen Faktoren, wie die geänderte Packung des Sediments, der Einfluss von Diatomeen und ihren extrapolymere Substanzen und die Feinfraktion im Sediment, die die beobachteten Änderungen in der Permeabilität bestimmen.

Änderungen der Nährstoffkonzentrationen und der Salinität im Porenwasser wurden an derselben Probenahmestelle zwischen Februar 2003 und April 2005 untersucht. Si(OH)_4 und NH_4^+ Porenwasserprofile zeigten in den oberen 4 – 6 cm des Sediments vermutlich aufgrund von Advektion und Assimilation durch das Mikrophytobenthos niedrige Konzentrationen. Die Konzentrationen nahmen unterhalb dieser Schicht zu. PO_4^{3-} Konzentrationen erreichten ihre höchsten Werte immer zwischen 3 und 7 cm Sedimenttiefe, wohingegen NO_3^- and NO_2^- höchste Konzentrationen in den oberen Sedimentzentimetern zeigten. Die gemittelten Konzentrationen der Nährstoffe des Porenwassers der oberen 5 cm zeigten für Si(OH)_4 , NH_4^+ and PO_4^{3-} in beiden Jahren ähnliche Verläufe: niedrigste Konzentrationen im Frühling und im späten Sommer bzw. beginnenden Herbst und zwei Konzentrationsmaxima, eines während des Sommers und eines während des Winters. Ein kleiner Peak in den Konzentrationen dieser Nährstoffe tritt außerdem im Frühjahr auf, wahrscheinlich aufgrund der abgesetzten Phytoplanktonblüte. Vermutlich ist dieses Muster das Ergebnis aus sich ändernder Temperatur, geänderten Lichtbedingungen und einer geänderten Menge an organischem Material, das dem Sediment zugeführt wird. NO_3^- im Porenwasser hingegen folgte der gleichen Dynamik wie NO_3^- in der überliegenden Wassersäule, mit geringen Konzentrationen im Sommer und Herbst und hohen Konzentrationen im Winter und Frühling. Im Winter und Frühling wurde die Nährstoffdynamik an der Probenahmestelle zusätzlich durch einfließendes Grundwasser mit hohen Konzentrationen von Si(OH)_4 und NH_4^+ beeinflusst. Hohe NO_3^- Konzentrationen im einströmenden Wasser wurden im Winter und Frühling 2004 / 2005 beobachtet.

Zeitliche Veränderungen der Mikrophytobenthosbiomasse und des organischen Gehalts des Sediments wurde zwischen Februar 2003 und November 2004 an ebenfalls derselben Probenahmestelle untersucht. In den oberen 6 bis 10 cm des Sediments wurde eine hohe Biomasse des Mikrophytobenthos gefunden. Es konnte keine eindeutige Saisonalität festgestellt werden und die Biomasse war hoch im Vergleich zu der Phytoplanktonbiomasse des überliegenden Wassers und zu Mikrophytobenthosbiomassen in anderen intertidalen oder subtidalen Gebieten. Zusätzlich wurden im Juni 2004 Proben entlang eines Transekts von der Hochwasserlinie bis zu einer Wassertiefe von 4 m unterhalb der Niedrigwasserlinie genommen. Höchste Mikrophytobenthosbiomassen wurden in der Nähe der Niedrigwasserlinie und im flachen Sublitoral gefunden.

Der organische Gehalt des Sediments war niedrig, aber von hoher Qualität. Basierend auf dem Kohlenstoff : Chlorophyll *a* Verhältnis von 40, waren ungefähr 50 % des organischen Kohlenstoffs in den oberen 5 cm des Sediments im Mikrophytobenthos gebunden. Organisches Material, das nicht mit lebendem Mikrophytobenthos assoziiert war, korrelierte mit der Biomasse, was einen schnellen Umsatz der Mikrophytobenthosbiomasse vermuten lässt. Das C : N : P Verhältnis was sehr nah zu dem Redfield - Verhältnis, was

zusätzlich als ein Indikator für organisches Material mit hoher Qualität im Sediment gesehen werden kann.

Der permeable Sand im flachen Sublitoral stellt durch eine Kombination von ausreichenden Lichtbedingungen mit permanenter Advektion von partikulärem Material, gelösten Nährstoffen, O₂ and CO₂ vermutlich ein Optimumhabitat für das Mikrophytobenthos dar.

Chapter 1

General introduction

Permeable sands are a dominant sediment type along world's shore line (Emery 1968). These areas are of significant socio – economic value. They e.g. provide productive fishing grounds, are major sources for raw materials and form popular beaches. At the same time these coastal zones are affected by habitat destruction, eutrophication and water contamination (Huettel et al. 2003).

Despite their ecological and economic importance these sands have been poorly studied with respect to their role in coastal cycles of matter. Long time these sediments were thought to be biogeochemical deserts that did not significantly contribute to the cycling of matter, because of their low organic matter content (Boudreau et al. 2001). Thus, studies about these sediments are rare. The difficulty of sampling of permeable sediments including retaining in situ gradients and intact pore water profiles (Jahnke et al. 2005) adds to this. However recent studies indicate that these sandy sediments may be very efficient in transformation of organic matter (Shum and Sundby 1996, Boudreau et al. 2001).

One key characteristic of these sands is their high permeability, allowing rapid pore water exchange (advection) in the upper layer of the sediment (Reimers et al. 2004, Precht and Huettel 2004) through interactions between currents at the boundary layer and sea – bed topography. The main transport processes, advection and enhanced dispersion (Huettel and Webster 2001, Reimers et al. 2004), may be induced by bottom current – sediment interactions (Huettel et al. 1996) and by pore pressure variations due to the passage of surface gravity waves (Precht and Huettel 2003).

The lower permeability limit allowing advective pore water transport that significantly exceeds diffusive transport is approximately 10^{-12} m^2 (Huettel et al. 1996). In sandy sediments the permeability exceeds normally 10^{-12} m^2 , and the

advective pore water flow is an additional solute transport mechanism in sandy sediments. In contrast, transport in silty and muddy sediments is restricted to molecular diffusion, bioturbation, and bioirrigation (e.g. Janssen et al. 2005).

Advective pore water transport may be important for the coastal cycles of matter through the acceleration of deposition and mineralization processes (Marinelli et al. 1998) and coastal permeable sands may function like expansive biocatalytical filter systems (Huettel et al. 1998). Suspended particles and phytoplankton are filtered from the water column, thus increasing the deposition rate (Huettel and Rusch 2000). In the sediment, organic particles are exposed to higher mechanical stress, higher bacterial abundances and higher exo – enzyme concentrations than in the water above, which accelerate their decomposition (Crossland et al. 2005). Advective transport of oxygen and other electron acceptors in the sediment (Lohse et al. 1996, Ziebis et al. 1996), and export of decomposition products (e.g. nutrient and CO₂) out of the sediment (Gehlen et al. 1995, Huettel et al. 1998) further enhance sedimentary degradation. The effect of advective pore water flow may be shown by high benthic primary production (Nelson et al. 1999, Jahnke et al. 2000). In most regions, sufficient light for photosynthesis by benthic microalgae commonly reaches the sediment, especially at water depths less than 50 m (e.g. Cahoon and Cooke 1992). This further adds to the complexity of the benthic system.

As already mentioned only recently the importance of these permeable sediments in the cycle of organic matter was recognized (Shum and Sundby 1996, Boudreau et al. 2001). Therefore until now just a few studies have investigated the role of permeable sediments and especially in the shallow subtidal these are rare.

To assess the role of permanent submerged sandy sediments in coastal cycles of matter, the EU - project COSA ("Coastal sands as biocatalytical filters", EVK3 – CT2002 – 0076) was initiated. The aim was to understand the mechanisms and to develop an effective management concept to ensure sustainable use of

permeable sediments. Figure 1 shows parameters and expected fluxes which were investigated in the COSA project.

This work is part of this project, in which five research institutes and two environmental agencies focus on the ecological role and management of near shore marine sandy sediments. Time series and intense field campaigns focussing on experiments were done to get data as a basis for identifying mechanisms, process modelling and attempting prognostic simulations.

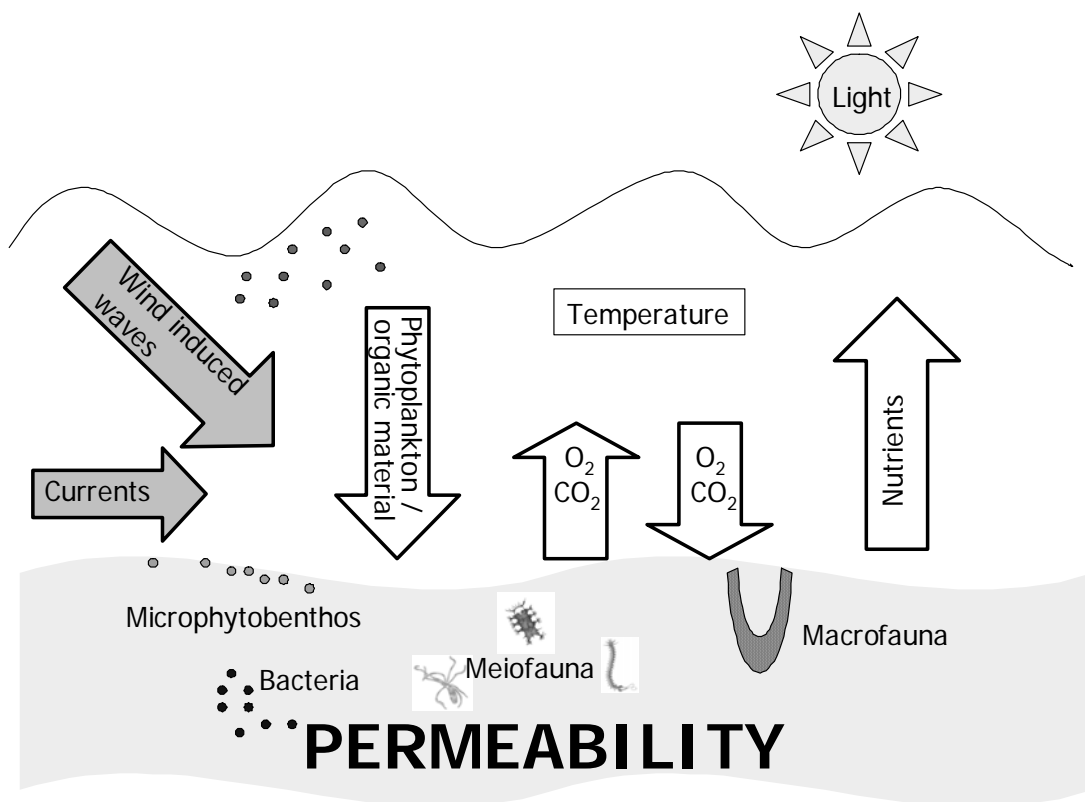


Figure 1: Scheme of potential factors influencing fluxes, the main fluxes and groups of organisms in sandy permeable sediments.

This study was conducted at a shallow subtidal site near the island of Sylt, Germany, in the List tidal basin, a semi - enclosed back - barrier lagoon in the northern Wadden Sea.

From 1990 until 1995 a former interdisciplinary research project investigated changing ecosystems of the Wadden Sea in the List tidal basin between the barrier islands of Sylt and Rømø. Sandy sediments predominate in the basin. Approximately 57 % of the area belong to the shallow subtidal, 33 % to the intertidal and 10 % are deep channels. Mainly the intertidal and the water column were investigated, while the subtidal was scarcely studied (Gätje and Reise 1998). Where budgets were attempted, data for the lower intertidal were used as an approximation for the sandy shallow subtidal.

The COSA sampling site in the shallow subtidal, at the so called "Hausstrand" was chosen because the intertidal area of this location has already been intensively investigated for the diversity and zonation of the benthic fauna (see Armonies and Reise 2000 and references therein). Recently a study on the influence of permeability on transport processes and mineralization rates at this site in the intertidal was published (de Beer et al. 2005), almost adjacent to the shallow subtidal site of this study.

As this study is part of the comprehensive project COSA, the aim was to focus on the temporal dynamics of sediment properties, permeability, pore water nutrient concentrations, microphytobenthos and organic matter at this subtidal exposed sandy sediment over a two years period, to get an idea of the shallow subtidal sediments in general, and also especially in this area as a base for the interpretation of experimental results and modelling. A parallel study was conducted in the water column in the Lister Ley (Loebl 2005) and other comparative studies were done near Hel peninsula in the Baltic Sea (e.g. Weslawski et al. in prep.).

Chapter 2 describes the sediment properties and permeability variations and the factors which may have influenced these properties over a two years period.

Chapter 3 reports on the variation of pore water nutrient concentrations and of salinity during two years and some influencing factors.

Chapter 4 presents the microphytobenthic biomass and quality and quantity of organic matter over two years period.

In a final chapter, a general discussion will combine the results from the individual studies presented in the chapters outlined above.

Chapter 2

Permeability of a shallow subtidal sandy system – mainly driven by wind

2.1 Abstract

Permeability of the sediment is a key factor for sedimentary processes. Changes in sediment permeability and the potential forcing factors were measured monthly (March 2003 – April 2005) at a shallow (0.5 m at low tide) subtidal sandy site of the Island Sylt in the northern Wadden Sea (Germany). The permeability of the upper 5 cm and of the whole core (10 - 15 cm length) was measured monthly and ranged for the upper 5 cm between $1.42 \times 10^{-11} \text{ m}^2$ and $8.09 \times 10^{-11} \text{ m}^2$ and for the whole core between $1.01 \times 10^{-11} \text{ m}^2$ and $3.36 \times 10^{-11} \text{ m}^2$. These ranges are assumed to enable advective pore water exchange all the time. Permeability varied seasonally with highest values in winter and spring, and lowest values in summer and autumn. Redundancy analysis (RDA) showed that the only significant and main influencing factor explaining sediment permeability was the mean average wind speed on the sampling day, suggesting that wave induced turbulence increases sediment permeability. The triplot of the RDA showed that permeabilities during autumn, in the year 2003, were influenced by the EDTA - extractable carbohydrate content in the sediment. Permeabilities during the summer months in both years were influenced by the amount of fine fraction in the sediment. The results suggest that the shallow permeable subtidal sediment at the study site was influenced all the time by wind induced waves, leading to a seasonality of the permeability. Probably a combination of factors, like changed consolidation of the sediment, diatoms and their extracellular polymeric substances and the trapping of fine particles in the sediment is also contributing to the observed dynamics of permeability.

2.2 Introduction

The predominant sediment types in shelf areas world wide are sandy deposits with high permeabilities (Boudreau et al. 2001). Permeability of the sediment is a key factor for sedimentary processes, such as exchange rates and penetration depths of solutes (Forster et al. 1996, Huettel et al. 1996, Shum and Sundby 1996). The high permeability of sandy sediments permits rapid pore water exchange in the upper sediment layer (Reimers et al. 2004, Precht and Huettel 2004). Since this rapid exchange allows a fast transport of dissolved and particulate organic matter and electron acceptors like oxygen into and metabolic products (e.g. nutrients, CO₂) out of the sea bed (Shum and Sundby 1996, Marinelli et al. 1998), permeability is also a central factor determining organic matter deposition and degradation rates in sandy deposits (Boudreau et al. 2001).

Despite the importance of sediment permeability, only very few measurements of coastal sediments are available, and little is known about the processes that control its dynamics. Physical as well as biological factors determine the permeability of sediments. It depends on grain size, sorting, compaction of the sediment (Hsü 1989) and the viscosity and density of the pore fluid (Klute and Dirksen 1986). Benthic diatoms are the major producers of exopolymeric substances (Grant et al. 1986), a mix of polysaccharides and other compounds (Underwood et al. 1995). These extracellular polymeric substances facilitate cell attachment and locomotion and reduce sediment permeability and erosion (e.g. Grant and Gust 1987, Decho and Lopez 1993, Yallop et al. 1994, Underwood et al. 1995). They can also alter the cohesivity of sediments (Grant and Gust 1987, Dade et al. 1990) and the adsorption of particulate organic matter and cells on the matrix (Roemer et al. 1984, Decho and Lopez 1993). All this may influence the sediment permeability (Cahoon 1999).

Subtidal sediments in the List tidal basin are continuously exposed to currents and wind induced waves, so small and light particles are removed from the sediments and sands are the prevalent sediment type (Gätje and Reise 1998,

Stal 2003). These sands may have a high permeability showing seasonal changes due to wind effects. To test this hypothesis, permeability was measured monthly at a subtidal station during a two - year period. The study included grain size, microphytobenthos and extracellular polymeric substances as factors that potentially influence the permeability.

2.3 Materials and Methods

2.3.1 Sampling site

The study was conducted at a shallow subtidal site near the island of Sylt, Germany (55° 00' 47.7'' N, 008° 25' 59.3'' E; Figure 1), in the List tidal basin, a semi - enclosed back - barrier lagoon in the northern Wadden Sea. The tidal amplitude of the diurnal tide is ~ 2m. The water depth at the sampling site ranged from 0.5 – 2.5 m depending on the tidal phase. Sediments at the experimental site are well to moderately well sorted medium sand with a median particle size of 350 µm. The origin is mainly aeolic, blown in from dunes of the island (Austen 1994). Tidal currents and wind induced wave action are the most important hydrodynamic forces. Currents at the sampling site were up to 90 cm s⁻¹ (Wenzhöfer pers. comm.). Salinity varies on average between 27.5 in spring and 31 in summer. Benthic polychaetes were present in relatively low abundances (Weslawski et al. in prep., Armonies and Reise 2000). Further details of the study site are provided by Austen (1994) and Gätje and Reise (1998).

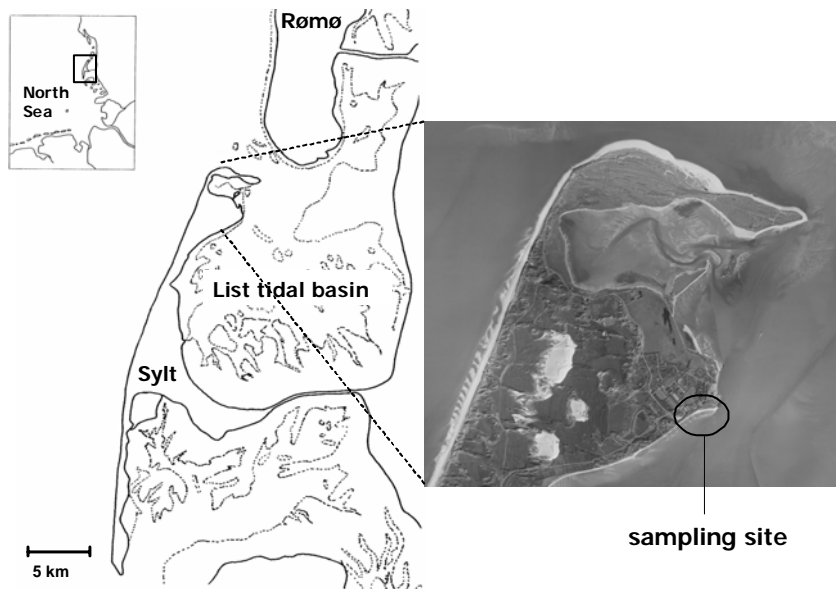


Figure 1: Study area in the northern Wadden Sea. Spring low tide is stippled. Circle marks the sampling site (Foto from the Wadden Sea National Park Office Schleswig – Holstein).

2.3.2 Sampling

Sampling was done between March 2003 and April 2005 at monthly intervals. Fifteen sediment cores with an inner diameter of 3.6 cm and a length of 15 - 20 cm were taken randomly during low tide. The water level above the sediment was at least 50 cm. The cores were hand collected to avoid sediment disturbances. They were carefully pushed into the sediment, closed watertight with a rubber stopper, lifted and closed carefully from beneath with a second stopper. All following procedures were performed in the nearby (500 m) lab as soon as possible.

2.3.3 Wind data

Data on wind speed and wind direction (hourly means) were obtained from the Deutsche Wetterdienst (German weather Bureau) and were measured at the Weather station at List. From these data, daily average wind speeds and median wind directions were calculated.

2.3.4 Permeability measurement

Permeability describes how easy a fluid flows through a porous medium. Sediment permeability k of three replicate cores was determined by using the constant head method (Klute and Dirksen 1986). A setup of the measurement device is shown in Figure 2. With the device, different hydraulic pressures can be applied to a sediment core. The amount of water that flows through a core at a given hydraulic pressure is recorded.

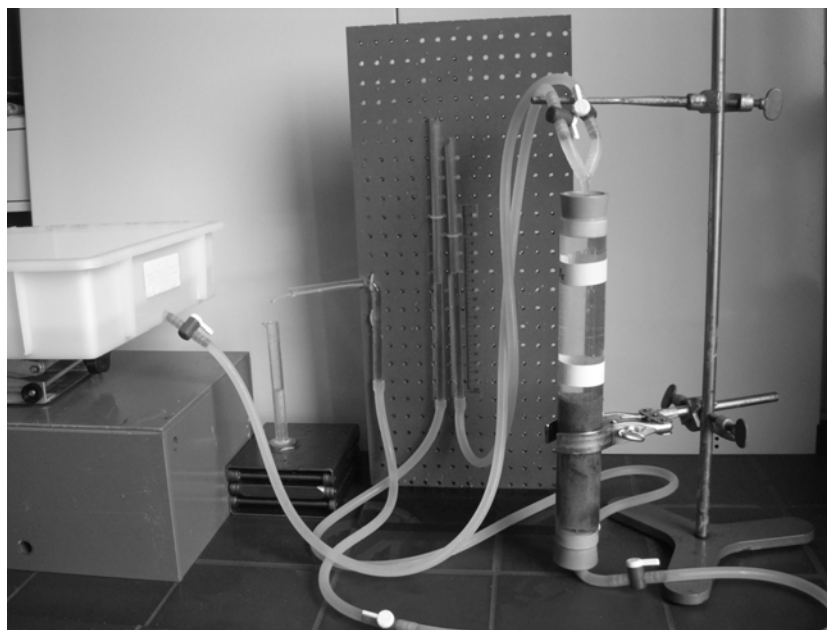


Figure 2: Setup of the measurement device for measuring the permeability of the sediment.

The hydraulic conductivity is calculated with equation [1] and transformed into permeability with equation [2].

$$K = (V \cdot L) / (h \cdot A \cdot t) \quad [1]$$

K = hydraulic conductivity (cm s^{-1})

V = volume of water collected (cm^3)

L = length of core (cm)

h = pressure head (cm)

A = surface area of core (cm^2)

t = time (s)

$$k = Km/dg \quad [2]$$

$$\begin{aligned} k &= \text{permeability (cm}^2\text{)} \\ K &= \text{hydraulic conductivity (cm s}^{-1}\text{)} \\ m &= \text{viscosity (g cm}^{-1} \text{s}^{-1}\text{)} \\ d &= \text{density (g cm}^{-3}\text{)} \\ g &= 981 \text{ cm s}^{-2} \end{aligned}$$

First, permeability of the entire cores (10 – 15 cm) was determined. Then, the permeability of the upper 5 cm of the sediment core was determined after carefully removing the lower part of the core.

2.3.5 Porosity

Sediment porosity was determined by slicing three cores into three 5 cm intervals and assessing the water content of the slices after being oven - dried at 65 °C for 48 h. The water content was determined from the weight loss upon drying. The density of the sand was calculated from the wet weight and the volume of the sediment sample. The porosity was then calculated from the density of the sand, the wet weight and the dry weight of the sample without correcting for the salt content (Daalsgard et al. 2000).

2.3.6 Grain size distribution

The grain size distribution of the sediment was determined on the same samples used for porosity measurements. The samples were rinsed twice with freshwater to remove the salt and avoid aggregation, dried and then dry - sieved through a set of standard sieves suited to the intervals of the Wentworth scale (mesh sizes: 2000 μm , 1000 μm , 500 μm , 250 μm , 125 μm , 63 μm) by shaking the samples for 15 minutes. The samples were then weighed and the sorting and the median were calculated by using GRADISTAT Version 4.0, excluding the biggest (> 2000 μm) and the smallest (< 63 μm) sediment fraction.

2.3.7 Chlorophyll *a* and carbohydrate concentration in the sediment

Eight sediment cores were sliced in 1 cm intervals down to a depth of 15 cm. The samples of corresponding depths were pooled and sub samples for the further analysis were taken. The samples were frozen at -20 °C and freeze dried before further analysis. All measurements were done in triplicate for each depth centimetre. The homogenization procedure and the method reliability was tested before with the parameter chlorophyll *a*, by taking 8 cores, taking sub samples and then homogenizing the rest and taking sub samples of the homogenized sediment. The variation of the mean of the eight single cores was $\pm 2 \mu\text{g chlorophyll } a \text{ g}^{-1}$ dry sediment ($\sim 10 \%$ of the chlorophyll *a* concentration).

2.3.7.1 Chlorophyll *a*

For chlorophyll *a* determination, approximately 1 g sediment of each depth interval was extracted with 7.5 ml acetone (90 %) and incubated for 24 hours at 4 °C in the dark. Samples were shaken in between a second time to assist the extraction. At the end of the extraction samples were centrifuged at 3600 rpm for 10 minutes. The supernatant was measured before and after acidification with 2 drops of HCl (10 %). Absorbance of chlorophyll *a* was measured spectrophotometrically (UVIKON XL) at 665 nm, with a turbidity correction made at 750 nm. Chlorophyll *a* and phaeopigments were calculated after Lorenzen (1967).

2.3.7.2 Carbohydrates

Carbohydrates were quantified using a spectrophotometric assay (Dubois et al. 1956). The assay is based on the reaction of a carbohydrate - phenol mixture with concentrated sulphuric acid. The heat of this exothermic reaction results in the production of coloured compounds, which can be quantified using a glucose standard curve, which gives carbohydrate values in glucose equivalent concentrations. EDTA - extractable and total carbohydrates were determined to a depth of 10 cm. EDTA - extractable carbohydrates were determined as on

100 mg homogenized sediment, extracted for 15 minutes with 5 ml of 100 mM Na₂EDTA solution. After the extraction were the samples centrifuged 15 minutes at 3500 rpm. Two ml of the solution were transferred in a glass vial and 1 ml phenol (5 %) and 5 ml sulphuric acid (concentrated) were added. After 10 minutes the samples were carefully homogenized and incubated for another 30 minutes. The solution was transferred into cuvettes and absorbance was measured with a spectrophotometer (UVIKON XL) at 485 nm (Underwood et al. 1995). Total carbohydrates were determined on 50 mg of sediment. Two ml of Milli – Q water was added to the sediment in a glass vial and then the samples were handled as for the EDTA - extract described above. The measurements for each sediment centimetre (1 - 10 cm) were done in triplicate.

2.3.8 Statistical analysis

The statistical analyses were done using the software packages STATISTICA 6 (Stat Soft) and BRODGAR 2.4.5. (Highland Statistics). The permeability data were square root transformed before analysis, to reduce the outliers.

The influence of the two sampling years and the different seasons were tested using a two - factorial ANOVA design, with year and season as fixed factors. Although taken at the same locality, the samples were considered to be independent due to the temporal distances of at least three to four weeks. For each sampling, monthly mean values were calculated and the months were summarized to seasons (spring: March, April, May; summer: June, July, August; autumn: September, October; winter: November, January, February).

Temporal trends for the permeability were fitted by using the repeated Loess smoothing technique in BRODGAR.

The relationships between permeability, potential forcing factors and the sampling date over the sampling period were analyzed by using a redundancy analysis (RDA), performed with BRODGAR statistical software. Only data after July 2003 were used for the RDA, because some variable values were missing at prior sampling dates. All the data for the variables of the upper 5 cm were

highly collinear with the data from the depths below. Therefore, the statistical tests were done by taking the data of the different parameters just from the upper 5 cm to reduce the number of variables. All data used in the following statistical analyses can be found in the appendix of this chapter.

2.4 Results

2.4.1 Permeability

The permeabilities of the surface layer (0 - 5 cm) and the upper 10 - 15 cm of the sediment exceeded 10^{-11} m², thus the sediment was expected to allow advective pore water flow all the time (e.g. Huettel et al. 1998). Permeabilities of the upper 5 cm and the entire sediment core (10 – 15 cm) varied seasonally with highest values in winter and spring, and lowest values in summer and autumn.

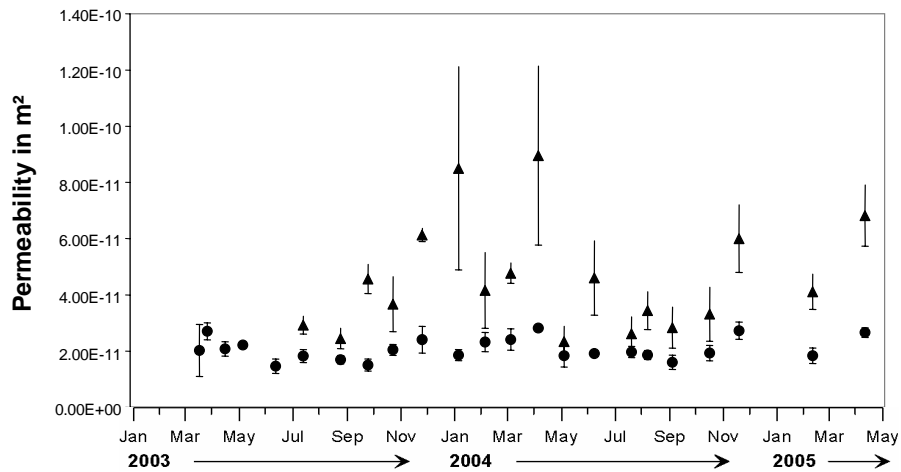


Figure 3: Sediment permeability time series of the surface layer (0 – 5 cm, triangles) and the entire core (points). Vertical bars depict the standard error between 3 parallel cores and reflect spatial variability in permeability.

A significant difference in permeability was observed between the seasons for the upper 5 cm (ANOVA, $p < 0.05$); (Table 1; Figure 4) and the entire core (ANOVA, $p < 0.05$); (Table 1; Figure 5). Mean permeability of the upper 5 cm of the sediment was $4.12 \times 10^{-11} \text{ m}^2 \pm 1.85 \times 10^{-11} \text{ m}^2$ during this study. In the entire core the mean permeability was $2.07 \times 10^{-11} \text{ m}^2 \pm 5.43 \times 10^{-12} \text{ m}^2$. The spatial variability, indicated by the standard error, was higher during winter and spring than in summer and autumn (Figure 3).

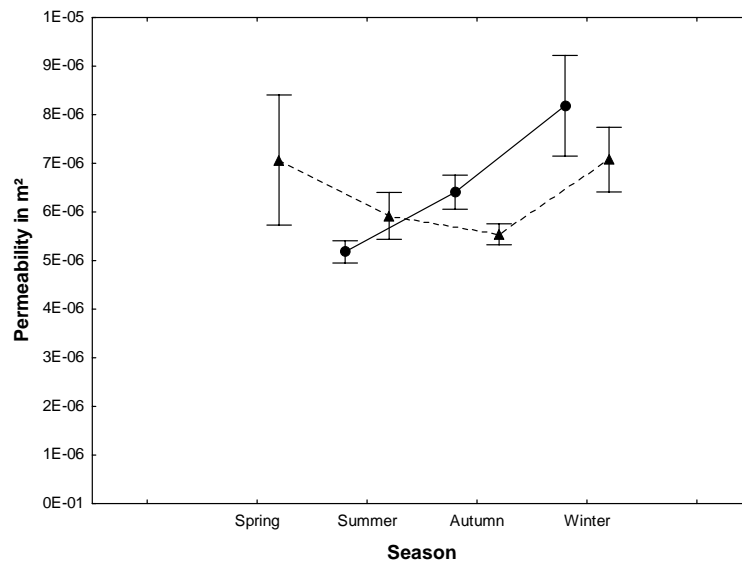


Figure 4: Mean root transformed permeability data for the upper 5 cm with standard error, summarized in seasons.
(●: year 2003; ▲: year 2004; in 2003 no spring data are available)

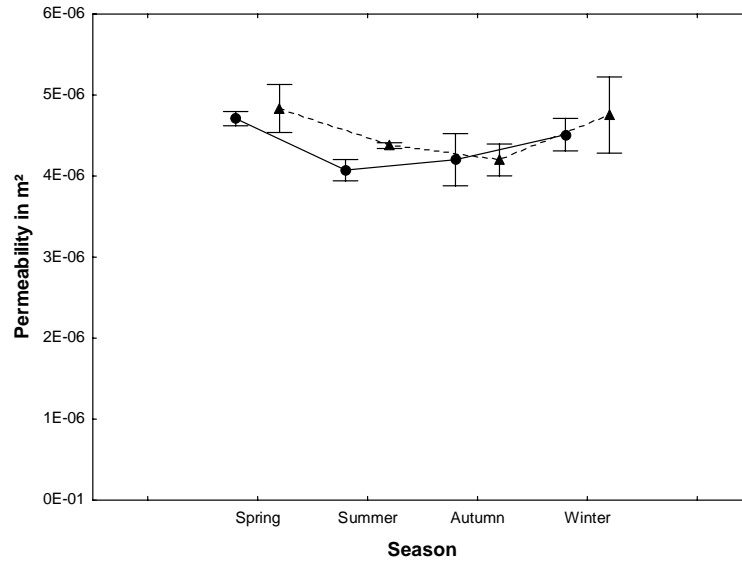


Figure 5: Mean root transformed permeability data for the upper 10-15 cm with standard error, summarized in seasons. (●: year 2003; ▲: year 2004)

Clear seasonal trends in permeability can be distinguished using the repeated Loess smoothing technique (Figure 6), with the highest permeabilities being observed during winter and the lowest in summer. The changes are much more pronounced in the upper sediment layers than in the whole 15 cm of the sediment.

