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Phosphorus recycling and availability in the western Wadden Sea

Fosfor recycling en beschikbaarheid in de westelijke Waddenzee
(met een samenvatting in het Nederlands)

Regeneração e disponibilidade de fósforo no Mar de Wadden Ocidental
(com sumário em português)

Proefschrift
ter verkrijging van de graad van doctor aan de Universiteit Utrecht op gezag van de rector magnificus, prof.dr. G.J. van der Zwaan, ingevolge het besluit van het college voor promoties in het openbaar te verdedigen op woensdag 17 december 2014 des middags te 2.30 uur

door
Catarina Maria de Freixo Leote
geboren op 23 februari 1983 te Lisboa, Portugal

Promotor: Prof.dr. P. Van Cappellen
Copromotor: Dr. E. Epping

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Para os meus pais, Eurico e Luisa,
por todos os motivos e mais alguns

"Segue o teu destino,
Rega as tuas plantas,
Ama as tuas rosas.
O resto é a sombra
De árvores alheias.

A realidade
Sempre é mais ou menos
Do que nós queremos.
Só nós somos sempre
Iguais a nós-próprios.

Suave é viver só.
Grande e nobre é sempre
Viver simplesmente.
Deixa a dor nas aras
Como ex-voto aos deuses.

Vê de longe a vida.
Nunca a interrogues.
Ela nada pode
Dizer-te. A resposta
Está além dos deuses.

Mas serenamente
Imita o Olimpo
No teu coração.
Os deuses são deuses
Porque não se pensam."

Ricardo Reis

"The important thing is not to stop questioning. Curiosity has its own reason for existing"

Albert Einstein

CONTENTS

Chapter 1

Introduction

1. The chemistry of phosphorus and its economical, biological and environmental importance

Phosphorus (P) is a relatively scarce element on the planet, ranking about 10th in terms of abundance in the upper crust and with an average concentration of 0.1% by weight (Canfield et al. 2005). It shows a diverse chemistry and exists in oxidation states between −3 and +5 (PH_3 to P_2O_5). Its pentavalent state, usually as part of the orthophosphate ion (PO_4^{3-}) is by far the most abundant and the only one stable under natural aqueous conditions, meaning that biological systems are limited to the +5 state (Canfield et al. 2005). In aquatic media and depending on pH, P can exist in the form of phosphoric acid (H_3PO_4), di-hydrogen phosphate ($H_2PO_4^{-}$), hydrogen phosphate (HPO_4^{2-}), and phosphate (PO_4^{3-}), with pK_a values of 2, 7, and 12. In seawater, with a pH of approximately 8, HPO_4^{2-} is the dominant form (87%), followed by PO_4^{3-} (12%) and $H_2PO_4^{-}$ (1%). As a tri-valent anion, PO_4^{3-} interacts with dissolved cations and positively charged interfaces, with 99.6% of PO_4^{3-} and 44% of HPO_4^{2-} species being complexed by sodium (Na^{+}), magnesium (Mg^{2+}), and calcium (Ca^{2+}) in seawater (Kester and Pytkowicz 1967) (Figure 1).

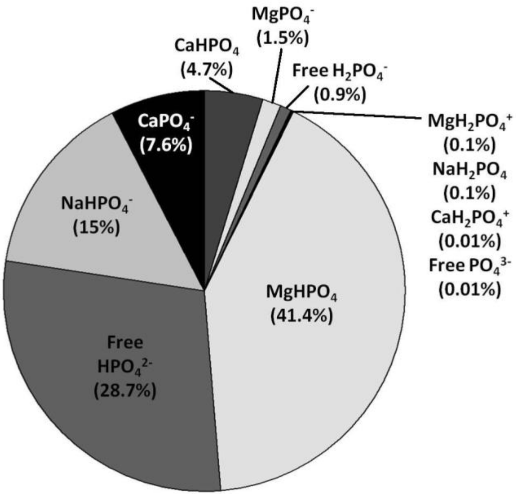

Figure 1. P speciation in seawater. Adapted from Ruttenberg (2004).

Phosphorus is an essential element for life for which, in spite of recent research suggesting arsenic as a potential replacement in microbial DNA, no substitute is known (Cressey 2012). Essential biological compounds such as proteins, enzymes, and DNA/RNA contain phosphate, while cell membranes and bones are composed of phospholipids and calcium phosphate, respectively. Even energy in the cells is handled in the form of the phosphate compound adenosine triphosphate (ATP) (Canfield et al. 2005; Nausch and Nausch 2007).

In addition to being a fundamental element for life, P has significant economical value. It is widely used as fertilizer, herbicide/pesticide, water softener, food supplement/preservative, chemical buffer, fungicide, and anti-corrosion agent in the fields of chemical industry, agriculture, ceramics, water treatment, and metallurgy (Williams 1979). In order to meet this demand, man exploits terrestrial rock reserves mainly in the form of the Ca-P mineral apatite. Even though P reserves are formed at a much lower rate than human utilization, making it a limited resource, the total P mined throughout the history of the planet is less than 0.15% of the known reserves (Griffith 1979).

However, mankind has affected the P cycle in the past years since activities like mining, forest clearing, extensive fertilizer use in agriculture and increased industrial and domestic disposal of high P containing sewage have increased its transfer from terrestrial to aquatic systems (Stumm 1973; Nausch et al. 1999). Since P is often the limiting nutrient in natural environments, the estimated 2–3 fold increase in the riverine P flux to the oceans since the beginning of the 20th century has significantly impacted freshwater and marine coastal ecosystems, often resulting in eutrophication (Crouzet et al. 1999; Ruttenberg 2004; Clarke et al. 2006). The minimization of the P transfer between reservoirs becomes essential to reduce its loss and harmful accumulation and the application of adequate policies requires a good understanding of the distribution and exchange of P between the multiple reservoirs.

2. The phosphorus cycle

Phosphorus is distributed between several reservoirs on the planet. Marine sediments and land rocks represent the largest reservoir (8.4–40.3 x 10^{20} g and approximately 50% of total P) followed by land soil (9.6–19.9 x 10^{16} g). In addition to the sedimentary reservoir, ocean waters contain a large amount of dissolved P (9.0 x 10^{16} g), mostly between 300 and 3300 m depth. Important fractions are also "stored" in oceanic and especially land biota (0.5–1.4 x 10^{14} and 26.0–30.0 x 10^{14} g) while the atmospheric P reservoir is almost negligible (3.0 x 10^{10} g) when compared with the other pools. The total biologically active pool, comprising the organic and dissolved (in-)organic fractions, accounts for only about 0.01% of sedimentary/rock P and only 1% corresponds to living biomass. The residence time, depending on the difference between input and output fluxes from a specific reservoir, is largest for sedimentary and rock deposits (4.2–20.1 x 10^7 years), followed by land soil (4.3–23.1 x 10^2 years) and dissolved P in the deep sea (15.0 x 10^2 years) (Ruttenberg 2004).

The cycle of P, shown in Figure 2 in a simplified version, takes about 1 x 10^9 years to be completed, with the diagenetic transformation of P into sedimentary rock as the slowest step (Pierrou 1979). Briefly, P is concentrated in the ocean sediments as phosphorite, a sedimentary rock containing at least 20 % of apatite [$Ca_{10}(PO_4)_6(OH,F,Cl)_2$] (Griffith 1979). Tectonic uplift or volcanic activity will expose the high P content rocks to physical and chemical weathering forces resulting in the formation of soils at an annual flux of 20 x 10^{12} g P (McConnel 1979; Ruttenberg 2004). After soil formation, P becomes available for uptake by terrestrial biomass with 63–236 x 10^{12} g P year^{-1} being incorporated in plants (Pierrou 1979; Ruttenberg 2004). Later transport to aquatic systems occurs via groundwater transport and surface runoff. The anthropogenic impact on the P cycle is particularly important in this step due to the use of fertilizers in agriculture. Fertilizers represent an additional and faster source of P to soils compared with the slower supply due to natural weathering, thereby increasing the mass transfer of P to aquatic systems. Before reaching the estuarine zone and ultimately the ocean, P will likely be exchanged between different reservoirs, being temporarily stored and recycled several times due to uptake by algae and macrophytes, exchange with the sediments, degradation of organic material, sorption, precipitation, and resuspension (Froelich et al. 1982; Meybeck 1982; Santschi 1995).

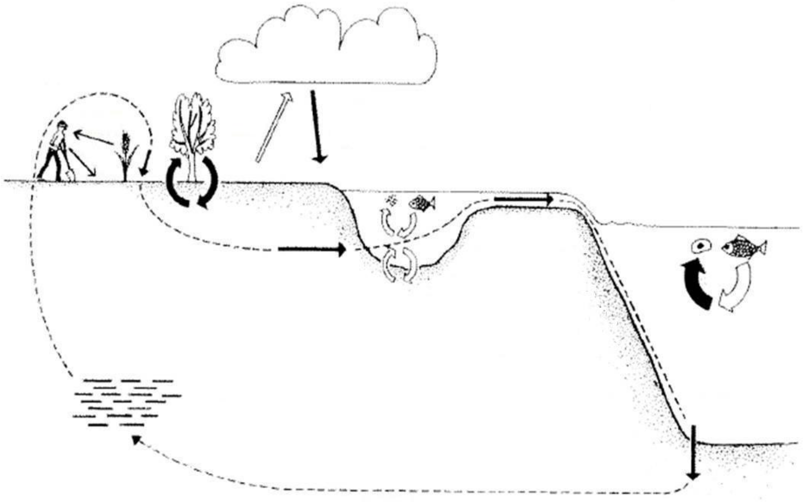

Figure 2. Simplified cycle of phosphorus. Adapted from Pierrou (1979).

3. Phosphorus in the marine environment

River runoff represents the largest flux of P to the marine environment and has been estimated at 17.4–39 x 10^{12} g P $year^{-1}$ (Pierrou 1979; Froelich et al. 1982; Ruttenberg 2004) while Meybeck (1982) estimated a transport of 2 x 10^{12} g P $year^{-1}$ in the dissolved form and 20 x 10^{12} g P $year^{-1}$ as particulate P. Additional fluxes such as the deposition of atmospheric P, adsorbed to particulate matter or dissolved in sea spray, constitutes only a minor flux of 0.6–3.5 x 10^{12} g P $year^{-1}$

(Pierrou 1979; Ruttenberg 2004) whereas groundwater P discharge to the coastal zone still remains poorly quantified.

Riverine concentrations of dissolved inorganic P are thought to be largely controlled by sorption onto particulate matter (Froelich 1988; Lebo 1991). In the estuary zone, freshwater is mixed with waters of higher salinity. As a consequence of increased anion competition for sorption sites, P is released from the particulate matter, increasing the dissolved P concentration. An additional increase in the concentration of dissolved P in estuaries results from the recycling of organic P (Lebo 1991; Spiteri et al. 2008). Conversely, P uptake by biota and adsorption to newly formed metal organic rich colloids tend to remove P from the dissolved pool.

3.1 Water column

One important feature of the P cycle in the water column is the conversion of dissolved P to the particulate form due to uptake by algae/bacteria through primary production (Corner 1973). After reaching the coastal zone, part of the discharged P will be taken up by primary producers for growth together with carbon (C), nitrogen (N), and silica (Si) at a ratio of about 106C:16N:15Si:1P (Redfield 1958; Brzezinski 1985). Phosphorus is often limiting both the growth rates and biomass formation since C is always in excess as HCO_3^-/CO_2 and N can be introduced in the aquatic system by organisms fixing atmospheric N_2 (Capone and Carpenter 1982). The dissolved inorganic form of P is preferred for uptake and further assimilation, even though scarcity may induce primary producers to exploit particulate and organic P, through extracellular enzymatic degradation to phosphate by the exoenzyme phosphatase (Fogg 1973; Nausch and Nausch 2006; 2007). Another strategy to meet the P demand for biosynthesis is excess uptake, followed by storage as polyphosphates, to be used when P is not available (Fogg 1973). This may point to a higher accumulation of P in living biomass than initially thought, even though attempts to measure it in the water column revealed very low concentrations (Solórzano and Strickland 1968). The use of the Redfield ratio to assess nutrient limitation is no longer straightforward since under apparent external limitation, algae cells can still meet their demands for P by consuming their internal reserves and through a fast preferential degradation of organic P over N in the water column (Ruttenberg 2004). Overall, the oceanic uptake of P by phytoplankton has been calculated as 600–1300 x 10^{12} g P year^{-1} of which up to 30% will deposit in the bottom sediments, to be recycled and returned to the water column or stored for a prolonged period of time in marine sediments (Stumm 1973; Pierrou 1979; Ruttenberg 2004).

3.2 Sediments

In addition to the organic form, particulate P reaching the sediments includes P bound/sorbed to iron (Fe), Ca, and manganese (Mn) compounds and clays and terrestrial detrital apatite (Froelich et al. 1982). Part of the deposited material, like terrestrial detrital apatite or refractory organic matter, will not react in the sediment and be buried. Degradable organic material and loosely bound P, however, can be transformed in the sediment, exchanging P between dissolved and particulate forms. The dissolved fraction may, to some extent, exchange with the overlying water, while particulate forms usually remain stored in the sediment. Thus, sediments are complex reactive sites for P, which may act both as a source and a sink for P in the water column. The timing and magnitude of sedimentary P processing may control the availability of dissolved P in the productive water column, thereby directing the trophic system that relies on primary production for food and energy.

3.2.1 Production

The main process responsible for the increase of dissolved P concentrations in the porewater is the degradation (oxidation) of organic material by consortia of heterotrophic microorganisms, in a process called mineralization. The concentrations of organic matter and microbial communities in sediments are much higher than in the water column, resulting in rates of respiration 1–2 orders of magnitude higher in sediments than in the water column (Jørgensen 1977). A range of electron acceptors is used in the oxidation of organic matter, with the stronger oxidants, yielding the highest amounts of energy, being used first. Given the stoichiometric coupling between the oxidation of organic matter and the consumption of electron acceptors such as oxygen (O_2), Fe, and Mn oxides, nitrate or sulfate, the degradation of organic matter can be described by the following set of equations (Jørgensen 1983; Chester 2000). Oxygen is the strongest oxidant widely available to biota being consumed first in a process often referred to as aerobic mineralization:

$$5\ (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 690\ O_2 \rightarrow 530\ CO_2 + 80\ HNO_3 + 5\ H_3PO_4 + 610\ H_2O$$

As O_2 becomes depleted at higher depth, the redox potential in the sediment decreases and mineralization proceeds under anoxic conditions. The next most favorable oxidant for organic matter mineralization after O_2 is nitrate which can be used in denitrification or dissimilatory nitrate reduction to ammonium (DNRA):

$5\ (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 472\ HNO_3 \rightarrow 276\ N_2 + 520\ CO_2 + 5\ H_3PO_4 + 886\ H_2O$ (denitrification)

$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ HNO_3 \rightarrow 69\ NH_3 + 106\ CO_2 + H_3PO_4 + 53\ H_2O$ (DNRA)

Subsequently, oxides of Fe and Mn are used as electron acceptors:

$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236\ MnO_2 + 472\ H^+ \rightarrow 236\ Mn^{2+} + 106\ CO_2 + 8\ N_2 + H_3PO_4 + 336\ H_2O$

$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212\ FeO_3 + 848\ H^+ \rightarrow 424\ Fe^{2+} + 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 530\ H_2O$

When nitrate and Fe and Mn oxides are absent or in very low concentrations, sulfate is used as an electron acceptor:

$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 55\ SO_4 \rightarrow 55\ S^{2-} + 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 106\ H_2O$

Once sulfate is depleted, C can be used as an electron acceptor in acetate fermentation to methane, according to the following equation (Canfield et al. 2005):

$CH_3COOH + 4\ H_2 \rightarrow 2\ CH_4 + 2\ H_2O$

Manganese/Fe oxide and sulfate reduction result in the production of reduced manganeous (Mn^{2+}) and ferrous (Fe^{2+}) ions and sulfide (HS^- and H_2S). These compounds tend to diffuse to the upper oxic layer where they will be oxidized, regaining their power as electron acceptors at the expense of stronger oxidants like O_2 and nitrate. These species also interact chemically, resulting in the precipitation of Fe-sulfide minerals like mackinawite (tetragonal $Fe_{(1+x)}S$), greigite (cubic Fe_3S_4), and pyrite (FeS_2) (Price 1976). Once formed, these minerals, and especially pyrite, will not be dissolved easily, thereby removing sulfur (S) and Fe from the redox system. The availability of Fe oxides is then decreased in the longer term, since re-oxidation is limited by physical and biological mechanisms transporting deeper anoxic sediments into more oxidized surface layers.

The distribution of electron acceptors according to their oxidizing potential (Figure 3) results in a vertical diagenetic zonation in the sediment with well defined redox reaction zones and a redox boundary, where the conditions in the sediment change from oxidizing (positive redox potential) to reducing (negative redox potential).

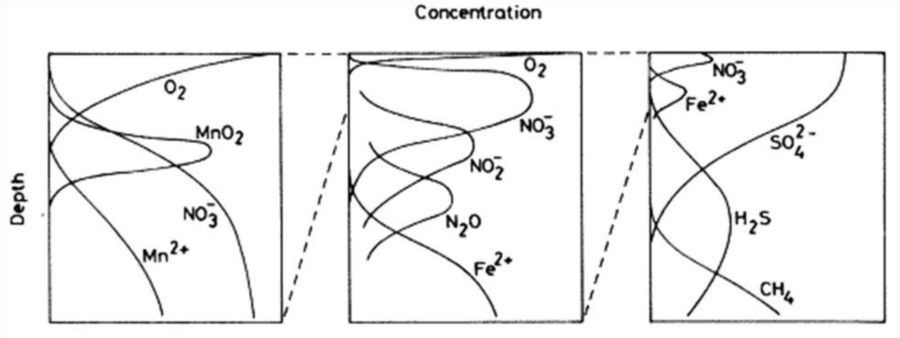

Figure 3. Vertical distribution of oxidizers and their reduced forms in the sediment to illustrate the diagenetic distribution of electron acceptors used in mineralization. From Jørgensen (1983).

The rate of mineralization depends not only on the availability of electron acceptors, but foremost on the quality and availability of the organic material (Jørgensen 1983). The compounds that are easier to metabolize will be degraded first, so that the relative concentration of refractory material increases with time, i.e with depth in a sediment (Berner 1980). As a consequence of organic matter degradation (with a typical preferential degradation of P over N and C), the porewater will be enriched in dissolved inorganic P (Ingall and Van Cappellen 1990; Edlund and Carman 2001). A fraction of the dissolved P will be released to the overlying water whereas the remaining will be retained in the sediment.

3.2.2 Retention

Sediments are known for retaining P, hampering the release to the water column for a variable period of time. Short-term retention occurs in the dissolved form, with P (and other nutrients) being temporarily stored in the porewater before transport to the overlying water. However, this is a highly transient condition, with longer term retention involving the conversion of dissolved P into a particulate form (Figure 4). Depending on the chemical stability of the particulate P formed and on sediment conditions such as O_2 availability and pH, the time scale of retention ranges between hours/days to permanent (Jensen and Thamdrup 1993; Jensen et al. 1995; Ruttenberg and Goni 1997).