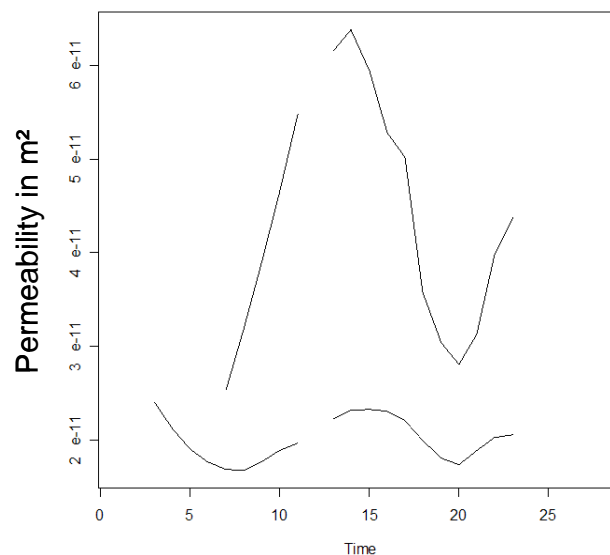


Figure 6: Trend modelled with the Software BRODGAR using the repeated Loess smoothing technique. Gaps are missing values. Time stands for the months of the permeability time series (2003: 1-12; 2004: 13-24; 2005: 25-28).

Table 1: Results of the two-factorial ANOVAs for the different variables with the two factors year and season. P-values below 0.05 are considered as significant and are shown in bold.

		dF	MS	F	p
Permeability 10-15 cm core	year	1	1.01E-13	0.844	0.374853
	season	3	4.71E-13	3.941	0.033482
	year*season	3	2.00E-14	0.167	0.916450
	Error	13	1.20E-13		
Permeability of the upper 5 cm (without spring)	year	1	1.62E-13	0.1877	0.676302
	season	2	4.17E-12	4.8452	0.041823
	year*season	2	8.17E-13	0.9490	0.426764
	Error	8	8.61E-13		
Wind speed	year	1	0.0996	0.0554	0.817849
	season	3	8.6758	4.8303	0.019798
	year*season	3	1.9956	1.1111	0.382866
	Error	12	1.7961		
Grain size median of the upper 5 cm	year	1	566	19.11	0.000909
	season	3	81	2.73	0.090159
	year*season	3	19	0.65	0.595725
	Error	12	30		
Fine fraction in % of the upper 5 cm	year	1	0.000163	0.1222	0.732727
	season	3	0.008880	6.6380	0.006819
	year*season	3	0.002071	1.5485	0.252889
	Error	12	0.001338		
Porosity of the upper 5 cm	year	1	0.000234	1.13	0.309160
	season	3	0.001016	4.90	0.018914
	year*season	3	0.000384	1.85	0.191347
	Error	12	0.000207		
Mean chlorophyll <i>a</i> Content of the upper 5 cm	year	1	16.413	3.9294	0.068992
	season	3	2.123	0.5083	0.683408
	year*season	3	24.228	5.8004	0.009632
	Error	13	4.177		
Mean EDTA - extractable carbohydrate content of the upper 5 cm (without spring)	year	1	200997	11.3104	0.009886
	season	2	39412	2.2178	0.171275
	year*season	2	4017	0.2261	0.802599
	Error	8	17771		
Mean total carbohydrate Content of the upper 5 cm (without spring)	year	1	6262629	2.75431	0.135575
	season	2	95509	0.04200	0.959075
	year*season	2	250911	0.11035	0.896859
	Error	8	2273756		

2.4.2 Wind data

The mean wind speed of the sampling days ranged between 2.98 m s^{-1} (July 2003) and 10.50 m s^{-1} (February 2004). The seasons were significantly different, with higher values in winter and spring and lower in summer and autumn (ANOVA, $p < 0.05$); (Table 1; Figure 7). The permeability correlated better with the mean wind speed of the sampling day than with the wind speed the day before the sampling. Wind speed showed the same seasonal pattern as the permeability.

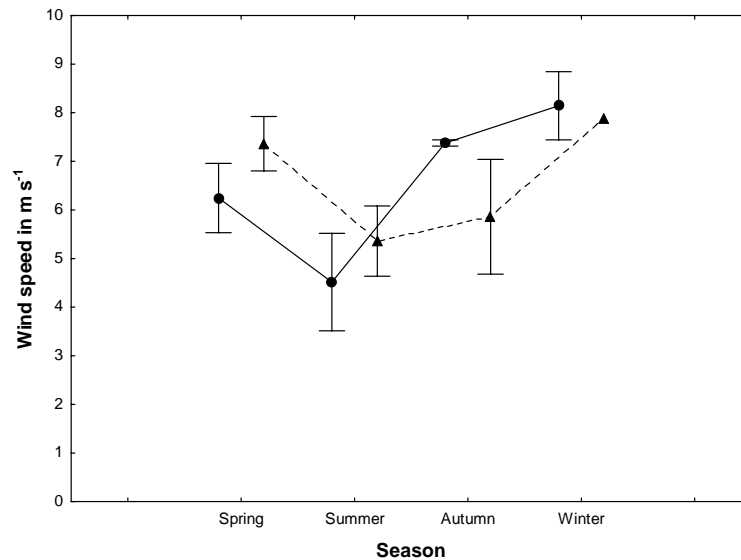


Figure 7: Mean wind speed with standard error, summarized in seasons. (●: year 2003; ▲: year 2004)

2.4.3 Porosity

Mean values for the porosity, averaged over all sampling dates were for the upper five centimetre of the sediment 0.449 ± 0.026 and for the whole upper 15 cm 0.397 ± 0.042 (data not shown). As for permeability, higher values were observed in winter and spring and lower values in summer and autumn (ANOVA; $p < 0.05$); (Table 1; Figure 8).

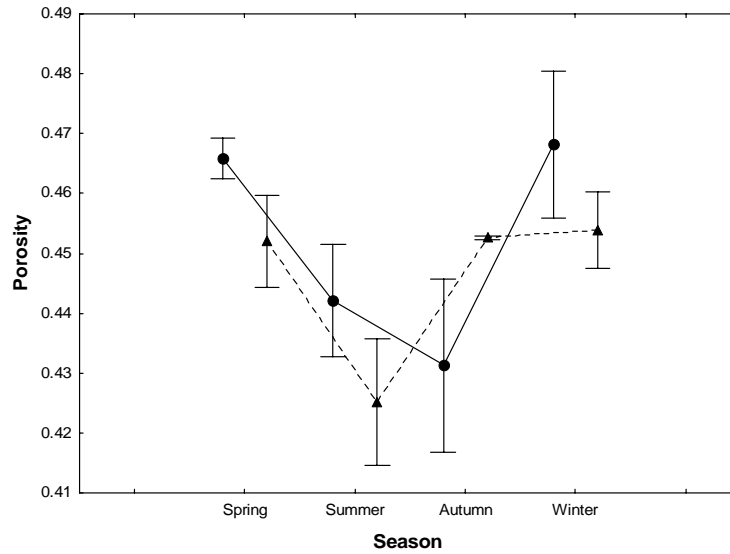


Figure 8: Mean porosity data for the upper 5 cm with standard error, summarized in seasons. (●: year 2003; ▲: year 2004)

2.4.4 Grain size and fine fraction

The sediment was well to moderately well sorted sand with a mean grain size for the upper 5 cm of $346 \mu\text{m} \pm 9 \mu\text{m}$ and for the whole upper 15 cm of $350 \mu\text{m} \pm 13 \mu\text{m}$ (data for the upper 15 cm not shown). There was no seasonal variation of the mean grain size during each year, but a significant difference between the two years (Table 1; Figure 9), but this difference was very small ($3 \mu\text{m}$). The fine particle content of the sediment was very low the whole time and the influence on the median grain size was not indistinguishable. The fine particle content in the upper 5 cm of the sediment varied significantly with the seasons (ANOVA, $p < 0.01$) (Table 1; Figure 10) and was lower during the winter months than during summer.

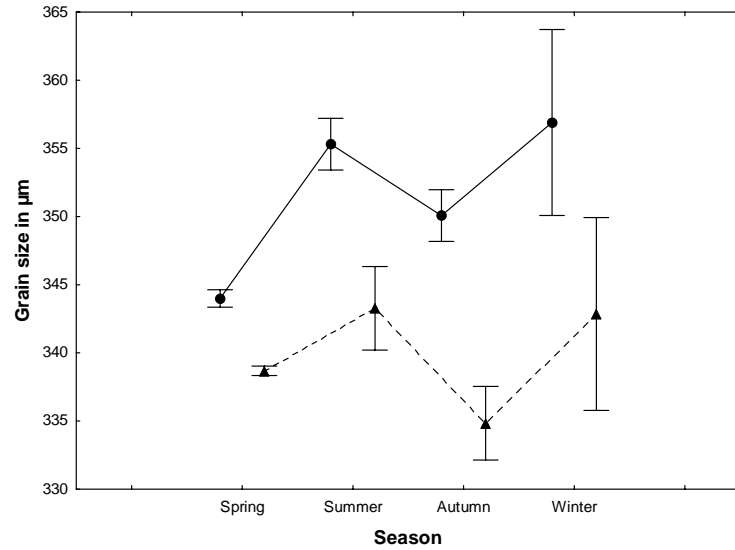


Figure 9: Mean median grain size data for the upper 5 cm with standard error, summarized in seasons. (●: year 2003; ▲: year 2004)

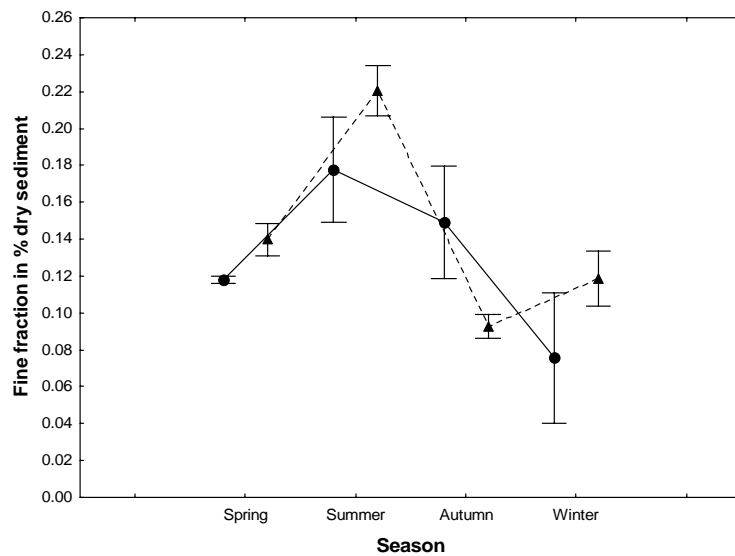


Figure 10: Mean fine fraction data for the upper 5 cm with standard error, summarized in seasons. (●: year 2003; ▲: year 2004)

For the fine fraction of the sediment, a seasonal variation was observed with highest values during summer and was opposite to the trends seen for permeability, mean wind speed and porosity. No seasonal variation was observed for the median grain size distribution.

2.4.5 Chlorophyll *a* content in the sediment

The mean microphytobenthic biomass in the upper 5 cm of the sediment, measured as chlorophyll *a* showed little temporal variability (Figure 11). During winter the contents in the sediment were slightly lower, but the differences were not significant. In summer 2004 concentrations were lower than during the rest of the sampling period. This led to a significant season * year interaction (Table 1; ANOVA, $p < 0.01$). The chlorophyll *a* profiles showed high chlorophyll *a* contents in the upper 2 - 4 cm, decreasing to minimum values reached at 8 – 10 cm depth during the whole sampling time (Figure 12). The chlorophyll *a* content of the sediment did not follow any clear seasonal pattern.

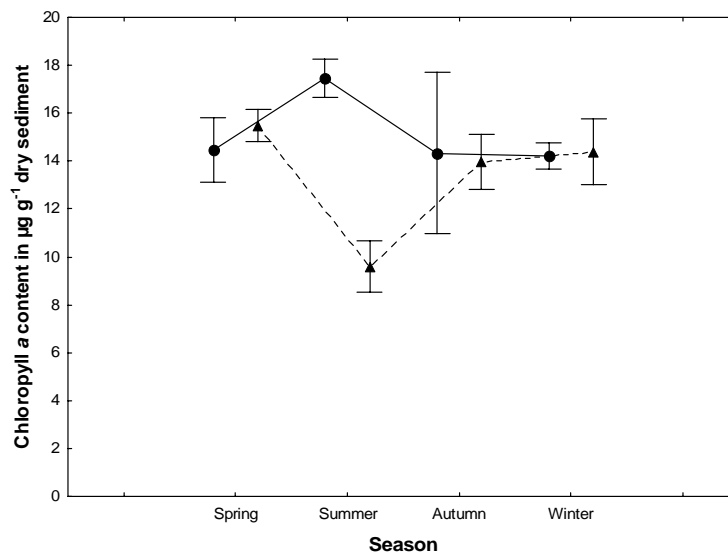


Figure 11: Mean chlorophyll *a* content for the upper 5 cm with standard error, summarized in seasons. (●: year 2003; ▲: year 2004)

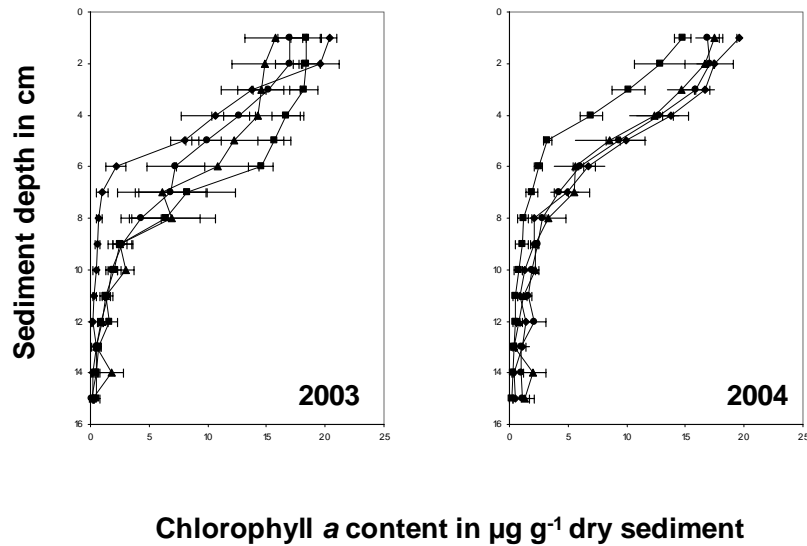


Figure 12: Chlorophyll *a* depth profiles for the years 2003 and 2004. The error bars mark the standard error of the mean of the months which were put together into seasons. ♦: spring, ■: summer, ▲: autumn, ●: winter.

2.4.6 Carbohydrate contents in the sediment

The mean EDTA - extractable carbohydrate content of the sediment varied between 234.7 (October 2004) and 886.2 (September 2003) $\mu\text{g g}^{-1}$ glucose equivalents g^{-1} dry sediment in the upper 5 cm of the sediment. The mean EDTA - extractable carbohydrate contents of the upper sediment of 2003 and 2004 were significantly different (Table 1; Figure 13). The EDTA - extractable carbohydrates and chlorophyll *a* correlated significantly in the 1 - 10 cm of the sediment ($p < 0.001$) (Figure 14).

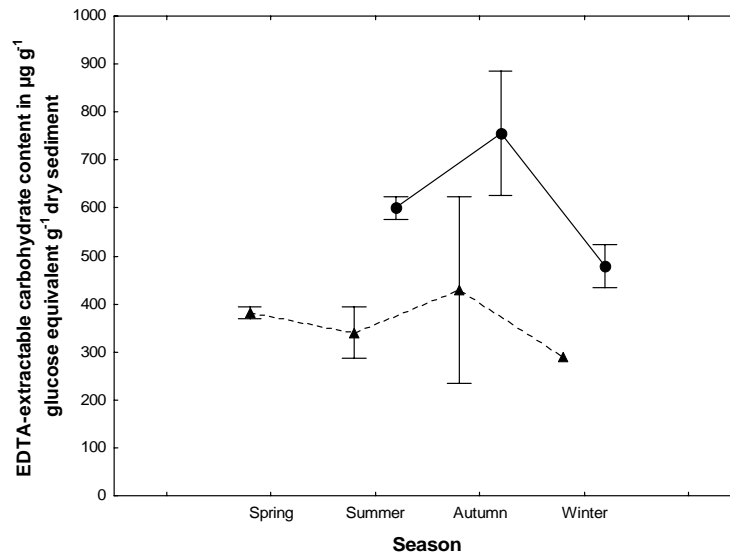


Figure 13: Mean EDTA - extractable carbohydrate content of the sediment for the upper 5 cm with standard error, summarized in seasons.
 (●: year 2003; ▲: year 2004; in 2003 no spring data are available)

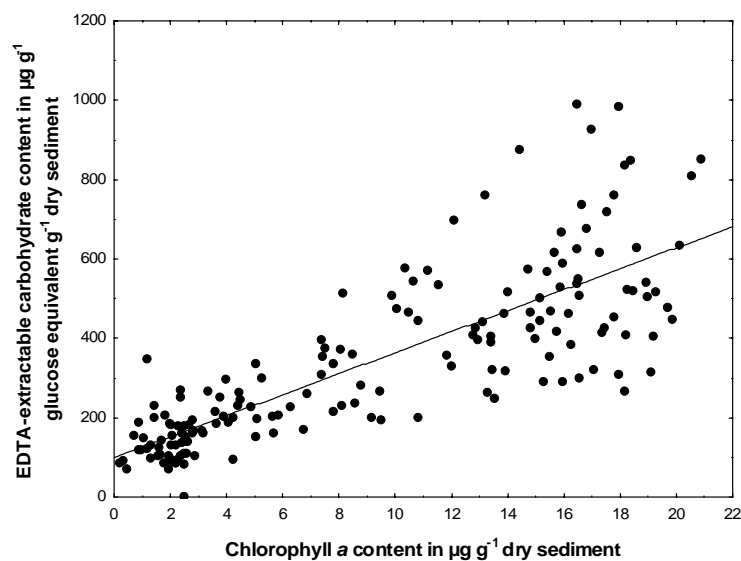


Figure 14: Correlation of the EDTA - extractable carbohydrates with chlorophyll a in the sediment for all sampling dates and sediment depth from 1 - 10 cm.
 ($r^2 = 0.6466$, $p < 0.001$, $y = 26.45x + 99.36$)

The mean total carbohydrate content of the upper part of the sediment ranged between 1080.6 (May 2004) and 6883.6 $\mu\text{g g}^{-1}$ glucose equivalents g^{-1} dry sediment (August 2003). No significant difference between the two years, or

the different seasons was found in the total carbohydrate content of the upper part of the sediment (Table 1; Figure 15). Also, there was no correlation of the total carbohydrates and the chlorophyll *a* concentration of the sediment (Figure 16).

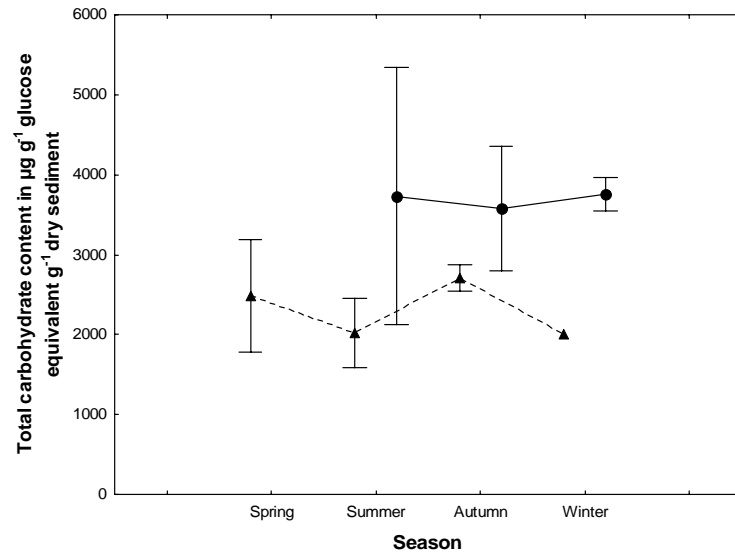


Figure 15: Mean total carbohydrate content of the sediment for the upper 5 cm with standard error, summarized in seasons. (●: year 2003; ▲: year 2004; in 2003 no spring data are available)

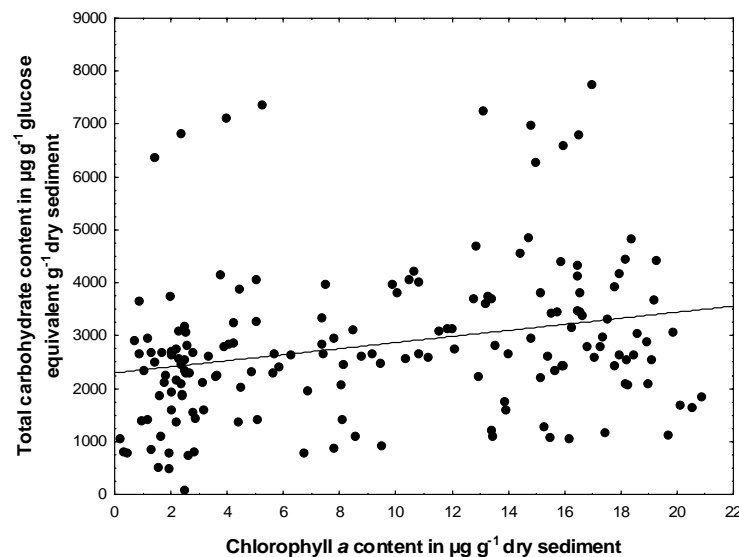


Figure 16: Correlation of the total carbohydrates with chlorophyll *a* in the sediment for all sampling dates and sediment depth from 1 - 10 cm. ($r^2 = 0.0676$, $p < 0.001$, $y = 57.37x + 2297.68$)

2.4.7 Redundancy Analysis

To determine which physical or biological factor described above influenced the permeability the most, a redundancy analysis was done with the explanatory variables in Table 2. Data between July 2003 and April 2005 were used. The variables which are highly collinear were determined before. All the data for the variables of the upper 5 cm were highly collinear with the data from the depths below. The RDA was performed by taking the data of the different parameters for the upper 5 cm to reduce the number of variables. The permeability data were square root transformed before analysis. The triplot of the first two axes (eigenvalues 0.431 and 0.114) for the RDA analysis are shown in Figure 17.

The first axis alone explains already 54 % of the variation of the response variables. The most important and the only significant variable influencing the permeability is the mean average wind speed on the sampling day ($p = 0.004$). The correlation of the variables with the axes and canonical effects of the variables is shown in Table 2. The second important variable, but not significant is the mean EDTA - extractable carbohydrate content of one horizon in the upper 5 cm of the sediment.

Variables with longer arrows in the triplot (Figure 17) are more important as response variable. Those variables pointing in the same direction show positive correlation and those with inverse direction show negative correlation. The intensity of this correlation increases as the angle between the variables diminishes. Two variables with an angle direction of 90° are not correlated. Samples positioned close to an arrow of a variable show a strong relationship with the factor. The permeability of the upper 5 cm (Perm5) is highly correlated with the porosity (P) and the mean average wind speed (WS), but the wind speed is much more important. The mean average wind speed, porosity and the mean concentration of chlorophyll *a* in the 5 upper cm are negatively correlated to the fine fraction of the sediment. The mean content of the EDTA - extractable carbohydrates, the mean content of the total carbohydrates of the

upper 5 cm of the sediment as well as the mean median grain size of the upper 5 cm of the sediment correlate with each other, but not with the other variables.

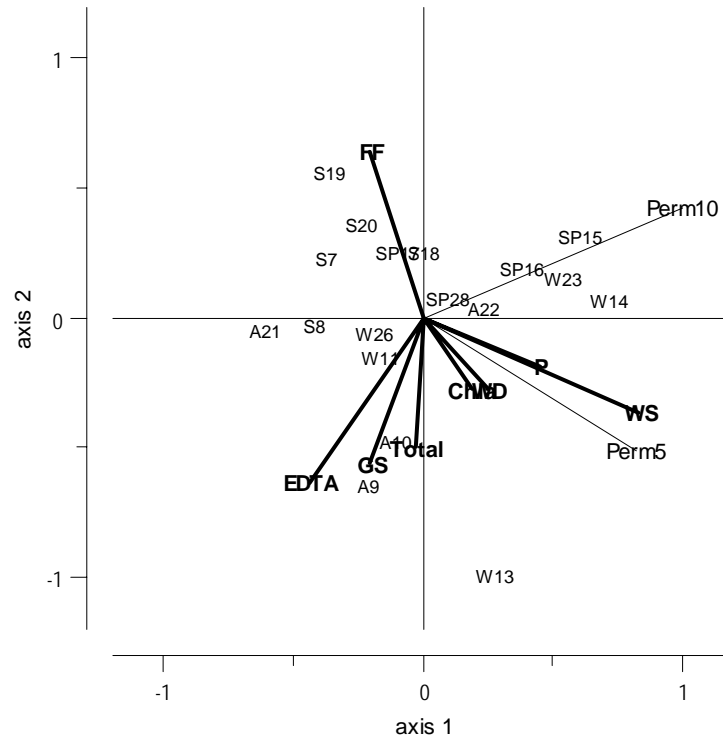


Figure 17: Triplot based on redundancy analysis of variation (samples) of permeability of the upper 5 cm (Perm5) of the sediment and upper 10 - 15 cm of the sediment (Perm10) with respect to 8 explanatory variables (thick lines). The lines display the approximately correlation coefficients between these two sets of variables. Abbreviations: (Perm5) mean permeability of the approximately upper 5 cm of the sediment, (Perm10) mean permeability of 10 - 15 cm long sediment cores, (S7) July 2003, (S8) August 2003, (A9) September 2003, (A10) October 2003, (W11) November 03, (W13) January 2004, (W14) February 2004, (SP15) March 2004, (SP16) April 2004, (SP17) May 2004, (S18) June 2004, (S19) July 2004, (S20) August 2004, (A21) September 2004, (A22) October 2004, (W23) November 2004, (W26) February 2005, (SP28) April 2005, (WS) mean average wind speed on the sampling day, (WD) mean wind direction on the sampling day, (FF) mean fine fraction in % of the upper 5 cm of the sediment, (P) mean porosity of the upper 5 cm of the sediment, (GS) mean median grain size of the upper 5 cm of the sediment, (Chla) mean chlorophyll a content of 1 cm horizon of the upper 5 cm of the sediment, (EDTA) mean EDTA-extractable carbohydrate content of 1 cm horizon of the upper 5 cm of the sediment, (Total) mean total carbohydrate content of 1 cm horizon of the upper 5 cm of the sediment.

The samples can be classified according to their position in the graph into distinct groups. The summer samples dominate the upper left part of the graph, autumn the lower left part. Winter and spring dominate the upper right part. Permeability in summer was mainly influenced by the fine fraction in % of the upper 5 cm of the sediment. Permeability in autumn (especially in 2003) was influenced by the carbohydrate content in the sediment. Sample W13 (January 2004) is a clear outlier. At that time the sampling station was ice covered.

*Table 2: Redundancy analysis: correlations of the variables and canonical coefficients of the variables with the two axes of the RDA. ** Significantly related at $p < 0.01$*

Variables	Correlation with axes		Canonical coefficients of environmental variables	
	Axis 1	Axis 2	Axis 1	Axis 2
mean average daily wind speed (ms^{-1})	0.84**	-0.37	1.082 **	-0.511
mean average daily wind direction ($^{\circ}$)	0.25	-0.28	-0.213	0.106
mean fine fraction of the upper 5 cm (% dry sediment)	-0.20	0.64	0.239	0.685
mean porosity of the upper 5 cm of the sediment	0.45	-0.19	-0.343	0.317
mean median grain size of the upper 5 cm of the sediment (μm)	-0.20	-0.57	-0.047	-0.207
mean chlorophyll <i>a</i> content of 1 cm in the upper 5 cm of the sediment ($\mu\text{g g}^{-1}$ dry sediment)	0.19	-0.28	0.538	0.432
mean EDTA - extractable carbohydrate content of 1 cm in the upper 5 cm of the sediment (μg glucose equivalent g^{-1} dry sediment)	-0.44	-0.64	-0.689	-0.618
mean total carbohydrate content of 1 cm in the upper 5 cm of the sediment (μg glucose equivalent g^{-1} dry sediment)	-0.03	-0.50	0.433	-0.146

2.5 Discussion

To date, just a few permeability data are available. They are mostly for intertidal sediments and do not cover an entire seasonal cycle. Rusch et al. (2001) made measurements in the intertidal in different months and they found temporal variation of permeability to be unrelated to seasons. In contrast, permeability measurements in this study showed a clear seasonal signal for the upper 5 cm and for the upper 15 cm of the sediment with higher values in winter and spring and lower values in summer and autumn.

The redundancy analysis showed that the mean average wind speed of the sampling day had the biggest and only significant influence on the sediment permeability in this study. Wind generated waves are already known as an important forcing factor on physical properties of the sediment (e.g. Cadée and Hegeman 1974, Frostick and McCave 1979, Grant et al. 1986, Madsen et al. 1993, de Jonge and van Beusekom 1995, Nelson et al. 1999, Lucas et al. 2000), overriding the importance of tidal currents. Beside other factors like porosity, fine fraction, chlorophyll *a* and carbohydrate content of the sediment, changed consolidation of the sediment due to enhanced resuspension because of wind generated waves is the most likely explanation for the observed changes in permeability dynamics. Porosity, fine fraction, chlorophyll *a* and carbohydrate content of the sediment may influence the permeability, but this was not significant.

The redundancy analysis showed that the EDTA - extractable carbohydrate content of the sediment was the second important influencing factor of permeability, but this factor was not significant. In particular, the permeability of autumn samples of the year 2003 was influenced by the EDTA - carbohydrates in the sediment. Carbohydrates comprise a major fraction of extrapolymeric substances (EPS) produced by microphytobenthos (Staats et al. 1999). Extrapolymeric substances are known to stabilize sediments, trap fine

particles thereby possibly influencing the permeability of sediments. This stabilization has been described for the intertidal and the subtidal, for muddy sediments and sandy sediments (e.g. Vos et al. 1988, Grant et al. 1986, Yallop et al. 1994). The carbohydrates are bound to the cells with different strength. At this study site the microphytobenthos is dominated by benthic diatoms (Wiktor pers. comm.). Extracellular carbohydrates are excreted as a part of the mechanism of motility from epipelagic diatoms (de Brouwer and Stal 2001) or as a result of "overflow metabolism" due to nutrient limitation during photosynthesis (Blanchard et al. 2000).

The carbohydrates of EPS can be extracted with different reagents and measured as glucose equivalents (Underwood et al. 1995). In this study the EDTA - extractable carbohydrates were measured, because they are more tightly associated with the cell walls or sediment particles and may have a strong stabilising influence on the sediment (e.g. Decho and Lopez 1993, de Winder et al. 1999, de Brouwer et al. 2000, Stal 2003). Sand grains are relatively uncharged and so a relatively small fraction of carbohydrates can be adsorbed to sandy sediments. Therefore, the colloidal carbohydrate fraction which can be extracted with water is rapidly removed from the system by pore water flows, and is, as such, probably not so important for stabilization of permanently water covered subtidal sediments (Madsen et al. 1993, de Brouwer et al. 2000, Rusch et al. 2001), or they might be rapidly degraded (Rusch et al. 2001, Stal 2003). The mean EDTA - extractable carbohydrate content in this study correlated significantly with mean chlorophyll *a* content of the sediment, indicating that benthic diatoms were the main producers of these carbohydrates. Several authors found a high influence of carbohydrates on sediment stabilization, if there was a significant correlation between chlorophyll *a* and carbohydrates (see Riethmüller et al. 2000). The relationship of chlorophyll *a* and carbohydrates is determined by several factors: algal composition (e.g. ratio between diatoms and other algal groups (e.g.

cyanobacteria, flagellates), ratio between motile (epipelagic) and non - motile (epibenthic) diatoms (Madsen et al. 1993) and nutrient availability (Cook et al. in prep.).