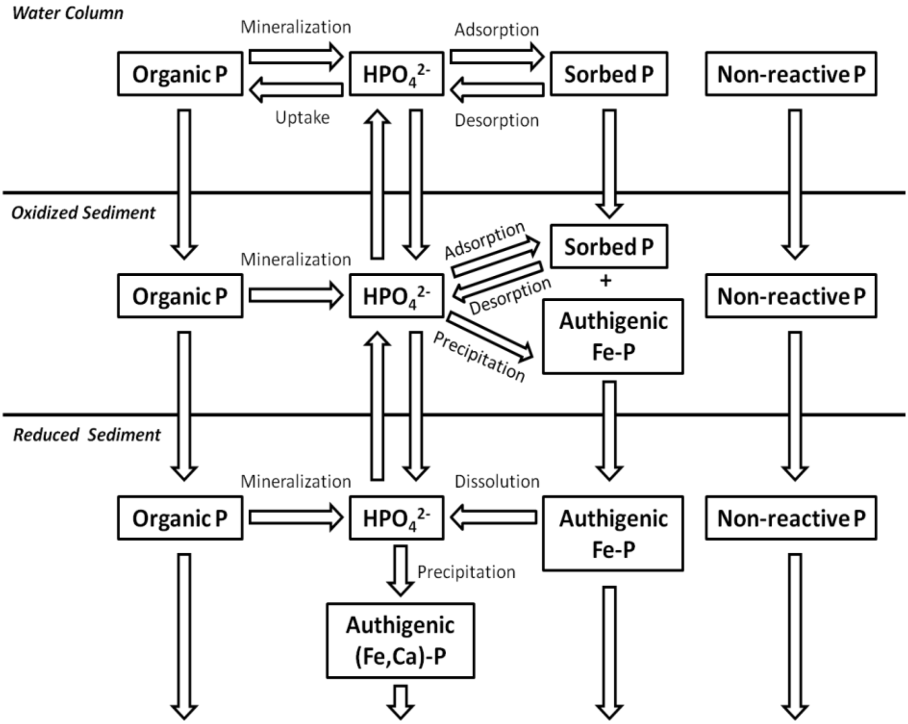

Figure 4. Phosphorus distribution in the sediment

Close to the sediment surface, the availability of O_2 allows for the presence of metal oxides, particularly of Mn, aluminum (Al), and Fe, which have a high sorption capacity for P and act as a filter before P release to the overlying water (Krom and Berner 1980a, 1981; Sundby et al. 1992; Matthiesen et al. 2001). In addition to metal oxides, clay minerals and calcite/aragonite are also known for adsorbing P (Pomeroy et al. 1965; Millero et al. 2001). Sorption is a chemical binding process based on the electric charges between adsorbant and adsorbate, creating the so-called “sorption sites” (Peinemann and Helmy 1977; Lijklema 1980; Goldberg and Sposito 1984). The extent of sorption depends on the concentration of sorption sites and on the concentrations of dissolved and adsorbed fractions of P, as well as of all ions that can compete for the sorption sites. A list of well-known competitors for P sorption in marine sediments includes sulfate (Caraco et al. 1989; Geelhoed et al. 1997), bicarbonate (Millero et al. 2001), silicate (silicon hydroxide) (Tuominen et al. 1997; Tallberg et al. 2008), humic and fulvic acids (Hawke et al. 1989; Weng et al. 2008), and hydroxyl ions (Neméth et al. 1998; Gao and Mucci

2001; Mustafa et al. 2006). Consequently, a higher salinity or pH result in decreased adsorption or even desorption of P (Hawke et al. 1989; Yao and Millero 1996; Koski-Vähälä et al. 2001). Once adsorbed to the surface of clay minerals and metal-oxides, P may migrate to their inner structure. This so-called "slow-sorption" or solid state diffusion increases the solid phase stability of P, allowing retention for a longer time period (Froelich 1988).

Another process resulting in longer term storage is the precipitation of authigenic minerals containing P. The availability of O_2 at the oxic/anoxic interface allows for the precipitation of Fe-P minerals, such as strengite, ferrihydrite, akageneite, and amorphous oxides (Slomp et al. 1996a; Hyacinthe and Van Cappellen 2004). Deeper in the sediment, the increase of the dissolved P concentrations, due to the mineralization of organic matter, P release from diatom cell polyphosphates and dissolution of Fe bound P and fish bones, results in exceeding the saturation constants for the precipitation of other authigenic P minerals, such as vivianite or carbonate fluorapatite (Van Cappellen and Berner 1988; Slomp et al. 1996b; van der Zee et al. 2002; Diaz et al. 2008). While the prevalence of vivianite as an oceanic authigenic mineral is unclear and may be restricted to areas with high Fe loading, apatite represents the largest P pool on the planet and the major form of oceanic P burial (Ruttenberg and Berner 1993) with 8–13 x 10^{12} g P year^{-1} that deposit in the sediment being converted to carbonate fluorapatite (Pierrou 1979; Ruttenberg 2004). Large accumulations of apatite result in the slow formation of the large sedimentary deposits of phosphorites, which remove P from the oceanic pool for such a long time period that it can be considered as permanent retention (Ruttenberg 2004). Other recently discovered authigenic minerals, that may significantly contribute to oceanic P removal are aluminophosphates often enriched with rare earth elements (Rasmussen 2000).

An important characteristic of sediment P is the "sink-switching", which is the transfer of P from one reservoir to another. Exchange between reservoirs often occurs several times before release to the overlying water, enhancing the retention period in the sediments (Ruttenberg and Berner 1993; Slomp et al. 1996b; Louchouarn et al. 1997). However, the efficiency and duration of sediment P storage also depends on the mechanisms transporting P to the overlying water. If transport is fast, the time for conversion of dissolved P into a particulate form will be less and consequently, retention will be lower.

3.2.3 Transport

The production and retention processes affecting the concentration of dissolved P in the porewater have been discussed above. However, for release to the overlying water, P must be transported to the sediment-water interface.

Various transport processes tend to resolve the concentration gradients, resulting in sediment-water exchange of solutes. Molecular diffusion can often be assumed as the main transport process. In that case, the magnitude of the benthic flux can be estimated using Fick’s first law of diffusion: $F = -\phi D_{sed}\, dC/dz$, which relates the flux F, with the diffusion coefficient D_{sed} (a coefficient of proportionality per unit of area that depends on the nature of the medium, the diffusing material and temperature) and the vertical concentration gradient dC/dz (Krom and Berner 1980b, 1981; Sundby et al. 1992). Since molecular diffusion can only occur in the sediment’s pore space, the effective diffusion will be lower than in a bulk solution. To account for the reduction in effective diffusion area and for the increased path length between two points, the diffusion coefficient in the bulk solution D, is multiplied with porosity and divided by tortuosity (Lerman 1979).

The effect of waves, strong tidal currents or groundwater discharge also results in the displacement of pore water relative to the sediment matrix, or sometimes even in the resuspension of sediment (Huettel et al. 1998; Burnett et al. 2003; Beck and Brumsack 2012). The transport of solutes is then enhanced by advective processes, in addition to molecular diffusion. Advective mass transfer is quantified as the product between the concentration/density of the solute/particle and the flow velocity which is regarded as the driving force of the flux. In porewater the flow velocity depends on the properties of the fluid (viscosity, density) and of the sediment (porosity, grain size, sorting) (Lerman 1979).

The activity of benthic macrofauna may also assume an important role in transporting both sediment particles and porewater. Some benthic macrofauna mix the sediment top layer in a process called bioturbation (Krantzberg 1985; Aller 1994; Boudreau 1998). Even though both particles and porewater are mixed, the effect of bioturbation is more significant for the mixing of particulate material like organic matter and inorganic sediment particles. On the other hand, bioirrigation due to the ventilation of burrows represents a very efficient mechanism for the exchange of water and solutes between deeper sediment layers and the overlying water (Aller and Aller 1998; Kristensen and Hansen 1999). Bioturbation and bioirrigation are highly variable both temporarily and spatially and difficult to quantify, since they depend on the species composition of the macrofauna community and several abiotic factors that will affect their activity such as temperature, food availability, and grain size.

3.2.4 Release

The sediment-water exchange can be mathematically described as the sum of all transport and reaction (production and retention) terms (Berner 1980). The description is far from straightforward since several processes are involved at the same time. The transport term, for example, is usually the result of molecular diffusion and advection/bioirrigation acting together, while the availability of P in the porewater depends on the cumulative action of several processes. Besides mineralization, desorption and dissolution of P minerals are responsible for an increase in the dissolved P concentrations, while biological uptake, adsorption, and precipitation will remove P from the porewater. However, the mineralization of organic matter is assumed to represent the main process for the production of dissolved P in the porewater while sorption is usually the most efficient reversible process temporarily retaining P. By controlling the availability of dissolved P, these two process are often assumed as the main controls on P release to the overlying water (Krom and Berner 1980a; Froelich et al. 1982; Sundby et al. 1992). Temperature, pH, redox conditions, salinity, and O_2 and organic matter availability are known to strongly affect both mineralization and sorption and to vary significantly on a seasonal and (horizontal and vertical) spatial scale. Consequently, seasonal and spatial changes in the release of P are expected, especially in coastal areas, where the environmental conditions are extremely variable (Nur and Bates 1979; Gunnars and Blomqvist 1997).

4. Phosphorus in shallow coastal environments

Shallow coastal environments share several characteristics that render them particularly complex when compared with open ocean settings. Examples are the higher interaction between sediment and water column, the increased complexity of sediment nutrient recycling and the high spatial and temporal heterogeneity in the environmental conditions.

The high riverine input of organic matter and nutrients boosts primary production in coastal waters. Consequently, in spite of covering only a small fraction of the ocean, coastal areas account for 18–33% of the total primary production in the ocean and, due to the reduced water depths, most of organic matter recycling takes place in the sediments (Jørgensen 1983). As a consequence, O_2 is quickly consumed. Aerobic mineralization is limited to the top mm of sediment and accounts for roughly 10% of total mineralization (Jørgensen 1977; 1983). Thus, most organic material in coastal areas is degraded under anoxic conditions, unlike the open ocean. Denitrification accounts for about 20%, while sulfate reduction is responsible for 20–50% of total mineralization in organic rich environments (Jørgensen 1977). The contribution of Fe/Mn oxides to total mineralization is usually very small, except when their availability is particularly high (Canfield et al. 2005). Nevertheless, their effect on the transient behavior of P in the sediment is important, due to the close coupling between the P, Fe, and S cycles. The sorbed/precipitated Fe-P reservoir is the main temporary pool in most coastal environments (van Raaphorst and Kloosterhuis 1994; Slomp et al. 1996, 1997) with P being released following the reductive dissolution of Fe oxides due to mineralization (Krom and Berner 1980a; Sundby et al. 1992; Jensen et al. 1995). Given the importance of sulfate reduction in coastal areas, large amounts of sulfide are produced in the sediments, which will quasi-permanently remove Fe from the system through the precipitation of Fe-sulfides with no sorptive capacity, such as pyrite (Krom and Berner 1980a; Caraco et al. 1989). The sorption capacity of the sediment is then almost irreversibly decreased, since Fe will no longer be re-oxidized and retain P in the oxic layer.

The reduced water column depth also renders the sediment more vulnerable to changing environmental conditions. Considering a generalized seasonal scenario, in winter, lower temperatures and a reduction in the availability of labile organic matter lead to low mineralization rates and increased O_2 availability. The balance between precipitation and reductive dissolution of Fe and Mn oxides is favored towards the precipitation, increasing the concentration of sorption sites and enhancing the retention (Sundby et al. 1986; Sundbäck and Granéli 1988; Spears et al. 2006). The lower production of P, allied to a stronger potential for retention, results in lower concentrations in the porewater. Since the concentrations in the water column are usually higher in winter, due to the lower uptake by phytoplankton, the concentration gradient between the overlying water and the sediment is reduced. Transport by molecular diffusion will be lower and so is the expected release. Nevertheless, advective transport due to waves and bottom currents, usually higher in winter due to storms, potentially enhances the release and may compensate for the lower diffusive transport. On the other hand, in spring, the bloom of primary producers supplies the sediment with fresh organic material, which may enhance mineralization and O_2 consumption, especially as water temperature increases. The thickness of the oxic layer decreases and Fe oxides are reduced in the oxidation of organic matter and reduced compounds. This reductive dissolution results in the release of sorbed/precipitated P to the porewater and lowers the sorption capacity of the sediment. Allied to the higher production rate, the concentration gradient between the sediment and the overlying water increases, promoting the exchange (Sundby et al. 1986; Boström et al. 1988; Jensen et al. 1995; Gunnars and Blomqvist 1997). In addition, the activity of macrofauna, usually higher in spring and summer when temperatures are higher, may further enhance the release.

Summarizing, nutrient riverine discharge results in high primary productivity in coastal areas. Due to the low depth, a large fraction of the fresh organic material reaches the sediment, where it will be degraded. Part of the newly formed inorganic nutrients will be exchanged with the overlying water, potentially replenishing the water column and sustaining phytoplankton growth. Since primary producers are the basis of trophic systems, their success determines the fate of the whole ecosystem. The study of the availability of nutrients is then vital to understand natural biological systems.

4.1 The western Wadden Sea

The Wadden Sea is a confined coastal area reaching from Den Helder in the Netherlands to Ejsberg in Denmark, separated from the North Sea by a chain of barrier islands (Figure 5). It represents the largest coherent tidal flat area in the world with a large biodiversity and economical importance, which resulted in its recognition as a UNESCO World Heritage Site in 2009. Nevertheless, it suffers a significant anthropogenic impact through tourism, fisheries, sand extraction, mussel production, and freshwater discharge from areas highly impacted by agriculture.

Our study site comprises its westernmost basin, the Marsdiep, which covers approximately 700 km^2. Freshwater discharge and coastal North Sea water are considered the main nutrient sources for this area, whereas atmospheric deposition of nutrients is of minor importance, especially for P. Freshwater discharge originates mainly from Lake IJssel with sluices in Den Oever and Kornwerderzand, and to a minor extent from the harbours of Den Helder and Harlingen (van Raaphorst et al. 2000). Tidal exchange with the North Sea occurs through the Marsdiep and Vlie inlets. Nutrient supply from both sources mainly includes inorganic P (de Jonge et al. 1996) and particulate organic P to be mineralized in the Wadden Sea sediments (Postma 1954; Beck and Brumsack 2012).

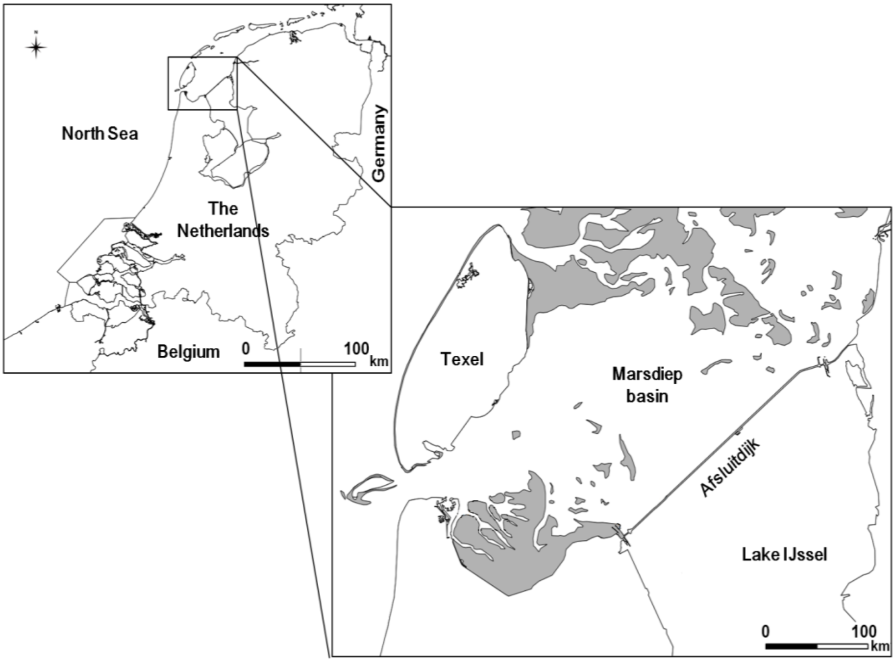

Figure 5. Map of the Wadden Sea

From the mid 1930s until the 1980s, the Wadden Sea experienced a more than 10-fold increase in the P and N loading from Lake IJssel and from the coastal zone fuelled by the rivers Rhine and Meuse (van Raaphorst and de Jonge 2004). The elevated nutrient supply induced several changes such as an increase in primary production and mineralization rates, sporadic anoxia, increased turbidity, proliferation of opportunistic macroalgae, seagrass decline, and changes in the benthic and pelagic communities (van Beusekom and de Jonge 2002; van Beusekom 2005). These eutrophication signs led to the implementation of more stringent environmental policies in the bordering countries of the Wadden Sea, such as the removal of P from washing powders and restrictions in the use of fertilizers. By the end of the 1980s, the discharge of total P and N had decreased to values 2.5 and 5-fold the initial ones. Nowadays, P concentrations are close to the pre−1950s background concentrations while N is still 5.5 fold higher, resulting in a high N/P ratio (van Raaphorst and de Jonge 2004; Colijn and van Beusekom 2005).

During the period of eutrophication, primary production increased from 20 g C m^{-2} (1950) to 520 g C m^{-2} (1986) and remained high until the 2000s (van der Veer et al. 1989; Cadée and Hegeman 1993; de Jonge 1997; Philippart et al. 2000; Kuipers and van Noort 2008). Concomitant changes in productivity and species composition were observed for several trophic levels, suggesting a direct coupling between nutrient input in terms of quantity and elemental ratios, primary production and the transfer of primary carbon to higher trophic levels (Philippart and Cadée 2000; Philippart et al. 2007; Kuipers and van Noort 2008). Nowadays, the high N/P ratio and the presence of a phytoplankton community typical from P limited systems, suggests P as the limiting factor of the Wadden Sea trophic system. The study of P dynamics is then essential to understand the western Wadden Sea ecosystem.

The capacity of the sediments to recycle and temporarily retain large amounts of P makes them potentially responsible for the remaining relatively high primary production. The importance of the Wadden Sea sediments for nutrient recycling has already been suggested by Postma (1954) with import of organic material from the North Sea followed by mineralization in the Wadden Sea and export to the coastal zone. Nowadays, in addition to mineralization of autochthonous and allochthonous organic matter, the released P may also include P stored in the sediment during the high loading period. At present, some information is available regarding sediment P dynamics in the western Wadden Sea. Postma's formulation was confirmed by the modeling study of van Raaphorst et al. (1988), who estimated that 70% of P reaching the sediment is recycled and released back to the overlying water. Some studies indicate an accumulation of P in the sediment during winter/beginning of spring and release in the end of spring/summer (van Raaphorst and Kloosterhuis 1994), suggesting a mineralization/sorption control on the sediment-water exchange (Sundby et al. 1986; Jensen et al. 1995). However, in spite of the sediments' large capacity for short-term storage of P, most P appears to be in a non-easily exchangeable Ca-bound form with the bioavailable fraction corresponding to only 10–20% of the total pool (de Jonge et al. 1993; van Raaphorst and Kloosterhuis 1994; van Beusekom et al. 1999). Unfortunately, most of the available data is biased towards intertidal sediments and seasonal information is limited.

The limitations of the available data set become critical when trying to understand P cycling in the Wadden Sea, given its high complexity. Even though it shares some characteristics with estuaries, the western Wadden Sea doesn't behave like a conventional estuary, since freshwater discharge is controlled by sluices since the construction of the Afsluitdijk, separating Lake IJssel from the Wadden Sea (Oost and de Boer 1994) (Figure 5). The construction of the dike resulted in a generalized sedimentation regime leading to an average depth of 3.3 m. The shallowness allied to strong tidal currents and frequent storms results in frequent but unpredictable sediment resuspension, disrupting the sediment surface and altering the release of P and the sorption equilibrium (Berger et al. 1987; Dastgheib et al. 2008; Hommersom et al. 2009; Nauw et al. 2013). Another factor affecting sorption is a changing salinity, since the presence of competing ions for the sorption sites will reduce adsorption or induce desorption (Hawke et al. 1989; Yao and Millero 1996). Intermittent freshwater discharge, dependent on the opening of the sluices results in a variable salinity gradient ranging from 0 on Lake IJssel or 15 close to the sluices to 32 in the North Sea inlets (Dame et al. 1991; van Aken 2008). As a consequence of freshwater discharge, vertical stratification is sometimes observed (de Vries et al. 2012), in disagreement with a past view of a well mixed estuary, further complicating the transport of nutrients released from the sediment to the surface of the water column, where light availability, and phytoplankton growth, are maximum. In addition, nutrients from freshwater discharge or sediment release are only temporarily available in the western Wadden Sea basin, since the microtidal semi-diurnal regime results in an exchange of approximately 1% of the total water volume per tide and in a residence time of the water mass of 5–15 days (Ridderinkhof et al. 1990; Nauw et al. 2013). Approximately 1/3 of the total area of the western Wadden Sea is intertidal and contains active macrofauna and benthic phytoplankton communities (Dame et al. 1991; Beukema et al. 2002). Macrofauna is known to significantly affect the sediment-water exchange of nutrients due to bioirrigation and bioturbation while microphytobenthos may affect P release by acting as a biological filter taking up P before its release, but also by increasing pH and O_2 concentrations at the sediment surface due to photosynthesis, simultaneously increasing the oxic layer and potentially the sorption capacity and the competition for sorption sites by the hydroxyl ions (Carlton and Wetzel 1988; Furumai and Ohgaki 1988; Sundbäck and Granéli 1988; Seitzinger 1991; Epping and Jørgensen 1996; Koski-Vähälä et al. 2001).

Thus, a robust seasonal sampling scheme, including subtidal and intertidal sediments and covering the whole range of grain sizes present in the basin is needed to fully understand sediment P. Additionally, a complete view of the P cycle in the western Wadden Sea will only be complete if the water column is monitored for full tidal cycles, to understand the spatial and temporal distribution of P.

Objectives and outline of the thesis

The work presented in this thesis was part of the IN PLACE project (Integrated Network for Production and Loss Assessment in the Coastal Environment) which aimed at the quantification of the carrying capacity of the western Wadden Sea. It involved 6 cruises to the western Wadden Sea basin and several field trips to the Balgzand tidal flat. This thesis intended to re-assess the cycling of P in the western Wadden Sea, 3 decades after the introduction of policies to reduce freshwater P loading and to investigate its present availability to primary producers, as the basis of the ecosystem. Even though the main focus was on the contribution of the sediments, this study integrated both water column and sediment data. Field, laboratory, and modeling work were combined to quantify the seasonal and tidal variation of P availability and sediment-water exchange and to identify the major processes controlling the release of P from the sediment. The 4 chapters of this thesis aim at (1) the identification of a method for proper quantification of P sorption to marine sediments, (2) the characterization and quantification of the sedimentary P pool of the western Wadden Sea, (3) the quantification of sediment P release in the same area throughout the year and identification of the main processes affecting the release, and (4) the comparison between the contribution of sediment release, freshwater discharge and primary production to the pelagic availability of P in the western Wadden Sea.

In marine sediments, the majority of the temporary P pool corresponds to P sorbed to Fe/Mn oxides and clay particles. Information on sorption kinetics and maximum sorption capacity is achieved with incubations of sediment in a P solution. By starting the incubations at different initial concentrations, different equilibrium pairs of adsorbed/dissolved concentrations are obtained. These can be plotted to obtain an isotherm, a curve describing the distribution of a compound between the dissolved and solid phase and considered to be independent of the amount of adsorbent used. Although that doesn’t seem to always be the case, studies of P sorption to marine sediments often ignore this fact. **Chapter 2** demonstrates the bias induced in the sorption isotherms when different particle concentrations are used on incubations of marine sediment/Fe-coated sand in a seawater P solution. A model reproducing P sorption was developed using R as a programming language to extrapolate the incubations to a longer time scale and guarantee equilibrium conditions. The use of an alternative isotherm expression, based on the Metastable Adsorption Theory was suggested to correct for the particle concentration effect and allow the comparison between studies performed at different particle concentrations.

On **chapter 3** a characterization and quantification of the different sedimentary P pools in the western Wadden Sea was done, allowing to estimate the potential P release from the sediments and to investigate the possibility of a significant storage of P in the sediment during the period of high freshwater loading. Sequential extractions are useful to identify different functional groups of stored P and were used in our study to identify the easily exchangeable, redox sensitive, non-easily reducible Fe/Mn bound, Ca bound/apatite, and refractory organic P pools from subtidal and intertidal sediments. The different pools were compared with sediment parameters such as median grain size, porosity, sorting, specific surface area, organic C content, and porewater concentrations of ammonium and phosphate to find which factors can be related with the storage. Based on a relationship found between median grain size and P content, a budget of potentially bioavailable P was calculated for the western Wadden Sea. An estimation of the seasonal release was made, based on the difference in stored P between winter and the end of summer.

Chapter 4 provides a more reliable estimation of sediment P release. The sediment-water exchange can be directly measured in situ or with whole core incubations in the laboratory or calculated using depth profiles of porewater nutrient concentration. In this chapter, the measured, using whole core incubations, and the calculated exchange are presented for the main nutrients. Based on grain size and organic C measurements, porewater profiles, measured and calculated exchange, and presence/absence of macrofauna, different reactive zones were identified, with different processes controlling the release of P (and other nutrients) from the sediment. Median grain size was used once more as an independent variable in the extrapolation of the sediment-water exchange of P for the western Wadden Sea basin, and a seasonal and annual estimation of total release from the sediment was given. Assuming P as the limiting nutrient, the contribution of sediment release to primary production was assessed.

Given the present P limited and relatively high primary production, in spite of the significant decrease in P loading from freshwater discharge, **chapter 5** aims to identify the main sources of P to the water column in the modern western Wadden Sea. The pelagic concentrations of nutrients and chlorophyll *a* were compared, to assess the availability of nutrients, and especially P, to the phytoplankton community and to understand the relationship between phytoplankton growth and nutrient recycling and release from the sediment. The contributions, in terms of nutrient supply, of exchange with the North Sea, freshwater discharge and sediment release were compared, and the main sources of P throughout the year in the western Wadden Sea were identified.

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Chapter 2

Phosphate sorption from seawater solutions: Particle concentration effect

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Abstract

Phosphate sorption experiments were performed with beach sand artificially coated with iron(III) (hydr)oxides and with a natural intertidal sandy sediment. Initial fast sorption was followed by a much slower exchange of phosphate between sorbent and seawater solution. A two-step kinetic model was developed to reproduce the time series sorption data. Because in many cases equilibrium was not reached at the end of the two-week experiments, the model was extrapolated to a nominal duration of one year to construct (near-) equilibrium isotherms. The results for both the iron(III) coated sand and the intertidal sediment showed a clear particle concentration effect, with higher sorption densities and steeper sorption isotherms at lower solid-solution ratios. Thus, while the commonly used Langmuir and Freundlich isotherms successfully reproduced individual experimental data series, the corresponding parameter values were dependent on the particle concentration. The particle concentration effect was accounted for by modifying the Freundlich isotherm according to the Metastable Equilibrium Adsorption (MEA) theory of Pan and Liss (1998a). The MEA-modified isotherm accounted well for the mixed suspensions of iron(III) coated sand, however, over-predicted phosphate sorption to the iron(III)-coated sand obtained under stagnant conditions. Although a mechanistic interpretation of the sorption process cannot be inferred from a fit to the MEA-modified Freundlich isotherm, the resulting parameter values facilitate the comparison of sorption studies carried out at variable solid-solution ratios.

1. Introduction

Dissolved inorganic phosphorus (P), mainly in the form of aqueous phosphate (PO_4), is a major nutrient, often limiting primary production in marine and freshwater environments. Large quantities of P can be temporarily or permanently stored in sediments (Tallberg et al. 2008), with PO_4 sorbed to iron (Fe), aluminum and manganese (hydr)oxides typically representing the largest exchangeable P reservoir under oxic conditions (Sundby et al. 1992; van Raaphorst and Kloosterhuis 1994; Slomp et al. 1998; Gao and Mucci 2001, 2003). Sorption and desorption of PO_4 are thus key processes controlling the availability of P in aquatic environments, especially in shallow, nearshore areas (Froelich 1988; van der Zee et al. 2007; Spiteri et al. 2007).

The affinity and maximum sorption capacity of a sediment for PO_4 are usually expressed in the form of an isotherm, which relates the amount sorbed with the dissolved concentration at equilibrium. Isotherms are experimentally obtained by incubating the sediment with solutions containing variable initial dissolved PO_4 concentrations under well-defined temperature, pH, and background electrolyte conditions. After an arbitrary period of time, the distribution between the dissolved and sorbed phases is assumed to have reached equilibrium. The amount sorbed (or desorbed) is calculated from the difference between the initial and final concentrations of dissolved PO_4. A plot of the amount sorbed, normalized to the mass of the incubated sediment, versus the final concentrations of dissolved PO_4 yields a sorption isotherm (Krom and Berner 1980; Jensen and Andersen 1992; Slomp et al. 1998; Zhou et al. 2005).

Ideally, an isotherm should be unique for a given sediment, temperature, and solution composition. In particular, the isotherm should be independent of the solid to solution ratio under which the sorption experiments are conducted (Limousin et al. 2007). However, deviation from this ideal behavior is often observed, with the sorbed concentration at a given dissolved concentration decreasing with increasing sediment mass per unit volume solution. This is referred to as the solid-solution ratio effect, solids effect, or particle concentration effect. The effect is fairly ubiquitous and has been observed with a wide variety of natural sorbents, including soils (Cox et al. 1993; Chang et al. 2002; Koopmans et al. 2004) and suspended particulate matter (Benoit 1995; Rawling et al. 1998), as well as freshwater (Voice and Weber Jr. 1985; Servos and Muir 1989), estuarine (Turner et al. 1999; Hatje et al. 2003), and marine sediments (Higgo and Rees

1986; van Raaphorst and Kloosterhuis 1994; Du and Hayashi 2006). Even single, well-characterized mineral sorbents such as kaolinite (Puls et al. 1991) and goethite (Pan and Liss 1998b) have shown this supposedly anomalous behavior. Moreover, different sorbates such as metals (Pan and Liss 1998a; Benoit and Rozan 1999; Chang et al. 2002; Hatje et al. 2003), organic compounds (Voice et al. 1983; Weber Jr. et al. 1983; Servos and Muir 1989; Turner et al. 1999), nutrients, including PO_4 (van Raaphorst and Kloosterhuis 1994; Koopmans et al. 2004; Jianbo et al. 2009), and actinides (Higgo and Rees 1986) exhibit the particle concentration effect (O'Connor and Connolly 1980; Mackay and Powers 1987; Sohn and Kim 2005). The diversity of sorbent plus sorbate combinations where the particle concentration effect has been observed, points to a widespread behavior.

In this study, the effect of the particle concentration on the sorption of PO_4 was studied. Since Fe oxides often represent the main pool of sorption sites for PO_4 in oxic marine sediments, artificial sediment consisting of quartz sand coated with amorphous Fe(III) oxide was used as one of two sorbents, the other being a natural sandy sediment. The use of the artificially Fe coated sediment minimizes artifacts related to multiple sorbents and the presence of additional sources or sinks due to, for example, microbial activity. The main goal of this study was to assess the importance of the particle concentration effect for PO_4 sorption from seawater and its potential implications for benthic-pelagic coupling in nearshore marine environments.

2. Methods

2.1 Artificial and natural sediments

Beach sand was collected on the North Sea coast of the Dutch Wadden Sea island of Texel, sieved (250–500 µm), placed in a muffle oven at 500°C for 4 hours to remove organic matter, and rinsed at least 3 times with Milli-Q water. After drying, an Fe(III) hydroxide coating was applied using a procedure adapted from Chardon (2000). Briefly, the sand was immersed in an acidified 0.6 M $FeCl_3$ solution and then dried in the oven at 60–80°C for 2–4 hours. After drying, the sand was quickly neutralized with a 5% NH_4OH solution after which it was rinsed with Milli-Q water to remove non-adhering Fe oxides. Upon drying at 60–80 °C, the sediment was sieved to remove the remaining non-adhered Fe oxide dust formed during oxidation. Natural intertidal sandy sediment was collected in the Balgzand tidal flat in the Dutch western Wadden Sea and used fresh (wet) in the incubations, which started approximately 2 hours after collection. Intertidal sediment from the Balgzand area has previously been described by van Raaphorst and Kloosterhuis (1994).

2.2 Sediment Fe and P extractions

To quantify the amount of Fe coated to the sand, the Fe and PO_4 contents of the natural sediment, and the amounts of sorbed PO_4 before and after the sorption incubations, acid-extractions were performed. Known weights of natural sediment or artificially Fe(III) coated sand were added to 40 ml of 1 M Suprapure HCl in Falcon tubes. After mixing for 16 hours, samples were collected and filtered (0.2 µm pore diameter Acrodisc filter, Supor® membrane) for PO_4 and Fe(II) analysis. The analyses were performed on a TRAACS-800 auto-analyzer according to the methods of Murphy and Riley (1962) and Gibbs (1979), respectively. The detection limit and precision for the PO_4 analysis were 0.01 and 0.007 µM; the Fe(II) analysis had a detection limit and precision of 0.05 and 0.1 µM. The samples were kept at 4°C until analysis. The extraction procedure used corresponds to the last step of the sequential extraction protocol described by Lukkari et al. (2007), which is expected to dissolve the Fe coating and release all sorbed (= adsorbed and coprecipitated) PO_4.

2.3 Sorption incubations at different particle concentrations and mixing speeds

Phosphate under the form of K_2HPO_4 was added to low nutrient North Atlantic seawater diluted with Milli-Q water to a salinity of 27 psu at a pH of 8 (±0.05). Six solutions were prepared with concentrations of dissolved PO_4 ranging from 0 to 150 µM (for 20 g l^{-1} particle concentration), 0 to 200 µM (for 100 g l^{-1} particle concentration), and 0 to 250 µM (for 200 g l^{-1} particle concentration), which is well within the range found in Wadden Sea sediments, which goes up to 1200 µM (Chapter 3). Polypropylene Falcon tubes were filled with 50 ml of each solution and dry Fe coated sand was added to a final particle concentration of 20, 100, and 200 g l^{-1}. Prior to incubation, the artificial sediment was equilibrated for a week in a PO_4 containing seawater solution (220 µM K_2HPO_4, 27 psu), yielding an average pre-loading of 0.93 µmol PO_4 g^{-1}, which is within the range of the 0.02–1.78 µmol g^{-1} found in the North Sea and the 0.23–2.25 µmol g^{-1} found in the Wadden Sea tidal flats (van Raaphorst and Kloosterhuis 1994; Slomp et al.1998). This procedure was followed to reproduce the native loading of natural marine sediments and resemble our experiments to natural conditions. The tubes were placed in a vertical tube rotator at a defined speed (1, 2.5, 11 or 27 rpm) and incubated at a temperature of 10–12°C, for a maximum duration of 14 days. At regular intervals, the tubes were left standing for approximately a minute, to allow the sand particles to settle and 2 ml samples were collected, filtered (0.2 µm pore diameter Acrodisc filter, Supor® membrane), acidified with 2 µl of 5 N Suprapure HCl, and kept at 4°C until analysis of PO_4 and Fe(II), using the methods described above. Samples were replaced by equal volumes of low nutrient North Atlantic seawater (27 psu), to maintain a similar particle concentration throughout the experiment. Identical incubations were also performed using the upper centimeter of the intertidal sediments. However, the initial PO_4 concentrations used were lower (ranging from 0 to 100 µM), as the sorption capacity was expected to be less than for the Fe coated sand. pH was measured in the beginning and after 2 weeks of incubation. No consistent change was observed and variation throughout the experiment was lower than 0.1.

2.4 Sorption incubations under stagnant conditions

Stirred suspensions may not provide conditions representative of those encountered in sediments deposited at the seafloor. Hence sorption experiments were also conducted with stagnant Fe coated sand. Acid cleaned (1 M HCl) syringes (ca. 30 ml) were sealed with parafilm at the tapered end and filled with 38.5 g of artificially Fe coated sand. Subsequently, 9.5 ml of PO_4 amended seawater (0–1 mM initial PO_4 concentration, 27 psu, also within the range of concentrations found in North Sea (up to 800 µM) and Wadden Sea sediments (up to 1.2 mM) (Slomp et al. 1998; Chapter 3) was added to each syringe to fully saturate the sediment while carefully avoiding the inclusion of air bubbles. The incubation at higher PO_4 concentrations was needed to guarantee that the equilibrium concentration after 2 weeks was within the range normally found in sediment porewater, due to the high sorption capacity of the packed sediment. After sealing the top with a cap, the sediments were left stagnant at 10–12°C. The syringes were sacrificed at different times up to a maximum of 14 days by replacing the parafilm on the bottom of the syringe by a 0.2 µm pore diameter Acrodisc filter (Supor® membrane). A filtered porewater sample was collected by centrifugation for 12 minutes at 1900 rpm. Samples were acidified, stored and analyzed as described above. No consistent or significant variation on pH was observed between the beginning and end of the incubation.

2.5 Kinetic model

A numerical model describing the time-dependent PO_4 sorption dynamics in a batch experiment was developed in the software environment R (R Development Core Team 2011) in order to estimate experimental rate constants and extrapolate sorption trends to incubation periods exceeding the length of the experiments (14 days). Based on the literature (e.g., van der Zee and van Riemsdijk 1986; McGechan and Lewis 2002; Limousin et al. 2007) and our own data, the overall process of sorption was described by the simultaneous action of four processes: fast and slow sorption, and fast and slow desorption. Five state variables were included in the model: (1) *P*, the concentration of dissolved PO_4; (2) *Sf*, the concentration of "fast" sorption sites; (3) *Ss*, the concentration of "slow" sorption sites; (4) *PSf*, the concentration of PO_4 sorbed onto "fast" sorption sites; and (5) *PSs*, the concentration of PO_4 sorbed onto "slow" sorption sites. Sorption and desorption were described according to Langmuir kinetics (van der Zee and van Riemsdijk 1986), with sorption depending on a kinetic sorption constant, the dissolved PO_4 concentration plus the available sorption sites concentration, and desorption depending on a kinetic desorption constant and the corresponding sorbed PO_4 concentration. This implies that we assume that each sorption site retains one molecule of PO_4 and that all sites are energetically independent of the adsorbed quantity. The following differential equations describe the variations in time of the different PO_4 pools:

$$dP/dt = -(kaf \times P \times Sf + kas \times P \times Ss) \times Cp + (kdf \times PSf + kds \times PSs) \times Cp \quad (1)$$

$$dSf/dt = -kaf \times P \times Sf + kdf \times PSf \quad (2)$$

$$dSs/dt = -kas \times P \times Ss + kds \times PSs \quad (3)$$

$$dPSf/dt = kaf \times P \times Sf - kdf \times PSf \quad (4)$$

$$dPSs/dt = kas \times P \times Ss - kds \times PS \quad (5)$$

where *kaf* and *kas* are the fast and slow sorption rate constants (in $l\ \mu mol^{-1}\ h^{-1}$), *kdf* and *kds* the fast and slow desorption rate constants (in h^{-1}), *P* the dissolved PO_4 concentration (in $\mu mol\ l^{-1}$), *Sf* and *Ss* the fast and slow sorption site concentrations (in µmol g^{-1}), *PSf* and *PSs* the fast and slow sorbed PO_4 concentrations (in µmol g^{-1}), and *Cp* the particle concentration of sediment (in g l^{-1}).

The parameters *kaf*, *kas*, and *kdf* were estimated by fitting the measured dissolved PO_4 concentrations versus time using the FME package (Soetaert and Petzold 2010). Initial model trials applied to our results suggested that the slow desorption rate constant, *kds*, was very small ($<10^{-5}$ h^{-1}) and a non-significant parameter at the time scale of the experiments. Therefore, *kds* was set to zero, implying that the slow process is irreversible, which is corroborated by the literature (van der Zee and van Riemsdijk 1986; Limousin et al. 2007). Initial dissolved PO_4 concentration and sediment concentration were known experimental parameters. The total (i.e., fast plus slow) sorbed PO_4 resulting from the pre loading was also known, but the distribution of pre-loaded PO_4 sorbed among fast and slow sites not. Therefore, initial values of *PSf* and *PSs* were estimated as *PSf_0 = PStotal x f.fast* (6) and *PSs_0 = PStotal x (1 – f.fast)* (7), where *PStotal* is the total amount of pre-loaded PO_4, and *f.fast* is the fraction sorbed onto fast sites. The latter fraction was estimated from the model fit to the data.

2.6 (Near-) equilibrium isotherms

Because in many of the sorption experiments the dissolved PO_4 concentrations did not reach stable values by the end of the incubation period, the kinetic model described in the previous section was run forward in time to a total duration of 1 year. In what follows, it is assumed that the calculated concentrations after 1 year represent (near-) equilibrium values. Isotherms were then constructed by plotting the calculated total sorbed PO_4 concentration ((initial – final dissolved PO_4 concentration) + pre-loaded PO_4 concentration), normalized per sediment weight, versus the corresponding dissolved PO_4 concentration remaining in solution. The 2-site Langmuir and Freundlich expressions were used to fit the experimental isotherms yielding estimates for the maximum sorption capacities (Q_{max1} and Q_{max2}, in µmol g^{-1}) plus equilibrium constants (K_1 and K_2, in l μmol^{-1}) for the 2-site Langmuir model, and the empirical parameters K_{fr} (in l g^{-1}) and *n* for the Freundlich model. In order to estimate sorption parameter values that are independent of the experimental particle concentration, the modified Freundlich isotherm proposed by Pan and Liss (1998a) was also applied: $PS = K_{sp} \times Cp^{-m} \times P^{\beta}$ (8), where *PS* is the sorbed PO_4 concentration, K_{sp} an equilibrium sorption constant, independent of the dissolved PO_4 and particle concentrations, *Cp* the particle concentration, and *m* and *β* empirical constants. The fitting of the MEA isotherm was done using function nls from R (R Development Core Team 2011) and the error minimization routines developed by Bolster and Hornberger (2006) for the Freundlich and 2-site Langmuir isotherms.