The mean chlorophyll *a* content of the upper 5 cm showed no significant seasonal differences during the two sampling years, but the second summer had significantly lower chlorophyll *a* contents. Also the EDTA - extractable carbohydrate content as well as the total carbohydrate content of the sediment showed no seasonal differences. Several authors (e.g. Pinckney et al. 1995, Brotas and Plante - Cuny 1998) also found no seasonal pattern especially for sandy sediments. The chlorophyll *a* profiles in the sediment showed high values several cm down into the sediment, probably due to burial of diatoms through physical forces (Rusch et al. 2000) or active migration (Kingston 1999, Cadée and Hegeman 1974).

Rusch et al. 2001 also found for the intertidal no influence of chlorophyll *a* and carbohydrates on sediment permeability. They suggested that the permeability may be modified by carbohydrates, but the concentrations were low and apparently insufficient to cause measurable changes in permeability. Underwood and Paterson (1993b) discussed that during calmer weather periods diatom enhanced stability through carbohydrates may play a significant intermediary role in promoting sediment consolidation by binding settling sediment particles with exopolymer material. This mechanism may also reduce the permeability during calmer periods.

Microorganisms are also known to alter other sediment characteristics beside the stability, including grain size and porosity (Wachendoerfer et al. 1994). EPS produced by microorganisms may play a key role for the formation of a matrix, which influences the porosity of the sediment and enhances the deposition of fresh sediment (Underwood and Paterson 1993a). Underwood and Paterson (1993a) found that the sediment became much more stable, because of the compaction. Because bioturbators were absent, the sediment became more

closely packed and more difficult to erode. Therefore, sediment packing plays an important role in sediment stability also.

The triplot of the redundancy analysis showed that the permeability during summer months was influenced by the fine fraction of the sediment. Probably due to a combination of lower wind speeds and higher phytobenthos activity the fine fraction was not so easily resuspended from the sediment. The fine fraction in % was significantly seasonally different with higher amounts in summer and autumn compared to lower amounts in winter and spring. The fine fraction of the sediment is known as one possible factor influencing the sediment permeability (Cahoon 1999, Regh et al. 2005, Volkenborn et al. *subm. a, b*), but the amount present in our sediments were small ($< 0.2\%$) and had no significant influence on the sediment permeability.

Other possible factors determining the sediment permeability are the sorting, the grain size of the sediment (Hsü 1989). The redundancy analysis showed no significant influence of the grain size on the dynamics of permeability. The median grain size showed no seasonal pattern. The median grain size was significantly smaller in the second year, but the difference was small. The sediment was moderately well or well sorted, with no seasonal differences.

The shallow permeable subtidal sediment at the study site was influenced all the time by wind induced waves, leading to a seasonality of the permeability at this site because of changed consolidation of the sediment due to enhanced resuspension of the sediment. Wind, however could not explain all the variability in permeability and other factors such as the EPS and fine fraction content of the sediment may also have an influence on permeability albeit with a much lower statistical certainty than wind. However the physical forces of waves determined through the wind are much more important at this site than the biological parameters, suggesting that higher wind speeds will lead to higher permeabilities.

Appendix:

Results for the different measured parameters. Data are the mean of three different measurements. The numbers in italics are the standard error of the three replicates. For chlorophyll a and carbohydrates the mean concentration of the upper 5 cm was calculated. NA: not determined

Date	Mean Permeability 10-15 cm in m ²	Mean Permeability of the upper 5 cm in m ²	Mean Median Wind Speed in m s ⁻¹	Mean Median Wind Direction	Mean Median Grain size in µm	Mean Fine Fraction of the upper 5 cm of the sediment in %	Mean Porosity of the upper 5 cm	Mean Chlorophyll a content of the 5 upper cm in µg g ⁻¹	Mean EDTA-extractable carbohydrate content of the 5 upper cm in µg glucose equivalent g ⁻¹	Mean Total carbohydrate content of the 5 upper cm in µg glucose equivalent g ⁻¹
March 03 (21.03.2003)	2.37E-11 <i>9.25E-12</i>	NA	7.48	130	NA	NA	NA	14.20 <i>2.71</i>	NA	NA
April 03 (17.04.2003)	2.08E-11 <i>2.56E-12</i>	NA	5.01	140	343.35 <i>1.56</i>	0.12 <i>0.03</i>	0.46 <i>0.01</i>	16.92 <i>2.10</i>	NA	NA
May 03 (06.05.2003)	2.22E-11 <i>1.18E-12</i>	NA	6.24	260	344.64 <i>1.88</i>	0.12 <i>0.02</i>	0.47 <i>0.01</i>	12.29 <i>2.72</i>	NA	NA
June 03 (12.06.2003)	1.47E-11 <i>2.55E-12</i>	NA	6.40	250	354.80 <i>1.95</i>	0.23 <i>0.05</i>	0.46 <i>< 0.01</i>	18.27 <i>0.28</i>	567.34 <i>23.63</i>	2695.20 <i>166.46</i>
July 03 (14.07.2003)	1.83E-11 <i>2.27E-12</i>	2.92E-11 <i>3.14E-12</i>	4.18	90	352.33 <i>3.30</i>	0.17 <i>0.02</i>	0.43 <i>0.01</i>	18.28 <i>1.40</i>	645.33 <i>82.68</i>	1609.44 <i>138.54</i>
August 03 (28.08.2003)	1.70E-11 <i>1.51E-12</i>	2.45E-11 <i>3.61E-12</i>	2.98	220	358.84 <i>0.90</i>	0.13 <i>0.01</i>	0.44 <i>0.02</i>	15.82 <i>0.42</i>	588.39 <i>91.49</i>	6883.59 <i>246.47</i>
September 03 (25.09.2003)	1.51E-11 <i>2.12E-12</i>	4.57E-11 <i>5.17E-12</i>	7.31	220	351.97 <i>4.02</i>	0.12 <i>0.02</i>	0.45 <i>0.01</i>	17.71 <i>0.38</i>	886.24 <i>44.45</i>	4352.99 <i>149.72</i>
October 03 (24.10.2003)	2.05E-11 <i>1.93E-12</i>	3.67E-11 <i>9.72E-12</i>	7.44	190	348.17 <i>5.67</i>	0.18 <i>0.04</i>	0.42 <i>0.02</i>	10.96 <i>0.85</i>	625.80 <i>45.53</i>	2801.57 <i>209.19</i>
November 03 (24.11.2003)	2.22E-11 <i>4.76E-12</i>	5.11E-11 <i>2.36E-12</i>	7.44	190	350.08 <i>0.50</i>	0.11 <i>0.01</i>	0.48 <i>< 0.01</i>	13.66 <i>2.36</i>	500.67 <i>11.44</i>	3584.72 <i>509.60</i>
December 03	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
January 04 (06.01.2004)	1.86E-11 <i>1.94E-12</i>	8.50E-11 <i>3.61E-11</i>	8.85	160	363.72 <i>2.09</i>	0.04 <i>0.02</i>	0.46 <i>0.01</i>	14.70 <i>1.14</i>	542.33 <i>90.25</i>	4128.40 <i>226.59</i>
February 04 (05.02.2004)	3.32E-11 <i>3.40E-12</i>	4.16E-11 <i>1.35E-11</i>	10.50	250	347.34 <i>4.78</i>	0.16 <i>0.02</i>	0.48 <i>0.02</i>	14.59 <i>0.87</i>	391.27 <i>58.51</i>	3515.16 <i>119.36</i>
March 04 (05.03.2004)	2.41E-11 <i>3.79E-12</i>	4.77E-11 <i>3.62E-12</i>	8.02	120	338.01 <i>3.79</i>	0.15 <i>0.04</i>	0.47 <i>0.01</i>	16.83 <i>1.14</i>	405.52 <i>62.04</i>	3131.61 <i>289.88</i>
April 04 (05.04.2004)	2.82E-11 <i>5.23E-13</i>	8.96E-11 <i>3.18E-11</i>	7.83	220	338.93 <i>2.85</i>	0.14 <i>0.02</i>	0.45 <i>0.02</i>	14.84 <i>1.85</i>	380.79 <i>51.45</i>	3231.39 <i>206.23</i>
May 04 (04.05.2004)	1.84E-11 <i>4.01E-11</i>	2.34E-11 <i>5.46E-12</i>	6.25	190	339.11 <i>3.97</i>	0.12 <i>0.02</i>	0.44 <i>0.01</i>	14.74 <i>2.02</i>	361.00 <i>57.57</i>	1080.59 <i>53.62</i>
June 04 (07.06.2004)	1.92E-11 <i>5.75E-13</i>	4.60E-11 <i>1.32E-11</i>	6.68	250	337.43 <i>3.40</i>	0.22 <i>0.04</i>	0.41 <i>0.01</i>	11.06 <i>2.31</i>	421.86 <i>86.48</i>	2228.20 <i>44.49</i>
July 04 (17.07.2004)	1.97E-11 <i>1.96E-12</i>	2.61E-11 <i>6.02E-12</i>	4.20	110	347.83 <i>1.08</i>	0.25 <i>0.02</i>	0.41 <i>0.01</i>	7.53 <i>1.82</i>	240.89 <i>40.09</i>	1182.98 <i>123.59</i>
August 04 (05.08.2004)	1.86E-11 <i>1.58E-12</i>	3.44E-11 <i>6.70E-12</i>	5.20	100	344.55 <i>2.58</i>	0.20 <i>0.03</i>	0.45 <i>0.02</i>	10.18 <i>2.21</i>	357.61 <i>80.34</i>	2658.93 <i>136.96</i>
September 04 (03.09.2004)	1.60E-11 <i>2.57E-12</i>	2.83E-11 <i>7.28E-12</i>	4.68	120	332.13 <i>3.02</i>	0.10 <i>0.03</i>	0.45 <i>< 0.01</i>	15.12 <i>1.08</i>	624.53 <i>95.19</i>	2867.17 <i>80.81</i>
October 04 (16.10.2004)	1.93E-11 <i>2.75E-12</i>	3.31E-11 <i>9.57E-12</i>	7.04	135	337.54 <i>2.70</i>	0.09 <i>0.02</i>	0.45 <i>0.01</i>	12.81 <i>2.17</i>	234.70 <i>36.22</i>	2542.60 <i>124.11</i>
November 04 (17.11.2004)	2.73E-11 <i>3.06E-12</i>	6.00E-11 <i>1.20E-11</i>	7.88	145	335.78 <i>5.46</i>	0.10 <i>0.08</i>	0.45 <i>0.01</i>	15.75 <i>1.69</i>	288.20 <i>45.23</i>	2004.69 <i>372.32</i>
December 04	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
January 05	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
February 05 (08.02.2005)	1.83E-11 <i>2.76E-12</i>	4.11E-11 <i>6.30E-12</i>	NA	NA	349.93 <i>1.92</i>	0.13 <i>0.02</i>	0.46 <i>< 0.01</i>	13.00 <i>1.35</i>	NA	NA
March 05	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
April 05 (08.04.2005)	2.66E-11 <i>171E-12</i>	6.82E-11 <i>1.09E-11</i>	NA	NA	NA	NA	NA	15.26 <i>1.28</i>	NA	NA

Chapter 3

Seasonal nutrient dynamics in pore water of a shallow subtidal permeable sediment: the effect of groundwater and microphytobenthos

3.1 Abstract

Seasonal pore water nutrient dynamics in a permeable shallow subtidal sandy sediment near the island Sylt in the northern Wadden Sea (Germany) were investigated between February 2003 and April 2005. Si(OH)_4 , NH_4^+ and PO_4^{3-} pore water profiles showed low concentrations in the upper 4 - 6 cm of the sediment probably due to advection and assimilation by microphytobenthos. Concentrations increased below this layer. PO_4^{3-} concentrations always reached maximum values between 3 and 7 cm sediment depth. NO_3^- and NO_2^- reached maximum concentrations in the upper centimetres. The mean pore water concentrations of the upper 5 cm of the sediment showed the same dynamics for Si(OH)_4 , NH_4^+ and PO_4^{3-} in both years: lowest concentrations in spring and late summer / early autumn and two concentration peaks during summer and during winter. In addition weak peaks of these nutrients occurred also during spring, probably reflecting the depositing phytoplankton bloom. It is suggested that this pattern is the result of changing temperature, light conditions and organic matter loading on the sediment. NO_3^- showed different dynamics and closely followed the dynamics of the overlying water column with low concentrations in summer and autumn and high concentrations in winter and spring. The nutrient dynamics at the sampling site were also influenced by inflowing water from below with low salinities, containing high concentrations of Si(OH)_4 and NH_4^+ . High NO_3^- concentrations were only observed during winter and spring 2004. The pore water concentrations in the upper 5 cm of the sediment were always higher than the concentrations in the overlying water column, suggesting that the sediment is a nutrient source for the

microphytobenthos in the upper cm of the sediment and potentially also for the water column.

3.2 Introduction

Permeable sands are a dominant sediment type on continental shelves (Emery, 1968, Riedl et al. 1972). These sediments usually contain a relatively small amount of organic matter. But low organic carbon and nutrient concentrations in coastal sands may reflect high turnover rates and not low activity (Huettel et al. 1998, Boudreau et al. 2001). In sediments with permeabilities exceeding $10^{-12} - 10^{-11} \text{ m}^2$ advection and enhanced dispersion dominate pore water transport (Huettel and Webster 2001, Reimers et al. 2004). Advective solute exchange rates increase with increasing permeability. These transport processes are induced by bottom current – sediment interactions (Huettel et al. 1996) and by pore pressure variations, caused by the passage of surface gravity waves (Precht and Huettel 2003). High advective flushing rates enhance the mineralization of the trapped organic matter and stimulate the benthic oxygen consumption and prevent the accumulation of nutrients in the pore water (Ehrenhaus and Huettel 2004). Flume experiments have shown that advective pore water flows enhance the nutrient efflux (Huettel et al. 1998), as well as the oxygen penetration (Ziebis et al. 1996) and consumption (Forster et al. 1996) in permeable sediments.

The pore water dynamics in shallow water sediments may be influenced by two additional factors: groundwater intrusion and microphytobenthos. In recent years investigations on the influence of submarine groundwater discharge on biogeochemical cycles has started (e.g. Burnett et al. 2003). Coastal zones are known as areas with fresh or brackish water inflow (Johannes 1980), which may influence the pore water nutrient concentrations. At shallow sites, sufficient light for photosynthesis by microphytobenthos reaches the sediment (Cahoon and Cooke 1992, Nelson et al. 1999). Uptake of nutrients by microphytobenthos may influence the nutrient fluxes from the sediment

(Sundbäck et al. 1991). These factors add to the complexity of the organic matter and nutrient dynamics in benthic system.

Here, the temporal dynamics of nutrients and salinity in pore water of a shallow subtidal permeable sediment are reported. Samples were taken at least once per month between February 2003 and April 2005 at a shallow sandy subtidal sampling station near the island of Sylt in the northern Wadden Sea, to evaluate seasonal patterns and to identify possible influencing factors.

3.3 Materials and Methods

3.3.1 Sampling site

Samples were taken in a permeable sand in the shallow subtidal near the island of Sylt (Germany) in the northern Wadden Sea (55°00'47.7'' N, 08°25'59.3'' E; Figure 1). Water depth at the sampling site ranged from 50 - 250 cm, depending on the tidal phase. The sediment at the sampling site consisted of well to moderately well sorted medium sand with a median particle size of 350 µm. The origin of the sediment is mainly aeolic (Austen 1994). The mean porosity was 0.397 ± 0.003 and was higher during winter and spring than in summer and autumn. The mean permeability of the upper 10 to 15 cm sediment was $2.07 \times 10^{-11} \pm 6.63 \times 10^{-12} \text{ m}^2$. The permeability varied also seasonally with higher values during winter and spring than during summer and autumn. Permeability ranged between $1.01 \times 10^{-11} \text{ m}^2$ and $3.36 \times 10^{-11} \text{ m}^2$ (see Chapter 2) - a range within which advective porewater flow was expected to take place (Huettel et al. 1998). Tidal currents and wind induced waves are the dominant hydrodynamic forces. Currents at the sampling site were up to 90 cm s^{-1} (Wenzhöfer pers. comm.).

Benthic macrofauna biomass was low and dominated by small polychaetes, present in relatively low abundances (Weslawski et al. in prep.).

Further details of the study area are provided by Austen (1994) and Gätje and Reise (1998).

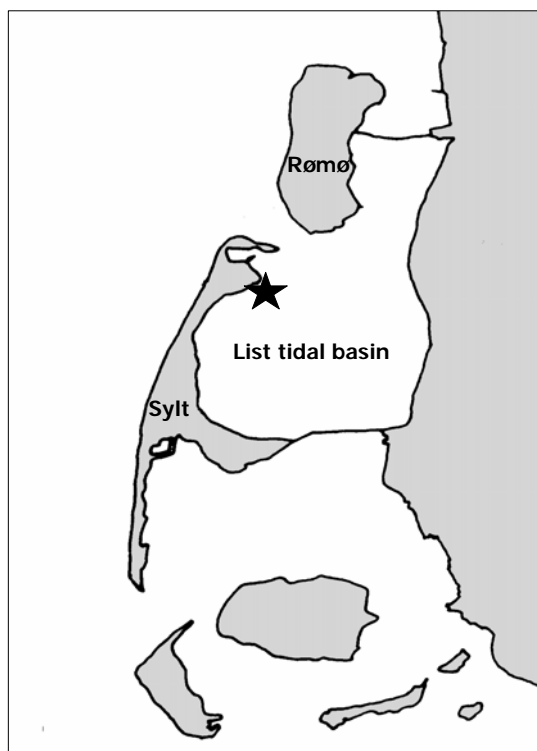


Figure 1: Sampling site in the List tidal basin in the northern Wadden Sea near the island Sylt (Germany). The star shows the sampling station.

3.3.2 Sampling

Sediment samples were taken at least once per month between February 2003 and April 2005 during low tide. The sediment cores with an inner diameter of 3.6 cm and a length of 30 cm were taken randomly by hand, to avoid sediment disturbance. The water level above the sediment was at least 50 cm. The cores were carefully pushed into the sediment (15 - 20 cm deep), closed with a rubber stopper, lifted and closed carefully from beneath with a second stopper. All following procedures were performed in the nearby (500 m) lab as soon as possible.

Water samples of the overlying water were taken twice per week at two nearby sampling stations in the frame of long term investigations of nutrient and phytoplankton dynamics in the List tidal basin. The water was filtered through Nuclepore filters and frozen, except samples for dissolved silicon, which were stored in a fridge until further analysis.

3.3.3 Pore water extraction

Eight cores with an inner diameter of 3.6 cm were sliced in 1 cm intervals to a depth of 15 cm. Sediment slices were pooled together and the pore water blown out with nitrogen (Billerbeck et al. subm.). The pore water was filtered through 0.45 μm nylon filters and stored in a fridge (for dissolved silicon and salinity determination) or frozen until further analysis (ammonium, phosphate, nitrate and nitrite).

The homogenization procedure and the method reliability was tested before based on $\text{Si}(\text{OH})_4$ measurements. From eight cores, sub samples were taken of each layer and pore water was blown out from each sample. After homogenizing the rest of each sediment layer, the pore water was blown out. The $\text{Si}(\text{OH})_4$ concentrations in each layer from each core and the concentrations in the pooled layers were compared.

3.3.4 Pore water and water analysis

The concentration of the dissolved silicon was measured photometrically after dilution of the pore water (Grasshoff et al. 1983). Ammonium, phosphate, nitrate and nitrite concentrations in the pore water as well as nitrate concentrations in the water column were measured with an autoanalyzer (Bran & L bbeck; methods modified from Grasshoff et al. 1983). The dissolved silicon, ammonium, phosphate, nitrite concentrations of the water column were determined by hand with a photometer (Grasshoff et al. 1983). Pore water salinity was measured with a hand refractometer (Reichert Scientific Instruments), salinity of the overlying water column with a salinometer (Autosal, Model 84001), methods were compared with each other.

3.3.5 Data presentation

Data are presented as means \pm standard error. The temporal and vertical dynamics of salinity and different concentrations were plotted with Surfer (Golden Software, version 8). The gridding method was krigging with a linear variogram model. The slope was one, the anisotropy ratio 10.

3.4 Results

3.4.1 Salinity

The salinity of the pore water ranged between 17 (November 2004, 14 cm depth) and 33 (October 2003, 15 cm depth) (Figure 2).

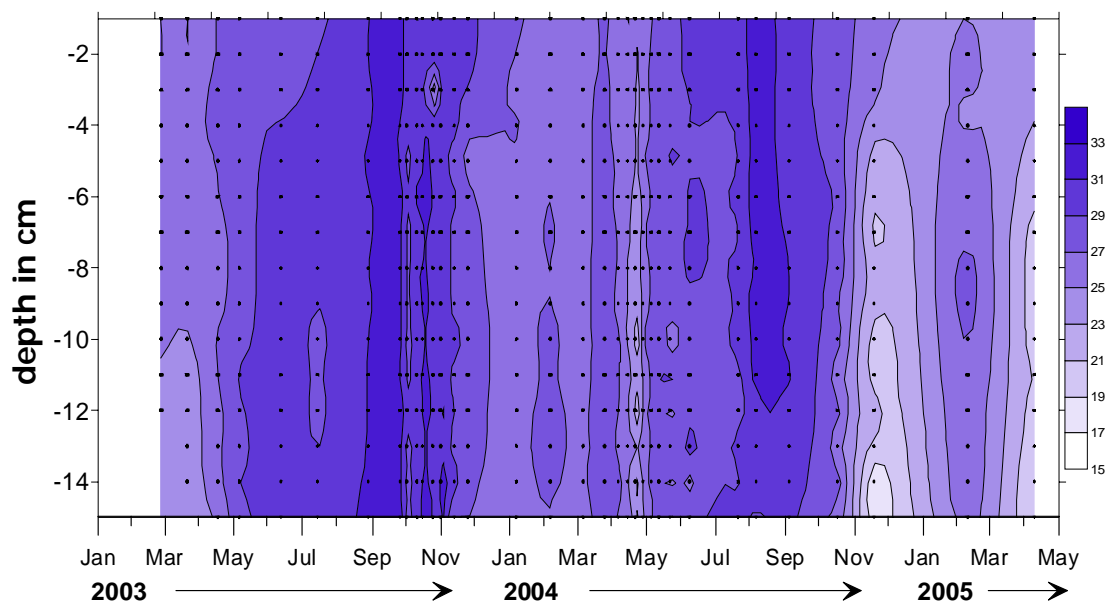


Figure 2: Vertical distribution of salinity in the pore water at the sampling site from February 2003 to April 2005. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The colour is proportional to the salinity.

The mean salinity of the overlying water column was 29.28 ± 0.07 and ranged between 26.05 (February 2004) and 31.65 (November 2003). The salinity of the water column showed higher values during the summer months than during winter and spring. This seasonality was more distinct in the year 2003 (Figure 3). It should be noted that salinity of the overlying water was measured with a salinometer, which gives much more accurate results than the refractometer (± 1 unit; pore water). Pore water salinity of the upper 5 cm in the sediment followed the trend of the overlying water column with salinities in the same

range until November 2004. In November 2004 the mean salinity of the pore water of the upper 5 cm dropped in comparison to the water column. In November 2004, February 2005 and April 2005 the salinity in the deeper sediment layers was much lower than in the upper 5 cm of the sediment (Figure 2).

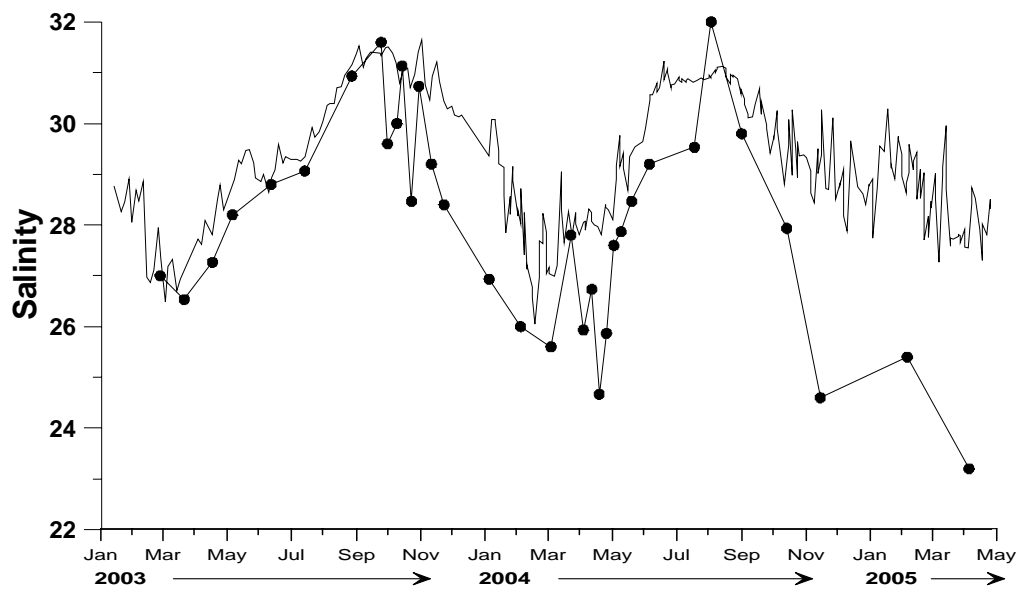


Figure 3: Mean salinity in the upper 5 cm of the sediment (dotted line) and in the water column (line).

3.4.2 Dissolved silicon

Dissolved silicon concentrations in the upper centimetres (2 - 6 cm) were always low, and then increased deeper within the sediment (Figure 4). During winter and spring there were spikes of high concentrations in deeper layers coinciding with spikes of low salinity. Mean dissolved silicon concentration of the pore water in the upper 5 cm of the sediment was $28 \pm 3 \mu\text{mol l}^{-1}$, the mean concentration of the pore water in the 6 to 15 cm sediment depth was $70 \pm 8 \mu\text{mol l}^{-1}$. The concentration range of the pore water was between $0.57 \mu\text{mol l}^{-1}$ (May 2003, 1 cm depth) and $290.15 \mu\text{mol l}^{-1}$ (April 2003, 14 cm depth) (Figure 4).

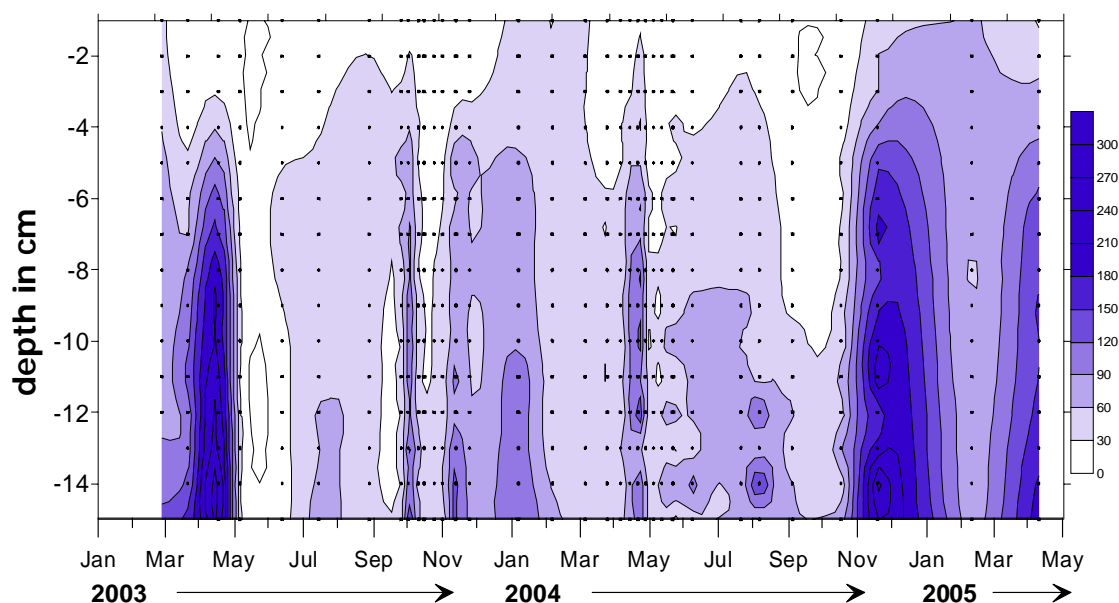


Figure 4: Vertical distribution of Si(OH)_4 in $\mu\text{mol l}^{-1}$ in the pore water at the sampling site from February 2003 to April 2005. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The colour is proportional to pore water concentrations.

Dissolved silicon concentration of the overlying water column ranged between $0.13 \mu\text{mol l}^{-1}$ (April 2005) and $45.94 \mu\text{mol l}^{-1}$ (March 2004), reaching their seasonal maximum between November and April. The mean Si(OH)_4 concentration in the pore water of the upper 5 cm in the sediment was nearly always higher than the concentration in the overlying water column (Figure 5). In November 2004 the mean concentration of the pore water of the upper 5 cm strongly increased, remained high in February and April 2005. In November 2004, February 2005 and April 2005 were also in the deeper sediment layers higher Si(OH)_4 concentrations in the pore water than in the rest of the sampling time (Figure 4).

The mean pore water concentrations in the upper 5 cm showed two maxima per year. The first one was reached during winter months, before the maximum in the water column. The second one was reached during summer months. The pore water concentrations decreased at the beginning of autumn and the concentrations in the water column and in the pore water were in a similar range. In both years a general pattern could be observed: low concentrations in spring, increasing concentrations during summer, then decreasing concentrations to minimum concentrations in late summer / early autumn, before concentrations increased again during winter months. At the end of April in the years 2003 and 2004, an additional short peak of dissolved silicon in the pore water concentrations occurred. In 2004 this small peak coincided with lower salinities in the pore water.

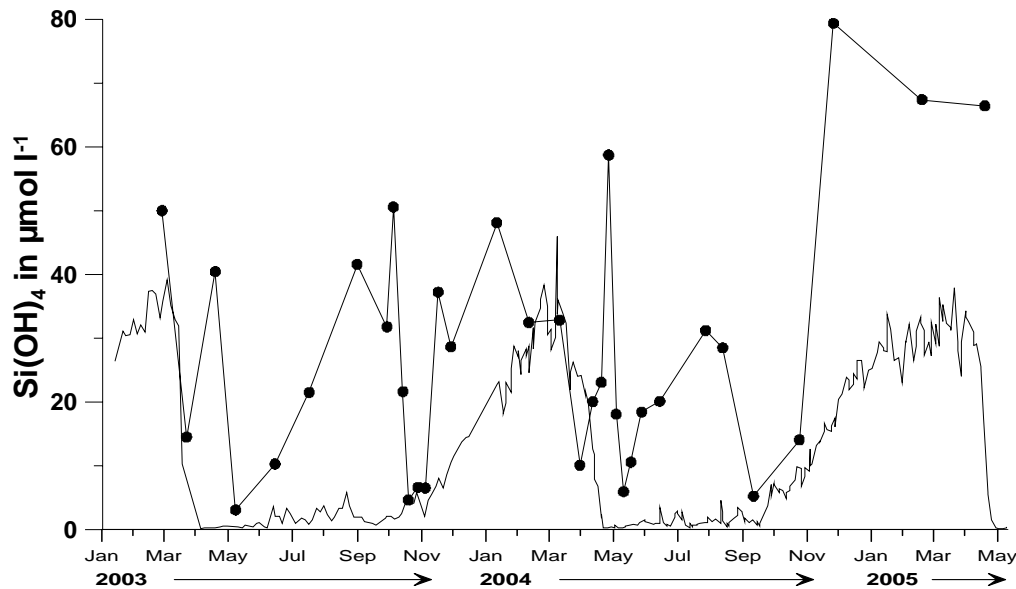


Figure 5: Mean Si(OH)_4 concentration of the pore water in the upper 5 cm of the sediment (dotted line) and in the water column (line).

Figure 6 compares the nutrient profiles during the different seasons. In spring and winter, nutrient concentrations were generally higher than during summer and autumn during the whole sampling period. This is also visible in Figure 4, where higher concentrations are mainly found in April 2003, November 2004, January 2005 and April 2005. These high Si(OH)_4 concentrations often coincide with low salinities in deeper sediment layers (Figure 2). The variation of the concentration was higher during winter and spring (see error bars in Figure 6) than during summer.