3. Results

3.1 Sorbents

The artificially Fe coated sand had grain size diameters ranging between 250 and 500 µm and a specific surface area of 0.32 m^2 g^{-1} (measured on a BET Micromeritics Tristar3000), which was similar to the specific surface area of the sand measured prior to coating. The coating provided an Fe content of approximately 14.30 µmol Fe g^{-1} of sediment. X-ray diffraction spectra did not identify any crystalline Fe mineral phase, suggesting that the coating was mainly composed of X-ray amorphous Fe oxyhydroxides. The natural intertidal sediment was principally composed of sand with a mean grain size of 201 µm and a silt fraction of 2.5%. The sediment had an Fe content of 23.20 µmol g^{-1} and a total PO_4 content of 3.30 µmol g^{-1}, of which 0.4 µmol g^{-1} was HCl extractable.

3.2 Sorption experiments

The sorption experiments performed with artificially Fe coated sediment at a particle concentration of 200 g l^{-1} and a mixing rate of 1 rpm are illustrated in Figure 1. At low initial dissolved PO_4 concentrations, the artificial sediment, pre-loaded with PO_4, released PO_4 to solution, resulting in a logarithmic increase in the dissolved PO_4 concentration with time. Almost no change in dissolved PO_4 was observed for the incubations run at an initial concentration of 50 µM. At initial concentrations of dissolved PO_4 exceeding 50 µM, the sediment removed PO_4 from solution, resulting in an exponential decrease in the dissolved PO_4 concentration with incubation time.

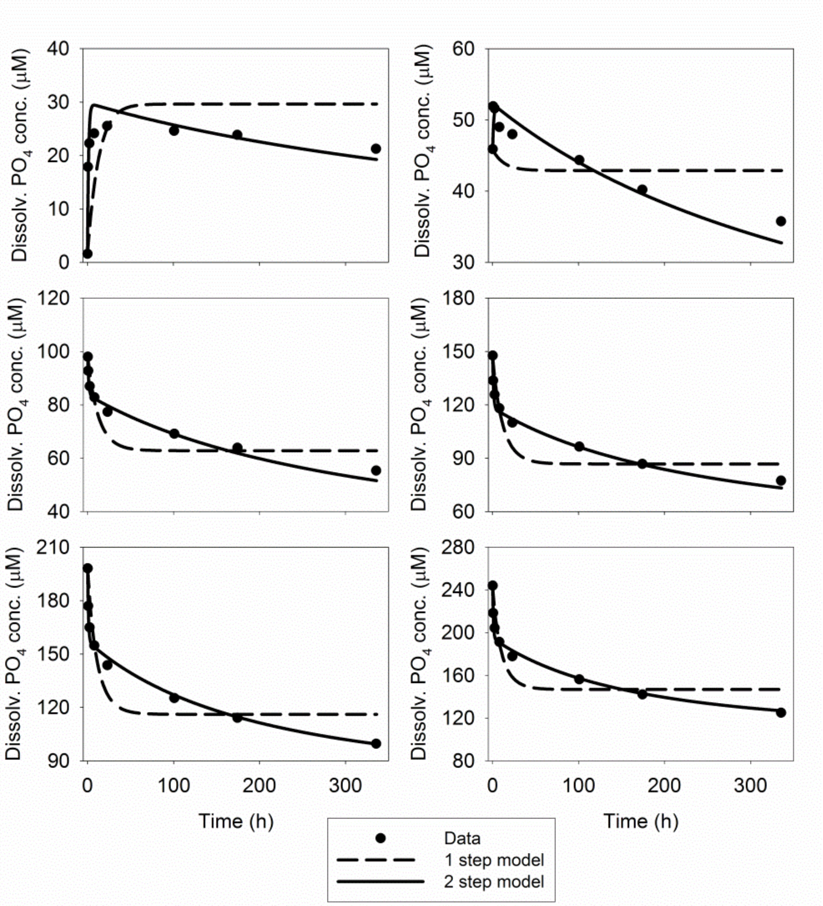


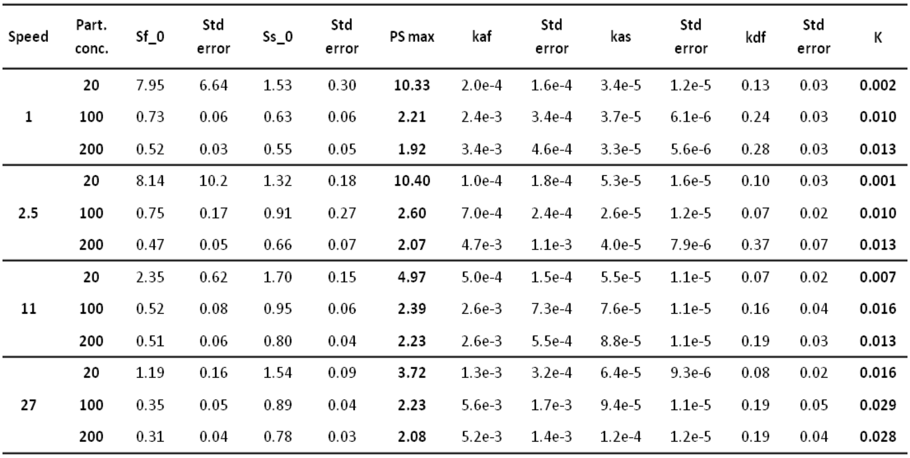
Figure 1. Experimental and modeled time series of dissolved PO_4 concentrations from the six incubations started at different initial PO_4 concentrations, with suspended Fe coated sand at a particle concentration of 200 g l^{-1} and mixed at 1 rpm. Dashed lines correspond to the model with one sorption process included and solid lines correspond to modeled results with the inclusion of 2 sorption processes in the model (fast and slow). Note that the model including only one sorption process clearly cannot reproduce the slow PO_4 exchange after 336 h.

In many cases, the PO_4 concentration in solution continued to change after two weeks of incubation with an average change of 18%, implying that equilibrium had not yet been established between dissolved and sorbed PO_4. This effect was especially conspicuous for the incubations with the highest initial dissolved PO_4 concentrations, where the change in concentrations between 7 and 14 days could be as high as 50%. Rather than increasing the incubation time, which may introduce artifacts (e.g., due to microbial activity when using natural sediments), the numerical model described in section 2.5 was used to extrapolate the data trends to a nominal equilibration time of 1 year. After the extrapolation, even though final equilibrium had not been reached, the changes in concentration were always lower than 0.15% and simulations showed that longer equilibration times did not significantly alter the computed isotherms. The one-year isotherms are therefore considered to be representative of near-equilibrium conditions.

3.3 Sorption kinetics

Modeling the dissolved PO_4 concentration during the sorption incubations using only one kinetic expression for sorption and one for desorption yielded poor fits (Figure 1), as this approach did not reconcile the initial fast kinetics with the slower continued change in dissolved PO_4 concentration during the later stage of the incubations. Including both a fast and a slow sorption process significantly improved the fit to the experimental data for all experimental runs (Figure 1), which is a prerequisite for a meaningful extrapolation of the trends beyond the time span of the incubations. For each combination of particle concentration and mixing speed, a single set of parameter values was estimated by collectively fitting the data from the 6 incubations run with different initial dissolved PO_4 concentrations.

Table 1. Estimated parameters (and associated standard deviations) for the kinetic model including two sorption steps (fast and slow) and applied to all data from the suspended incubations with Fe coated sand. Separate datasets are presented for each different particle concentration/mixing speed combination. PS_{max} corresponds to Sf_0 + Ss_0 + PS_0 (pre-loaded PO_4). K corresponds to kaf/kdf. Units are rpm for speed, g l^{-1} for particle concentration, µmol g^{-1} for Sf_0, Ss_0 and PS_{max}, l $µmol^{-1}$ h^{-1} for kaf and kas, h^{-1} for kdf, and l $µmol^{-1}$ for K. (See text for details)



Speed	Part. conc.	Sf_0	Std error	Ss_0	Std error	PS max	kaf	Std error	kas	Std error	kdf	Std error	K
1	**20**	7.95	6.64	1.53	0.30	**10.33**	2.0e-4	1.6e-4	3.4e-5	1.2e-5	0.13	0.03	**0.002**
	100	0.73	0.06	0.63	0.06	**2.21**	2.4e-3	3.4e-4	3.7e-5	6.1e-6	0.24	0.03	**0.010**
	200	0.52	0.03	0.55	0.05	**1.92**	3.4e-3	4.6e-4	3.3e-5	5.6e-6	0.28	0.03	**0.013**
2.5	**20**	8.14	10.2	1.32	0.18	**10.40**	1.0e-4	1.8e-4	5.3e-5	1.6e-5	0.10	0.03	**0.001**
	100	0.75	0.17	0.91	0.27	**2.60**	7.0e-4	2.4e-4	2.6e-5	1.2e-5	0.07	0.02	**0.010**
	200	0.47	0.05	0.66	0.07	**2.07**	4.7e-3	1.1e-3	4.0e-5	7.9e-6	0.37	0.07	**0.013**
11	**20**	2.35	0.62	1.70	0.15	**4.97**	5.0e-4	1.5e-4	5.5e-5	1.1e-5	0.07	0.02	**0.007**
	100	0.52	0.08	0.95	0.06	**2.39**	2.6e-3	7.3e-4	7.6e-5	1.1e-5	0.16	0.04	**0.016**
	200	0.51	0.06	0.80	0.04	**2.23**	2.6e-3	5.5e-4	8.8e-5	1.1e-5	0.19	0.03	**0.013**
27	**20**	1.19	0.16	1.54	0.09	**3.72**	1.3e-3	3.2e-4	6.4e-5	9.3e-6	0.08	0.02	**0.016**
	100	0.35	0.05	0.89	0.04	**2.23**	5.6e-3	1.7e-3	9.4e-5	1.1e-5	0.19	0.05	**0.029**
	200	0.31	0.04	0.78	0.03	**2.08**	5.2e-3	1.4e-3	1.2e-4	1.2e-5	0.19	0.04	**0.028**

Table 1 summarizes the estimated parameters and initial concentrations for the different particle concentration and mixing speed combinations. The initial density of fast sorption sites (*Sf_0*) varied between 0.31 and 8.14 µmol g^{-1} and decreased, for all mixing speeds, with increasing particle concentration. The same trend was observed for the initial slow sorption site density (*Ss_0*), which ranged between 0.55 and 1.70 µmol g^{-1}. The sorption rate constant for the fast sites (*kaf*) ranged between 1.00 x 10^{-4} and 5.60 x 10^{-3} l $µmol^{-1}$ h^{-1}, while for the slow sites (*kas*) it varied between 2.59 x 10^{-5} and 1.19 x 10^{-4} l $µmol^{-1}$ h^{-1}. Both rate constants showed increasing trends with particle concentration. The fast desorption rate constant (*kdf*) ranged between 0.07 and 0.37 h^{-1} but exhibited no (clear) relationship with respect to the particle concentration.

3.4 Particle concentration effect

The (near-) equilibrium sorption isotherms obtained by extrapolating the kinetic results to 1 year are shown in Figure 2 for the experiments run at a mixing speed of 1 rpm. As can be seen, the amount of PO_4 sorbed per unit of mass of Fe coated sand decreased with increasing particle concentration. The particle concentration effect was more prominent for a change in particle concentration from 20 to 100 g l^{-1} than from 100 to 200 g l^{-1}. Furthermore, the isotherms at the higher particle concentrations (100 and 200 g l^{-1}) appeared to reach site saturation, which was not the case at the lower particle concentration (20 g l^{-1}).

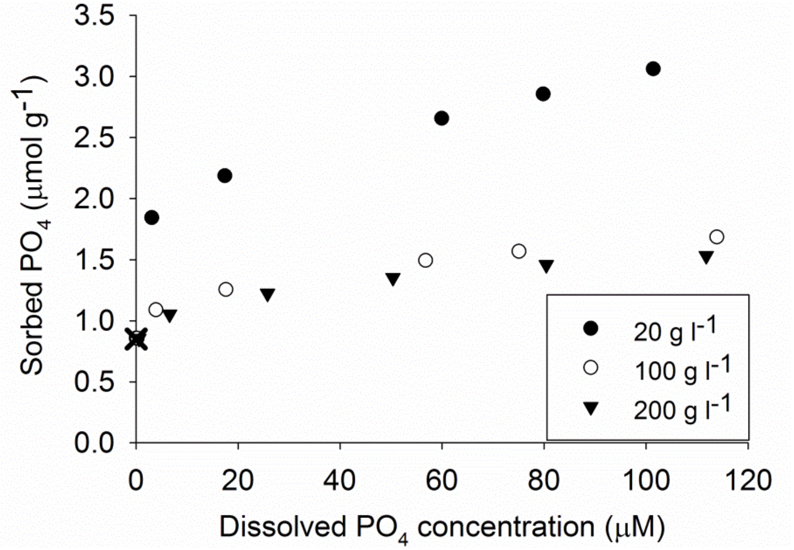


Figure 2. Sorbed PO_4 concentration versus dissolved PO_4 concentration (isotherms) for the Fe coated sand suspensions mixed at 1 rpm, obtained by extrapolating the time series data to 1 year of equilibration using the kinetic model (see text for details). Results for the three particle concentrations used, 20, 100, and 200 g l^{-1}, show the particle concentration effect even for long incubation times. The cross indicates the pre-loaded PO_4 concentration.

The isotherms for the various combinations of particle concentration and mixing rate were fitted to the 2-site Langmuir and Freundlich equations and the estimated parameters are summarized in Table 2. For the data corresponding to the incubation mixed at 1 rpm, the maximum sorption capacities estimated from the 2-site Langmuir equation were approximately twice as high for the 20 g l^{-1} particle concentration (Q_{max1} = 2.94 µmol PO_4 g^{-1}; Q_{max2} = 1.82 µmol PO_4 g^{-1}) than those obtained for 100 and 200 g l^{-1} (Q_{max1} = 1.06 and 0.90 µmol PO_4 g^{-1}; Q_{max2} = 1.06 and 0.99 µmol PO_4 g^{-1}). The estimated K_1 value for the lower particle concentration was around half the estimated values for the 100 and 200 g l^{-1} incubations: 7.00 x 10^{-3} versus 1.30 x 10^{-2} and 1.40 x 10^{-2} l μmol^{-1}, respectively. The values of K_2 were much higher than K_1 and showed a distinct decrease with increasing particle concentration: 41.56, 20.67, and 11.31 l μmol^{-1}, for particle concentrations of 20, 100, and 200 g l^{-1}, respectively. For the data at the other mixing speeds, the 2-site Langmuir parameters showed similar trends, except for K_2, which exhibited large and inconsistent variations between particle concentrations.

Table 2. Estimated parameters for the 2-site Langmuir and Freundlich isotherms applied to all data obtained with the Fe coated sand suspensions, after extrapolation of the incubation time to 1 year using the kinetic model. Also given are the 95% confidence limits.

Mixing speed (rpm)	Particle conc. (g l^{-1})	Langmuir				Freundlich	
		Q_{max1}	Q_{max2}	K_1	K_2	K_{fr}	n
1	20	2.94±4.10	1.82±0.25	6.9e-3±0.02	41.56±22.29	1.50±0.17	6.80±0.03
	100	1.06±0.22	1.06±0.05	0.01±6e-3	20.67±6.36	0.96±0.10	8.90±0.03
	200	0.90±0.04	0.99±0.01	0.01±2e-3	11.31±1.29	0.88±0.08	8.79±0.02
2.5	20	5.36±4.72	1.80±0.05	2e-3±3e-3	203.98±25.28	1.57±0.27	8.33±0.04
	100	0.94±0.63	1.26±0.24	0.03±0.08	48.52±57.28	1.23±0.05	9.88±0.01
	200	0.83±0.38	1.14±0.11	0.02±0.03	77.60±58.91	1.12±0.13	12.29±0.03
11	20	2.82±0.16	2.23±0.02	6e-3±7e-4	7.42±0.52	1.95±0.18	9.32±0.02
	100	0.94±0.05	1.43±0.01	0.02±2e-3	362.97±23.40	1.52±0.11	20.13±0.02
	200	0.94±0.01	1.29±2e-3	0.01±4e-4	482.52±9.63	1.40±0.12	27.84±0.02
27	20	1.81±0.07	1.86±0.02	0.02±2e-3	163.63±7.38	1.69±0.14	8.25±0.02
	100	1.00±0.04	1.22±0.02	0.03±5e-3	198.49±24.40	1.27±0.14	11.15±0.03
	200	0.95±1e-3	1.13±6e-4	0.03±1e-4	203.56±1.16	1.19±0.16	12.02±0.04

The Freundlich isotherm parameter K_{fr} had estimated values of 1.50, 0.96, and 0.88 l g^{-1}, while *n* had values of 6.80, 8.90, and 8.79 for the 20, 100, and 200 g l^{-1} incubations, respectively. The decrease in the parameter K_{fr} and the increase of *n* with the particle concentration was observed for all mixing speeds. All fits summarized in Table 1 had R^2 > 0.91. Taken together, the results indicate that the sorption isotherms depend on the experimental particle concentration.

3.5 Effect of mixing rate on sorption

The relative effects of the mixing speed (1, 2.5, 11, and 27 rpm) and particle concentrations (20, 100, and 200 g l^{-1}) on the amounts of sorbed PO_4 measured after 14 days of incubation are compared in Figure 3, panels A, B, and C. The results for 1 and 2.5 rpm were similar at each of the particle concentrations. This is also true for the 11 and 27 rpm results, although systematically more PO_4 is sorbed at these higher mixing speeds.

The isotherm calculated by extrapolating to 1 year the data of the incubations obtained at the maximum mixing speed of 27 rpm is shown on Figure 3D: the particle concentration dependency was similar to that observed at 1 rpm mixing speed (compare Figures 2 and 3D). Fitting of the 2-site Langmuir isotherm to the data in Figure 3D yielded Q_{max1} values of 1.81, 1.00, and 0.95 µmol g^{-1}, and Q_{max2} values of 1.86, 1.22, and 1.13 µmol g^{-1} at particle concentrations of 20, 100, and 200 g l^{-1}, respectively. The K_1 and K_2 values for particle concentrations of 20, 100, and 200 g l^{-1} were 0.02, 0.03, and 0.03, and 163.63, 198.49, and 203.56 l μmol^{-1}, respectively. The estimated Freundlich parameters K_{fr} and n for 20, 100, and 200 g l^{-1} were 1.69, 1.27, and 1.19 l g^{-1}, and 8.25, 11.15, and 12.02, respectively. Overall the parameters describing the isotherms at the different mixing speeds were quite comparable, with the exception of K_2 (Table 2)

3.6 Sorption under stagnant conditions

The results for the sorption experiments with the Fe coated sand in a packed sediment column (no stirring) are illustrated in Figure 4. In order to obtain an acceptable range in dissolved PO_4 concentrations at the end of the experiments, similar to natural porewater concentrations, initial dissolved PO_4 concentrations of up to 1000 µM were required. The general time series trends observed were similar to those found in the suspended sediment sorption experiments (compare Figures 1 and 4A). However, the estimated maximum sorption capacities (Langmuir isotherm) in the stagnant systems were significantly lower than for the mixed suspensions, with values of 0.53 and 0.09 µmol g^{-1} for Q_{max1} and $Q_{max\ 2}$, respectively, whereas K_1 was higher (0.07 l μmol^{-1}) and K_2 lower (11.11 l μmol^{-1}) than for the experiments with suspensions (Figure 4B). For the Freundlich isotherm, the K_{fr} and n values were estimated at 0.12 l g^{-1} and 2.49, respectively, that is, both lower values than the ones observed for the mixed suspensions. All fits had $R^2 > 0.99$.

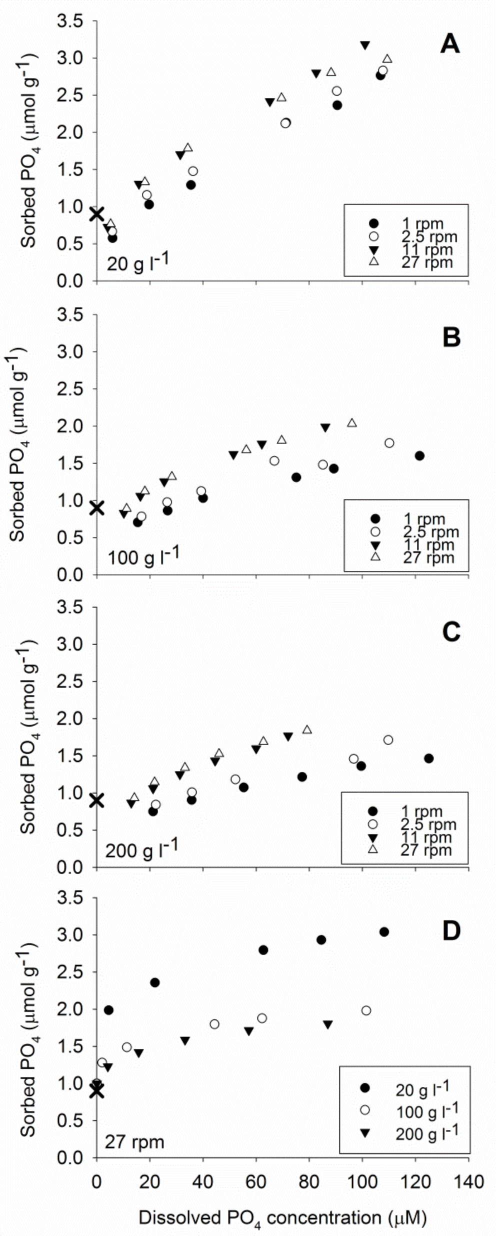


Figure 3. A–C – Isotherms for all the suspended incubations of Fe coated sand plotted separately for each particle concentration. Plots show the data obtained after 14 days of incubation. Panel D presents the isotherms for the incubations mixed at 27 rpm after extrapolation to 1 year, showing the persistence of the particle concentration effect. The cross indicates the pre-loaded PO$_4$ concentration.

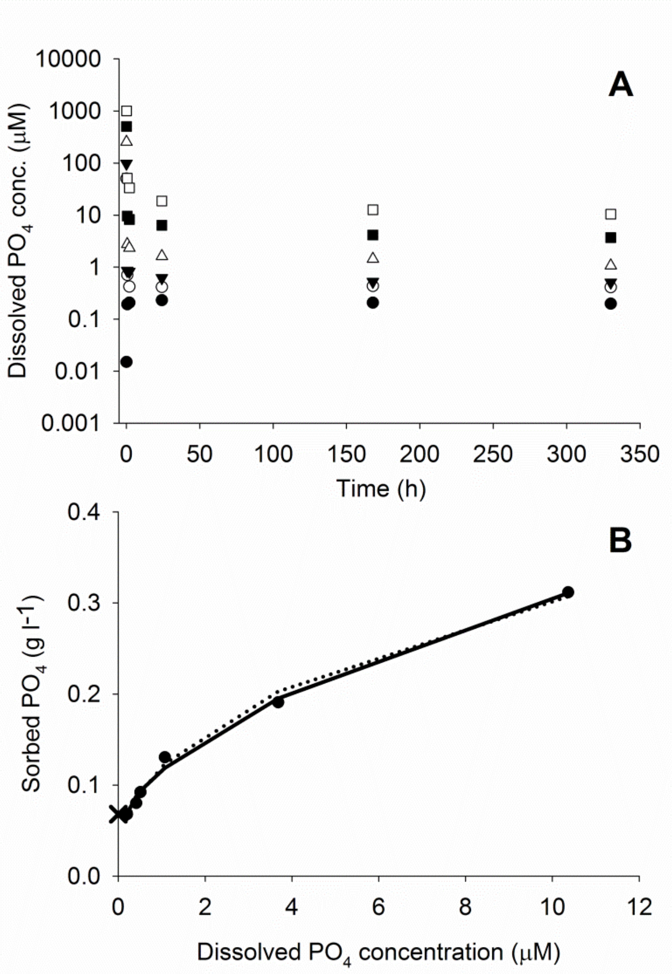


Figure 4. Results from the incubation of Fe coated sand performed under stagnant conditions: A – Variation of dissolved PO_4 with time for the different initial concentrations. Note that equilibrium was apparently reached after 14 days; B – Sorbed PO_4 versus dissolved PO_4 concentration after 14 days of incubation (isotherm) and fit of the 2-site Langmuir (solid line) and Freundlich (dotted line) isotherm equations. Estimated parameters for the Langmuir equation, Q_{max1}, Q_{max2}, K_1 and K_2, are 0.53 and 0.09 µmol l^{-1} and 0.07 and 11.11 l $µmol^{-1}$; Estimated K_{fr} and n for the Freundlich equation are 0.12 l g^{-1} and 2.49, respectively. Both fits have R^2 > 0.99. The cross indicates the pre-loaded PO_4 concentration.

3.7 Application of the Metastable Adsorption Theory

In order to account for the particle concentration effect, the Freundlich equation, modified according to Metastable Equilibrium Adsorption (MEA) theory (Equation 8, section 2.6), was applied to the entire set of isotherms for the mixed suspensions of Fe coated sand. As shown on Figure 5, a single set of parameters was able to reproduce the isotherms obtained at the different particle concentrations. The corresponding parameter values of K_{sp}, m, and β in Equation (8) were 4.04, 0.26, and 0.10, with standard errors of 0.26, 0.01, and 7 x 10^{-3}, respectively. The isotherm for sorption to the Fe coated sand under stagnant conditions, however, could not be adequately fitted with the same set of parameter values (see inset on Figure 5). In fact the isotherm derived for mixed suspensions of Fe coated sand overpredicted sorption under stagnant conditions.

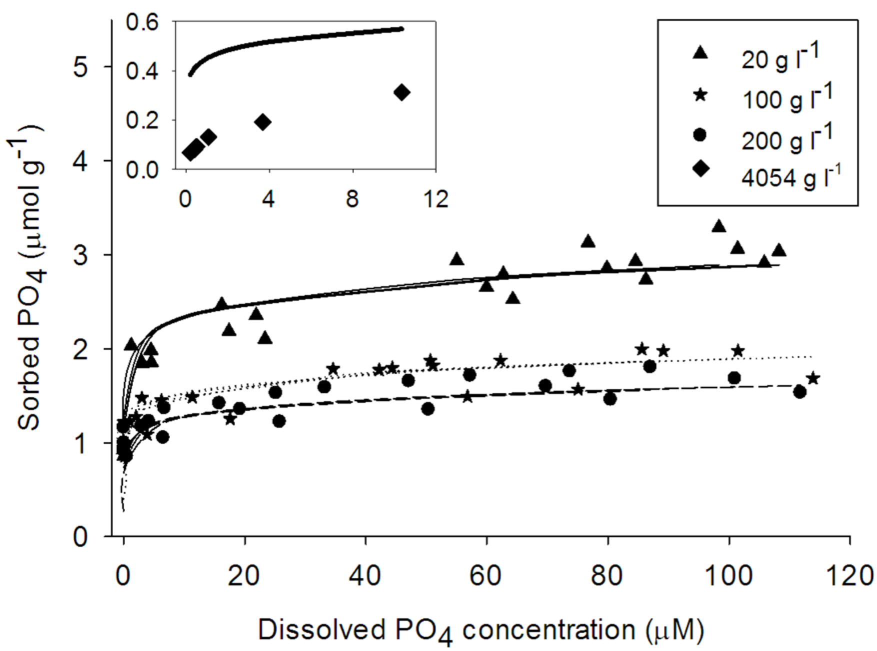


Figure 5. Isotherms for all incubations with Fe coated sand after extrapolation to 1 year (equilibrium). This includes suspended and stagnant sorption experiments (inset). The lines show model fits using a single Freundlich isotherm, modified according to the MEA theory, for all particle concentrations: 20 g l^{-1} (solid line), 100 g l^{-1} (dotted line), 200 g l^{-1} (dash line), and 4054 g l^{-1} (solid line in the small plot). The estimated parameters K_{sp}, m, and β are 4.04, 0.26, and 0.10, with standard errors of 0.26, 0.01, and 7 x 10^{-3}, respectively.

3.8 Particle concentration effect for natural marine intertidal sediments

Sorption incubations with suspensions of the natural intertidal sediments at particle concentrations of 20 and 100 g l^{-1} revealed a particle concentration effect very similar to that observed for the artificially Fe coated sand (Figure 6): the specific sorption density (i.e., the amount of sorbed PO_4 per gram of sediment) decreased with increasing particle concentration. The Freundlich isotherm modified according to the MEA theory was also applied to the natural sediments. Estimated values of K_{sp}, m, and β were 0.77, 0.25, and 0.44, with standard errors of 0.06, 0.02, and 0.01, respectively.

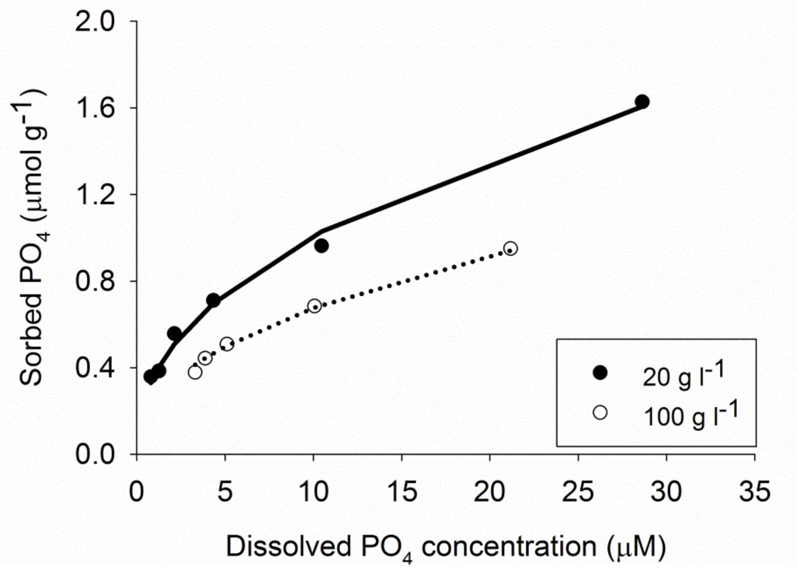


Figure 6. Isotherms for sorption experiments using natural intertidal sediment at two different particle concentrations, 20 and 100 g l^{-1}. Note that also in this case a particle concentration effect is observed. The lines show the fit of a single Freundlich isotherm, modified according to the MEA theory, applied to both the 20 g l^{-1} (solid line) and 100 g l^{-1} (dotted line) data. The estimated parameters K_{sp}, m, and β are 0.77, 0.25, and 0.44, with standard errors of 0.06, 0.02, and 0.01, respectively.

4. Discussion

Incubation experiments with a natural intertidal sediment and artificially Fe coated sand show that the extent and kinetics of PO_4 sorption depend on the particle concentration. In the experiments with mixed suspensions, increasing particle concentration results in less PO_4 sorbed per unit of mass of sediment. In addition, the apparent sorption capacity is significantly lower in the stagnant sediment incubations compared to the suspensions. Sorption of PO_4 to variable concentrations of Fe coated sand cannot be captured by a single Langmuir or Freundlich isotherm, even when allowing for two distinct sorption sites.

4.1 Particle concentration effect in the literature

Although a particle concentration effect has been reported for many different sorbent and sorbate combinations (O'Connor and Connolly 1980; Limousin et al. 2007), it is not universally observed (Maraqa et al. 1998; Pan et al. 1999). Furthermore, a variety of explanations have been proposed for the particle concentration effect. For example, it has been suggested that the effect is an artefact due to the presence of colloids, which contribute erroneously to the measured dissolved phase concentrations (Voice et al. 1983; Voice and Weber Jr. 1985; Higgo and Rees 1986; Servos and Muir 1989; Turner et al. 1999; Fehse et al. 2010). Other explanations include reactor wall effects (Rawling et al. 1998), competition between the sorbate and chemical species desorbing from the solid phase (Du and Hayashi 2006), flocculation or aggregation, which decrease the accessibility to sorption sites (Utomo and Hunter 2010), presence of large volume particles with low sorption capacity (Benoit 1995; Benoit and Rozan 1999), and sorbate dilution with increasing particle concentration, for which Chang and Wang (2002) propose a correction based on dimensional analysis. Particle-particle interactions such as increased desorption resulting from increased collision frequency (Di Toro 1985; Mackay and Powers 1987) or increased sorption due to enhanced surface area caused by particle abrasion and breakdown (Barrow and Shaw 1979) have also been put forward.

4.2 Particle concentration effect on PO_4 sorption

The use of artificially Fe-coated sand as the sorbent helps eliminate a number of the explanations for the particle concentration effect proposed in the literature. Quartz beach sand was selected for its resistance to abrasion and the X-ray amorphous Fe coating should provide PO_4 sorption sites not unlike those found in many oxic marine sediments (Froelich 1988; Jensen and Thamdrup 1993; Slomp et al. 1996). The sand was collected nearby the Balgzand area, where the intertidal sediment originates, so no major differences in mineral composition are expected, apart from the Fe content and lower grain size of the intertidal sediment. The coated sand grains have a specific surface area (0.32 m^2 g^{-1}) and diameters (250–500 µm) which fall within the typical ranges for sandy sediments (Slomp et al. 1998). The Fe content of the coated sediment (14.28 µmol g^{-1}) is also comparable to values measured on nearshore marine sediments varying from 3.3 to 21.3 µmol g^{-1} (van Raaphorst and Kloosterhuis 1994) and to the 23.2 µmol g^{-1} found for the intertidal sediment used in the present study. The native adsorbed PO_4 concentration in the Fe-coated sand, induced by the pre-loading, represents an average value similar to the ones found for North Sea and Wadden Sea sediments (van Raaphorst and Kloosterhuis 1994; Slomp et al. 1998).

The incubations with artificially Fe coated sand and low nutrient seawater should exclude interferences of organic compounds or other chemical species that may compete with PO_4 for sorption sites (e.g., dissolved silicate). The release of colloidal Fe from the coatings during the incubations is also ruled out by the dissolved Fe concentrations measured at the end of the incubations. These concentrations were always well below the detection limit (<0.05 µM) in all filtered samples, which implies a negligible contribution of Fe colloids smaller than 0.2 µm. The fairly uniform size distribution of the sand grains further excludes a particle concentration effect due to the presence of large volume particles (Benoit 1995; Benoit and Rozan 1999), while extensive tests showed that sorption of PO_4 to the walls of the polypropylene vials was insignificant.

Particle-particle interactions are also unlikely to explain the observations, as these interactions are expected to increase both when the particle concentration and the mixing speed increase. However, while sorption increased with a higher mixing speed, it decreased with increasing particle concentration (Figure 3). Similarly, an increase in sorption sites due to particle abrasion would be higher at a particle concentration of 200 g l^{-1}, which does not agree with the observations. Sorbate dilution, as proposed by Chang and Wang (2002), also failed to explain our data: their suggested isotherms, corrected for the particle concentration, could not fit our data with one single set of parameters.

The effect of mixing speed on PO_4 sorption (Figure 3A–C) raises the possibility that the particle concentration effect is an artefact related to the mixing regime.

Several mixing devices were tested and the vertical tube rotator proved to be the most efficient in keeping the particles continuously in suspension, unlike a rolling table and an orbital shaker. The results show that for the two highest rotation speeds (11 and 27 rpm) the sorption isotherms are indistinguishable and yield the highest sorption capacity. Nonetheless, even under these optimal mixing conditions, a clear particle concentration effect is observed (Figure 3D).

4.3 Sorption kinetics

In previous studies on PO_4 sorption to marine sediments, incubation times ranged between 24 and 48 h (Krom and Berner 1980; Jensen and Andersen 1992; Sundby et al. 1992; Slomp et al. 1998; House and Denison 2000; Wang et al. 2005; Zhou et al. 2005). Longer durations often introduce artefacts due to mineral dissolution and precipitation processes or microbial activity. For example, van Raaphorst and Kloosterhuis (1994) found that changes in dissolved PO_4 concentrations in suspensions of natural marine sediments persisted after 700 hours. They attributed this to a continuous supply of PO_4 from organic matter mineralization by microorganisms. A similar explanation does not apply to our incubations with Fe coated sand as organic matter and microbial activity were absent. Yet, in these experiments, stable dissolved PO_4 concentrations were often not reached at the end of the 14-day (336 hours) incubations (Figure 1). The variable incubation times and, presumably, the absence of equilibrium in many previous PO_4 sorption studies hinders the comparison of reported sorption capacities and partition coefficients (McGechan 2002), and can lead to misunderstandings in terms of sorption irreversibility (Limousin et al. 2007). Moreover, the particle concentration effect may have been overlooked in previous experiments on PO_4 sorption to marine sediments because of short incubation times (Pan and Liss 1998b). In our experiments, particle concentration and mixing effects became clearly apparent only after 8–24 hours. It seems thus essential to consider the time-dependent PO_4 sorption behaviour.

The 2-site kinetic model is able to reproduce the dissolved PO_4 concentration time series for the incubations with the Fe coated sand and nearshore marine sediment. The combination of a fast plus reversible and a slow plus irreversible (or extremely slowly reversible) sorption step is in line with previous work (Parfitt et al. 1975, Peinemann and Helmy 1977, Nyffeler et al. 1984, van der Zee and van Riemsdijk 1986, Froelich 1988, Ler and Stanforth 2003, Badruzzaman et al. 2004, Boujelben et al. 2008 and Reddy and DeLaune 2008). The slow process has been ascribed to solid state diffusion, surface precipitation, chemisorption or inner sphere surface complexation to surface metal ions. The exact mechanism leading to the irreversible sorption of PO_4 to the Fe coated sand cannot be determined from the available data, although the precipitation of a discrete ferric PO_4 phase at the surface of the sorbent particles can probably be excluded. The P/Fe molar ratios at the end of the sorption incubations were between 0.04 and 0.13, that is, a similar range as obtained by Slomp et al. (1996; 1998) for North Sea sediment containing poorly crystalline ferrihydrite and akageneite, but quite different from the ratios for ferric phosphates in estuarine sediments (0.7–0.8, Hyacinthe and Van Cappellen 2004) and wastewater activated sludge Fe-P precipitates (0.3–1, Caravelli et al. 2010) or a variety of ferric phosphate minerals (0.4–1, Fytianos et al. 1998, Matthiesen et al. 2001 and Gunnars et al. 2002).

The rate constants obtained by fitting the kinetic model to the dissolved PO_4 concentration time series data are in agreement with literature values for natural sorbent materials. The fast sorption (1.00×10^{-4}–5.60×10^{-3} l μmol^{-1} h^{-1}) and desorption constants (0.07–0.37 h^{-1}) yield apparent equilibrium sorption constants ($K = kaf/kdf$) for the fast process between 1.50×10^{-3} and 0.03 l μmol^{-1} (Table 1). The latter values fall within the same order of magnitude as the reported by van der Zee and van Riemsdijk (1986) and Koopmans et al. (2002) for sandy soils, by Ku et al. (1978), Mayer and Kramer (1986), Furumai et al. (1989), and Wang et al. (2005) for lake sediments, and with the values for aragonite and Fe coated sand obtained by Millero et al. (2001), Boujelben et al. (2008), and Jianbo et al. (2009) (Table 3). The estimated concentrations of fast and slow sorption sites vary between 0.31 and 8.14 µmol g^{-1}, and 0.55 and 1.70 µmol g^{-1}, respectively (Table 1), similar to PO_4 sorption capacities found in the literature (Table 3).

Table 3. Literature values for parameters estimated using the Langmuir isotherm equation (on which our numerical model is based) applied to data from comparable PO_4 sorption studies.

Sediment type	PS max (µmol g^{-1})	K (l µmol^{-1})	Reference
Sandy soils	6.8 – 16.3	0.01 – 0.05	(van Der Zee and van Riemsdijk 1986)
Lake	3.2 – 70.1	3.1×10^{-5} – 0.02	(S. Wang et al. 2005)
Natural and synthetic Fe coated sand	9.3 – 15.8	1.6×10^{-2} – 1.9×10^{-2}	(Boujelben et al. 2008)
Sandy soils	3.3 – 24.8	3×10^{-3} – 0.19	(Koopmans et al. 2002)
Lake	19.2 – 30.2	0.01 – 0.06	(Furumai and Ohgaki 1989)
Fe coated sand	7.9	0.08	(Jianbo et al. 2009
Lake	36.3 – 71.6	3×10^{-3} – 0.69	(Ku et al. 1978)
Lake	29.7 – 151.8	0.03 – 0.11	(Mayer and Kramer 1986)
Aragonite	15.5	0.04	(Millero et al. 2001)

When analyzing the error structure of the estimated sorption sites concentration from the 2-site kinetic model (Table 1) it can be seen that the standard errors are higher for the lower particle concentrations and mixing speeds and decrease with increasing particle concentration and mixing speed. A similar observation was made for the confidence intervals of Q_{max1} and $_2$ from the Langmuir fits (Table 2). The use in sorption incubations of low particle concentrations in combination with poor mixing yields unreliable results. In order to have a reproducible and reliable outcome, vigorous mixing and particle concentrations higher than 100 g l^{-1} should be used.