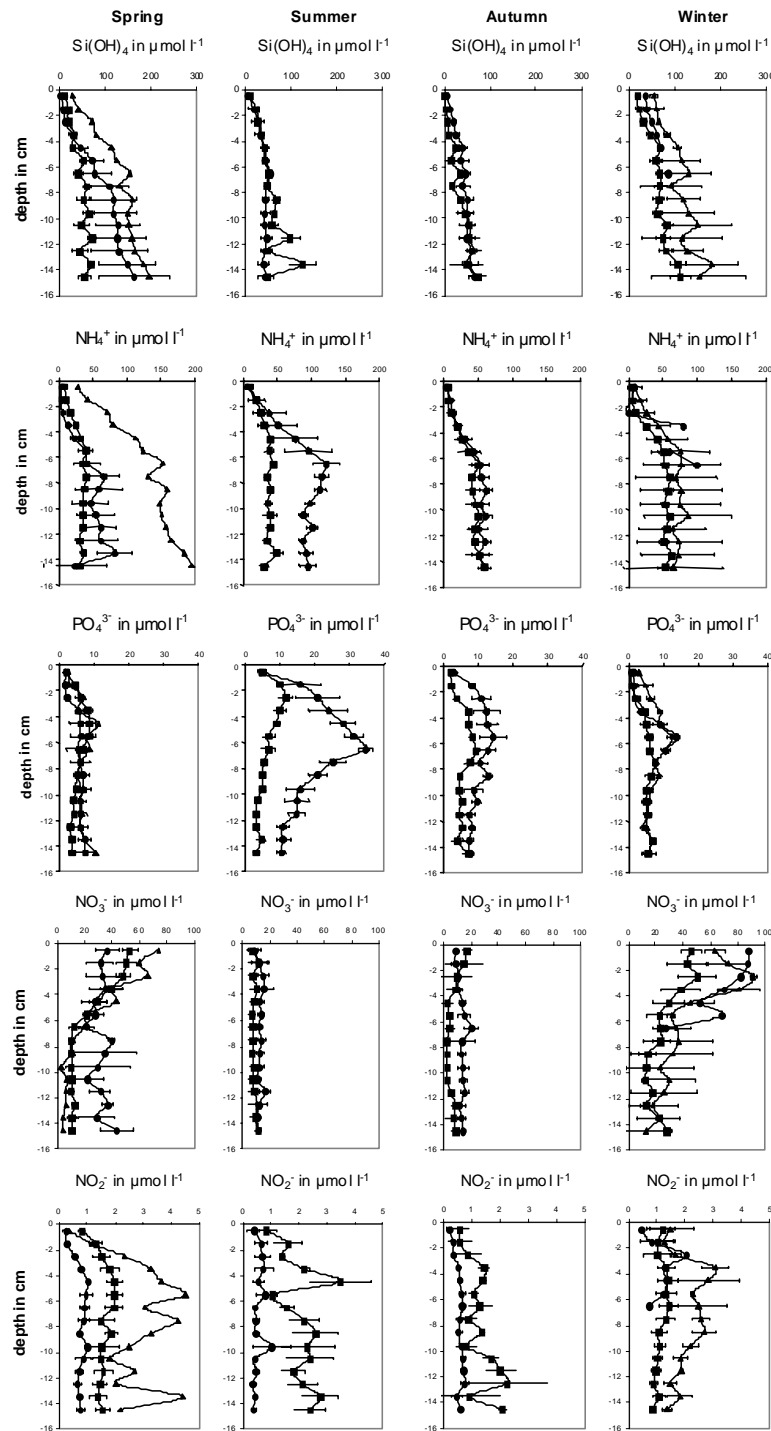


Figure 6: Seasonal distribution of pore water Si(OH)_4 , NH_4^+ , PO_4^{3-} , NO_3^- and NO_2^- with SE.
 ●: 2003 (winter 2002 / 2003: 1 sampling, spring 2003: mean of 3 samplings, summer 2003: mean of 3 samplings, autumn 2003: mean of 6 samplings),
 ■: year 2004 (winter 2003 / 2004: mean of 4 samplings, spring 2004: mean of 9 samplings, summer 2004: mean of 3 samplings, autumn 2004: mean of 2 samplings),
 ▲: year 2005 (winter 2004 / 2005: 1 sampling spring 2005: mean of 2 samplings), all the profiles are presented with standard error.

3.4.3 Ammonium

Ammonium concentrations in the upper centimetres (2 - 6 cm) were always low, and then increased below with depth (Figure 7). Mean ammonium concentration of the pore water in the upper 5 cm of the sediment was $20 \pm 2 \mu\text{mol l}^{-1}$, and the mean concentration in 6 to 15 cm sediment depth horizon was $54 \pm 5 \mu\text{mol l}^{-1}$. The concentration of the pore water ranged between $0.58 \mu\text{mol l}^{-1}$ (February 2004, 1 cm depth) and $172.67 \mu\text{mol l}^{-1}$ (April 2003, 14 cm depth) (Figure 7).

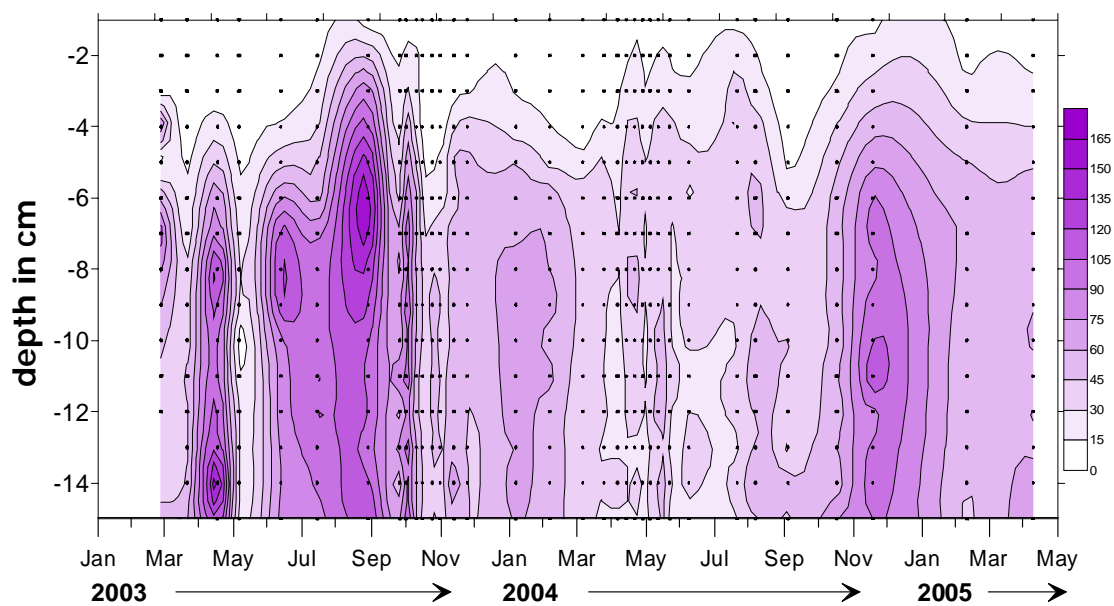


Figure 7: Vertical distribution of NH_4^+ in $\mu\text{mol l}^{-1}$ in the pore water at the sampling site from February 2003 to April 2005. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The colour is proportional to pore water concentrations.

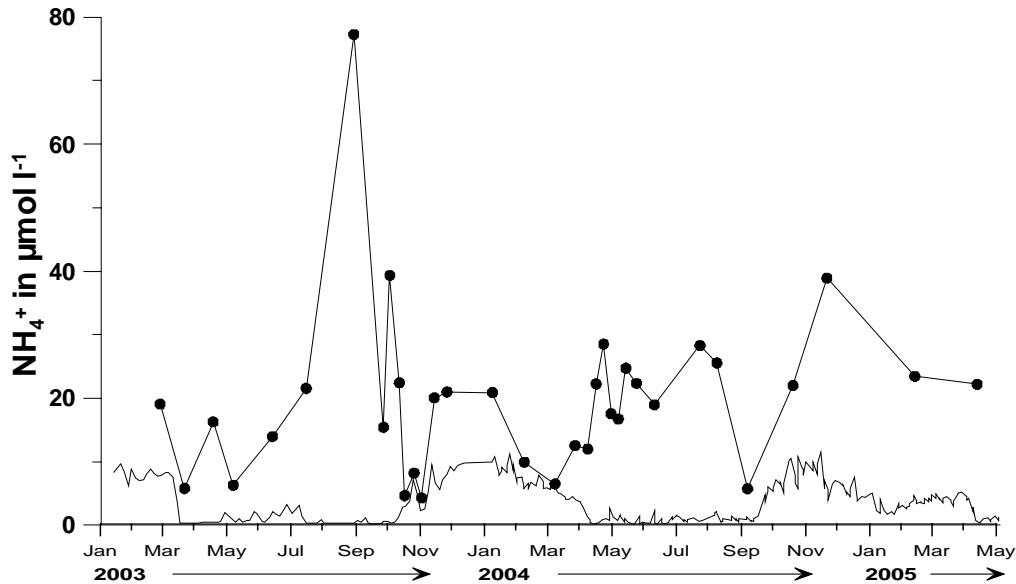


Figure 8: Mean NH_4^+ concentration of the pore water in the upper 5 cm of the sediment (dotted line) and in the water column (line).

The ammonium concentration of the overlying water column ranged between $0.18 \mu\text{mol l}^{-1}$ (May 2004) and $11.52 \mu\text{mol l}^{-1}$ (November 2004) with the highest concentrations being observed between October and April each year. The mean NH_4^+ concentration in the pore water of the upper 5 cm in the sediment was always higher than the concentration in the overlying water column and showed again two peaks per year. The first one occurred during winter months, the second one during summer months. During spring and late summer / early autumn, minimum values were reached in the pore water and the concentrations in the water column and in the pore water were similar. A comparison of the profiles (Figure 6) show that the concentrations in spring and winter were high and the shape of the NH_4^+ profiles is similar to the profiles of $\text{Si}(\text{OH})_4$ during spring and winter. The NH_4^+ profiles in summer 2003 show a higher concentration than in summer 2004 (compare Figure 6).

Once again, in both years the general pattern as already described for dissolved silicon in the pore water could be observed: low concentrations in spring, increasing concentrations during summer, then decreasing concentrations with minimum values in late summer / early autumn, before concentrations increased again during winter months. The peak during summer 2003 was much higher than in 2004. Once again at the end of April in year 2003 and 2004, an additional short peak of ammonium in the pore water concentrations occurred (more pronounced in 2003). In 2004 this small peak coincided with lower pore water salinities.

3.4.4 Phosphate

In contrast to Si(OH)_4 and NH_4^+ maximum concentrations of PO_4^{3-} in the pore water were present between 3 – 7 cm sediment depth. Mean phosphate concentration of the pore water in the upper 5 cm of the sediment was $7 \pm 1 \mu\text{mol l}^{-1}$, the mean concentration of the pore water in 6 to 15 cm sediment depth was $8 \pm 1 \mu\text{mol l}^{-1}$. Pore water concentration ranged between $0.52 \mu\text{mol l}^{-1}$ (January 2004, 1 cm depth) and $36.69 \mu\text{mol l}^{-1}$ (June 2003, 7 cm depth) (Figure 9).

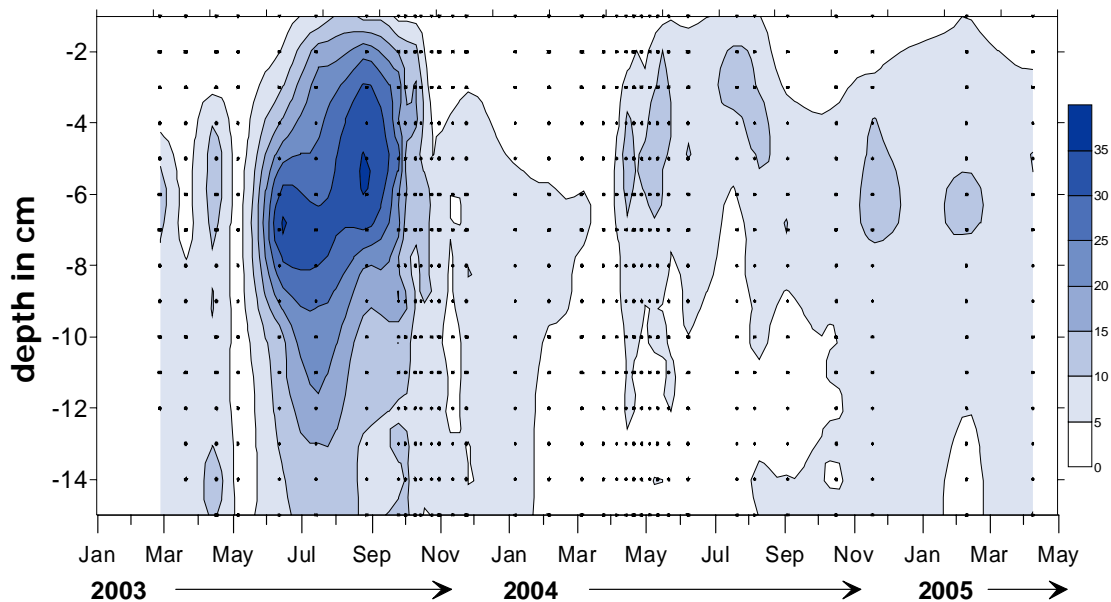


Figure 9: Vertical distribution of PO_4^{3-} in $\mu\text{mol l}^{-1}$ in the pore water at the sampling site from February 2003 to April 2005. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The colour is proportional to pore water concentrations.

The phosphate concentration of the overlying water column ranged between below $0.01 \mu\text{mol l}^{-1}$ (April 2003) and $1.20 \mu\text{mol l}^{-1}$ (January 2003) (note the different Y – axis in Figure 10). The phosphate values in the water column were lower from April to June in each year in comparison to the rest of the year. In summer 2003 the concentrations in the water column were higher than in 2004. The mean PO_4^{3-} concentration in the pore water of the upper 5 cm in the sediment was always substantially higher than the concentration in the overlying water column. The highest PO_4^{3-} concentration in the pore water of the upper 5 cm in the sediment was reached in both years during summer (Figure 10). In 2003 the highest concentration was reached in August coinciding with the maximum values in the water column.

Once again, the pattern for the pore water could be distinguished: lower concentrations during spring, increase during summer, decrease in late summer / early autumn, before the concentrations increased again during winter. Here again a small peak at the end of April in 2003 and 2004 occurred.

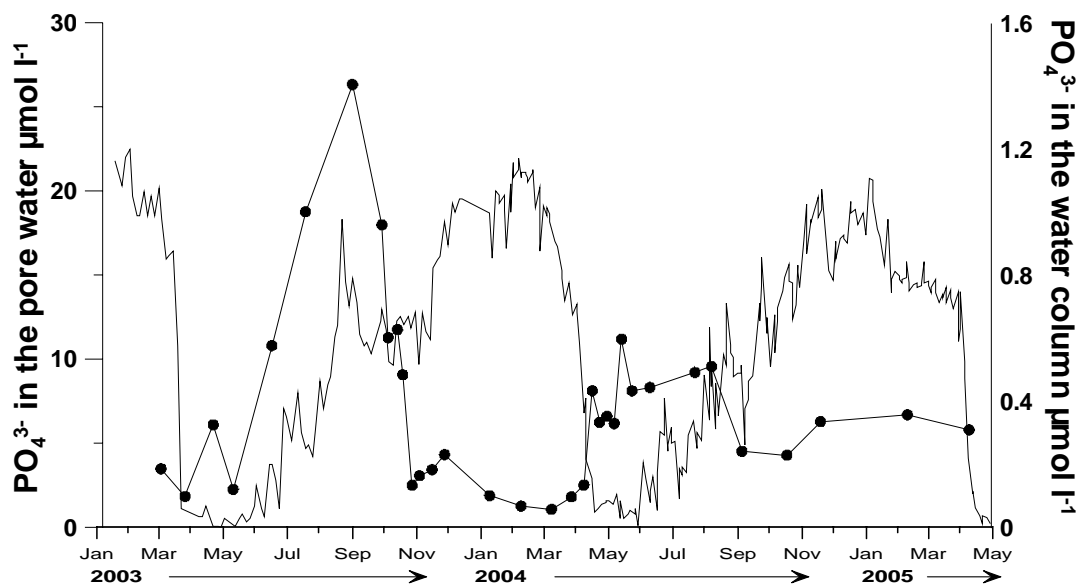


Figure 10: Mean PO_4^{3-} concentration of the pore water in the upper 5 cm of the sediment (dotted line) and in the water column (line).

A comparison of the profiles in Figure 6 shows that the concentrations in summer and autumn were highest, especially in summer 2003. They resemble the NH_4^+ profile. The high PO_4^{3-} concentrations in summer 2003 are also visible in Figure 9.

3.4.5 Nitrate

The highest nitrate concentrations in the pore water were generally reached in the upper 4 cm of the sediment. During winter and spring months there was always a subsurface maximum in pore water concentrations. Mean nitrate concentration of the pore water in the upper 5 cm of the sediment was $32 \pm 4 \mu\text{mol l}^{-1}$. The mean concentration of the pore water in the 6 to 15 cm sediment depth horizon was $16 \pm 2 \mu\text{mol l}^{-1}$. Concentrations in the pore water ranged between $1.36 \mu\text{mol l}^{-1}$ (September 2004, 6 cm depth) and $107.05 \mu\text{mol l}^{-1}$ (November 2004, 3 cm depth) (Figure 11).

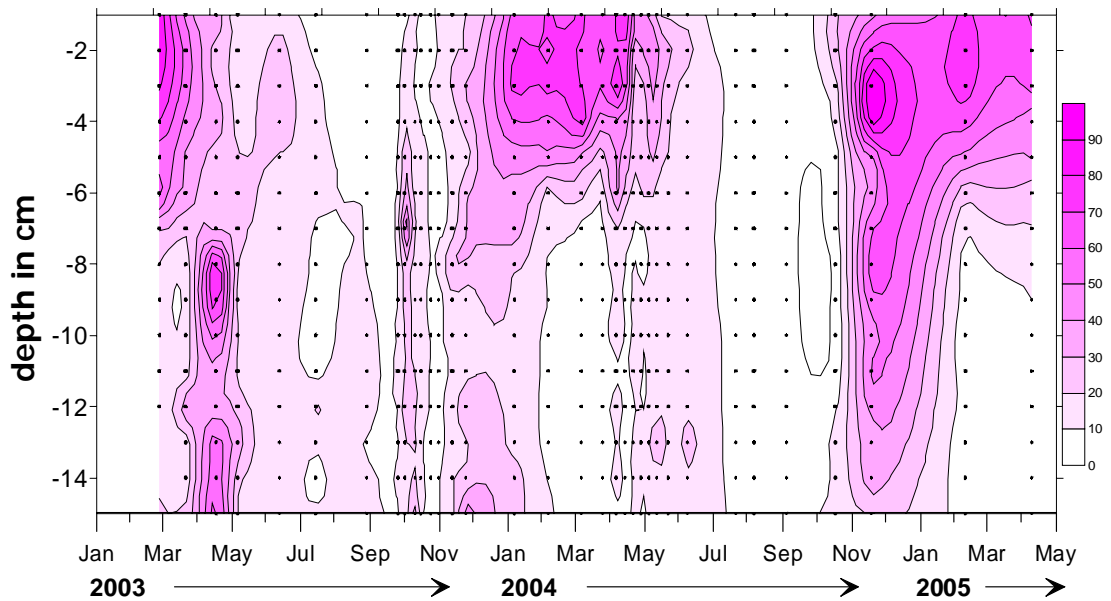


Figure 11: Vertical distribution of NO_3^- in $\mu\text{mol l}^{-1}$ in the pore water at the sampling site from February 2003 to April 2005. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The colour is proportional to pore water concentrations.

The nitrate concentration of the overlying water column ranged between below $0.01 \mu\text{mol l}^{-1}$ (September 2004) and $67.38 \mu\text{mol l}^{-1}$ (February 2004). The nitrate values in the water column as well as for mean values in the pore water of the

upper 5 cm of the sediment were lowest between April and November in 2003 and between May and November in 2004. The mean NO_3^- concentration in the pore water of the upper 5 cm in the sediment was always higher than in the overlying water column (Figure 12). The mean profiles in Figure 6 also show that the NO_3^- concentrations were highest in spring and winter. As mentioned previously maximum values were almost always in the upper sediment centimetres except in April 2003 (Figure 11) when high values coincided with low salinity, high $\text{Si}(\text{OH})_4$ and NH_4^+ concentrations in deeper layers.

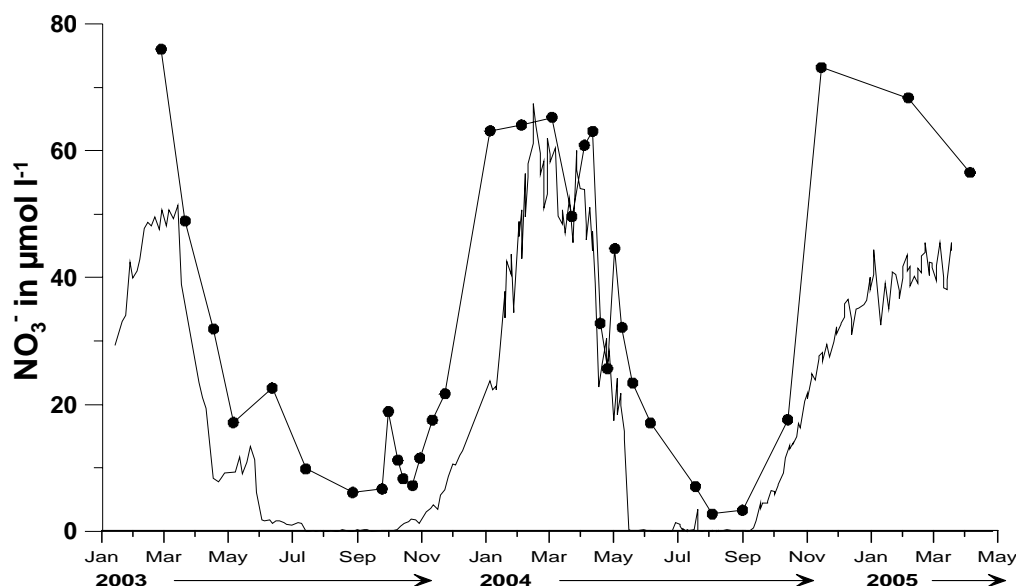


Figure 12: Mean NO_3^- concentration of the pore water in the upper 5 cm of the sediment (dotted line) and in the water column (line).

3.4.6 Nitrite

Mean nitrite concentration of the pore water in the upper 5 cm of the sediment was $1.16 \pm 0.13 \mu\text{mol l}^{-1}$, the mean concentration of the pore water in 6 to 15 cm sediment depth was $1.31 \pm 0.14 \mu\text{mol l}^{-1}$. Pore water concentration ranged between $0.06 \mu\text{mol l}^{-1}$ (September 2003, 1 cm depth) and $6.57 \mu\text{mol l}^{-1}$ (May 2004, 9 cm depth) (Figure 13).

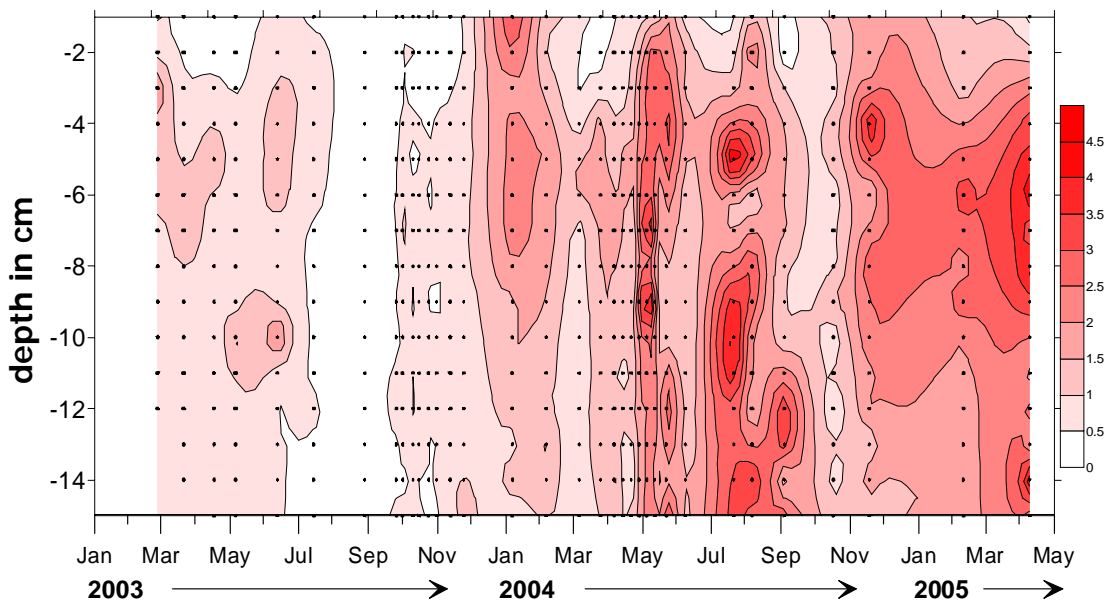


Figure 13: Vertical distribution of NO_2^- in $\mu\text{mol l}^{-1}$ in the pore water at the sampling site from February 2003 to April 2005. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The colour is proportional to pore water concentrations.

The nitrite concentration of the overlying water column ranged between $0.01 \mu\text{mol l}^{-1}$ (August 2003) and $2.39 \mu\text{mol l}^{-1}$ (January 2004). The nitrite values in the water column as well as the mean values in the pore water of the upper 5 cm were lower between April and November in 2003. In 2004 the same seasonal signal was visible for the water column, but in the pore water the concentrations were always relatively much higher (Figure 14). The mean NO_2^-

concentration in the pore water of the upper 5 cm in the sediment was always higher than the concentration in the overlying water column, except during March and April in 2003 and 2004. Comparing the concentration profiles in Figure 6, there is no seasonal trend obvious; the maximum concentrations were always in sediment depths below the NO_3^- maxima.

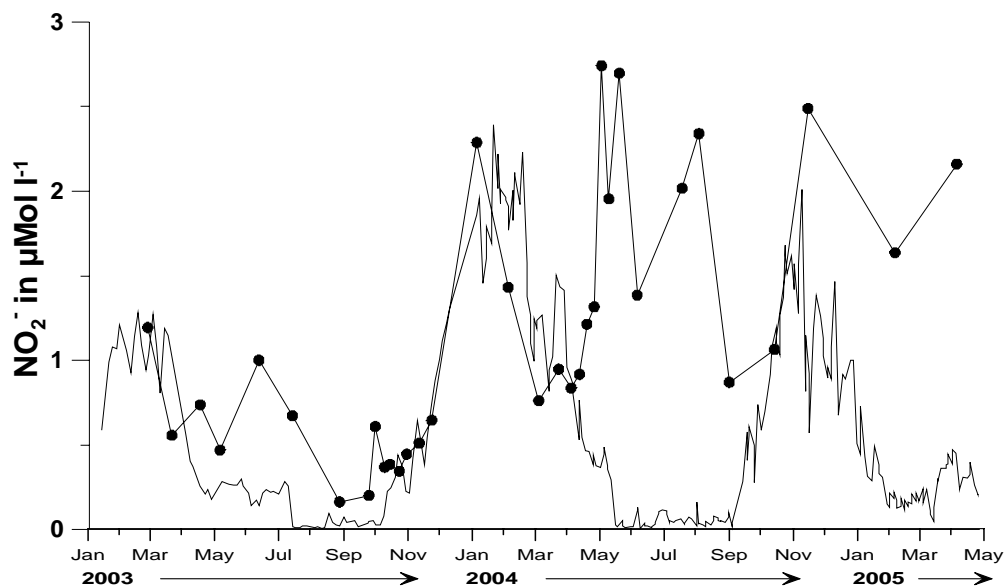


Figure 14: Mean NO_2^- concentration of the pore water in the upper 5 cm of the sediment (dotted line) and in the water column (line).

3.5 Discussion

From the vertical distribution over time and the temporal variation of salinity and nutrient concentrations, two general patterns are evident. 1) Lower salinities in deeper sediment layers coincided with high Si(OH)_4 , NH_4^+ and sometimes NO_3^- concentrations indicating the intrusion of water with low salinities and high nutrient concentrations. 2) High Si(OH)_4 , NH_4^+ and PO_4^{3-} concentrations were observed in the upper sediment horizon during summer, especially in 2003, whereas low values were observed during spring and late summer / early autumn. During winter the concentrations in the pore water of all the nutrients were high and followed the same dynamics as the overlying water column. In this discussion the focus will be on these two aspects.

Inflow of waters with lower salinities

In recent years a discussion about the influence of submarine groundwater discharge on biogeochemical cycles has started (e.g. Burnett et al. 2003). Submarine groundwater does not have to be exclusively terrestrial. It may also be a combination of rainwater and brackish water. Seldom is there a straightforward way to evaluate the source or the driving force of submarine groundwater discharge. The salinity of pore waters of many coastal sediments is lower than that of sea water due to the presence of brackish or fresh groundwater, flowing in through convection, hydraulic head, tidal pumping and wave set - up (Crossland et al. 2005). Water flow is especially important where underlying coastal sediments consists of coarse, unconsolidated sands of glacial or marine origin (Valiela et al. 1990) like at our sampling station. The geological composition of the northern tip of Sylt is determined by sand and clay (Bayerl and Higelke 1994), which leads to irregular groundwater inflow into the investigated area (e.g. Zipperle and Reise 2005).

Groundwater inflow rates into coastal zone are, among others influenced by the terrestrial groundwater recharge rate, which is affected by precipitation and evatranspiration (Crossland et al. 2005) and the groundwater storage capacity (Johannes 1980). The inflow of water with low salinities was most pronounced at the end of the year 2004 and beginning of 2005. Probably this was the result of more precipitation in 2004 (mean of monthly means 2003: 49.63 ± 5.73 mm, mean of monthly means 2004: 56.78 ± 6.46 mm) and lower temperatures in 2004 especially during summer (Figure 15). The high summer temperatures in 2003 probably led to a higher evaporation and a lowering of the groundwater table whereas lower temperatures and higher precipitation in 2004 led to a higher groundwater table and in a consequence a more pronounced water inflow, lower pore water salinities and higher Si(OH)_4 and NH_4^+ pore water concentrations in deeper sediment layers.

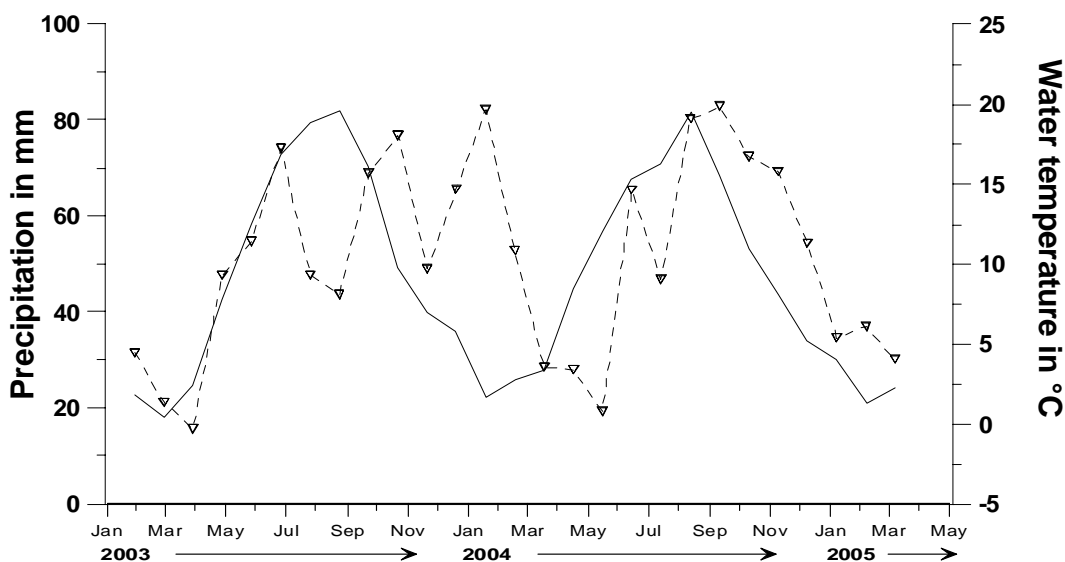


Figure 15: Mean monthly precipitation (stippled line with triangles) and mean monthly water temperature (line) over the sampling time.

Because of high nutrient concentrations in groundwater compared to those in seawater, groundwater is an important source for nutrients, despite low flow rates. According to Johannes (1980), the nutrient loading of coastal waters is primarily due to nitrate because nitrification converts most of the ammonium to nitrate. Phosphate is adsorbed by sediment surfaces and so groundwater concentrations of phosphate are relatively low. Concentrations vary widely, but the upper ranges of dissolved inorganic nitrogen are sometimes two to three fold higher than those of the receiving seawater (Valiela et al. 1990). Whereas the low PO_4^{3-} concentrations in the intruding groundwater were also found at our site, ammonium instead of nitrate dominated the groundwater nitrogen at our site. Only in April 2003 did low salinities coincide with higher NO_3^- concentrations in deeper sediment layers. For the rest of the sampling period, low salinities coincided with higher Si(OH)_4 and NH_4^+ concentrations in deeper sediment layers. These concentrations were higher than expected from inflowing fresh groundwater with its origin just from precipitation, so there has to be an additional source than precipitation alone.