While the 2-site kinetic model and the 2-site Langmuir isotherm can reproduce the data for the various individual particle concentration and mixing speed combinations tested, this does not necessarily imply a mechanistic interpretation of the processes involved, nor does it confer a physical meaning to the estimated parameters. Therefore, caution must be taken on the conclusions drawn from the estimated fast or slow process parameters. In addition, the kinetic model in itself does not explain the particle concentration effect. The latter can therefore not be explained simply by differences in the rate at which equilibrium conditions are approached.

4.4 Metastable Equilibrium Adsorption (MEA) theory

Pan and Liss (1998a; 1998b) discuss the particle concentration effect within the framework of the MEA theory. The premise of MEA is that adsorbate molecules are in a metastable equilibrium state, rather than in the ideal equilibrium state. That is, a given adsorption density (moles of sorbate per unit of surface area or weight of sorbent) may correspond to different chemical potentials, depending on the organization of the sorbate at the solid-solution interface. Therefore, the adsorption density cannot be regarded as a thermodynamic state variable, like the dissolved concentration, but as a metastable state variable. In the ideal equilibrium state, where the adsorption density corresponds to a unique value of chemical potential, the molecules have full opportunity (and time) to freely adsorb and desorb until they all occupy the lowest energy state. If changes in the particle concentration (C_p) affect the metastable equilibrium state, then the sorption isotherm should explicitly depend on C_p. Pan and Liss further assume a power law dependence of the apparent equilibrium constant of adsorption, where $K \alpha Cp^{-m}$, with $m \geq 0$. This then yields the semi-empirical Freundlich-type isotherm of Equation (8) given in section 2.6.

As shown in Figures 5 and 6, the MEA-modified Freundlich isotherm adequately reproduces the data obtained in the mixed suspensions of Fe coated sand and natural intertidal sediment. When the isotherms obtained at the different mixing speeds are fitted individually to Equation (8), separate sets of parameter values improve the model fits. The differences between the estimated parameter sets, however, are neither large nor show consistent trends. The effect of mixing speed on the (near-) equilibrium isotherms is, therefore, considered to be non-significant. Similar successful applications of the MEA-based Freundlich isotherm include Zn sorption onto goethite (Pan and Liss 1998b) and PO_4 sorption onto Nile particulate matter and Saharan dust (Pan et al. 2002). However, it is important to mention that even though the MEA-modified Freundlich isotherm successfully fits our experimental data it doesn’t provide any mechanistic explanation for the particle concentration effect and is only valuable for comparison of the sorption parameters.

Even though the MEA-modified Freundlich isotherm can be used to correct for the particle concentration effect in the mixed suspension experiments, the same set of K_{sp}, m, and β values is unable to reproduce the isotherms from the stagnant incubations. Possibly, this reflects micro-scale gradients in dissolved PO_4 concentration with lower concentrations near the grain surfaces, or reduced accessibility to sorption sites at the grain surfaces because of the particle packing. Both would tend to lower the apparent sorption capacities of the packed versus the freely suspended Fe coated sands.

4.4 Mixed versus stagnant conditions: environmental implications

The relatively large differences between mixed and stagnant conditions illustrated by the inset in Figure 5 imply that the apparent PO_4 sorption capacity and the relative distribution of reversibly and irreversibly bound PO_4 may be significantly different depending on whether the sorbent particles are present in suspension or reside in deposited sediments. Although the formation of Ca-PO_4 minerals cannot be completely ruled out, due to the high PO_4 concentrations present (up to 1 mM), it is not likely that the observed removal of PO_4 was due to precipitation instead of sorption. The different PO_4 solutions were prepared an hour before the sorption experiment started. No evidence of precipitation with Ca or Mg was observed since the solution remained transparent and clear. In addition, a sample of the solution was taken right before being added to the sediment and the PO_4 concentrations were similar to the expected. When added to the Fe coated sand, a fast removal from solution was observed with most PO_4 being removed within the first 30 min (Figure 4), which contrasts with the relatively slow rates (5 h up to several days) found for apatite formation (Atlas and Pytkowicz 1977, Van Cappellen and Berner 1988, Slomp et al. 1996, Gunnars et al. 2004). The presence of $CaCO_3$ to favor the precipitation when in contact with the coated sand is also not likely (Martens et al. 1978, Van Cappellen and Berner 1988, Gunnars et al. 2004), since our artificial sediment was mainly composed of quartz particles to which an Fe coating was applied. Considering the discrepancies observed between suspended and stagnant incubations, it may thus not be straightforward to extrapolate isotherms measured in laboratory suspensions to estimate sorption parameters applicable to sediments at a different particle concentration (Barrow 1983).

In addition, environmental particles may experience large changes in particle density and mixing regimes during their life-time. For instance, sediments deposited along riverbeds and in intertidal or shallow areas are frequently resuspended, thus making a transition from a stagnant, high particle concentration state to a well-mixed, lower particle concentration state. In addition, the dissolved PO_4 concentration in interstitial pore waters and in the overlying water column may differ considerably, depending on the season. In coastal areas of the Northern hemisphere, the dissolved nutrient concentrations, including PO_4, typically increase in the water column during winter, while they may be low in sediment porewaters. A resuspension event may therefore cause an increased PO_4 uptake from the water column, because the sorption capacity of the particles may increase as a result of a lower particle concentration and efficient mixing with the aqueous phase. Resuspended particles may scavenge dissolved PO_4 from the water column before settling back to the bottom. Oppositely, during summer, when the water column nutrient concentrations are low and the porewater dissolved concentrations high, sediment resuspension could result in nutrient PO_4 release through desorption. However, because prior equilibration within the sediment took place at a high particle concentration under stagnant conditions, much of the sorbed PO_4 may be irreversibly bound to the particles and hence no longer exchangeable. The particle concentration effect may also have implications for aeolian dust depositing in the ocean (Pan et al. 2002). Usually seen as nutrient suppliers, depending on the initial loading, they may also work as scavengers in the presence of high nutrient concentrations as found in coastal areas, due to low particle concentration and consequent increased sorption capacity.

Conclusions

Sorption of PO_4 from seawater solutions onto marine intertidal sediments and artificially Fe coated sand exhibits a particle concentration effect, even for long incubation times and fully mixed suspensions. The estimation of sorption capacities and equilibrium constants using standard isotherm equations therefore yields parameter values that are dependent on the particle concentration, which hinders the comparison of data obtained at variable solid to solution ratios. However, for the mixed suspensions of Fe coated sands and intertidal sandy sediment, the particle concentration effect on the observed PO_4 sorption isotherms can be described by modifying the Freundlich isotherm according to the Metastable Equilibrium Adsorption theory (Pan and Liss 1998a), which then yields isotherm parameters that are independent of particle concentration. The results further show lower sorption capacities in packed columns of Fe coated sand compared to the mixed suspensions, possibly because of micro-scale concentration gradients and reduced accessibility of sorption sites. The effects of particle concentration and the mixing regime should therefore be taken into account when representing PO_4 sorption in environmental models by using isotherms modified in order to correct for this effect, since the amount of work needed to fully correct for the particle concentration effect is not realistic in experimental settings. The particle concentration effect also has implications in the natural environment. Sorption will be maximum when the particle concentration is lowest meaning that during a resuspension event the sediments will be more efficient in adsorbing PO_4 than in a packed sediment column. On the other hand, PO_4 sorbed during a resuspension event will more likely desorb than if it was bound to the particles at a high particle concentration. This manuscript draws attention for the first time, to previously overlooked aspects of sorption experiments applied to marine sediments such as the incubation time, the mixing and the use of different particle concentrations, which can significantly bias the final results. Several recommendations are suggested to allow the comparison of the results from different studies.

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Chapter 3

A budget of bioavailable inorganic phosphorus in the sediment for the western Wadden Sea

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Abstract

This paper provides quantitative and qualitative information on the sediment phosphorus (P) pool for the western Wadden Sea. Total extractable P concentrations in the sediment were lower than 4 µmol g^{-1}, with the exception of a depositional area of fine sediment where P concentrations reached 45 µmol g^{-1}. Most P was in a non-bioavailable form, with the bioavailable inorganic fraction corresponding to 12–42% of the total extractable pool and being mainly composed of Fe-bound P. A strong negative relationship between median grain size and bioavailable inorganic P content was found based on which a budget was calculated for the periods of maximum (February/March) and minimum (November) content of bioavailable inorganic P in the top 9 cm of sediment. The sediment P budget decreased from 1.0×10^8 moles in February/March to 0.6×10^8 moles in November. Assuming that the seasonal difference was due to release to the overlying water, an exchange of 4.0×10^7 moles of P was estimated, which has the potential to fuel approximately 40% of the current annual primary production of ~200 g C m^{-2}.

1. Introduction

The Wadden Sea is a shallow coastal area separated from the North Sea by a chain of barrier islands stretching from The Netherlands to Denmark. Nutrient supply, both in particulate and dissolved form, mainly occurs through freshwater input and import from the North Sea, partly in the form of organic matter to be recycled in the Wadden Sea sediments (Postma 1954; van Beusekom and de Jonge 2002; van Beusekom 2005). From 1935 to late 1980s the Wadden Sea experienced a strong increase in the freshwater load of total nitrogen (N) and phosphorus (P) (Philippart et al. 2000). During this period, primary production almost doubled with indications of a shift from N to P limitation (Cadée 1986; Philippart and Cadée 2000; Philippart et al. 2000). In the 1990s, measures to reduce eutrophication drastically decreased the nutrient (and especially P) discharge levels (de Jonge 1997; Philippart et al. 2000; van Raaphorst and de Jonge 2004; Colijn and van Beusekom 2005). In spite of the apparent coupling between freshwater nutrient supply and primary production, the decrease in nutrient loading was followed by a minor decline in productivity in the years after (de Jonge 1990; Cadée and Hegeman 1993; de Jonge et al. 1996; de Jonge 1997; van Beusekom 2005), which may point at the role of sediments in buffering the bioavailability of P in the water column.

Sediments are well known for their capacity to store P (Krom and Berner 1980; van Raaphorst and Kloosterhuis 1994; Boers et al. 1998; Reddy et al. 1998; Heidenreich and Kleeberg 2003). This storage can be quasi permanent with the precipitation of minerals containing P, such as apatite (Morse and Cook 1978; Ruttenberg and Berner 1993; Slomp et al. 1996b; van der Zee et al. 2002), or temporary, where P remains exchangeable, primarily through sorption onto iron (Fe) and manganese (Mn) oxides, and aluminium (Al) minerals (Einsele 1938; Sundby et al. 1992; Danen-Louwerse et al. 1993; Jensen et al. 1995; Slomp et al. 1996a, 1998; Rozan et al. 2002; Jiang et al. 2006; Spears et al. 2006; Tallberg et al. 2008). Temporary retention of P, bound to Fe and Al, is particularly intense in small grain size areas (Andrieux-Loyer and Aminot 2001). Similarly, organic P also tends to appear associated with the finer fraction. On the other hand, apatite or Ca bound P doesn't appear to be related with any specific grain size fraction (Andrieux-Loyer and Aminot 2001).

At present, the Wadden Sea sediments are likely proportionally contributing with more nutrients to the water column, since the nutrient supply by freshwater has decreased. This is opposite to the pre−1990s situation, when inorganic nutrient supply was thought to be mainly via freshwater discharge (van Beusekom 2005). The mineralization of autochthonous and allochthonous organic matter (Postma, 1954; van Beusekom and de Jonge 2002) and the adsorption/desorption from the sediment play then a major role in the magnitude and timing of the exchange with the water column.

The goal of this study was to construct a sediment P budget for the western Wadden Sea and to evaluate the potential of the sediments to supply the overlying water with P. The vertical distribution of P pools in the sediment is presented on a seasonal basis for both subtidal and intertidal areas, covering the range of grain sizes prevailing in the area. Sediment sorption incubations provide additional information on the adsorption/desorption potential of the sediments throughout the seasons. Sediment P content is evaluated in relation to a selection of sediment characteristics in order to identify the controls on the fractionation and release from the sediment. Conservative estimates are presented for the annual sediment P release by comparing minimum and maximum contents of bioavailable inorganic P in the sediment.

2. Materials and methods

2.1 Study area

The western Wadden Sea (Figure 1) has a total area of approximately 700 km^2 and an average water depth of 3.3 m. The tidal frequency is of 1.9 tides d^{-1}, with a mean tidal range in Den Helder of 1.4 m (de Jonge et al. 1993). The western Wadden Sea mainly includes the Marsdiep tidal basin and 1/3 of the total area consists of intertidal flats. The basin sediments are composed of sand (94–99%) with a minor silt fraction and are sometimes intercalated with relict peat. The Balgzand is one of the largest tidal flats in the basin, with an exposure time of approximately 4.5 h during every tidal cycle (van Raaphorst and Kloosterhuis 1994). Reported oxygen penetration depths for the Balgzand tidal flat varied between 2 mm in summer and 4 mm in winter (van Duyl and Kop 1990).

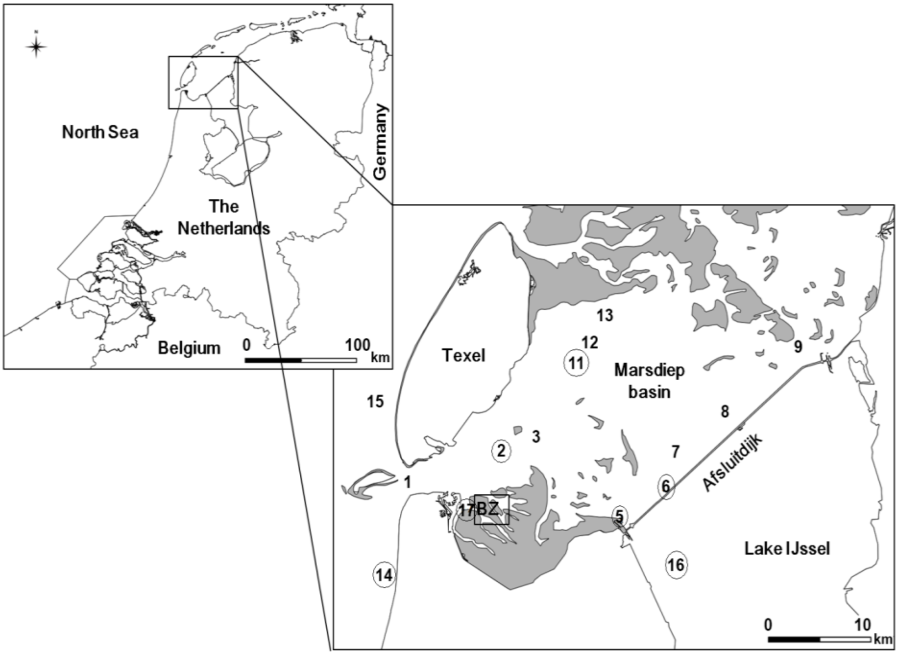

Figure 1. Map of the location of the western Wadden Sea and identification of the sampled subtidal stations (1–17) within the Marsdiep basin. The stations that have been sampled seasonally are marked with a circle. The open rectangle indicates the Balgzand (BZ) tidal flat area, where the intertidal stations (BZ18–84) were located.

2.2 Sampling scheme

Sixteen subtidal stations (1–17) were selected in the Marsdiep tidal basin, North Sea and Lake IJssel (Figure 1) six of which (2, 5, 6, 11, 14, and 17) were seasonally sampled. The stations were chosen to cover the seawater and freshwater end-members and the range of sediment grain sizes of the basin. The samples were taken seasonally in April and November 2009, February, March, May, and September 2010. For each station, 10 to 14 sediment cores (i.d. 6 cm) were collected using a Barnett-Watson multicorer. Sediment was used for porewater extractions, for solid phase analysis and sorption experiments, and for sequential extractions to determine the fractionation of P.

For the Balgzand tidal flat, 9 stations (BZ18–84) were sampled in December 2009 and June 2010. For each station, 8 cores (i.d. 6 cm) were taken manually for porewater extraction and solid phase analysis. To determine the fractionation and sorption of P, the upper 1 cm of sediment was collected separately with a 5 ml syringe in 2 layers (0–0.5 and 0.5–1 cm).

2.3 Porewater and solid phase sampling

Six to ten cores (i.d. 6 cm) were sliced using a hydraulically activated core slicer, for the following depth intervals: 0–0.25, 0.25–0.5, 0.5–0.75, 0.75–1, 1–1.5, 1.5–2, 2–2.5, 2.5–3, 3–4, 4–5, 5–6, 6–7, 7–9, 9–11, 11–13, 13–15, 15–17, 17–19, 19–21, 21–23 cm. Porewater was extracted and directly filtered (0.2 µm pore diameter Acrodisc filter, Supor® membrane) by centrifugation (2000 rpm for 12 minutes). Slicing and centrifugation were performed at *in situ* temperature within 2–3h after core collection. Samples were stored in pony vials at −20°C for ammonium (NH_4) and at 4°C for dissolved inorganic P, after acidification with 5 N HCl suprapure (2 µl/ml of sample) to keep Fe and P in the dissolved state. After centrifugation the solid phase was stored in BD Falcon^{TM} Tubes, frozen and freeze dried for later determination of grain size distribution and particulate organic C content.

2.4 Sediment P fractionation

For the subtidal stations, 4 cores (i.d. 6 cm) were sliced (0–0.25, 0.25–0.5, 0.5–0.75, 0.75–1, 1–2, 2–3, 3–5, 5–9 cm) and the corresponding depth intervals were pooled and homogenized under a N_2 atmosphere to avoid oxidation of the anoxic sediment. Only the first layer, roughly corresponding to the reported oxygen penetration depths for these sediments, was processed under standard atmospheric conditions. For the intertidal stations both layers (0–0.25 and 0.25–0.5 cm) were treated as oxic. A 0.5 ml subsample of sediment was collected with a syringe and sequentially extracted in a BD Falcon^{TM} tube according to a slightly modified procedure of Lukkari et al. (2007a; 2007b) (Figure 2).

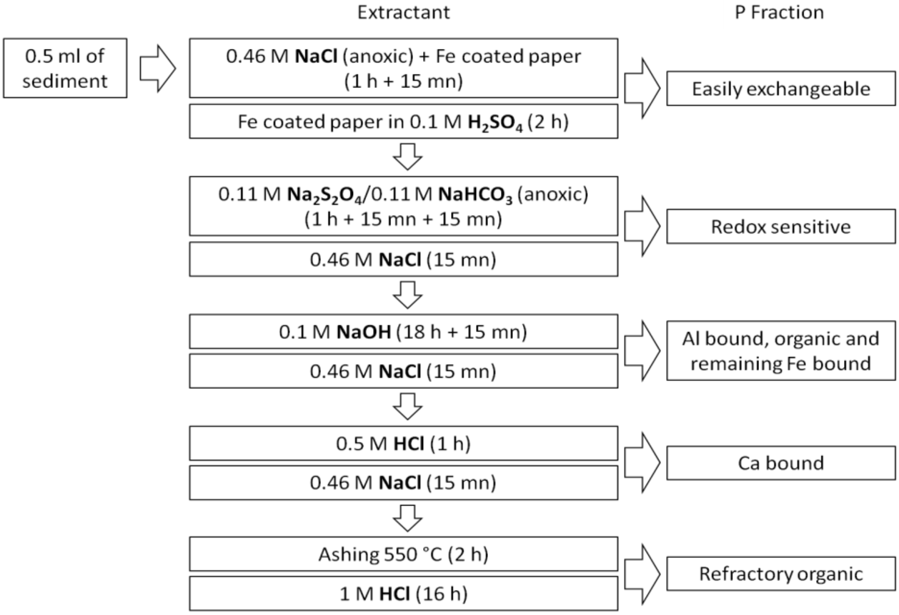

Figure 2. Scheme of the P fractionation procedure based on Lukkari et al. (2007a)

The first step of the extraction was modified to include a Fe oxide coated paper (Chardon 2000) in the solution, to create a permanent sink for desorbing P (van der Zee et al. 1987). Apart from the uppermost oxic layer, extractions were performed under a N_2 atmosphere in gas tight chambers. After each extraction step, samples were collected, acidified to a final pH of approximately 2 with 5 N HCl suprapure for the 1st, 2nd, and 3rd steps and stored at 4°C for the analysis of dissolved inorganic P (and Fe in September 2010). Total P was not analyzed in this extraction procedure. Separate 0.5 ml samples were taken for each slice to determine the dry mass after freeze drying.

To test reproducibility, full triplicates were run in September 2010 revealing coefficients of variation for P of 47, 12, 12, 12, and 27% for the 0.46 M NaCl, 0.11 M NaDB, 0.1 M NaOH, 0.5 M HCl, and 1 M HCl extractable P fractions. The coefficients of variation for Fe, following the same extraction procedure, were of 98, 25, 19, 12, and 6% for the fractions described above. The coefficients of variation were quite high, but in accordance with the values given by Lukkari et al. (2007a; 2007b). This is particularly the case for the 0.46 M NaCl extractable fraction, probably due to the relatively low concentrations measured for this fraction.