From the regression of salinity and Si(OH)_4 , the concentration of the inflowing water at a salinity of 0 would be $528.9 \mu\text{mol l}^{-1}$ (see Figure 16). Nutrient measurements of collected rain water (1992 – 1999; Martens unpublished data) showed that there was generally no Si(OH)_4 in the rainwater. Just a few measurements showed Si(OH)_4 , the highest amount to be $35 \mu\text{mol l}^{-1}$. The nutrients in the rainwater were dominated by NO_3^- (range 3 – $320 \mu\text{mol l}^{-1}$), but high concentrations of NO_3^- did not correlate significantly with low salinities in deeper layers (Figure 16). NH_4^+ concentrations correlated with lower salinities in deeper sediment layers, and extrapolating of this relation to a salinity of 0 would predict $197.6 \mu\text{mol l}^{-1}$ (see Figure 16). This value is much higher than the NH_4^+ content of rainwater, which ranged from below $1 \mu\text{mol l}^{-1}$ to $118 \mu\text{mol l}^{-1}$. An estimated yearly total nitrogen deposition of $1 \text{ g total nitrogen m}^{-2}$ (van Beusekom et al. 2001) and an average rainfall per year of 640 mm (2003 – 2004) imply an average concentration of $\sim 110 \mu\text{mol l}^{-1}$ total nitrogen (sum of NH_4^+ , NO_3^- , NO_2^- and organic bound) in the inflowing water, if the source of the

inflowing water originated just from precipitation. These estimates suggest that additional sources enrich the inflowing water with nitrogen and silica.

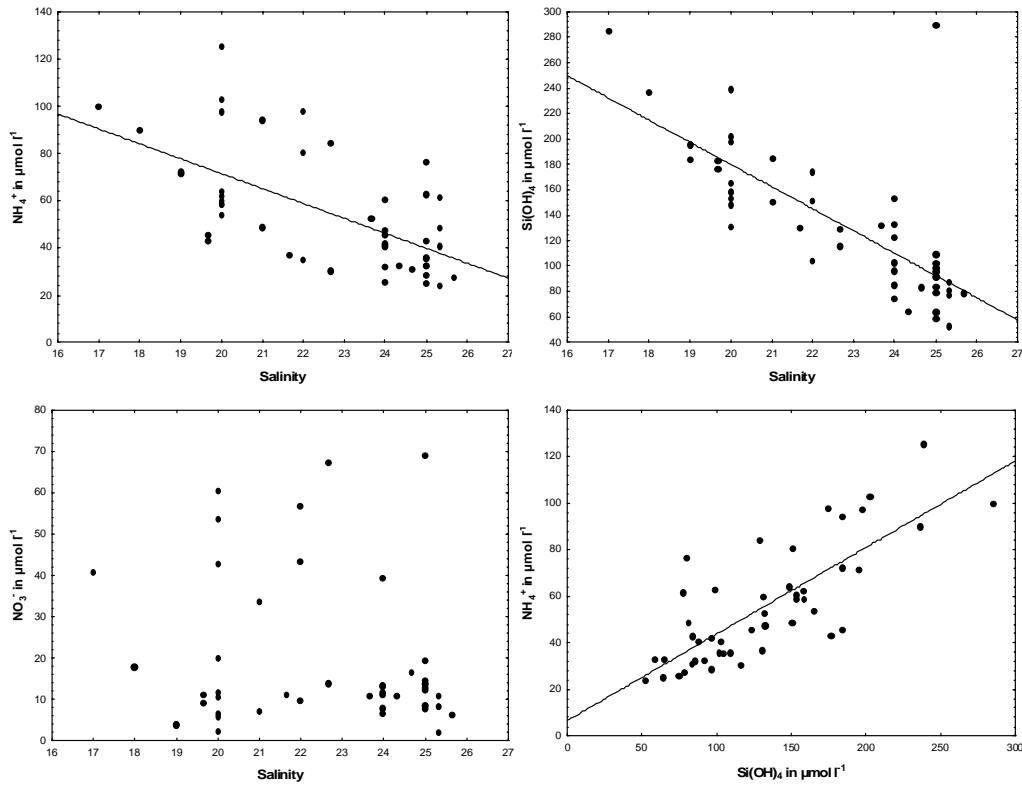


Figure 16: Upper left panel: correlation of salinity below 26 and corresponding NH_4^+ concentration in a sediment depth < - 6 cm ($r^2 = 0.3859$; $p < 0.001$; $y = -6.31x + 197.64$)

Upper right panel: correlation of salinity below 26 and corresponding Si(OH)_4 concentration in a sediment depth < - 6 cm ($r^2 = 0.5644$; $p < 0.001$; $y = -17.45x + 528.90$)

Lower left panel: correlation of salinity below 26 and corresponding NO_3^- concentration in a sediment depth < - 6 cm ($r^2 = 0.0291$; $p = 0.2464$; $y = -1.24x + 46.90$)

Lower right panel: correlation of Si(OH)_4 and corresponding NH_4^+ concentration with salinities < 26 and sediment depth < -6 cm ($r^2 = 0.6187$; $p < 0.001$; $y = 0.37x + 6.59$)

The ratios of Si(OH)_4 and NH_4^+ are different in the inflowing groundwater (salinity < 26 and depth < - 6 cm) and the rest of the pore water (salinity > 26 and depth > - 6 cm) (Figure 17), but in both cases a significant correlation is present. As Si(OH)_4 is not present in rain water and this nutrient correlates with NH_4^+ , there has to be an additional nutrient source for the inflowing groundwater than precipitation. The good correlation between Si(OH)_4 and NH_4^+ suggests a common source, which is most probably of biogenic origin. As already mentioned there is an extensive clay layer of marine origin in this region (Bayerl and Higelke 1994), which may be a nutrient source for the intruding water.

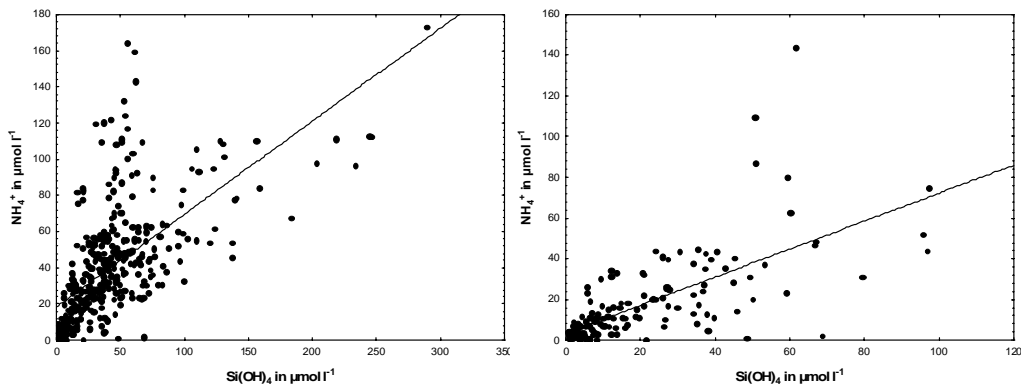


Figure 17: Left panel: correlation of Si(OH)_4 and corresponding NH_4^+ concentration with salinities > 26 and all sediment depths ($r^2 = 0.4104$; $p < 0.001$; $y = 0.51x + 18.3$)
Right panel: correlation of Si(OH)_4 and corresponding NH_4^+ concentration with salinities > 26 and sediment depth > -6 cm ($r^2 = 0.4733$; $p < 0.001$; $y = 0.69x + 3.54$)

Seasonality of mean pore water concentrations in the upper 5 centimetres

Nutrient concentrations in the sediment are among others controlled by transport (sediment - water exchange), nutrient release (by fauna, bacteria and dissolution) and uptake (by algae, plants, bacteria and adsorption) (e.g. Asmus 1986). Aim of this study was to determine seasonal trends of the pore water concentrations.

To emphasize the seasonal pattern of pore water concentrations, the mean concentration of Si(OH)_4 , NH_4^+ and PO_4^{3-} in the pore water of the upper 5 cm of the sediment were plotted against the water temperature (Figure 18). This interval (1 – 5 cm sediment depth) was used because this depth range was probably most affected by advective pore water transport and also mixing by ripple movement and resuspension (compare Surfer plots and Figure 6).

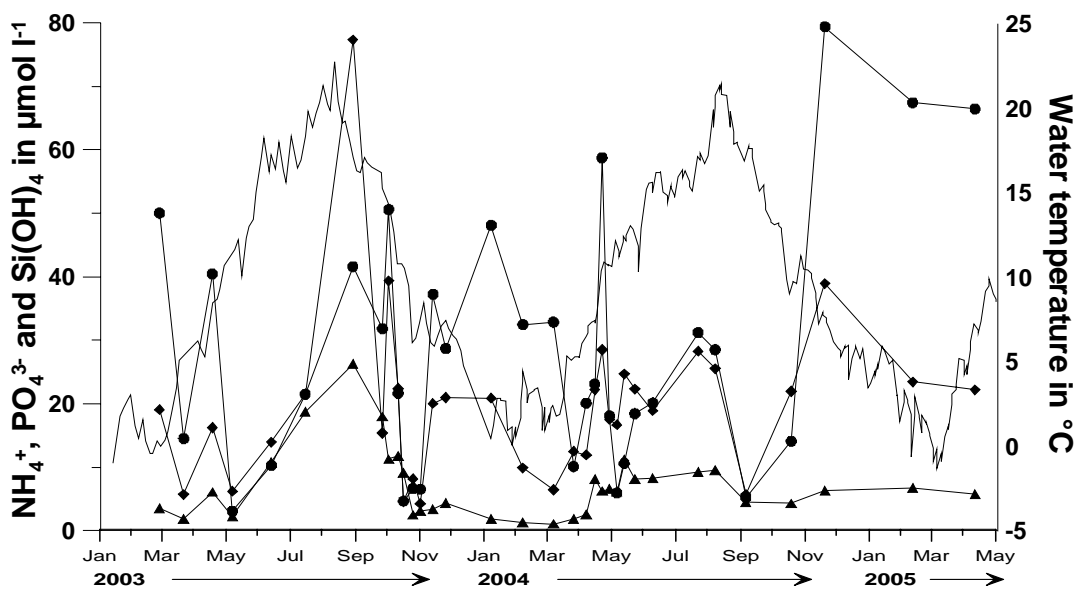


Figure 18: Mean concentration of the upper 5 cm of the sediment of NH_4^+ (\blacklozenge), PO_4^{3-} (\blacktriangle) and Si(OH)_4 (\bullet) and water temperature (line).

In both years the curves of mean concentrations in the upper 5 cm of all the three nutrients closely paralleled each other. Nutrient concentrations consistently showed peaks during summer and winter and minima during spring and late summer / beginning of autumn. In addition to this dominant cycle, a slight peak in pore water nutrient concentrations was observed in spring. In contrast, the concentrations in the water column showed higher concentrations only during winter months until March or April and remained low until autumn, except PO_4^{3-} concentrations, which increased already during summer.

Microphytobenthos is known to regulate the flux of regenerated nutrients from sediments by uptake (e.g. Sundbäck and Granéli 1988, Sundbäck et al. 1991, Nelson et al. 1999), particularly when it is abundant and productive. This study showed high microphytobenthic biomass the whole year (Chapter 4). Therefore, a large impact of microphytobenthos on the nutrient dynamics may be expected. The prevailing light conditions can be expected to regulate the extent to which microphytobenthos may regulate the nutrient fluxes. In addition to light, temperature and the input of organic matter by import of local pelagic primary production or organic matter from the North Sea may influence the nutrient dynamics. Figure 19 presents a conceptual explanation of the observed nutrient dynamics in the pore water (compare Figure 18).

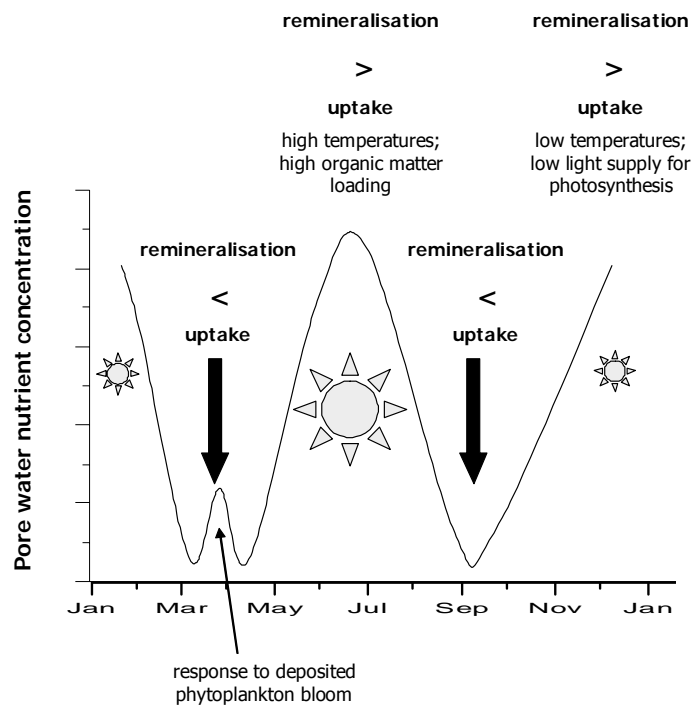


Figure 19: Conceptual model of seasonal pore water dynamics referring to mean concentrations in the upper 5 cm of the sediment of $\text{Si}(\text{OH})_4$, NH_4^+ and PO_4^{3-} .

The primary production in the water column of the List tidal basin is light and nutrient limited most of the year, and this is also most likely the case for the subtidal microphytobenthos. During winter and early spring, not enough light reaches the sediment and the sediment community will most likely be net heterotrophic (more carbon respired than produced). As such, remineralization rates are higher than the nutrient uptake by the microphytobenthos leading to higher nutrient concentrations in the pore water of the sediment. In spring, more light reaches the sediment and the sediments become more productive, but because the temperatures are still low, the remineralization rates do not increase to the same extent (e.g. Davis and McIntyre 1983; Kristensen 1993). As such, nutrient concentrations in the pore water decrease, because of increased uptake of the microphytobenthos relative to remineralization. At this point, the pore water concentrations and the concentrations of the overlying

water column are very similar. In spring a short peak of higher nutrient concentrations occurs, probably as a response on enhanced remineralization and dissolution of biogenic opal of deposited diatoms from the phytoplankton bloom in the water column. With increasing temperature and higher organic loading during summer (due to local primary production and import of organic matter from the North Sea; van Beusekom and de Jonge 2002), the remineralization rates increase as well and exceed the uptake of the microphytobenthos, which leads to higher nutrient concentrations in the pore water. In late summer the concentrations drop again. Several factors may contribute to this decrease like decreasing temperatures (Jahnke et al. 2005, Marinelli et al. 1998), decreasing input of organic matter due to nitrogen limited pelagic primary production (Colijn and Cadée 2003, Woodward and Owens 1990) and so lower remineralization rates within the sediment. But because there is still sufficient light, microphytobenthos continues to assimilate nutrients and hence their concentrations drop once again. At this point, the nutrient concentrations in the pore water and overlying water are very similar once again. In autumn and winter, low light levels lead to increasing concentrations in the pore water and in the water column, because of less primary production. During winter the inflowing water from below with high nutrient concentrations adds to the concentrations in the upper 5 cm of the sediment, which is visible especially in winter 2004 / 2005, with higher concentrations in deeper layers as well as in the upper 5 cm of the sediment.

The concentrations in the pore water were always higher than in the overlying water column, but the effect on the water column concentrations is probably only evident for PO_4^{3-} . This nutrient showed high concentrations in the pore water during summer 2003 compared to summer 2004. Also in the water column the concentrations in 2003 were higher than in 2004. Also the summer peak in the water column coincided with the peak values in the pore water.

Probably the concentrations of the other nutrients in the sediment were too low to show any effect on the water column concentrations.

During chamber experiments (Hedtkamp unpublished data), no nutrient fluxes from the sediment to the overlying water were detected, which may also be an indicator for the regulation of nutrient dynamics by microphytobenthos. Microphytobenthic biomass was all the time high even in several cm sediment depth (Chapter 4), so in these layers nutrients could be assimilated, before the microphytobenthos is mixed back to the sediment surface with enough light.

The nutrient dynamics in the sediment at this study site were influenced by advection, microphytobenthos, seasonal variations of temperature, light and organic matter loading and groundwater inflow of water with lower salinities and high nutrient concentrations.

Chapter 4

Shallow exposed subtidal sand: an optimum habitat for microphytobenthos?

4.1 Abstract

Seasonal dynamics of microphytobenthos and organic matter in a shallow subtidal sandy sediment were investigated near the island Sylt in the northern Wadden Sea (Germany) between February 2003 and November 2004. Throughout the upper 6 - 10 cm, and decreasing to low values at 15 cm a high standing stock of microphytobenthos was found with no apparent seasonality. Microphytobenthic biomass ranged from $13.2 \mu\text{g g}^{-1}$ to $21.4 \mu\text{g g}^{-1}$ in the upper cm to $0.1 \mu\text{g g}^{-1}$ at 15 cm depth. On a transect from the high water line down to a depth of ca. 4 m below the low water level, highest phytobenthos biomass was found near the low water tide mark and in the shallow subtidal. The organic matter content in these subtidal sediments was low but of high quality. Carbon ranged from $32.9 \mu\text{mol g}^{-1}$ to $427.4 \mu\text{mol g}^{-1}$, particulate organic nitrogen ranged from $1.9 \mu\text{mol g}^{-1}$ to $35.3 \mu\text{g g}^{-1}$ and organic phosphorus ranged from $0.09 \mu\text{mol g}^{-1}$ to $2.2 \mu\text{mol g}^{-1}$. Based on a carbon : chlorophyll *a* ratio of 40, about 50 % of the organic carbon was related to microphytobenthos in the upper 5 cm of the sediment. Organic matter not associated with microphytobenthos correlated with benthic biomass and this suggests a rapid turnover. The C : N : P values close to the Redfield ratio also indicate a good quality of the organic matter in the sediment, which is thus easy to degrade. The upper subtidal is suggested to be an optimum habitat for microphytobenthos by combining sufficient light conditions with permanent advection of particulate matter, dissolved nutrients, CO_2 and O_2 .

4.2 Introduction

Permeable sands are common coastal environments (Riggs et al. 1996), and sands cover approximately 70 % of the continental shelves (Emery 1968). Permeable sediments usually contain a relatively small amount of organic material. This led to the assumption that the biogeochemical activity in these sands is also low. Recently it has been shown that this is not the case (Shum and Sundby 1996, Boudreau et al. 2001). Permeability of the sediment is a key factor for sedimentary processes, with permeabilities above 10^{-12} m² allowing advective pore water flow (Huettel et al. 1998). Flume experiments have shown that advective pore water flows enhance the nutrient efflux (Huettel et al. 1998), as well as the oxygen penetration (Ziebis et al. 1996) and consumption (Forster et al. 1996) in permeable sediments. Through this process, the mineralization of the organic matter can be shifted from the sediment surface to deeper sediment layers (Huettel and Rusch 2000). Low organic content of permeable sediments may so be a consequence of high turnover rates (Huettel and Rusch 2000). Consequently, the contribution of sandy sediments to the degradation of organic matter on the continental shelf may have been underestimated.

Nelson et al. (1999) as well as D'Andrea et al. (2004) found high biomasses of benthic diatoms in permeable sediments with low organic matter content. So presumably the main sources for the organic matter in the sediment are the diatoms themselves.

Microphytobenthos (MPB) play an important role in the dynamics of shallow coastal systems, as primary sources of organic matter for ecological and biogeochemical processes and as modifiers of sediment dynamics. They may regulate the flux of regenerated nutrients from sediments, particularly when they are abundant and productive and they may also regulate oxygen flux into the sediment (e.g. Sundbäck et al. 1991, Cahoon 1999, Nelson 1999) and the oxygen concentrations within the sediment (e.g. Revsbech and Jørgensen 1983) through photosynthesis and respiration.

In this study the seasonal dynamics of benthic biomass and organic matter were investigated over a sampling period of two years in a shallow subtidal permeable sediment, to get an idea of changes in biomass and quality of organic matter. The investigations were carried out at a subtidal sandflat in the Wadden Sea. The pelagic primary production and biomass in this region shows a clear seasonal cycle probably due to light limitation (Colijn and Cadée 2003). Therefore also a clear seasonal cycle for the benthic biomass at our sampling station was expected as well.

4.3 Materials and Methods

4.3.1 Study site

Samples were taken in a permeable sand in the shallow subtidal near the island of Sylt (Germany) in the northern Wadden Sea (55°00'47.7'' N, 08°25'59.3'' E; Figure 1). Depending on the tidal range, the water depth at the sampling site ranged from 50 - 250 cm. The sediment at the sampling site was well to moderately well sorted medium sand with a median particle size of 350 μm , the origin of the sediment is mainly aeolic (Austen 1994). The mean permeability of the upper 10 to 15 cm sediment was $2.07 \times 10^{-11} \pm 6.63 \times 10^{-12} \text{ m}^2$. The permeability varied seasonally with higher values during winter and spring compared to summer and autumn, and ranged between $1.01 \times 10^{-11} \text{ m}^2$ and $3.36 \times 10^{-11} \text{ m}^2$. All the time the values allowed advective pore water flow (Huettel et al. 1998). Tidal currents and wind induced waves are the dominant hydrodynamic forces. At the sampling site current velocities up to 90 cm s^{-1} have been recorded (Wenzhöfer, pers. comm.). Benthic macrofauna was dominated by small polychaetes, which were present in relatively low abundances (Weslawski et al. in prep.). The microphytobenthos was dominated by diatoms (Wiktor pers. comm.). Salinity varies on average between 27.5 in spring and 31 in summer. Further details of the study area are provided by Austen (1994), Gätje and Reise (1998) and Armonies and Reise (2000).

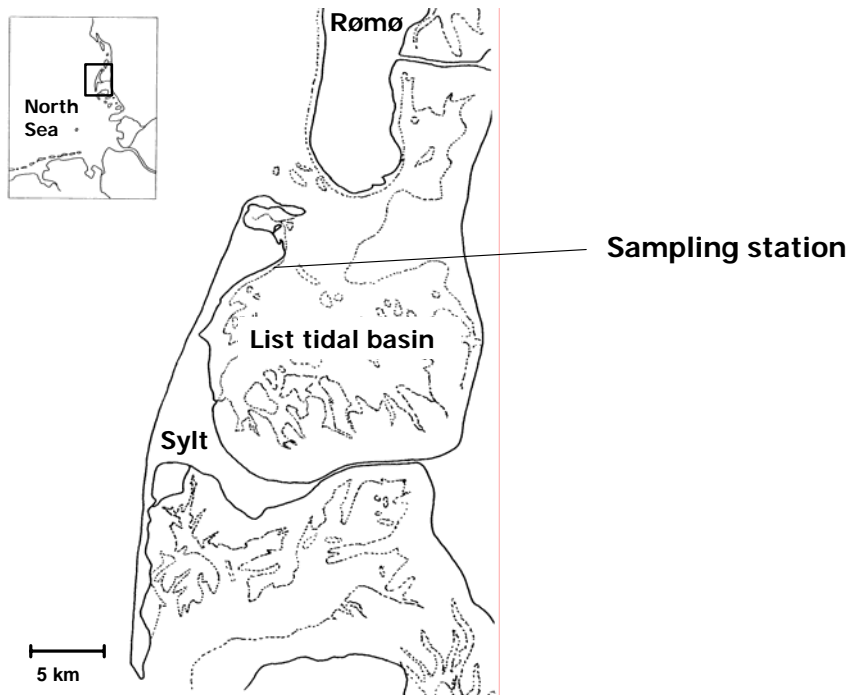


Figure 1: Sampling station in the northern Wadden Sea. Spring low tide is stippled.

4.3.2 Sampling

Samples were taken once per month between February 2003 and November 2004. The samples were taken during low tide; the water level above the sediment was still at least 50 cm. The sediment cores with an inner diameter of 3.6 cm were taken randomly by hand, to avoid sediment disturbance. All following procedures were performed in the nearby (500 m) lab as soon as possible. Eight cores with an inner diameter of 3.6 cm were sliced in 1 centimetre steps down to a depth of 15 cm. The samples of each centimetre were homogenized and sub samples for the further analysis were taken. The homogenization procedure was tested before. The samples were frozen at -20°C and freeze dried before further analysis. All the measurements were done in triplicate for each depth centimetre, and then the mean value was calculated for each centimetre. In June 2004 additional a transect of 300 m length with 11 stations from the high water line to a water depth of 4 m (at low tide) was

done. The samples were also hand collected, at the deeper stations through divers. Six cores per sampling station were sliced down to a depth of 10 cm and each depth centimetre was pooled and sub samples for chlorophyll *a* determination were taken.

4.3.3 Biomass

The biomass of the sediment was determined as chlorophyll *a*. For the chlorophyll *a* determination ca. 1 g freeze dried sediment of each depth centimetre was extracted with 7.5 ml acetone (90 %) and incubated for 24 hours at 4 °C in the dark. Samples were shaken in between to guarantee a good extraction. At the end of the extraction samples were centrifuged at 3600 rpm for 10 minutes and then measured at the wavelengths 665 nm and 750 nm before and after acidification with 2 drops of HCl (10 %) with a spectrophotometer (UVIKON XL) according to Lorenzen (1967). To calculate the biomass per m², the mean density of the sediment was determined (see appendix). The biomass of the overlying water was measured as chlorophyll. Samples were taken twice per week at two nearby sampling stations in the frame of long term investigations of nutrient and phytoplankton dynamics in the List tidal basin. 100 ml water were filtered through GF / C filters and frozen until further analysis. Chlorophyll was extracted with 10 ml acetone (90 %) for 18 hours. The samples were then centrifuged at 3500 rpm for 10 minutes. The absorbance was measured with a spectrophotometer (UVIKON XL) according to Jeffrey and Humphrey (1975).

4.3.4 Total organic carbon and total organic nitrogen content

Samples for the measurement of total organic carbon and the total organic nitrogen content of the sediment were homogenized by using a pebble mill after freeze - drying the sediment (cm 1 - 15). Approximately 60 mg of homogenized sand was weighed into silver cups, 30 µl of Milli - Q water was added followed by 10 µl of 6 N HCl, which was then repeated at least once to remove carbonates until no bubbles were visible anymore. Samples were dried

for at least 4 hours at 60 °C and measured with a C / N analyzer (Thermo - Finnigan Flash EA 1112). Helium was the carrier gas and aspartic acid was used as standard, furnace temperatures were 600 °C and 1000 °C.

4.3.5 Total organic phosphorus content

For total phosphorus as well as for inorganic phosphorus three sub samples (50 mg) were taken from the homogenized sediment (1 cm intervals). For total phosphorus the sediment was first ashed for two hours at 520°C. The samples were extracted for 18 hours with 5 ml 1 N HCl. After extraction the samples were centrifuged for 10 minutes at 2000 rpm. The dissolved phosphorus in the supernatant was determined spectrophotometrically after neutralization with NaOH with an autoanalyzer (Bran & L ubbe). The difference between the P content of the ashed and unashed samples (total phosphorus and inorganic phosphorus) is the amount of organic phosphorus (Aspila et al. 1976, van Beusekom and de Jonge 1997).

4.3.6 Statistical analysis

The statistical analyses were done using the software package STATISTICA 6 (Stat Soft). The influences of the two sampling years and the different seasons were tested using a two - factorial ANOVA design, with year and season as fixed factor. Although taken at the same locality, the samples were considered to be independent due to the temporal distances of at least three to four weeks. For each sampling, monthly mean values were calculated and the months were summarized to seasons (spring: March, April, May; summer: June, July, August; autumn: September, October; winter: November, January, February). Means are presented \pm standard error. All data used for the statistical analysis see in the appendix.

The temporal and vertical dynamics of the different sediment characteristics were plotted with Surfer (Golden Software, version 8). The gridding method was krigging with a linear variogram model. The slope was one, the anisotropy ratio 10.

4.4 Results

4.4.1 Microphytobenthos biomass

Microphytobenthos (MPB) biomass in the uppermost centimetre was high, with values ranging between $13.2 \mu\text{g g}^{-1}$ (October 2003) and $21.4 \mu\text{g g}^{-1}$ (April 2003) sediment or $190 - 310 \text{ mg chlorophyll } a \text{ m}^{-2}$. The mean chlorophyll *a* content in the first cm was $17.8 \pm 0.5 \mu\text{g g}^{-1}$ or $257 \pm 7 \text{ mg m}^{-2}$. Seasonal differences could be identified, but the patterns were not similar during both years (ANOVA, $p < 0.05$) (Figure 2; Table 1). In both years the highest biomass in the uppermost cm was reached in spring. In 2003, the lowest values were reached in autumn. In 2004 the minimum was reached during summer and was the lowest biomass in the sediment of the whole sampling period.

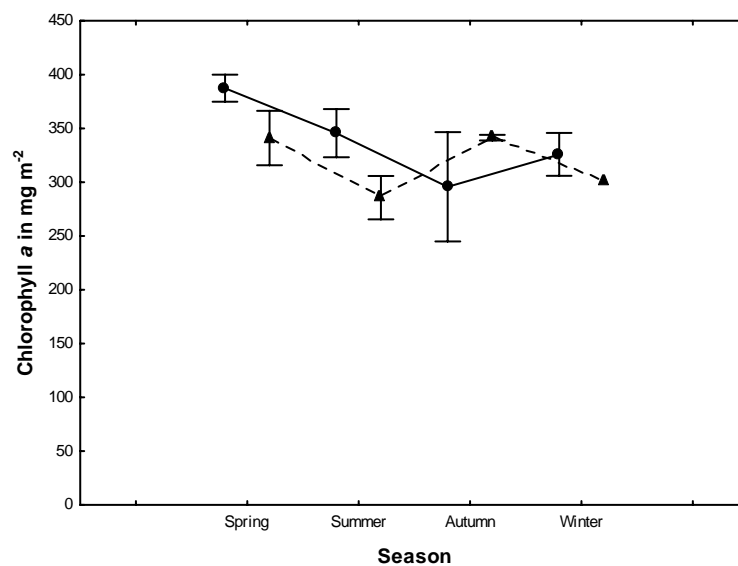


Figure 2: Mean chlorophyll *a* concentration of the first cm with standard error during spring, summer autumn and winter (●: year 2003; ▲: year 2004).

In comparison with the water column, the biomass of the MPB in the uppermost cm, was much higher than the phytoplankton biomass in the overlying water integrated over a water depth of 1.5 m (average water depth at the sampling site) (Figure 3). In contrast to the MPB, the chlorophyll in the water column

showed a clear seasonal pattern with a spring bloom in both years. The mean chlorophyll *a* concentration during the two years integrated over a water depth of 1.5 m was 8.6 mg m^{-2} and ranged between 71.3 mg m^{-2} (March 2003) and 1.50 mg m^{-2} (June 2004). On average, the MPB biomass was 30 times higher than the biomass in the water column.

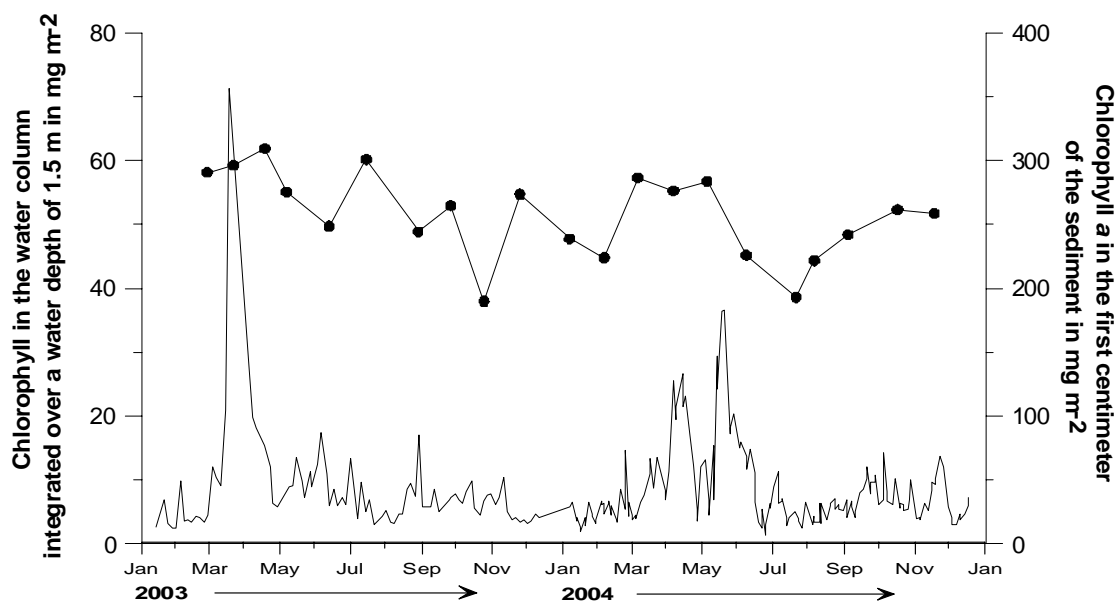


Figure 3: Chlorophyll *a* content in the upper centimetre of the sediment in mg m^{-2} (dotted line) and the chlorophyll content in the water column integrated over a water depth of 1.5 m in mg m^{-2} (line).