2.5 Sorption experiments

Sorption experiments were conducted to determine the sediment sorption capacity for P and to estimate EPC_0, the concentration of dissolved P for which adsorption is balanced by desorption and thereby no changes occur in the concentration in solution. Sorption experiments were run for all subtidal stations in March (2, 5, 11, 14, and 17) and September (2, 5, 6, and 11) 2010 and for the intertidal stations from Balgzand in June 2010 (BZ 18, 36, 70, and 84). BD Falcon^{TM} tubes were filled with 40 ml of one of six different P concentration solutions. The solutions were prepared using low nutrient North Atlantic seawater, diluted to the appropriate salinity for each station. The six initial P concentrations varied between 0 and 200 µM. For each station the range of concentrations was chosen on the basis of the concentration of dissolved P in the pore water in order to create conditions for both adsorption and desorption for a single series of incubations. Sediment from the upper two slices (0–0.5 cm, roughly corresponding to the oxic-anoxic boundary for these sediments) from the 4 cores used for the P fractionation was pooled and homogenized. Six subsamples of 0.5 ml were taken with a syringe and added to the tubes to yield an approximate particle concentration of 20 g l^{-1}. For stations 5 and 17 in March 2010 and stations 5 and 6 in September 2010 incubations were also run at a particle concentration of 150 g l^{-1} (van Raaphorst and Kloosterhuis 1994; Leote et al. 2013). The tubes were mixed on a roller table for 2 weeks in darkness at 15°C, close to *in situ* temperature. Samples for P analysis were taken immediately after adding the sediment and after 0.5, 2, 8, 24, 48, 96, 168, and 336 hours. The samples were acidified and stored at 4°C until further analysis. The sampled volume was replaced with low nutrient North Atlantic seawater diluted to *in situ* salinity to minimize the effect of a changing particle concentration. The tubes were opened for 15 minutes each day to prevent anoxic conditions.

2.6 Analytical procedures

Dissolved inorganic P, NH_4, and Fe analyses were performed on a TRAACS 800 Segmented Continuous Flow Analyzer according to the methods of Murphy and Riley (1962), Grasshoff et al. (1999), and Gibbs (1979), respectively. Calibration was performed using North Atlantic Low Nutrient Seawater, diluted to the sample's salinity and spiked with different volumes of a stock solution. Stock solutions of 10 mM NH_4Cl, KH_2PO_4, and $FeCl_3$ were prepared using analytical grade reagents. The detection limit and precision for the P analysis were 0.007 and 0.002 µM and the NH_4 and Fe(II) analysis had a detection limit and precision of 0.07 and 0.03 µM and 0.05 and 0.10 µM, respectively. Particulate organic C was determined as particulate C, after removal of all carbonates with 2 M HCl, on freeze dried and grinded sediment, according to the method of Verardo et al. (1990), using a Thermo-Interscience Flash EA1112 Series Elemental Analyzer with acetanilide (Thermo Finnigan) as a reference material for calibration. The detection limit was 100 ppm and precision 0.3%. Porosity was determined by weight loss after freeze drying. Grain size was determined using sediment samples homogenized after freeze-drying in a Coulter LS230.

2.7 Statistical analysis and calculations

To evaluate the relationships between P fractions and sediment characteristics, a Principal Component Analysis (PCA) was applied to our data using package STATS from software R (R Development Core Team 2011). The analysis was done for the surface (0–0.25 cm) and a deep layer (5–9 cm), using data from the April 2009 cruise, when the largest number of stations was covered. Two fractions of sediment P were compared: total extractable P, corresponding to the sum of all pools, and bioavailable inorganic P, which, in this study, corresponds to the 0.46 M NaCl + 0.11 M NaDB extractable fractions (de Jonge et al. 1993). Median grain size, porosity, sorting (calculated as (Φ 95% – Φ 5%)/2) and specific surface area (estimated by the Coulter LS230) were used as sediment characteristics. Porewater dissolved P and NH_4 were used as a proxy for mineralization, and particulate organic C was used as an indicator for organic matter availability in the sediment and deposition conditions. The data for total extractable and bioavailable inorganic P fractions, NH_4 and P porewater concentrations, median grain size, and total particulate organic C were all logarithmically transformed in order to improve the linearity of relationships. Data was standardized to mean = 0 and variance = 1 before analysis.

Budgets of bioavailable inorganic P for the entire western Wadden Sea were calculated for the months of February/March, when the content was maximum, and for November, when the content was minimum. For the budget of February/March, data from station 6 in February and stations 2, 5, 11, and 17 in March was used, while for November, data from stations 2, 5, 6, 11, and 17 was used. The sediment content of bioavailable inorganic P was extrapolated for the entire basin on the basis of the observed strong relationship between median grain size and P content from PCA. A map of median grain size distribution from the Rijkswaterstaat was available for grain size intervals of 0–60, 60–120, 120–150, 150–240, 240–300, and >300 µm. A power equation was used to relate sediment bioavailable inorganic P to the median grain size and to determine the content at the mid grain size value for each interval represented in the map. Data were multiplied by the total area represented by the grain size interval and the resulting values for all areas were added to yield the budget for the western Wadden Sea. The bioavailable inorganic P content between the two seasons was compared with a Student's t-test for significance and the difference in budgets between February/March and November was assumed to result from net release to the overlying water.

Isotherms to describe sorption equilibrium between a solid and a liquid phase frequently assume sorption as a process independent of the particle concentration. However, several studies have revealed that this is often not the case (O'Connor and Connolly 1980; Voice et al. 1983; van Raaphorst and Kloosterhuis 1994; Pan and Liss 1998b; Koopmans et al. 2004; Leote et al. 2013). The sorption isotherms in this study were fitted using the Freundlich equation modified according to the Metastable Adsorption theory (Pan and Liss 1998a; Leote et al, 2013). This approach allows the estimation of parameter values that are independent from the particle concentration chosen for the sorption assays, and is defined as $PS = K_{sp} \times Cp^{-m} \times P^{\beta} - NAP$, where PS is the sorbed P concentration, K_{sp} an equilibrium sorption constant, Cp the particle concentration, m, and β empirical constants, and NAP the native adsorbed P. Cp was known and NAP was determined experimentally as the 0.46 M NaCl extractable fraction, while K_{sp}, m, and β were estimated by fitting the expression to the experimental time series of dissolved P concentrations using the Solver tool from Microsoft Office Excel 2007. EPC_0 was estimated by assuming no net adsorption or desorption (i.e. setting PS to zero) and solving the equation for the estimated parameter values. The maximum sorption capacity was estimated by applying a Langmuir isotherm to the incubations performed at a lower particle concentration of 20 g l^{-1}, in order to minimize the error caused by the release of P due to organic matter mineralization. The isotherm was fitted to the data using the error minimization routine developed by Bolster and Hornberger (2006). The estimated sorption parameters were tested for the presence of linear correlations with sediment characteristics and different P pools using Microsoft Office Excel 2007.

3. Results and Discussion

3.1 Sediment characterization

The characteristics of the sediments that were seasonally sampled, averaged for all the sampling periods, are listed in Table 1. The median grain size of sediments from subtidal stations (2–17) ranged from 43 µm for station 6 to 389 µm for station 5, while the intertidal stations (BZ 18–84) showed a more uniform grain size distribution between 154 and 204 µm. Silt content was low and varied between 0.7 and 18.3% with the exception of station 6 which had a silt content of 72.3%. The grain size distribution and silt content were relatively uniform with depth, except for stations 5 and 11, which showed clear heterogeneity in composition down core. The sediment sorting varied between 0.7 (station 17) and 3.3 (station 6), and the higher values, indicating enhanced sorting, were found for the stations with a higher silt content. Sorting was generally constant for the first cm and increased down core. Porosity was very similar for all stations (0.34–0.40), apart from station 6 with an average porosity of 0.78. No seasonality was observed for median grain size, silt content, sorting or porosity. The organic C content was an order of magnitude higher for station 6 with an average value of 2.00 wt% while the contents for other stations were between 0.04 and 0.43 wt%, similarly to the values obtained for the North Sea, German Bight and Skagerrak (Slomp et al. 1996, 1998; van Raaphorst et al. 1990). Stations 2, 5, 6, and 17 showed higher contents in autumn and winter (data not shown), while stations 11 and 14 showed maximum values in spring. Active macrofauna, such as jackknife clams (*Ensis minor)*, gastropods (*Hydrobia sp*.), and small polychaetes, was observed at all stations, apart from 6.

Table 1. Physical and chemical characteristics from all subtidal and intertidal sediments that were seasonally sampled. Stations 2 to 17 are from subtidal areas while stations 18 to 84 are from the Balgzand (BZ) tidal flat.

Station	Mean Depth (m)	Median grain size (µm)	Silt (%)	Porosity	Sorting	Organic C (wt%)
2	3.6	231	4.7	0.40	1.3	0.10
5	2.8	389	5.4	0.38	1.9	0.16
6	2.7	43	72.3	0.78	3.3	2.00
11	6.2	300	9.3	0.38	2.3	0.43
14	11.0	323	2.3	0.34	1.6	0.06
17	3.4	229	0.7	0.34	0.7	0.04
BZ 18	~ 0.0	204	1.5	0.35	0.7	0.09
BZ 20	~ 0.0	198	2.9	0.40	0.8	0.09
BZ 36	~ 0.0	194	3.7	0.40	1.0	0.08
BZ 50	~ 0.0	184	6.1	0.40	1.7	0.12
BZ 52	~ 0.0	170	9.3	0.39	2.1	0.12
BZ 64	~ 0.0	174	8.5	0.40	1.6	0.08
BZ 70	~ 0.0	175	12.5	0.40	2.1	0.10
BZ 74	~ 0.0	172	18.3	0.45	2.6	0.15
BZ 84	~ 0.0	154	9.2	---	1.8	---

3.2 P and Fe in the sediment

3.2.1 Porewater concentrations of P and Fe

The concentrations of dissolved P in the porewater varied between 0 µM in the surface and 15 µM at 9 cm depth for the sandy stations (Figure 3). Station 6, however, showed concentrations of 900 µM in the porewater at 9 cm depth. Most stations showed lower concentrations at the surface, increasing with depth. Fe showed vertical profiles similar to P (Figure 3), suggesting that P is removed from the porewater by sorption/co-precipitation with Fe oxides. An exception was station 6, where higher concentrations were observed in the first cm, decreasing to zero at higher depths, likely due to the precipitation of Fe-S minerals (Thode-Andersen and Jørgensen 1989). The concentrations of dissolved Fe ranged between 0 and 48 µM.

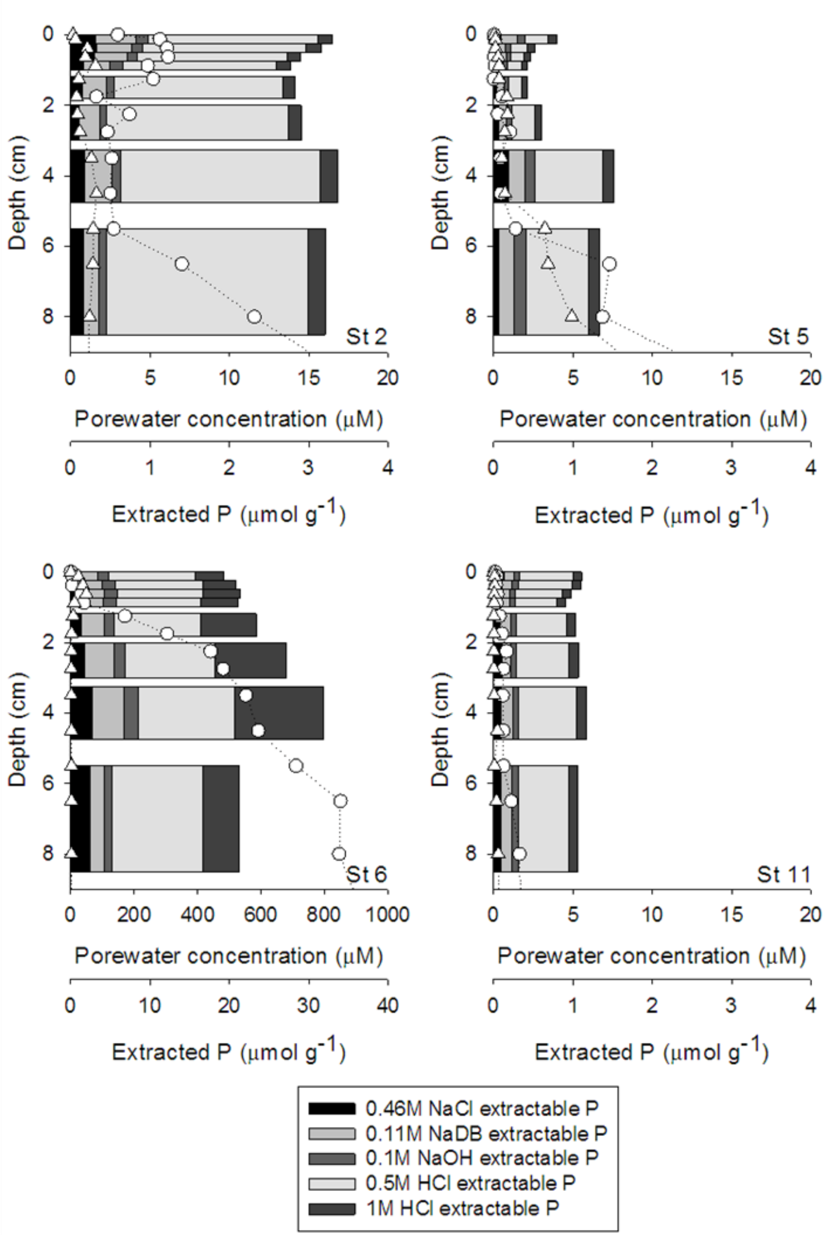

Figure 3. P fractionation for the subtidal stations 2, 5, 6, and 11 down to 9 cm depth. The results are from September 2010 cruise when stations 14 and 17 were not sampled. Note the different scale on station 6. Porewater concentrations of P (circles) and Fe (triangles) are also presented.

3.2.2 Total extractable P

The content of total extractable P in the sediment was quite low, ranging from 0.4 to 4.2 µmol g^{-1}, for most subtidal stations (1–17) and slightly higher for the intertidal stations (BZ 18–84), varying between 2.6 and 8.0 µmol g^{-1} (Table 2 and Figure 3). These results are similar to the sediment P contents of less than 5 µmol g^{-1} by de Jonge et al. (1993), between 0.89 and 6.52 µmol g^{-1} by van Raaphorst and Kloosterhuis (1994) and 7.25 µmol g^{-1} by Postma (1954), for intertidal, and mainly sandy areas in the western Wadden Sea. Yet, these concentrations are in the lower range of values observed for other temperate coastal systems (6–60 µmol g^{-1}) (Krom and Berner 1981; Sundby et al. 1992; Jensen and Thamdrup 1993; Jensen et al. 1995; Slomp et al. 1996a; Andrieux-Loyer and Aminot 2001; Lillebø et al. 2007; Tallberg et al. 2008), and for a compilation of several open ocean and continental margin settings (7–307 µmol g^{-1}) given by Filippelli (1997). Exceptions were stations 16, in the IJssel Lake, and station 6 with contents as high as 45 µmol g^{-1}, falling well within the values measured for other coastal areas (Table 2). Station 6 represents a fine grained depositional area of approximately 11 km^2 and relatively shallow (Table 1), that resulted from the closure of the Afsluitdijk, the dike separating the freshwater Lake IJssel from the Wadden Sea, since 1932 (Berger et al. 1987; Oost and de Boer 1994) and has been overlooked as a temporal or permanent repository of P in previous budgets for the western Wadden Sea.

Table 2. Seasonal P content in µmol g^{-1} from the sequential extractions. Subtidal stations (2–17) show range of values from 0 to 9 cm depth. Intertidal stations (BZ18–84) show range of values from 0 to 1 cm depth. Peat was collected from the sediment surface of station 11.

	0.46M	0.11M NaDB	0.1M NaOH	0.5M HCl	1M HCl	Total
February 2010						
St 2	0.28–0.71	0.21–0.49	0.14–0.24	1.26–1.88	0.21–0.50	2.31–3.27
St 5	0.15–0.77	0.14–0.57	0.07–0.17	0.17–0.60	0.14–0.57	0.66–2.69
St 6	3.14–11.18	2.57–6.42	0.77–2.20	8.74–12.24	2.87–9.95	18.84–41.99
St 11	0.18–0.41	0.13–0.20	0.09–0.13	0.43–1.64	0.16–0.26	1.04–2.61
St 17	0.16–0.32	0.28–0.34	0.10–0.13	0.99–1.69	0.21–0.25	1.82–2.47
March 2010						
St 2	0.36–0.51	0.22–0.27	0.10–0.12	1.11–1.58	0.22–0.26	2.07–2.74
St 5	0.28–0.57	0.11–0.25	0.05–0.14	0.28–0.66	0.13–0.44	0.85–2.06

St 11	0.27–0.47	0.12–0.59	0.07–0.17	0.63–1.27	0.21–0.44	1.40–2.82
St 14	0.06–0.31	0.02–0.19	0.02–0.07	0.30–0.86	0.11–0.26	0.51–1.63
St 17	0.18–0.24	0.19–0.22	0.10–0.15	0.98–1.42	0.19–0.23	1.66–2.21
Peat (St11)	0.85	0.77	1.63	4.67	3.12	11.04
April 2009						
St 2	0.26–0.41	0.32–0.44	0.03–0.11	1.09–1.76	0.18–0.37	1.97–2.72
St 5	0.09–0.24	0.13–0.41	0.08–0.23	0.12–0.40	0.09–0.76	0.51–1.63
St 6	1.89–3.49	1.23–5.64	0.30–0.95	7.52–11.25	1.39–2.17	12.44–23.13
St 11	0.10–0.34	0.16–0.54	0.07–0.26	0.28–2.07	0.14–0.96	0.75–4.17
St 14	0.06–0.18	0.03–0.14	0.03–0.07	0.47–1.12	0.15–0.21	0.89–1.71
St 16	1.87–10.02	1.27–12.14	0.22–4.91	4.18–13.21	1.28–7.43	11.03–45.35
June 2010						
St BZ 18	0.38–0.42	0.29–0.32	0.08–0.09	2.12–2.43	0.26–0.27	3.22–3.46
St BZ 36	0.34–0.41	0.17–0.22	0.08–0.09	2.34–2.58	0.31–0.33	3.40–3.48
St BZ 70	0.78–1.36	0.73–1.17	0.35–0.54	2.94–3.81	0.89–1.08	5.70–7.96
St BZ 84	0.88–0.94	0.56–0.64	0.16–0.19	3.70–3.83	0.44–0.50	5.84–6.01
Septemb 2010						
St 2	0.10–0.32	0.19–0.50	0.09–0.16	1.90–2.54	0.15–0.22	2.77–3.36
St 5	0.03–0.19	0.08–0.21	0.05–0.15	0.16–0.87	0.07–0.14	0.42–1.52
St 6	0.61–2.69	1.87–3.97	0.94–1.83	10.69–12.14	3.59–11.20	19.32–31.83
St 11	0.08–0.13	0.11–0.14	0.07–0.08	0.53–0.72	0.10–0.13	0.91–1.17
Novemb 2009						
St 2	0.20–0.57	0.01–0.12	0.05–0.13	1.21–2.22	0.23–0.28	2.25–3.11
St 5	0.24–0.36	0.06–0.08	0.11–0.39	0.30–1.26	0.21–0.61	1.19–2.54
St 6	2.59–10.22	0.86–4.40	0.67–2.04	9.64–12.15	1.82–8.75	16.05–37.40
St 11	0.13–0.25	0.02–0.04	0.01–0.12	0.33–0.68	0.15–0.28	0.64–1.33
St 17	0.21–0.39	0.05–0.24	0.09–0.11	1.62–2.51	0.20–0.25	2.22–3.11
Decemb 2009						
St BZ 18	0.24–0.25	0.20–0.21	0.08–0.09	1.84–1.95	0.27–0.31	2.66–2.79
St BZ 20	0.33–0.36	0.30–0.33	0.12–0.13	1.76–2.53	0.29–0.30	2.58–2.87
St BZ 36	0.36–0.40	0.29–0.30	0.13–0.14	1.98–2.65	0.32–0.34	3.17–3.75
St BZ 50	0.51–0.53	0.32–0.31	0.23–0.25	2.00–2.09	0.31–0.32	3.38–3.49
St BZ 52	0.45–0.46	0.28–0.29	0.24–0.25	1.93–2.47	0.30–0.33	3.20–3.78
St BZ 64	0.35–0.39	0.24–0.26	0.10–0.13	1.95–2.37	0.28–0.32	2.97–3.42
St BZ 74	0.54–0.62	0.40–0.41	0.13–0.14	1.97–2.29	0.39–0.40	3.46–3.84

3.2.3 P fractionation

Depending on the chemical form, the time scale of P retention in the sediment may range from quasi permanent to temporary. Therefore, it is essential to know its distribution between the main different pools, in addition to quantifying the total content. The sequential extraction procedure as described by Lukkari et al. (2007a; 2007b) was chosen since it focuses primarily on separating the more labile solid phase pools, which to a large extent determine the bioavailability of P throughout the year.