The average MPB biomass in the upper 5 and 10 cm of the sediment showed no significant seasonal differences, but a significant season * year interaction (ANOVA, $p < 0.01$ for both; Table 1). The integrated chlorophyll *a* content in the sediment was lowest in summer 2004 (Figure 4). The integrated chlorophyll *a* concentration of the upper 5 cm was $1020 \pm 48 \text{ mg m}^{-2}$, in the upper 10 cm it was $1277. \pm 81 \text{ mg m}^{-2}$.

Table 1: Results of the two-factorial ANOVAs for the chlorophyll a concentration with the two factors year and season. P-values below 0.05 are considered as significant and shown in bold.

		dF	MS	F	p
Chlorophyll a in the upper cm	year	1	501	0.816	0.382750
	season	3	3158	5.142	0.014598
	year*season	3	1243	2.024	0.160366
	Error	13	614		
Chlorophyll a in the upper 5 cm	year	1	87016	3.9324	0.068899
	season	3	11113	0.5022	0.687318
	year*season	3	128600	5.8117	0.009566
	Error	13	22128		
Chlorophyll a in the upper 10 cm	year	1	291858	4.5714	0.052077
	season	3	15846	0.2482	0.861168
	year*season	3	383716	6.0102	0.008482
	Error	13	63844		

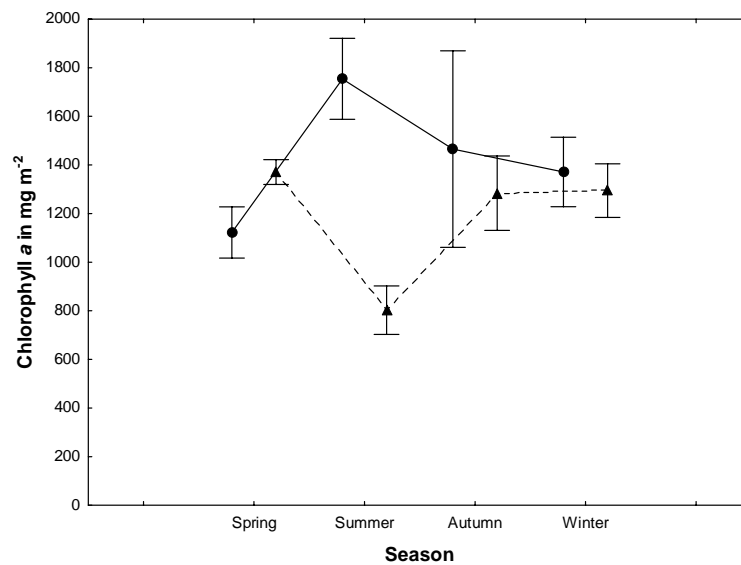


Figure 4: Mean chlorophyll a concentration in the upper 10 cm sediment layer with standard error during spring, summer, autumn and winter (●: year 2003; ▲: year 2004).

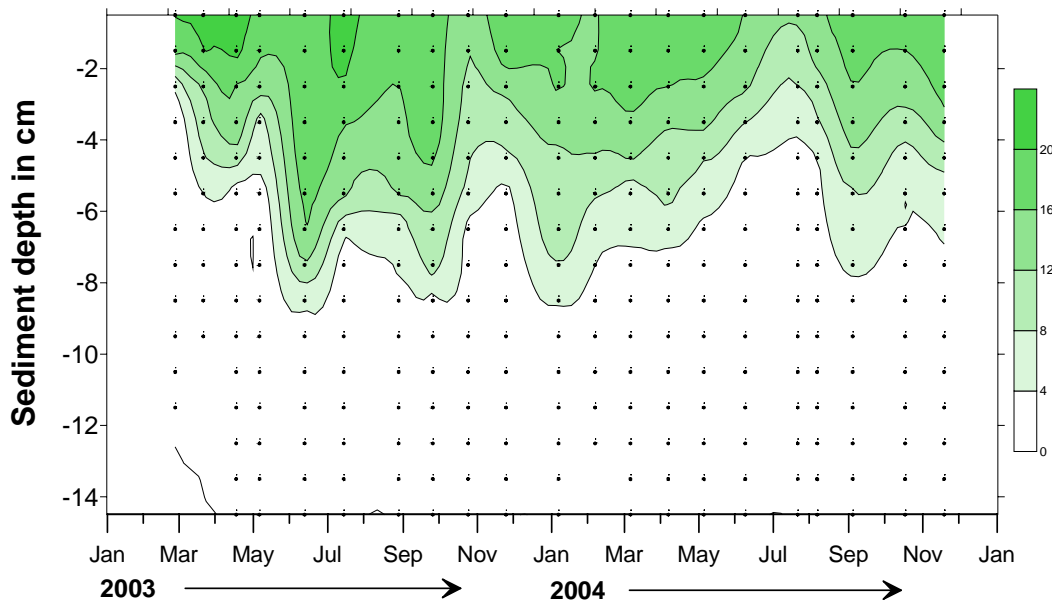


Figure 5: Vertical distribution of chlorophyll *a* in $\mu\text{g g}^{-1}$ at the sampling site during 2003 and 2004. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The darker the colour the more chlorophyll *a* in $\mu\text{g g}^{-1}$ was present in the sediment.

The highest chlorophyll *a* contents were always in the uppermost centimetre of the sediment, decreasing with depth to values below $0.1 \mu\text{g g}^{-1}$ between 6 – 10 cm (Figure 5). On average, $22 \pm 1.6 \%$ of the total microphytobiomass of the upper 10 cm sediment was present in the first cm of the sediment.

In July 2004, the MPB distribution was investigated along a transect from the mean high water line to the subtidal with a water depth of ca. 4 m during low tide. The stations 6 and 7 correspond approximately to the time series sampling station. Station 5 is already in the shallow subtidal. Samples at stations 1 - 5 were taken by foot, station 6 - 11 were taken by divers. Strong currents hampered the original sampling schema of one sampling station every 30 m. Figure 6 shows the chlorophyll *a* distribution in the sediment. The highest

biomass in the first centimetre of the sediment was measured at the stations 5, 3, 6 and 7 (Figure 6). Stations 5, 6 and 7 are already in the shallow subtidal. Integrated over the 10 sampled cm of the sediment, station 4, 2, 7 and 5 showed the highest biomass (Figure 6). Along this transect higher biomass in the upper cm as well as in the upper 10 cm are in the shallow subtidal. Relative high biomasses were found at all station down to a sediment depth of at least 5 cm.

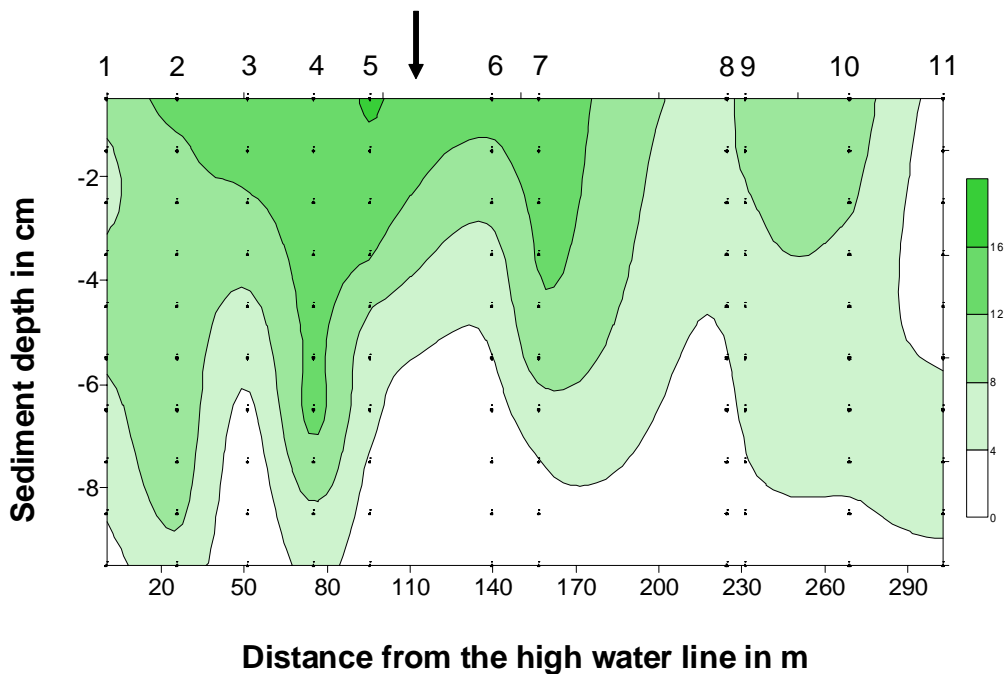


Figure 6: Vertical distribution of chlorophyll *a* in $\mu\text{g g}^{-1}$ along the transect from the normal high water line (0 m at the x-axis correspond Station 1) into the subtidal (302 m at the x-axis correspond Station 11). Dotted vertical lines represent a sampling station, Station numbers are shown along the top x-axis. The approximate position of the time series station is indicated with an arrow.

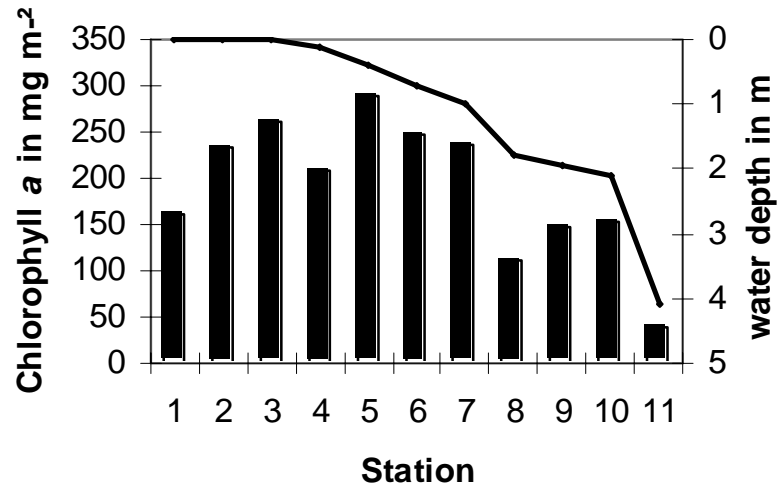


Figure 7: Chlorophyll a of the first centimetre of the sediment in mg m⁻² in relation to the water depth in m during low tide. Station 3 is situated at the low water line.

4.4.2 Total organic carbon

The total organic carbon content of the sediment was low with in average of 0.13 ± 0.002 % ($108.12 \pm 3.10 \mu\text{mol g}^{-1}$) and ranged between 0.30 % ($241 \mu\text{mol g}^{-1}$) in the first centimetre in May 2003 and 0.04 % ($32 \mu\text{mol g}^{-1}$) in 15 cm depth in November 2004. The vertical distribution is characterized by high values in the upper 4 – 6 cm and strongly resembles the chlorophyll *a* distribution in the sediment (Figure 5). Extreme high values up to 0.52 % were observed around about 9 cm in June and July 2004. Most of the time a surface maximum was present. The total organic carbon content of the first cm was 14.1 ± 0.7 % of the total amount in the upper 15 cm of the sediment. The mean total organic carbon content of 1 depth centimetre was $174.8 \pm 5.8 \mu\text{mol g}^{-1}$.

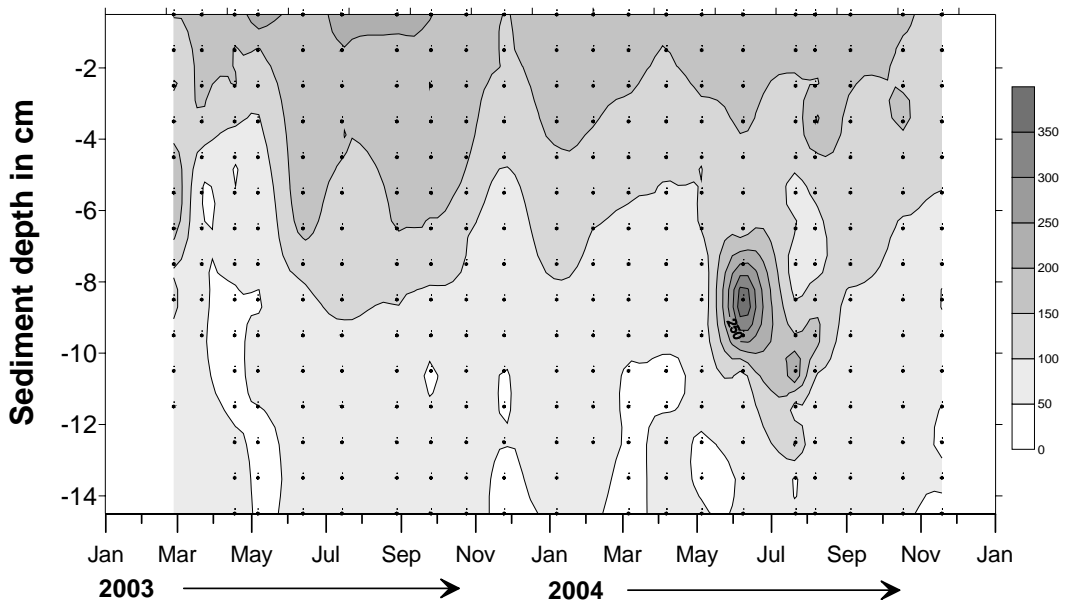


Figure 8: Vertical distribution of the total organic carbon content in $\mu\text{mol g}^{-1}$ at the sampling site during 2003 and 2004. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The darker the colour the more total organic carbon in $\mu\text{mol g}^{-1}$ was present in the sediment.

The total organic carbon concentration in the first centimetre was significantly lower in year 2004 (ANOVA, $p < 0.01$) and the seasons were also significantly different (ANOVA, $p < 0.05$) (Table 2), with highest amounts in summer and lowest in winter.

Table 2: Results of the two-factorial ANOVA for the total organic carbon concentration with the two factors year and season. P-values below 0.05 are considered as significant and are shown in bold.

		dF	MS	F	p
TOC in mol m ⁻² in the upper cm	Year	1	1042695	13.211	0.003024
	Season	3	418374	5.301	0.013172
	Year*Season	3	8256	0.105	0.955914
	Error	13	78926		

The total carbon content of the sediment correlated significantly with the chlorophyll *a* content of the sediment (Figure 9). The regression analysis suggests the presence of two types of organic matter. At minimum chlorophyll *a* contents a background amount of 50 – 100 $\mu\text{mol C g}^{-1}$ is present in the sediment. Superimposed on this a second type of organic matter is present that is related to the chlorophyll *a* content. A few outliers with high C content but low chlorophyll *a* are mostly from the high carbon samples from July 2004 at a sediment depth of 8 - 10 cm (Figure 8). Most, but not all carbon associated with the chlorophyll is from living MPB. Given a slope of 5.35 $\mu\text{mol C } \mu\text{g}^{-1}$ chlorophyll *a*, a total MPB derived carbon : chlorophyll *a* ratio of 64.2 $\mu\text{gC } \mu\text{g}^{-1}$ chlorophyll *a* can be inferred. Much of this MPB derived C will however be present as EPS and bacteria, however, so in order to estimate the fraction of C present as live cellular material a carbon : chlorophyll ratio of 40 (g / g; de Jonge 1980) was used. Using this factor, about 60 % of the chlorophyll related organic carbon is from living MPB. As outliers may have a large influence on the slope of the regression, the above relation was also recalculated based on a regression without values larger than 150 $\mu\text{mol g}^{-1}$ at chlorophyll *a* levels below 2 $\mu\text{g g}^{-1}$. This gives a slope of 5.97 $\mu\text{mol C } \mu\text{g}^{-1}$ chlorophyll ($r^2 = 0.7313$)

implying that about 56 % of the total organic carbon is from living MPB. In any case, the results show that living MPB is closely associated with a detritus pool, possibly derived from grazed MPB.

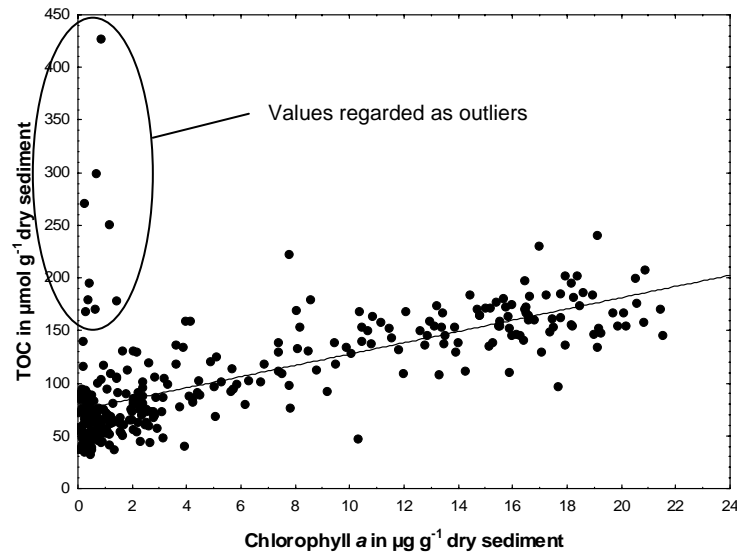


Figure 9: Total organic carbon content in $\mu\text{mol g}^{-1}$ dry sediment in relation to the chlorophyll a content in $\mu\text{g g}^{-1}$ dry sediment ($r^2 = 0.4524$, $p < 0.001$, $y = 5.35x + 74.3$).

In Figure 10 the percentage of total organic matter in MPB based on a carbon : chlorophyll ratio of 40 is shown. The percentage decreases from maximum values of 30 – 45 % near the surface to less than 5 % at 15 cm. Highest values are found in winter and spring. The values are lower than the above calculated value of about 56 %. This is possibly because two sources add to the detrital C pool: one independent of the benthic biomass and another one closely associated with benthic biomass. Also extrapolymeric substances (EPS) produced by microphytobenthos may influence the carbon : chlorophyll ratio in the sediment.

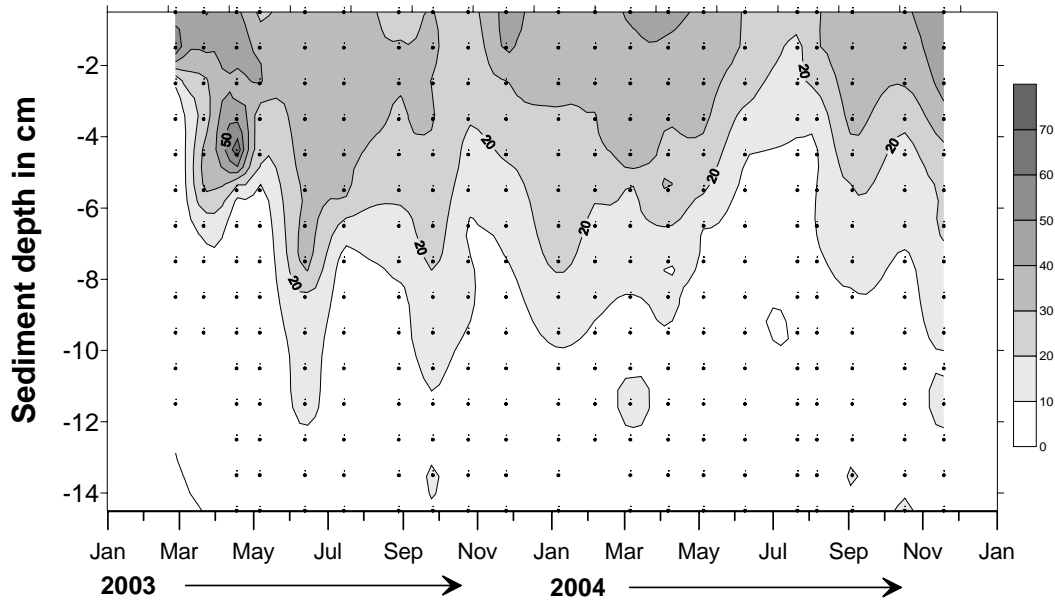


Figure 10: Percentage of total organic carbon which is associated with chlorophyll a in $\mu\text{g g}^{-1}$ over the sampling period estimated assuming a carbon : chlorophyll a of 40. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The darker the colour, the higher is the percentage.

4.4.3 Total organic nitrogen

The total organic nitrogen content of the sediment was also very low with in average 0.02 ± 0.0003 % of the sediment ($13.83 \pm 0.38 \mu\text{mol g}^{-1}$) and ranged between 0.0026 % ($1.86 \mu\text{mol g}^{-1}$) in January 2004 in the depth of 15 cm and 0.062 % ($8.50 \mu\text{mol g}^{-1}$) in August 2004 (15 cm depth). The vertical distribution (Figure 11) is very similar to the chlorophyll *a* distribution (Figure 5) and most of the time a surface maximum was present. The mean total organic nitrogen content in the first centimetre was $22.9 \pm 0.8 \mu\text{mol g}^{-1}$. The total organic nitrogen content of the first cm was 14.05 ± 0.54 % of the total amount in the sediment.

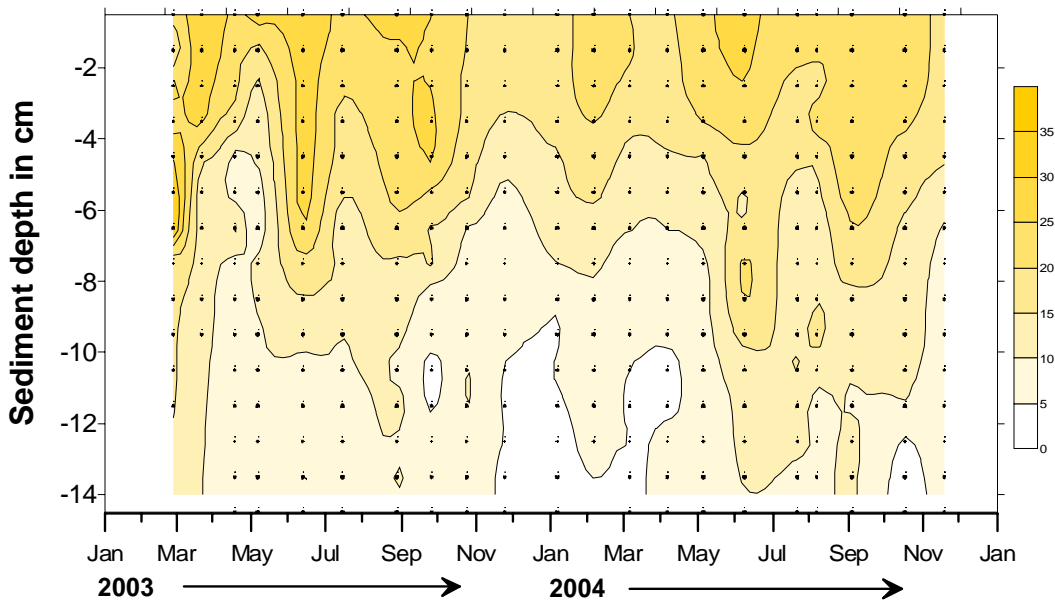


Figure 11: Vertical distribution of the total organic nitrogen content in $\mu\text{mol g}^{-1}$ at the sampling site during 2003 and 2004. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The darker the colour the more total organic nitrogen in $\mu\text{mol g}^{-1}$ was present in the sediment.

In 2004 the total organic nitrogen concentration in the uppermost centimetre was significantly lower than in 2003 (ANOVA, $p < 0.05$). Also significant differences between the seasons were present with lowest concentrations during winter (ANOVA, $p < 0.05$).

Table 3: Results of the two-factorial ANOVA for the total organic nitrogen concentration with the two factors year and season. P-values below 0.05 are considered as significant and are shown in bold.

		dF	MS	F	p
	Year	1	7453	4.816	0.046973
TON in mol m ⁻² in the upper cm	Season	3	6011	3.884	0.034924
	Year*Season	3	2028	1.311	0.313020
	Error	13	1548		

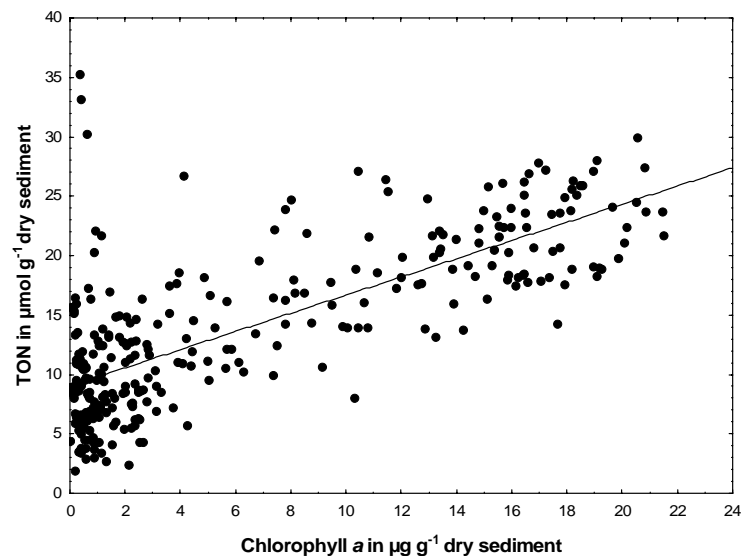


Figure 12: Total organic nitrogen content in $\mu\text{mol g}^{-1}$ dry sediment in relation to the chlorophyll *a* content in $\mu\text{g g}^{-1}$ dry sediment ($r^2 = 0.5579$, $p < 0.001$; $y = 0.76x + 9.04$).

The total organic nitrogen content of the sediment correlated significantly with the chlorophyll *a* content of the sediment (Figure 12). As for organic carbon, two different pools of organic nitrogen can be distinguished. A chlorophyll *a*

related and a chlorophyll *a* - independent pool. The slope of the chlorophyll *a* TON regression is about $0.76 \mu\text{mol } \mu\text{g}^{-1}$ chlorophyll ($0.82 \mu\text{mol } \text{g}^{-1}$ without the outliers shown in Fig 9). The percentage of organic nitrogen associated with benthic microalgae (based on a carbon : chlorophyll *a* ratio of 40 and the Redfield ratio C : N = 106 : 16) is shown in Figure 13. Values are highest at the surface (40 – 50 %) decreasing to values below 10 at depth.

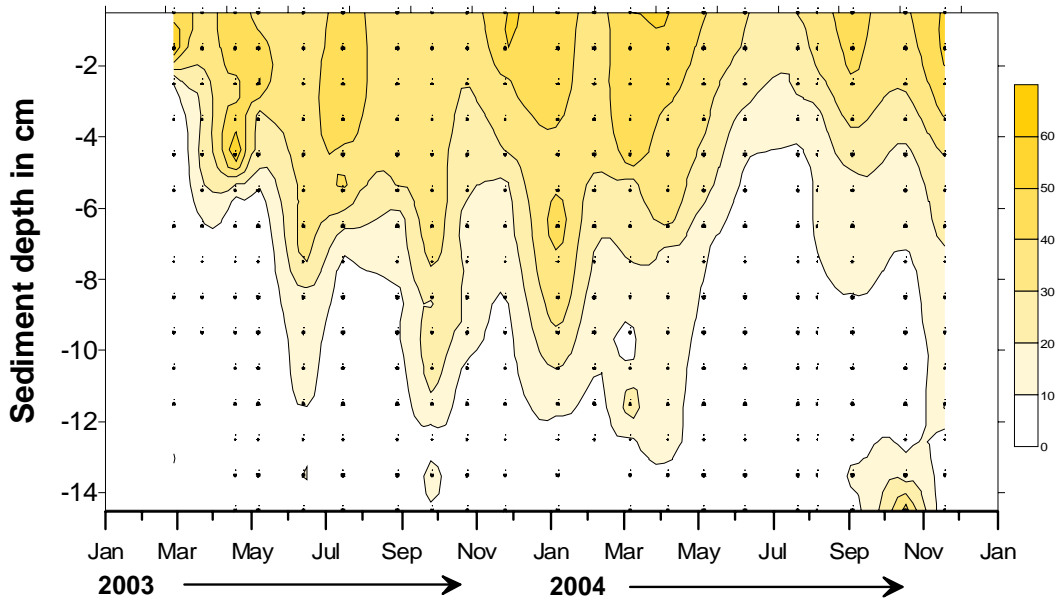


Figure 13: Percentage of total organic nitrogen which is associated with chlorophyll *a* in $\mu\text{g } \text{g}^{-1}$ over the sampling period. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The darker the colour, the higher is the percentage.

4.4.4 Total organic phosphorus

The total organic phosphorus content of the sediment was also very low with an average $1.75 \pm 0.05 \mu\text{mol g}^{-1}$ and ranged between $0.1 \mu\text{mol g}^{-1}$ in May 2003 in a depth of 13 cm and $2.2 \mu\text{mol g}^{-1}$ in November 2003 in a depth of 2 cm.

The vertical distribution of organic phosphorus was similar to the C and N and so also the chlorophyll *a* distribution in the sediment. The concentrations were highest in the upper few centimetres and ranged in the upper centimetre from $1.26 \mu\text{mol g}^{-1}$ in February 2003 to $2.09 \mu\text{mol g}^{-1}$ in May 2004. The first centimetre of the sediment contained $25.29 \pm 0.65 \text{ mol m}^{-2}$ or $17.22 \pm 0.78 \%$ of the total amount in the sediment (15 cm depth). Of the total (organic + inorganic) phosphorus concentration in the sediment $54.49 \pm 0.47 \%$ were organic bound.

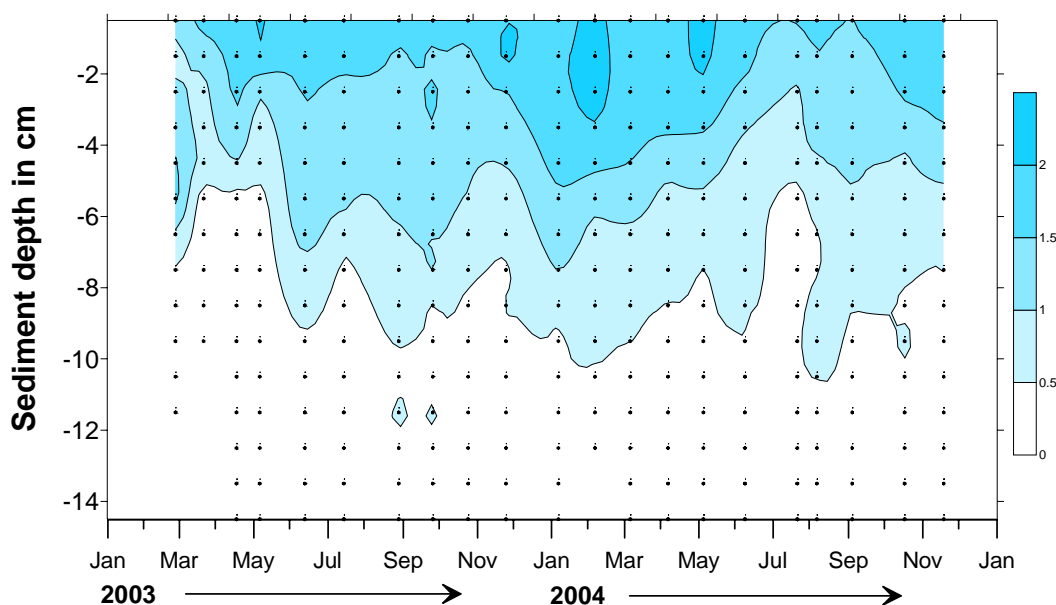


Figure 14: Vertical distribution of the total organic phosphorus content in $\mu\text{mol g}^{-1}$ at the sampling site during 2003 and 2004. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The darker the colour the more total organic nitrogen in $\mu\text{mol g}^{-1}$ was present in the sediment.

The total organic phosphorus concentration of the first cm of the sediment was neither influenced by the different seasons nor from the two different years (Table 4). The total organic phosphorus content in $\mu\text{mol g}^{-1}$ correlated significantly with the chlorophyll *a* content in $\mu\text{g g}^{-1}$ in of the sediment (Figure 15). Again a chlorophyll *a* dependent and a chlorophyll *a* - independent pool can be discerned. The P : chlorophyll *a* ratio is 0.075 (0.077 without the outliers).

Table 4.: Results of the two-factorial ANOVA for the total organic phosphate concentration with the two factors year and season. P-values below 0.05 are considered as significant and are shown in bold.

		dF	MS	F	p
TOP in mol m ⁻² in the upper cm	Year	1	10.27	1.835	0.200496
	Season	3	8.89	1.587	0.243930
	Year*Season	3	4.46	0.796	0.519400
	Error	12	5.60		

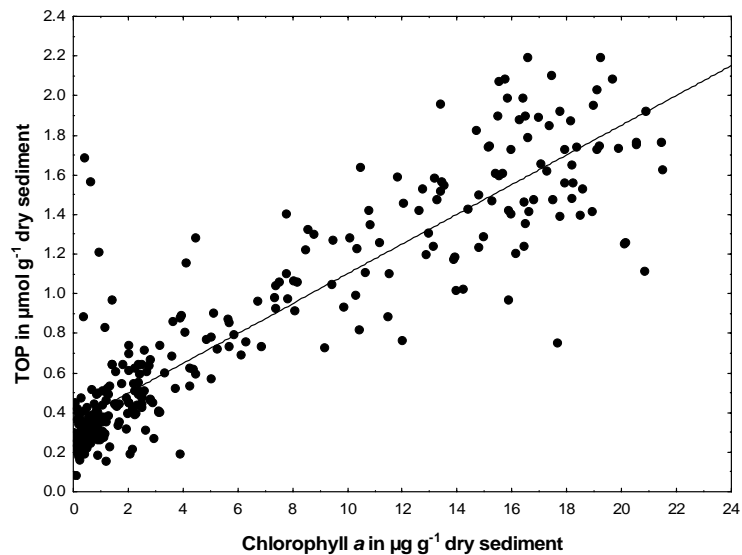


Figure 15: Total organic phosphorus content in $\mu\text{mol g}^{-1}$ dry sediment in relation to the chlorophyll *a* content in $\mu\text{g g}^{-1}$ dry sediment.
($r^2 = 0.8211$, $p < 0.001$, $y = 0.075x + 0.35$)

Based on the Redfield ratio (C : N : P = 106 : 16 : 1) and a carbon : chlorophyll ratio of 40, the amount of organic P associated with benthic microalgae biomass was estimated. Maximum values of around 30% were observed near the surface decreasing to low values at depth. (Figure 16).

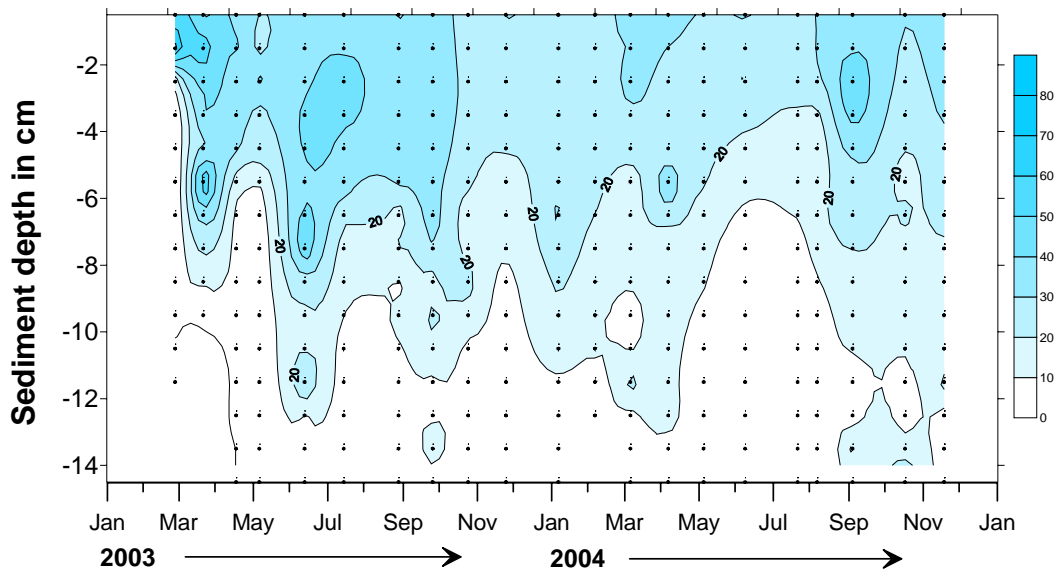


Figure 16: Percentage of total organic phosphorus which is associated with chlorophyll a in $\mu\text{g g}^{-1}$ over the sampling period. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The darker the colour, the higher is the percentage.

4.4.5 Nutrient and Carbon Ratios

In Figure 17 total organic carbon is plotted against total organic nitrogen. A significant correlation is present with C : N ratio of about 9.2. These values are higher than the Redfield ratio of 6.6. A plot of TOC versus TOP gives a C : P ratio of 129 (Figure 18), a plot of TOP versus TON gives a N : P ratio of 15.7 (Figure 19), which is close to the Redfield ratio. In all, the P : N : C ratio using all data is 1 : 15.7 : 137 indicating a relatively high C content. Omitting the outliers in Figure 9 changes the P : N : C ratio to 1 : 14.8 : 104.5, which is close to the Redfield ratio of 1 : 16 : 106.

In the upper part of the sediment at chlorophyll *a* levels higher than 2 $\mu\text{g g}^{-1}$ the P : N : C ratio is 1 : 16.6 : 114 which is also very close to the Redfield ratio. The C : N – ratio of individual samples ranged most of the time from 5 to 9 except during the winter months in the deeper sediment layers. The profiles showed just minor changes with depth over the whole sampling time except in the winter samples with higher ratios in the deeper layers. This might be related to the extreme low N values being close to the detection limit.

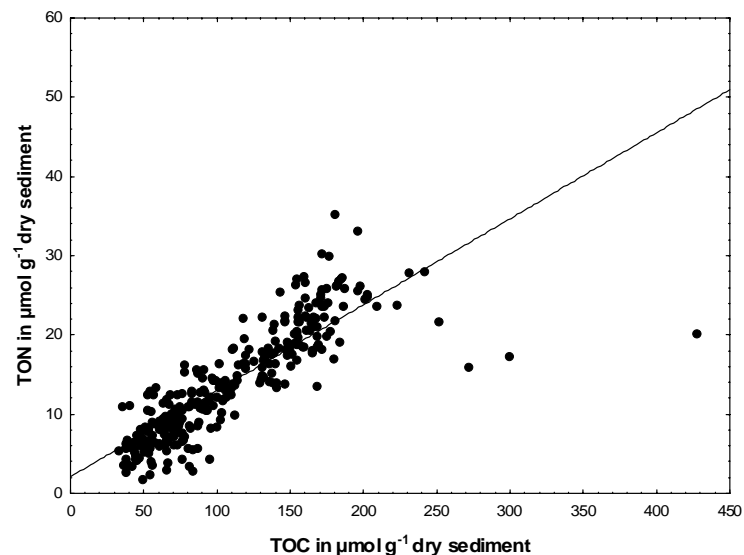


Figure 17: Total organic nitrogen content in $\mu\text{mol g}^{-1}$ dry sediment in relation to the total organic carbon content in $\mu\text{mol g}^{-1}$ dry sediment.
 ($r^2 = 0.7031$, $p < 0.001$, $y = 0.109x + 2.10$)

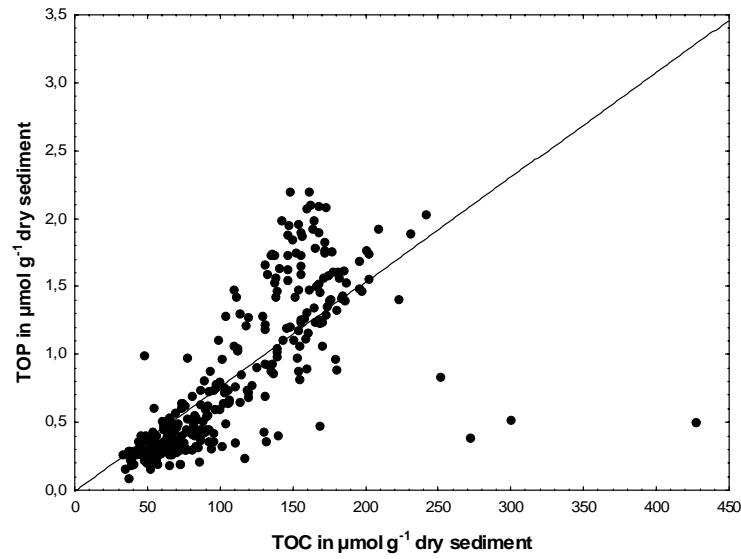


Figure 18: Total organic phosphorus content in $\mu\text{mol g}^{-1}$ dry sediment in relation to the total organic carbon content in $\mu\text{mol g}^{-1}$ dry sediment.
($r^2 = 0.5467$, $p < 0.001$, $y = 0.008x - 0.008$)

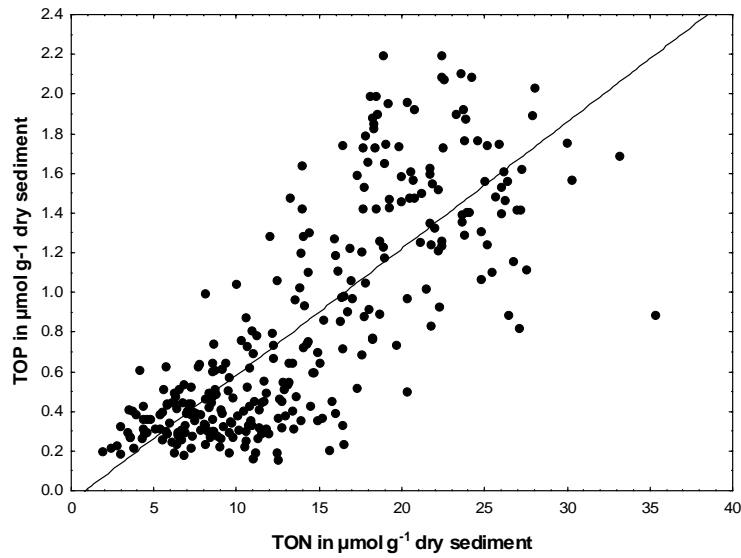


Figure 19: Total organic phosphorus content in $\mu\text{mol g}^{-1}$ dry sediment in relation to the total organic nitrogen content in $\mu\text{mol g}^{-1}$ dry sediment.
($r^2 = 0.6256$, $p < 0.001$, $y = 0.064x - 0.055$)

Table 5: Correlations of TOC, TON and TOP with r^2 , p -values and equations.

All data	r^2	p	equation
TOC in $\mu\text{mol g}^{-1}$: TON in $\mu\text{mol g}^{-1}$	0.7031	< 0.001	$y = 0.108545854x + 2.10330296$
TOC in $\mu\text{mol g}^{-1}$: TOP in $\mu\text{mol g}^{-1}$	0.5467	< 0.001	$y = 0.00770674704x - 0.00798245805$
TON in $\mu\text{mol g}^{-1}$: TOP in $\mu\text{mol g}^{-1}$	0.6256	< 0.001	$y = 0.0637987061x - 0.054844345$
Without TOC > 150 $\mu\text{mol g}^{-1}$ and chlorophyll a < 2 $\mu\text{g g}^{-1}$	r^2	p	equation
TOC in $\mu\text{mol g}^{-1}$: TON in $\mu\text{mol g}^{-1}$	0.8390	< 0.001	$y = 0.130859989x - 0.0798712433$
TOC in $\mu\text{mol g}^{-1}$: TOP in $\mu\text{mol g}^{-1}$	0.7615	< 0.001	$y = 0.0104064106x - 0.261753962$
TON in $\mu\text{mol g}^{-1}$: TOP in $\mu\text{mol g}^{-1}$	0.6504	< 0.001	$y = 0.0675730719x - 0.0923807756$
Chlorophyll a > 2 $\mu\text{g g}^{-1}$	r^2	p	equation
TOC in $\mu\text{mol g}^{-1}$: TON in $\mu\text{mol g}^{-1}$	0.8058	< 0.001	$y = 0.131545472x - 0.119350538$
TOC in $\mu\text{mol g}^{-1}$: TOP in $\mu\text{mol g}^{-1}$	0.6490	< 0.001	$y = 0.00979799767x - 0.12956808$
TON in $\mu\text{mol g}^{-1}$: TOP in $\mu\text{mol g}^{-1}$	0.5283	< 0.001	$y = 0.0603299947x + 0.121803972$

4.5 Discussion

Biomass

This study showed high biomasses of MPB measured as chlorophyll *a* during the whole sampling period of two years in the uppermost sediment centimetre ($17.84 \pm 0.51 \mu\text{g g}^{-1}$ and $257.43 \pm 7.34 \text{ mg m}^{-2}$). In comparison with chlorophyll *a* values in other studies, the chlorophyll *a* at this study site was always in the upper range of the reported values for the intertidal and for the subtidal (e.g. Heip et al. 1995, Schreiber and Pennock 1995, Cahoon 1999). Underwood and Kromkamp (1999) postulated, that in sandy sediments MPB biomasses are lower than in muddy sediments, but this was not valid for this sampling site. Miles and Sundbäck (2000) also found high biomasses in shallow sandy sediments.

Benthic microalgae are often 10^4 - 10^5 times more concentrated in sediments than in the water (per m^2) (Cahoon 1999). These high concentrations are also maintained under physical conditions such as wave - and tidal current - induced sediment disturbance that would be expected to disperse or destroy living cells (Cahoon 1999). These results are also in contrast to those of Cook et al. (2004), who postulated that exposure to wave energy reduced the biomass and productivity of MPB. Nelson et al. (1999) found 6 – 8 times higher chlorophyll *a* concentrations in the surface 5 mm of South Atlantic shelf sands than in the entire integrated overlying water column. Here in this study, the chlorophyll *a* concentration of the uppermost sediment centimetre averaged over the two years was 30 times higher than the average chlorophyll concentration in an estimated water column of 1.5 m. Thus it appears that even relatively exposed sites such as the one studied here may have extremely high MPB biomass and productivity.

Vertical distribution of biomass

At this sampling station these high biomasses were not just in the upper centimetre. High values were found throughout the upper 6 – 8 cm. On average 22 ± 2 % of the total chlorophyll *a* biomass in 15 cm were present in the upper sediment centimetre. The MPB consists mainly of diatoms (Wiktor pers. comm.) and the presence of viable diatoms in deeper sediment layers has also been described in other studies before. Diatoms are known to survive in darkness, to tolerate anoxia and sulphurous conditions and to compensate for low light levels by heterotrophy (e.g. Cadée and Hegeman 1974, de Jonge 1985, Admiraal 1984) for months without losing their photosynthetic capacity (e.g. Cadée and Hegeman 1977, Sundbäck and Granéli 1988, Nelson et al. 1999). Especially in sandy sediments, benthic microalgae may be present in deeper sediment layers through burial by physical forces such as waves and currents, bioturbation (Cadée and Hegeman 1974, Nelson et al. 1999, Rusch and Huettel 2000) or active migration of epipellic diatoms (Kingston 1999, Cadée and Hegeman 1974). At this sampling station the macrofauna densities were low and the burial of diatoms through waves and currents is probably the most important process.

Seasonality

Just the upper centimetre of the sediment showed significant differences of the chlorophyll *a* concentration with the seasons, with higher values during spring of both years. MPB biomass is known to show a high level of variability both within and between years (e.g. MacIntyre et al. 1996). Most populations of MPB show a peak in spring or summer (e.g. Cadée and Hegeman 1977). Many studies have documented a second bloom in the fall (e.g. Cadée and Hegeman 1974).

The mean chlorophyll *a* concentration of the upper 5 cm as well as integrated over 10 cm sediment depth at the sampling station showed no significant seasonal differences during the two sampling years, but the second summer had significantly lower chlorophyll *a* concentrations than the entire sampling

period. Factors, which contribute to the temporal variability of chlorophyll *a* in the sediment, are seasonal variations in day length, seasonal variations in temperature, seasonal variation in activity of benthic fauna and microbial communities (Nelson et al. 1999). Summer declines of benthic biomass are due to nutrient limitation or consumption by grazers (e.g. Underwood and Paterson 1993b). The results of this study suggest, that in terms of biomass, the MPB community of this sandy subtidal sandy sediment is rather stable all year round, at least compared to the large variation found in pelagic system (see also Sundbäck et al. 1996). Nelson et al. (1999) found that that physical disturbance of the sediments associated with wind – generated surface waves can be a significant factor driving variability in benthic microalgal biomass. Relatively low concentrations of surface chlorophyll *a* in general corresponded with periods when strong, sustained wind events were frequent (winter - spring and late summer and autumn) (Nelson et al. 1999), but this was not the case in this study (see Chapter 2).

Organic matter composition

The organic content of the sediment was low, but of high quality with a large share of living MPB and an organic matter composition close to the Redfield ratio (C : N : P = 106 : 16: 1). The total organic carbon content was in average 0.13 ± 0.002 % ($108.12 \pm 3.10 \mu\text{mol g}^{-1}$) and showed a clear seasonality with higher values during summer and autumn and the values were significantly higher in the first year. Such a seasonal cycle has been described before (e.g. Cadée and Hegeman 1977). The year 2003 was a sunny and warm year with low riverine discharge (<http://www.waterbase.nl>) and low nutrient input (van Beusekom et al. 2005) to the water column. MPB is known to produce extrapolymeric substances, high in carbon content under low nutrient conditions during overflow metabolism during photosynthesis (Blanchard et al. 2000). The carbohydrate measurements (Chapter 2) show higher values during summer and autumn 2003 than in the year 2004 and are so in line with the observations in this study (Figure 20). The total organic carbon content of the sediment

correlated significantly with the chlorophyll *a* content of the sediment. About 50 % of chlorophyll *a* associated carbon was probably associated with live MPB, based carbon : chlorophyll *a* ratio of 40 (de Jonge 1980). On average 16 % of the carbon was fixed in MPB, in the upper layer the amount was much higher. Cahoon (1999) reported that benthic microalgae typically represent a very small fraction of organic matter in the sediments, usually < 1 - 5 %. On the other hand, Cadée and Hegeman (1977) reported for the Dutch Wadden Sea that up to 40 % of total organic carbon comes from the chlorophyll *a*.

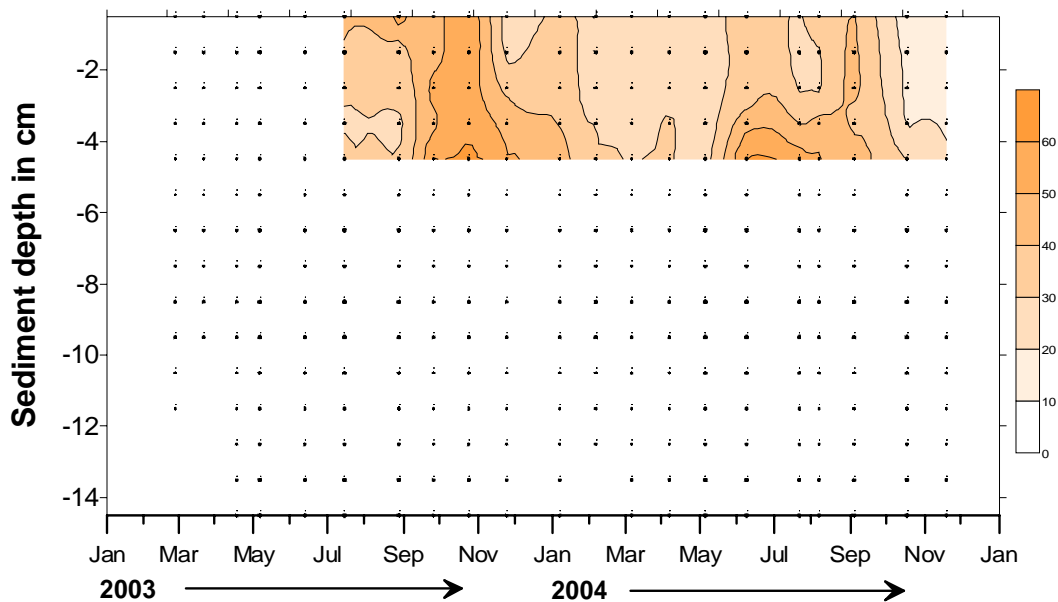


Figure 20: EDTA – extractable carbohydrate content : chlorophyll *a* content in the upper 5 cm of the sediment. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The darker the colour, the higher is the ratio.

The measured biomasses as well as the calculated associated carbon, nitrogen and phosphorus contents are just estimates. Microphytobenthic biomass is almost always measured and expressed in terms of chlorophyll *a*. There is no standard method for measuring chlorophyll *a*. Spectrophotometric methods,

particularly those that employ steps to eliminate interferences from pigment degradation products, like the method used in this study, give relatively accurate results. Benthic microalgae in low light flux habitats may accumulate relatively higher amounts of chlorophyll and / or accessory pigments per cell, so called "shade adaption" (e.g. Perry et al. 1981). This may lead to an overestimation of microphytobenthic biomass.

For the carbon : chlorophyll *a* ratio exist several values ranging between 10.2 and 153.9 and the ratio may also vary seasonally (de Jonge 1980). In this study the ratio carbon : chlorophyll *a* = 40 : 1 was taken to calculate the amount of carbon fixed per chlorophyll *a*. So there is a certain amount of uncertainty in these numbers, because the real value is not known.

Also for the C : N : P ratio of benthic diatoms different values are reported. In this study as the C : N : P ratio the Redfield ratio of 106 : 16 : 1 was taken to calculate the amount of nitrogen and phosphate bound in the MPB. Hillebrand and Sommer (1999) reported of a ratio for benthic diatoms of C : N : P = 119 : 17 : 1. Others reported of a C : N ratio of 10 : 1 for benthic diatoms (see Sundbäck and Granéli 1988 and references therein).

In this study a C : N : P ratio of 137 : 15.7 : 1 was found, by using the data of all depths. In the upper part of the sediment with chlorophyll *a* levels larger than 2 $\mu\text{g g}^{-1}$ the C : N : P ratio is 114 : 16.6 : 1 which is very close to the ratio of 119 : 17 : 1 for benthic diatoms reported by Hillebrand and Sommer (1999). This is an indicator for high quality organic matter which is thus easily degradable. Also the good correlations of the total organic carbon, total organic nitrogen and total organic phosphorus content with the chlorophyll *a* content of the sediment are supporting the high quality of the organic matter in this shallow subtidal sandy sediment.

Shallow subtidal: an optimum habitat?

One limiting factor for the primary production of MPB is the light flux to the sediment - water interface, which is a function of depth and turbidity. Subtidal sediments are relatively low light environments. In sandy sediments light can penetrate further. The euphotic zone in coarse sandy sediments is up to 4 mm (Colijn 1982) and due to the very high scatter relative to the absorption in the sand matrix, there can be a local maximum in scalar irradiance, just beneath the surface (Kühl et al. 1994). During winter in average approximately $1.7 \mu\text{E m}^{-2}\text{s}^{-1}$ and during summer $200 \mu\text{E m}^{-2}\text{s}^{-1}$ reached the sediment surface in a water depth of 1.5 m (mean amount of daylight; Loebel pers. comm.). Possible responses by benthic microalgae to the lower light levels, is the so called "shade adaption", the physiological and genetic adaption to low light intensities by increases in photosynthetic efficiency, by increasing their cellular pigments (e.g Perry et al. 1981). Benthic microalgae appear capable of sustaining growth at very low light intensities, in many cases of $5 - 10 \mu\text{E m}^{-2}\text{s}^{-1}$ and 1 % surface incident irradiance (Cahoon 1999). Admiraal et al. (1984) found that intertidal diatom species were able to grow in the range 0.3 to $40 \text{ E m}^{-2}\text{d}^{-1}$. Subtidal MPB is protected through optical filtering of the overlying water column. So MPB is not exposed so much to the potentially harmful effects of high visible and UV irradiance (Nelson et al 1999).

Because of permanent submersion in the shallow subtidal the MPB was not desiccated during low tide. The permeability of the sediment allowed all the time advection. Thus the sediment was continuously supplied with organic material transported from the overlying water column into the sediment. Due to enhanced mineralization through advection there were consistently higher nutrient concentrations in the sediment than in the overlying water column (Chapter 3). The MPB at the site has been shown to be limited by CO_2 in the absence of advection (Cook and Røy subm., Wenzhöfer et al. in prep.). Because of constant advection, the microphytobenthos is supplied all the time with CO_2

from the water column. High microphytobenthic biomass was observed throughout the entire advective zone (4 – 6 cm depth). This suggests that most of the benthic biomass remained in the dark for longer periods, as light penetrates only a few mm into the sediment. A large part of the microphytobenthos therefore presumably survived in a heterotrophic mode in this layer (Admiraal 1984). Because of advective pore water flow, the microalgae in this layer are not exposed to high concentrations of ammonia and sulphide (Nelson et al. 1999), which may become toxic compounds for benthic microalgae when they occur in high concentrations (Admiraal 1984). The viable diatoms below the euphotic zone, which start to photosynthesise when they are brought into light, are a pool of potential primary producers (e.g. Cadeé and Hegeman 1974, Nelson et al. 1999). After being mixed back to the surface sediments, the subsurface diatoms provide a population reservoir that helps to maintain benthic microalgal biomass at high levels despite physical and biological perturbations.

Our transect data showed higher biomasses in the upper centimetre of the sediment as well as integrated over the sediment depth of 10 cm in the shallow subtidal in comparison to the intertidal or the deeper subtidal. This is an indicator for high potential primary production at this shallow sandy site, because measurements of concentrations of photosynthetic pigments provide an indirect approach to “potential” production (Colijn and de Jonge 1984). The light penetration through the water column is one explanation for the differences in biomass between the intertidal, the shallow subtidal and the deeper subtidal sediments (Moreno and Niell 2004). Furthermore, the currents at the deepest stations were very strong, because the stations were right on the edge of one of the main tidal channels.

At this shallow exposed sandy subtidal site high biomasses were observed during the whole sampling time with a large potential of primary producers

below the surface, also in comparison with the intertidal and the deeper subtidal. The organic content was low, but of high quality indicating a rapid recycling of organic matter. For the intensive sedimentary mineralization with associated nutrient release also the high biomass may be an indicator.

Appendix A.

Mean sediment density (of the dry sediment) in g cm⁻³ for each depth centimetre (n = 32) with Standard Deviation and Standard Error. One cm³ sediment were taken with a syringe and weighed.

depth in cm	density in g cm ⁻³	SD	SE
1	1.44	0.07	0.01
2	1.45	0.07	0.01
3	1.46	0.08	0.01
4	1.46	0.07	0.01
5	1.46	0.07	0.01
6	1.45	0.07	0.01
7	1.43	0.07	0.01
8	1.43	0.08	0.01
9	1.44	0.07	0.01
10	1.42	0.07	0.01
11	1.44	0.06	0.01
12	1.43	0.07	0.01
13	1.43	0.08	0.01
14	1.42	0.08	0.01
15	1.43	0.08	0.01

B.

Chlorophyll a and Phaeophytin values of the whole sampling time in the upper centimetre and in 15 cm sediment. Data are the mean of three different measurements. NA: not determined. If there were not 15 cm available, this is indicated in the first column. The values are calculated then for this sediment depth.

Date	Chlorophyll a in the first cm in $\mu\text{g g}^{-1}$	Chlorophyll a in the first cm in mg m^{-2}	Chlorophyll a integrated over 15 cm sediment in mg m^{-2}	Phaeophytin in the first cm in $\mu\text{g g}^{-1}$	Phaeophytin in the first cm in mg m^{-2}	Phaeophytin integrated over 15 cm sediment in mg m^{-2}
February 03 (26.02.2003) (cm 1-12)	20.14	290.68	646.59	2.82	40.70	220.44
March 03 (21.03.2003) (cm 1-10)	20.53	296.24	1159.07	0.05	0.70	39.46
April 03 (17.04.2003)	21.44	309.38	1313.12	6.04	87.19	320.00
May 03 (06.05.2003)	19.08	275.38	934.68	0.88	12.77	106.08
June 03 (12.06.2003)	17.23	248.65	2196.20	1.09	15.76	214.35
July 03 (14.07.2003)	20.84	300.81	1695.60	1.59	22.91	183.67
August 03 (28.08.2003)	16.93	244.38	1570.27	1.13	16.35	161.49
September 03 (25.09.2003)	18.34	264.74	1960.33	1.35	19.54	191.45
October 03 (24.10.2003)	13.17	190.02	1104.25	0.75	10.78	90.50
November 03 (24.11.2003)	18.96	273.61	1148.35	1.29	18.63	106.25
December 03	NA	NA	NA	NA	NA	NA
January 04 (06.01.2004)	16.54	238.75	1678.85	3.69	53.20	545.28
February 04 (05.02.2004) (cm 1-13)	15.52	223.92	1426.44	3.17	45.71	379.75
March 04 (05.03.2004)	19.85	286.47	1517.96	3.33	48.02	359.10
April 04 (05.04.2004)	19.15	276.34	1472.38	3.84	55.46	479.69
May 04 (04.05.2004)	19.65	283.54	1309.89	4.27	61.64	355.32
June 04 (07.06.2004)	15.65	225.83	921.80	3.46	49.95	334.92
July 04 (17.07.2004)	13.38	193.16	620.73	2.58	37.30	223.14
August 04 (05.08.2004)	15.36	221.75	944.72	3.25	46.97	303.40
September 04 (03.09.2004)	16.77	241.98	1516.27	2.41	34.71	320.04
October 04 (16.10.2004)	18.14	261.77	1219.29	0.48	6.96	184.55
November 04 (17.11.2004)	17.92	258.59	1498.70	2.44	35.23	302.83

C.

Total organic carbon and total organic nitrogen values of the whole sampling time in the upper centimetre and in 15 cm sediment. Data are the mean of three different measurements. NA: not determined. If there were not 15 cm available, this is indicated in the first column. The values are calculated then for this sediment depth.

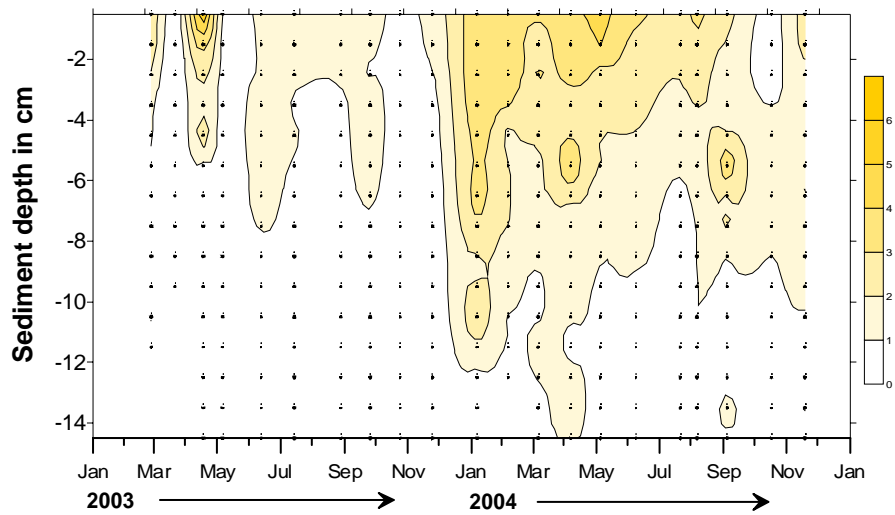
Date	TOC in the first cm in $\mu\text{mol g}^{-1}$	TOC in the first cm in Mol m^{-2}	TOC integrated over 15 cm sediment in Mol m^{-2}	TON in the first cm in $\mu\text{mol g}^{-1}$	TON in the first cm in Mol m^{-2}	TON integrated over 15 cm sediment in Mol m^{-2}
February 03 (26.02.2003) (cm 1-12)	155.15	2239.18	22126.91	22.37	322.85	3791.17
March 03 (21.03.2003) (cm 1-10)	176.37	2545.47	14179.90	29.96	432.33	2743.96
April 03 (17.04.2003)	171.26	2471.72	17741.42	23.73	342.45	2488.90
May 03 (06.05.2003) (N: cm 1-13)	241.21	3481.17	17327.24	28.00	404.09	2115.92
June 03 (12.06.2003)	184.78	2666.78	26712.92	27.23	393.01	3781.63
July 03 (14.07.2003)	208.58	3010.23	23996.89	23.71	342.26	2926.89
August 03 (28.08.2003)	230.59	3327.92	27573.35	27.87	402.27	3605.78
September 03 (25.09.2003)	202.40	2921.10	26374.45	25.11	362.40	3074.22
October 03 (24.10.2003)	174.43	2517.40	23337.36	19.91	287.30	2692.51
November 03 (24.11.2003)	147.36	2126.75	17865.77	19.13	276.13	2017.33
December 03	NA	NA	NA	NA	NA	NA
January 04 (06.01.2004)	164.84	2379.03	25343.98	17.77	256.52	2204.79
February 04 (05.02.2004) (cm 1-13)	159.50	2301.91	21016.19	22.51	324.85	2640.44
March 04 (05.03.2004)	154.90	2235.58	19191.45	19.79	285.59	2218.37
April 04 (05.04.2004)	152.19	2196.49	19989.16	18.99	274.10	2268.32
May 04 (04.05.2004)	167.42	2416.18	20191.92	24.17	348.84	2712.58
June 04 (07.06.2004)	180.89	2610.71	33127.54	26.16	377.61	3767.40
July 04 (17.07.2004)	167.48	2417.12	25970.50	22.16	319.78	3090.97
August 04 (05.08.2004)	177.30	2558.81	25780.34	20.51	295.99	3101.24
September 04 (03.09.2004)	160.82	2320.99	23958.57	20.73	299.13	3526.81
October 04 (16.10.2004)	156.03	2251.92	22412.28	23.84	344.13	2976.56
November 04 (17.11.2004)	136.88	1975.53	17959.42	17.63	254.41	2467.59

D.

Total organic phosphorus and total phosphorus values of the whole sampling time in the upper centimetre and in 15 cm sediment. Data are the mean of three different measurements. NA: not determined. If there were not 15 cm available, this is indicated in the first column. The values are calculated then for this sediment depth.

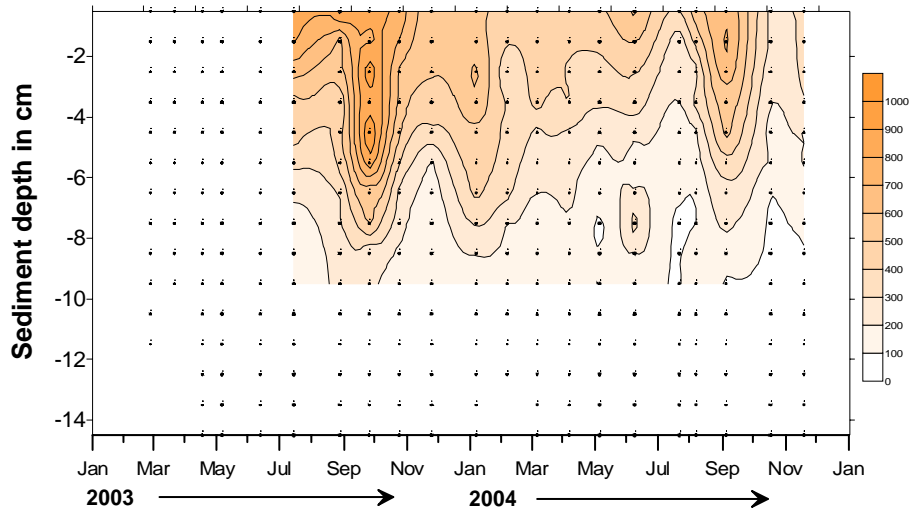
Date	TOP in the first cm in $\mu\text{mol g}^{-1}$	TOP in the first cm in Mol m^{-2}	TOP integrated over 15 cm sediment in Mol m^{-2}	TP in the first cm in $\mu\text{mol g}^{-1}$	TP in the first cm in Mol m^{-2}	TP integrated over 15 cm sediment in Mol m^{-2}
February 03 (26.02.2003) (cm 1-12)	1.26	18.21	141.80	2.69	38.79	338.16
March 03 (21.03.2003) (cm 1-10)	1.76	25.37	98.34	3.06	44.19	206.86
April 03 (17.04.2003)	1.77	25.53	151.76	2.96	42.68	273.74
May 03 (06.05.2003)	2.03	29.32	130.50	3.26	47.05	230.03
June 03 (12.06.2003)	1.62	23.41	201.26	2.67	38.56	363.45
July 03 (14.07.2003)	1.93	27.79	164.42	3.32	47.89	315.35
August 03 (28.08.2003)	1.89	27.32	192.04	3.28	47.38	363.24
September 03 (25.09.2003)	1.74	25.17	197.42	3.17	45.70	397.13
October 03 (24.10.2003)	1.59	22.91	164.60	2.84	40.96	326.29
November 03 (24.11.2003)	1.95	28.21	174.53	2.80	40.43	275.12
December 03	NA	NA	NA	NA	NA	NA
January 04 (06.01.2004)	1.79	25.82	226.73	3.04	43.89	391.06
February 04 (05.02.2004) (cm 1-13)	2.07	29.93	221.00	3.11	44.89	343.15
March 04 (05.03.2004)	1.73	25.03	201.18	2.67	38.54	311.02
April 04 (05.04.2004)	1.75	25.26	189.06	2.96	42.79	324.18
May 04 (04.05.2004)	2.09	30.15	195.33	3.21	46.35	315.52
June 04 (07.06.2004)	1.61	23.23	157.16	2.75	39.67	277.10
July 04 (17.07.2004)	1.52	21.90	124.56	2.46	35.45	219.17
August 04 (05.08.2004)	1.61	23.23	166.24	2.80	40.38	292.84
September 04 (03.09.2004)	1.48	21.30	160.03	2.35	33.96	298.28
October 04 (16.10.2004)	1.88	27.06	172.76	2.80	40.40	281.23
November 04 (17.11.2004)	1.73	25.02	180.61	2.62	37.77	285.91

E.

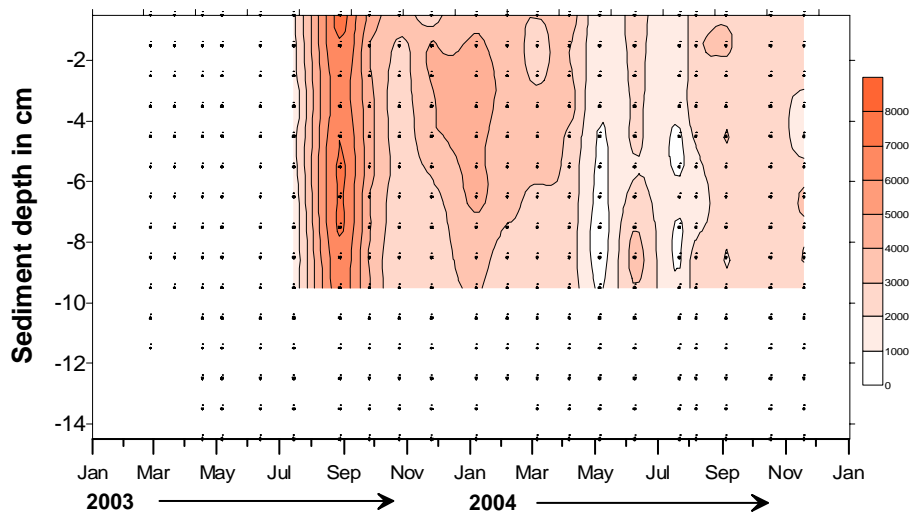


Vertical distribution of phaeophytin in $\mu\text{g g}^{-1}$ at the sampling site during 2003 and 2004. Vertical dotted lines represent the sampling date; each single dot represents also the sampled layer. The darker the colour the more phaeophytin in $\mu\text{g g}^{-1}$ was present in the sediment.

F.



Vertical distribution of EDTA – extractable carbohydrates in μg glucose equivalents g^{-1} dry sediment at the sampling site during 2003 and 2004.



Vertical distribution of total carbohydrates in μg glucose equivalents g^{-1} dry sediment at the sampling site during 2003 and 2004.

G.

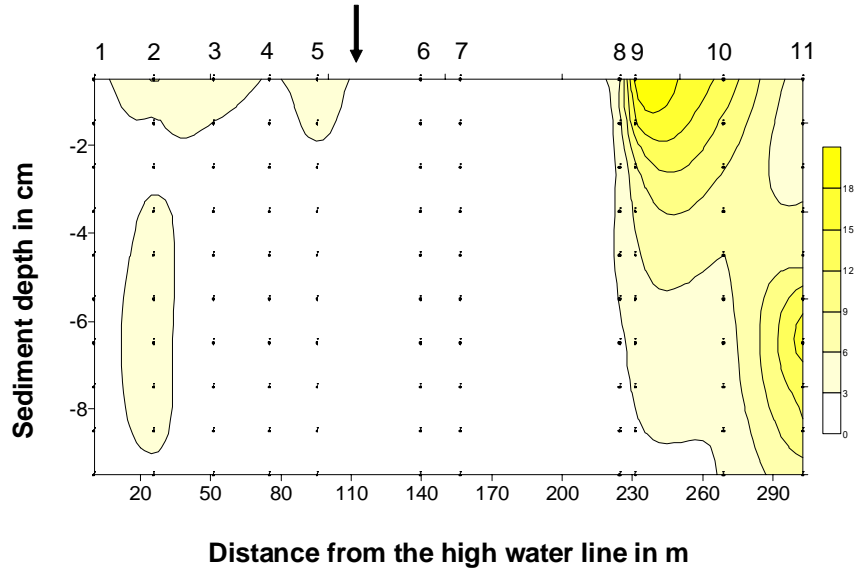
Transect data: Sediment density in g cm^{-3} for each depth centimetre and each sampled station. The shown number is the mean of three subsamples.

depth in cm	density in g cm^{-3} Station 1	density in g cm^{-3} Station 2	density in g cm^{-3} Station 3	density in g cm^{-3} Station 4	density in g cm^{-3} Station 5	density in g cm^{-3} Station 6	density in g cm^{-3} Station 7	density in g cm^{-3} Station 8	density in g cm^{-3} Station 9	density in g cm^{-3} Station 10	density in g cm^{-3} Station 11
1	1.63	1.67	1.77	1.54	1.77	1.80	1.73	1.81	1.35	1.48	1.69
2	1.63	1.66	1.70	1.75	1.82	1.82	1.72	1.90	1.35	1.71	1.62
3	1.53	1.74	1.70	1.67	1.83	1.76	1.69	1.80	1.91	1.64	1.71
4	1.74	1.85	1.71	1.73	1.79	1.81	1.74	1.78	1.93	1.75	1.68
5	1.69	1.68	1.69	1.76	1.82	1.75	1.69	1.78	1.91	1.77	1.75
6	1.79	1.73	1.69	1.67	1.79	1.78	1.80	1.68	1.84	1.43	1.39
7	1.76	1.84	1.79	1.70	1.83	1.67	1.81	1.77	1.78	1.66	1.20
8	1.80	1.81	1.76	1.70	1.82	1.69	1.74	1.84	1.80	1.30	1.21
9	1.71	1.81	1.83	1.69	1.75	1.69	1.83	1.73	1.82	1.46	1.23
10	1.69	1.69	1.83	1.71	1.73	1.74	1.82	1.55	1.81	1.56	1.42

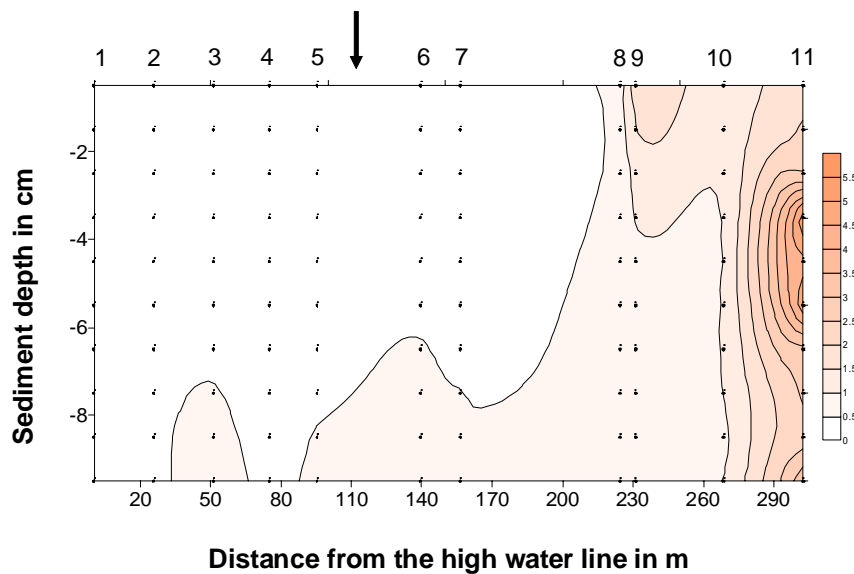
Transect data: Distance of the sampling station from the normal high water line in m, water depth of the sampling station during low tide in m. The third column shows the mean chlorophyll a in mg m^{-2} of three subsamples taken from 6 pooled cores per station. Column 4 contains the mean integrated chlorophyll a in mg m^{-2} of three subsamples taken from 6 pooled cores per station.

Station	Distance from the high water line in m	Water depth during low tide in m	Chlorophyll a in the upper cm in mg m^{-2}	Chlorophyll a integrated over 10 cm sediment in mg m^{-2}
Station 1	0	0	162.30	1177.12
Station 2	25.5	0	233.25	1815.44
Station 3	51	0	262.21	1160.72
Station 4	74.8	0.1	207.97	1985.00
Station 5	95.2	0.4	290.15	1524.26
Station 6	139.4	0.7	247.97	992.51
Station 7	156.4	1	236.30	1541.24
Station 8	224.4	1.8	110.65	706.48
Station 9	231.2	1.95	148.01	1033.04
Station 10	268.6	2.1	154.03	987.18
Station 11	302.6	4.1	38.20	424.58

H.



Vertical distribution of phaeophytin in $\mu\text{g g}^{-1}$ along the transect from the normal high water line (0 m at the x-axis correspond Station 1) into the subtidal (302 m at the x-axis correspond Station 11). Time series station is indicated with an arrow.



Phaeophytin : chlorophyll a in $\mu\text{g g}^{-1}$ along the transect from the normal high water line (0 m at the x-axis correspond Station 1) into the subtidal (302 m at the x-axis correspond Station 11). Time series station is indicated with an arrow.

Chapter 5

General discussion

Permeable sands are a dominant sediment type along the coasts (Emery 1968). The importance of these permeable sediments in the cycle of organic matter has been recognized recently (Shum and Sundby 1996, Boudreau et al. 2001). Therefore, until now only a few studies investigated the role of permeable sediments in the shallow subtidal. Aim of this study was to describe the temporal dynamics of permeability, pore water nutrients, microphytobenthic biomass and organic matter in a permeable shallow subtidal sandy sediment.

Key variables in the temporal dynamics were wind speed, microphytobenthos and the seasonal cycles of light and temperature. Following a short discussion on the seasonality of permeability, this chapter focuses on two further aspects. First the shallow subtidal permeable sand as an optimum habitat for microphytobenthos is compared to the intertidal and deeper subtidal. The seasonal dynamics of pore water constituents will be discussed in the second part of this chapter.

Seasonality of permeability

Permeability of the sediment as one key variable of sandy sediments varied seasonally, but allowed all the time advection. Higher values occurred in winter and spring and lower values during summer and autumn. Permeability correlated with the mean average wind speed in the sampling day, thus the shallow permeable subtidal sediment at the study site was influenced permanently by wind induced waves. This led to a seasonality of the permeability at this site. Presumably changed packing and loss of fine particles of the sediment due to enhanced resuspension of the sediment was caused by higher mean average wind speeds during winter and spring than in summer and autumn. Wind, however, could not explain all the variability in permeability.

Other factors, such as the EPS and the fine fraction of the sediment may also affect permeability, but explain less variability than wind.

Exposed shallow subtidal as optimum habitat for microphytobenthos?

The microphytobenthic biomass showed no clear seasonality at the sampling site and remained high throughout the year in contrast to other intertidal and subtidal regions with lower microphytobenthic biomass and pronounced seasonality (see e.g. Cahoon 1999, Heip et al. 1995). This suggests that the sampling site represents an optimum habitat for the microphytobenthos during the whole year. Transect data from the shore line down to the deeper subtidal show highest biomass at the shallow subtidal exposed site in comparison to the intertidal and the deeper exposed subtidal. Several factors may contribute to a shallow exposed subtidal optimum: 1) sufficient light conditions and 2) permanent submergence allow continuous advective exchange of the pore water. An overview on possible factors steering the spatial variation is shown in Figure 1.

Subtidal sediments are environments relatively low in light, and under these conditions it may be assumed that light is primarily limiting the primary production. During late summer also nutrient availability may become a limiting factor, indicated by high EPS concentrations in the sediment because of overflow metabolism during nutrient limitation (e.g. Stal 2003).

In sandy sediments light can penetrate further than in muddy sediments. The euphotic zone in coarse sandy sediments is up to 4 mm (Colijn 1982) and due to the very high scatter relative to the absorption in the sand matrix, there can be a local maximum in scalar irradiance just beneath the surface (Kühl et al. 1994). Subtidal microphytobenthos is protected from potentially harmful effects of high visible and UV irradiance through optical filtering by the overlying water column (Nelson et al. 1999). In the deeper subtidal less light is available, which

may explain the lower phyto-benthic biomass found in this habitat. Also current velocities are higher, leading to enhanced sediment mixing.

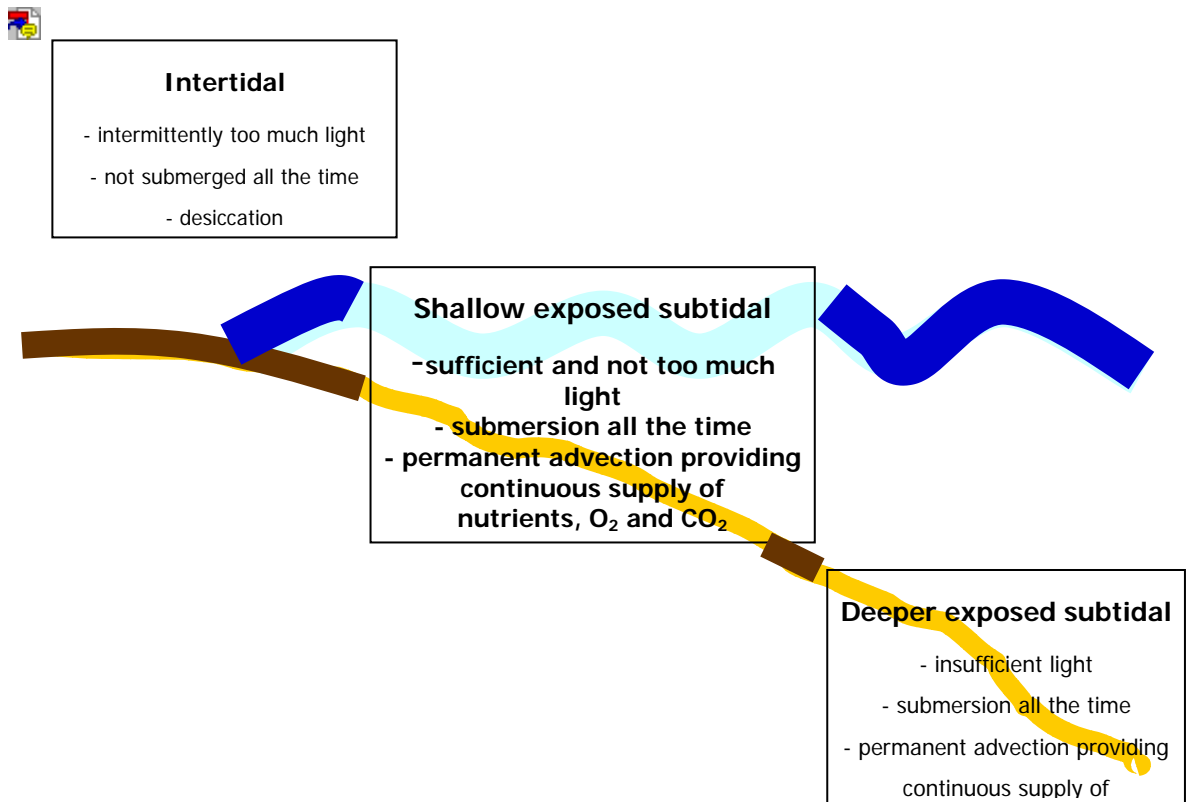


Figure 1: Scheme of advantages at the exposed shallow subtidal in comparison to the intertidal and the deeper subtidal sites.

An important characteristic of this shallow subtidal is the permanent submersion, preventing the microphytobenthos from desiccation during low tide exposure (e.g. Stal 2003). Permanent advection due to strong currents and wind induced waves is also regarded as a crucial factor. The sediment is continuously supplied with organic material transported from the overlying water column into the sediment. Due to enhanced mineralization through advection there were consistently higher nutrient concentrations in the sediment than in the overlying water column. In the intertidal, supply of organic material and nutrients through the water column is only possible when the tide is in. Furthermore, the pore water with the nutrients may drain out of the upper

sediment during low tide (Nielsen 1990, Billerbeck et al. *subm.*). The microphytobenthos at the site has been shown to be limited by CO₂ in the absence of advection (Cook and Røy *subm.*, Wenzhöfer et al. *in prep.*). Because of constant advection, the microphytobenthos is supplied all the time with CO₂ from the water column. Tidal exposure implies that CO₂ is intermittently not advected into the sediment.

High microphytobenthic biomass was observed throughout the entire advective zone (4 – 6 cm depth). This suggests that most of the benthic biomass remained in the dark for longer periods, as light penetrates only a few mm into the sediment. A large part of the microphytobenthos therefore presumably survived in a heterotrophic mode in this layer (Admiraal 1984). Because of advective pore water flow, the microalgae in this layer are not exposed to high concentrations of ammonia and sulphide (Nelson et al. 1999), which become toxic compounds for benthic microalgae when they occur in high concentrations (Admiraal 1984).

Grazing was probably not responsible for the spatial variation along the transect. Macrofauna densities were low (Weslawski et al. *in prep.*) and at moderate densities of some grazers are known to stimulate algal growth and gardening may be achieved by excretion of ammonia and mucus. In sand, mainly bioturbating macrofauna may depress microalgal growth by frequent burial (Reise 1996), but this was probably not the case in this study.

Seasonal characteristics

During this study seasonal patterns could be identified for permeability, pore water nutrient concentrations and organic matter degradation. Other parameters showed no clear seasonality, like the microphytobenthic biomass. The main factors driving seasonality in the advective zone are probably light, temperature and the import of organic matter. A conceptual model is presented in Figure 2.

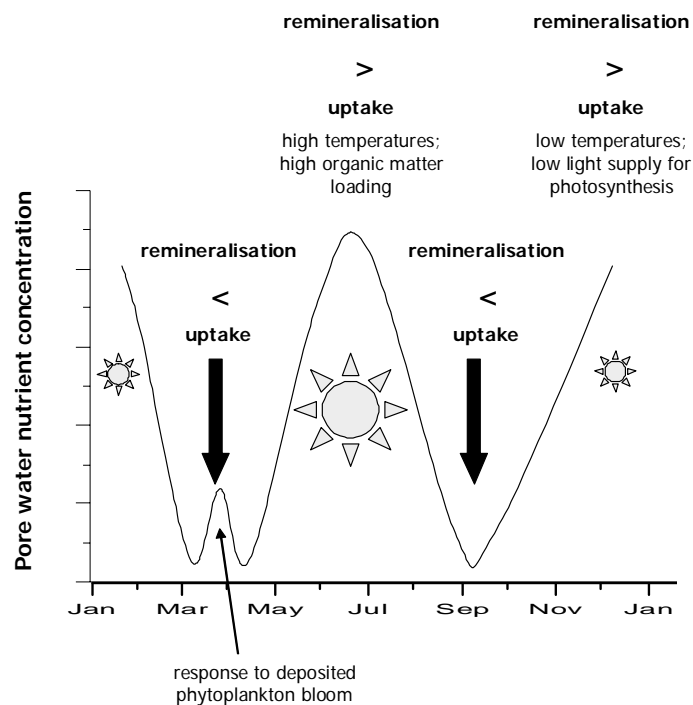


Figure 2: Scheme of seasonal pore water dynamics referring to mean concentrations in the upper 5 cm of the sediment of Si(OH)_4 , NH_4^+ and PO_4^{3-} .

An additional factor influencing the pore water nutrient concentrations especially in deeper sediment layers was water inflow from below with lower salinities and high Si(OH)_4 and NH_4^+ concentrations, also varying seasonally.

Winter

Increasing mean average wind speeds led to more wind induced waves and thus to high sediment permeability presumably because of changed consolidation and loss of fine particles from the sediment due to enhanced resuspension (Chapter 2). The water temperatures were low. Light reaching the sediment was probably insufficient for high primary production. Therefore the pore water concentrations in the upper 5 cm of the sediment remained high, being supplied by the transport of overlying water with high nutrient concentrations into the sediment and with additional remineralization in the sediment. Nutrient dynamics in the pore water and in the water column followed the same course during winter (Chapter 3). The microphytobenthic biomass was high (Chapter 4). Inflow of water with low salinities and high nutrient concentrations from below added to the nutrient concentrations in the sediment (Chapter 3).

Spring

During spring the mean average wind speed was higher than during summer and autumn and wind induced waves led to higher permeability of the sediment (Chapter 2). Mean pore water nutrient concentrations in the upper 5 cm of the sediment followed the same dynamics as nutrients in the water column. Water temperatures were still low. When the light was sufficient enough for the phytoplankton and microphytobenthos to commence with photosynthesis, the nutrient concentrations in the water column as well as in the sediment began to decrease. Following the phytoplankton bloom in the water column, a short peak in pore water nutrient concentrations occurred, presumably because of enhanced mineralization of deposited phytoplankton (Chapter 3). The benthic biomass in the upper first centimetre was higher during spring than during other sampling time in both years. Integrated over a sediment depth of 10 cm, the biomass showed no seasonality (Chapter 4). Also during spring, water of

low salinities and high nutrient concentrations was upwelling in the sediment (Chapter 3).

Summer

Permeability decreased in summer presumably because wind had calmed down and wind induced waves weak. More fine fraction in the sediment probably also led to reduced permeability (but this was not significant). Advection remained all the time possible (Chapter 2). High biomass was found in the first summer (2003), while in the second summer (2004) lowest biomasses of the whole sampling time were observed. There was enough light for photosynthesis in the sediment as well as in the water column, which led to high organic matter loading in the sediment. Because of higher temperatures and higher organic matter loading, remineralisation was higher than uptake by phytobenthos as indicated through the summer maximum of mean pore water concentrations in the sediment of Si(OH)_4 , NH_4^+ and PO_4^{3-} . This was more pronounced in summer 2003 with the higher temperatures than in summer 2004 (Chapter 3).

Late summer / early autumn

Permeability in late summer / early autumn was still lower than in winter and spring, presumably because of low wind speeds and weak wind induced waves. The permeability is probably also influenced by the extrapolymeric substances (EPS) content in the sediment, which is known to stabilize sediments and change permeability (Cahoon 1999). However this factor was not significant (Chapter 2). Nutrient concentrations in the upper 5 cm decreased and were about the same level as in the overlying water column at the beginning of autumn. Presumably the reason for this were lower water temperatures and thus reduced mineralization in the sediment. Also the organic matter input from the overlying water column was low because the primary production in the water column was probably nitrogen limited. Light for photosynthesis remained sufficient. The EPS content of the sediment increased at the end of

summer, indicating overflow metabolism of the microphytobenthos during nutrient limitation (Blanchard et al. 2000).

Autumn

When the light was too low for photosynthesis in the benthos and in the water column the mean nutrient concentrations in the upper 5 cm of sediment as well as in the overlying water column started to increase again and followed the same dynamics. Pore water nutrient concentrations were higher than in the overlying water column indicating that the sediment is a major source for the nutrient increase (Chapter 3). The benthic biomass remained at a high level (Chapter 4).

Concluding remarks

Some of the hypotheses on drivers, processes and fluxes could be confirmed during this study, whereas others need further investigations and others were incidentally recognized during sampling (Figure 3, extended version of the conceptual model presented in Chapter 1).

The study showed continuously high microphytobenthic biomass at the study site, suggesting that shallow exposed permeable sandy sediments are an optimum habitat. Through permanent advection, the sediment is an expansive filter system, supplying the benthos with particulate organic matter, oxygen and CO₂ and allowing a high microphytobenthic biomass throughout the year.

Comparing the phytoplankton biomass of the overlying water column and benthic biomass of the uppermost centimetre of the sampling site, the benthic biomass was consistently and substantially higher.

From end of spring until late summer probably enough light reaches the sediment at in the shallow subtidal to enable primary production (Loebl pers. comm., Hedtkamp unpublished data, Wenzhöfer et al. in prep.). Former studies in this area estimated a contribution of the microphytobenthos to total primary production to be 45 %, based on measurements in the intertidal (Gätje and Reise 1998). In this estimate the shallow subtidal with its high primary production (Hedtkamp unpublished data, Wenzhöfer et al. in prep.) is missing. The real value is probably substantially higher and needs more investigations over the entire depth range of the tidal channel in the List-tidal basin.

As the microphytobenthic biomass was high during the whole sampling period and was also high in deeper sediment layers, this could be an important food source for meio- and macrofauna. The macrofauna abundance was relatively low at the sampling site (Weslawski et al. in prep). In contrast the meiofauna

dominated by nematodes showed high abundances in comparison to other studies and other regions (Urban – Malinga pers. comm.).

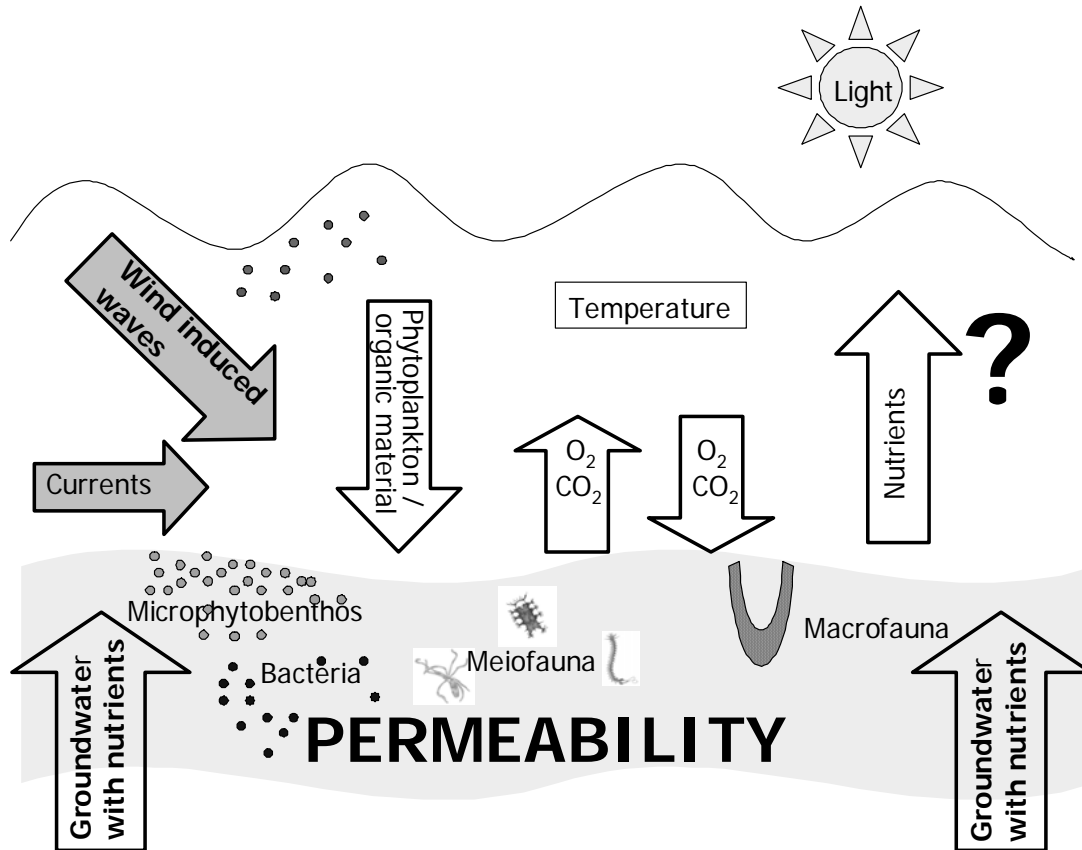


Figure 3: Scheme of factors influencing fluxes, the main fluxes and groups of organisms in exposed shallow subtidal permeable sand.

The organic content of the sediment at the sampling site was permanently low but of high quality. Approximately 50 % of the total organic carbon in the upper layers was associated with living microphytobenthos. Also the rest of the organic carbon correlated significantly with the chlorophyll *a* content of the sediment. Bacteria cell counts showed high cell numbers, comparable to numbers from sandy and muddy intertidal sediments. The activity of the bacteria was lower compared to muddy sediments but higher than in the water column and showed a temperature dependent variation (higher during summer than during winter) and correlated strongly with the chlorophyll *a* content of the

sediment (Böer pers. comm.). This also indicates organic matter which is easy to degrade. The sediment performs as an expansive biocatalytical filter system.

Nutrient fluxes from the sediment into the overlying water column were not measurable (Hedtkamp unpublished data) and lead to the question if this was a methodological problem or if there was no detectable flux to the water column, because nutrients are assimilated by the microphytobenthos before they could enter the water column. This topic needs more investigations.

One could argue, that the sampling station was not optimally chosen, because especially in winter 2004 and spring 2005 groundwater inflow with lower salinities and higher nutrient concentrations occurred and influenced the dynamics at the sampling station. However, these groundwater flows probably occur along the whole shore of the island of Sylt (see Bayerl and Higelke 1994, Zipperle and Reise 2005). Also recent studies showed that inflowing groundwater is a common phenomenon along coasts (e.g. Crossland et al. 2005 and references therein) which need more investigations.

This study shows that permeable sand in the shallow subtidal may attain a crucial role in the cycling of matter and in budget of ecosystem fluxes in a tidal basin of the North Sea coast.

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Kiel,

Stefanie Hedtkamp

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