The fraction extracted with 0.5 M HCl appeared the main fraction for all stations (Figure 3), corresponding to 23–77% of the total extractable pool, similarly to the findings of de Jonge et al. (1993) for the Marsdiep basin. The concentration for the sandy stations (median grain size >60 µm) ranged between 0.1–3.8 µmol g^{-1}, while for station 6 (median grain size <60 µm) it varied between 7.5–12.2 µmol g^{-1} (Table 2). This pool became slightly more important with depth, with station 5 showing a random vertical contribution. This fraction is assumed to represent the Ca bound fraction, which includes apatite of terrestrial and/or authigenic origin. Authigenic apatite may form in the sediment under high porewater P concentrations, i.e. in spring/summer when both desorption from the redox sensitive fraction and mineralization are at maximum (Ruttenberg and Berner 1993; Slomp et al. 1996b; Gomez et al. 1999; van der Zee et al. 2002; Anschutz et al. 2007). Such conditions were observed, especially for station 6 (Figure 3), and some of the Ca-bound P found in this depositional area, particularly the increase observed in April and September (Figure 4), may thus be of authigenic origin (Ruttenberg and Berner 1993, Slomp et al. 1996b, van Beusekom 1999).

The fractions extracted with 0.46 M NaCl and 0.11 M NaDB were similar in terms of concentrations and equally second most important (Figure 3). The concentrations ranged between 0.0–1.4 µmol g^{-1} and 0.0–1.2 µmol g^{-1} for the sandy stations, and between 0.6–11.2 µmol g^{-1} and 0.9–6.4 µmol g^{-1} for station 6, respectively (Table 2). These two fractions made a similar relative contribution throughout the year, between 5–29% and 2–27% of the total extractable P, respectively. The 0.46 M NaCl extractable pool includes all P that can be exchanged through sorption between the liquid and solid phases as well as porewater P. The 0.11 M NaDB fraction includes P bound to Fe and Mn oxides that can be released following reduction and solubilisation of these poorly crystallized oxides during anoxic mineralization of organic matter by microbes or re-oxidation of reduced compounds, such as H_2S (Al-Raei et al. 2009). These two pools together, assumed to represent the sediment P that is potentially exchanged with the porewater and the overlying water and may support benthic and pelagic primary production (inorganic bioavailable pool) corresponded to 12–42% of the total extractable P content. This agrees with the results of Jensen and Thamdrup (1993), Raaphorst and Kloosterhuis (1994), and Tallberg et al. (2008) for comparable coastal environments. In addition, the fact that these two pools showed a clear seasonal variation fits well with the assumption that they represent temporary sinks (Jensen and Thamdrup 1993; Jensen et al. 1995; Koski-Vahala et al. 2001). Even though the content decreased down core, the 0.46 M NaCl and 0.11 M NaDB extractable fractions never showed contributions lower than 3 and 1%, respectively. Again the exception was station 6 with both concentrations increasing with depth, possibly because the high Fe concentrations allow for the presence of a large pool of Fe oxides, as supported by the high 0.11 M NaDB extractable Fe content (Table 3), which likely compensate for the high reduction rates expected for this station, resultant from mineralization of organic matter.

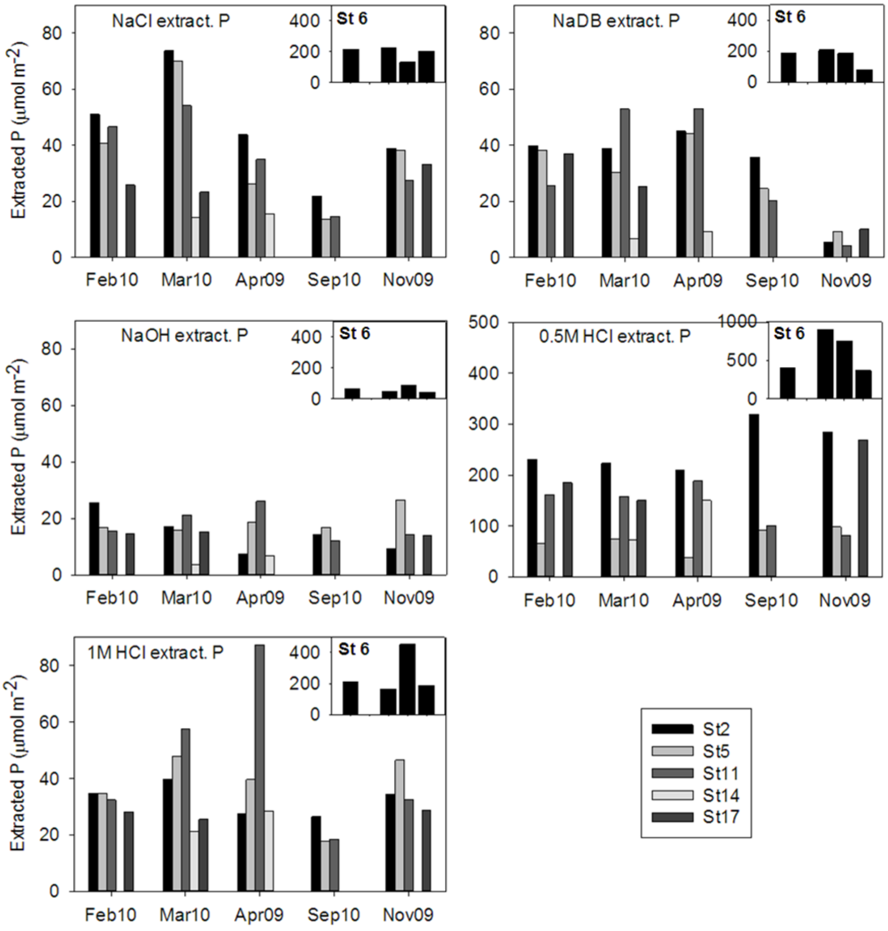

Figure 4. Seasonal variation on P fractionation for an integrated depth of 9 cm per square meter. Results are presented for all subtidal stations. The insets on the upper right side with a different scale are from station 6. Note that the 0.5 M HCl extractable P plot has a different scale.

Table 3. Extracted Fe in µmol g^{-1} from September 2010 cruise and December 2009 field trip to the Balgzand (BZ) tidal flat. Subtidal stations (2–11) show a range of values from 0 to 9 cm depth. Intertidal stations (BZ18–74) show range of values between 0 and 1 cm depth. Ratio corresponds to 0.11 M NaDB extractable Fe/P.

	0.46 M NaCl	0.11 M NaDB	0.1 M NaOH	0.5 M HCl	1 M HCl	Total	Fe/P
Sep 2010							
St 2	0.0	5.1–7.0	0.2–0.3	4.7–6.4	9.9–12.6	20.7–24.4	12.1
St 5	0.0	1.3–4.4	0.1–0.2	0.8–1.9	2.9–4.4	5.2–11.0	12.8
St 6	0.0–0.1	26.2–50.8	0.8–2.0	39.0–131.1	41.5–96.4	107.6–280.3	8.0
St 11	0.0	2.3–3.9	0.1–0.2	1.5–2.4	5.6–6.6	9.8–12.0	12.7
Dec 2009							
St BZ 18	0.0	4.9–13.7	0.2–0.2	3.8–4.0	9.2–10.4	18.3–28.0	20.6
St BZ 20	0.0	6.4–6.7	0.2–0.2	5.1–5.3	11.5–11.7	23.5–23.5	9.9
St BZ 36	0.0	6.2–7.4	0.2–0.3	5.2–5.3	12.0–12.9	24.5–24.9	10.1
St BZ 50	0.0	6.2–7.6	0.2–0.2	3.9–4.4	10.8–11.6	21.6–23.3	8.3
St BZ 52	0.0	5.7–5.7	0.2–0.2	4.6–4.6	12.0–12.4	22.4–22.8	7.8
St BZ 64	0.0	5.8–11.0	0.1–0.1	3.6–3.7	11.5–11.9	21.1–26.5	13.6
St BZ 74	0.0	6.8–7.9	0.2–0.3	4.2–4.3	12.9–13.4	24.7–25.4	7.5

The pool extracted with 1 M HCl after combustion, assumed to correspond to refractory organic P was the fourth most important fraction (Figure 3) and contributed 6–28% of the total extractable P. The concentrations ranged from 0.1–1.1 µmol g^{-1} for the sandy stations and from 1.4–11.2 µmol g^{-1} for station 6 (Table 2). This pool was approximately constant with depth for stations 11, 14, and 17. Station 2 showed a down core decrease, station 6 showed an increase, while station 5 revealed an erratic distribution. Even though refractory organic matter doesn’t often contain high amounts of P, in station 6, where the contribution of the refractory pool was higher, organic matter degradation may be more limited due to the decreased availability of oxygen and high organic matter content (Table 1), thereby retaining a higher content of P. In addition to refractory organic matter this pool may also include some P bound to non easily reducible Fe, as suggested by the high contents of Fe extracted in this step (Table 3).

The P fraction extracted with 0.1 M NaOH was the least important quantitatively (Figure 3), with a relative contribution of 2–12%. The concentrations varied between 0.0–0.5 µmol g^{-1} for the sandy stations and 0.3–2.2 µmol g^{-1} for station 6 (Table 2). Its contribution was approximately constant with depth for stations 11, 14, and 17. Stations 2 and 6 showed a down core decrease, while station 5 showed a random contribution of this pool. According to the procedure of Lukkari et al. (2007a), this pool is assumed to include the Al (clay) bound and organic fractions. However, since total P was not analyzed, our results only show the inorganic P fraction in this pool. Therefore, its relatively low importance may be explained by the fact that most of our sediment was relatively coarse with only minor admixtures of clays.

In some locations, the sediment was interspersed with ancient peat deposits. In order to assess the importance of peat to the sediment P budget, sequential extractions were additionally done on separate peat samples from station 11, collected in March 2010. The total extractable P content was slightly higher than for sandy sediments: 11.0 µmol g^{-1}, but much lower than the measured for station 6 (Table 2). However, the distribution between pools was different from the sediment samples, with the following contribution from each pool: 0.5 M HCl extractable (42%), 1 M HCl extractable (28%), 0.1 M NaOH extractable (15%), 0.46 M NaCl extractable (8%), and 0.11 M NaDB extractable (7%).

Concluding, 58–88% of the total extractable pool was found to be in a non-bioavailable form (1 M HCl, 0.5 M HCl, and 0.1 M NaOH extractable P) representing a long-term reservoir of P in the sediment. This is similar to what has been found for lake, deep sea, and coastal environments (Morse and Cook 1978; Fytianos and Kotzakioti 2005; Tallberg et al. 2008). The little or absent seasonal variation in the contents of the 0.1 M NaOH and 0.5 M HCl extractable P pools supports this idea, with the exception of the 0.5 M HCl extractable P for station 6 (Figure 4).

3.2.4 Seasonal variation

Since the distribution of P in the sediment is dynamic and depending on external input, oxygen availability, and redox conditions, it is vital to look at its seasonal distribution, especially for the inorganic bioavailable fraction (Figure 4). Considering P content integrated over a layer with 9 cm depth, the 0.46 M NaCl extractable pool showed the clearest seasonal variation, with higher contents in February/March, decreasing until September and increasing again in November. The 0.11 M NaDB extractable pool showed a similar pattern, with a less marked variation but higher contents in March and April decreasing until November. For the intertidal stations, higher concentrations were found in June, with slightly lower concentrations in December (Table 2). The lower bioavailable P contents observed in the warmer months of April and September and higher contents in the winter months of November, February, and March agree with van Raaphorst and Kloosterhuis (1994), van Raaphorst et al. (1988), and van Beusekom (1999) for the Wadden Sea. The spring increase in temperature and light promotes the blooming of phytoplankton (Rozan et al. 2002) and a reduction in water column P. At the same time, the concentration of dissolved P in the porewater will increase due to organic matter mineralization and reductive dissolution of Fe-P minerals (Holm and Lindstrom 1978; Krom and Berner 1981; Sundby et al. 1992; Grunwald et al. 2010), as confirmed by the strong coupling observed between porewater Fe and P concentrations (Figure 3). The reduction in thickness of the oxic layer, hence the reduction in sorptive capacity of the sediment allied to the strong gradient in dissolved P between porewater and water column results in enhanced release from the sediment and a reduction in the contents of 0.46 M NaCl and 0.11 M NaDB extractable P (Figure 4) (Krom and Berner 1980; Sundby et al. 1986; Furumai and Ohgaki 1989). The reversal occurs in fall and winter when the decrease in temperature and a lowered availability of organic matter slows down microbial activity, thereby increasing the availability of oxygen and favouring the precipitation of Fe oxides at the redox interface. Temporary storage of P until the next blooming season will then occur by sorption (Crosby et al. 1981; Slomp et al. 1996a; Gomez et al. 1999; Mayer and Jarrell 2000; Jiang et al. 2006) and/or co precipitation of Fe-P minerals (Hyacinthe and Van Cappellen 2004), thereby increasing the 0.46 M NaCl and 0.11 M NaDB extractable pools (Figure 4).

Oppositely, the 0.1 M NaOH extractable P was the most constant pool, with very similar contents throughout the year, similarly to the 0.5 M HCl extractable P pool (Figure 4). However, for the later pool, station 6 showed a clearly higher P content in April, decreasing until November and increasing again in February, possibly due to the formation of authigenic apatite. The 1 M HCl extractable pool, being associated with organic matter, showed a similar seasonal variation as the 0.46 M NaCl and the 0.11 M NaDB extractable pools for most stations (Figure 4). The exceptions were station 11, with a high content of 1 M HCl extractable P in April and station 6, where no clear seasonal pattern was observed, in spite of the variation between the different months.

3.2.5 Fe fractionation in the sediment

The content of total extractable Fe in September 2010 was similar for the sandy stations ranging from 5.2–28.0 µmol g^{-1} (Table 3) in agreement with the findings of van Raaphorst and Kloosterhuis (1994) for several tidal flats in the

Marsdiep and Vlie basins, using 0.1 M HCl as an extractant. Station 6 was an exception, showing a much higher extractable Fe content of 107.6–280.3 µmol g^{-1} (Table 3). The 0.46 M NaCl extractable Fe showed the lowest contribution (~0% of the total extractable Fe pool), followed by the 0.1 M NaOH (1–2%), the 0.5 M HCl (13–44%), the 0.11 M NaDB (19–49%), and the 1 M HCl extractable fraction (36–54%). All Fe fractions increased down core. The large fraction of Fe dissolved with 0.5 and 1 M HCl indicates a large presence of more crystalline Fe-minerals such as ferrihydrite and FeS minerals, in addition to the easily reducible amorphous Fe minerals extracted with 0.11 M NaDB (Slomp et al. 1996a).

3.2.6 Molar ratios of NaDB and total extractable Fe/P

The Fe/P ratio in the sediment provides qualitative information about the interaction between Fe and P, i.e. sorption or co-precipitation and the Fe-P minerals present.

The depth averaged ratio for the 0.11 M NaDB extractable Fe/P obtained for the subtidal sediments ranged between 8.0 for station 6 and 12.1–12.8 for stations 2, 5, and 11 (Table 3). The intertidal stations showed a larger variability with ratios between 7.5 (station 74) and 20.6 (station 18) (Table 3). In addition, a strong correlation between Fe and P content, especially for the 0.11 M NaDB extractable fraction was observed ($R^2 = 0.98$), similarly to previous studies (Jensen and Thamdrup 1993; van Raaphorst and Kloosterhuis 1994; Fytianos and Kotzakioti 2005) and confirms the closely coupled cycling of these two elements. The ratios obtained were similar to the measured by Jensen and Thamdrup (1993), de Jonge et al. (1993), Slomp et al.(1996a), and Grunwald et al. (2010) for the Aarhus bay, Kattegat and Skagerrak, the Wadden Sea, and the North Sea. However, they were much higher than the ratio of 2 found by Jensen et al. (1995) in late summer for the Aarhus bay. At this level the buffer capacity of the sediment for P sorption is exhausted, which does not seem to be the case in our sediments. Our ratios were also much higher than the 1.3–1.4 found by Hyacinthe and Van Cappellen (2004) for authigenic Fe-P phases, which may indicate that sorption and not co-precipitation is the main process retaining P in our sediments.

The depth averaged total extractable Fe/P ratios were lowest for station 2, with a ratio of 7.3, followed by stations 6, 5, and 11 with ratios of 7.9, 10.2, and 10.6, respectively. The intertidal stations showed total extractable Fe/P ratios of 6.5–8.5, which is also lower than the 0.11 M NaDB extractable Fe/P ratios. This suggests that a large fraction of P is bound to other cations than Fe, such as Ca, which is corroborated by the extraction results. An exception was station 6 with similar total extractable and 0.11 M NaDB extractable Fe/P ratios, indicating a stronger coupling between P and Fe cycling for this station (Figure 3 and Table 3).

3.3 Sorption experiments

Sorption experiments were conducted on sediments collected in March, June, and September 2010 to assess the sediment sorption capacity and to estimate EPC_0, the concentration of dissolved P at which adsorption and desorption are in equilibrium.

In general, the sediments released P when incubated at initial concentrations below 2 µmol P l^{-1}. At higher initial concentrations, the concentration of dissolved P decreased with time, suggesting adsorption by the sediment. After 100 h of incubation an increase in P concentration in solution was observed, especially for the incubations at higher particle concentrations, presumably as a consequence of P release from organic matter mineralization. Consequently, to reduce the effect of P added to the incubations by degradation of organic matter, only the incubations performed at a particle concentration of 20 g l^{-1} were used for the fitting of sorption isotherms.

Sorption isotherms are known to be sensitive to the time of incubation, temperature, particle concentration, ionic strength of the solution, etc, which hampers the comparison of the results obtained from different studies (Limousin et al. 2007; Leote et al. 2013). For that reason, to obtain isotherm parameters that are independent of the particle concentration, a modified Freundlich equation was used (see section 2.7). All isotherms were successfully fitted with $0.93 < R^2 < 1.00$ (Figure 5) and the parameters obtained are shown on Table 4. K_{sp} varied between 0.23 (station 17 in March 2010) and 2.62 (station 14 in March 2010) and was, in general, lower in March than in September. The exponent m ranged between −0.20 (peat from station 11 in March 2010) and 0.84 (station 14 in March 2010). β varied between 0.34 (station 84 in June 2010) and 0.90 (station 6 in September 2010) with stations 2 and 5 showing similar values in March and September. EPC_0 ranged between 0.1 µM (station 5 in September 2010) and 2.6 µM (station 2 in March 2010), with an average value of 1.1 µM, similar to the range reported by Slomp et al. (1998) for North Sea sediments, with incubations done for 48 h at a 1:1 ratio, but substantially lower than the 5–10 µM measured by van Raaphorst and Kloosterhuis (1994) for tidal flats in the Wadden Sea, with incubations done at a particle concentration of 50 g l^{-1} for 700 h. No seasonal or spatial pattern was observed for *m*, *β* or EPC_0. Q_{max} varied between 1 and 5.6 µmol g^{-1} with exceptionally high values of 43.9 µmol g^{-1} for station 6 and 17.5 µmol g^{-1} for the peat samples from station 11. For the stations that were sampled on a seasonal basis, Q_{max} only showed minor variation between the seasons, indicating that no major biases were induced in our incubations due to mineralization of organic matter. Apart from Q_{max}, sorption parameters did not show a clear correlation with sediment characteristics nor with the various P pools. Q_{max} showed a strong correlation with the 0.11 M NaDB, 0.1 M NaOH, 0.5 M HCl, 1 M HCl, and total extractable P pools with R^2 of 0.88, 0.76, 0.87, 0.87, and 0.89, as well as with the median grain size, specific surface area, solid phase, and porewater Fe and organic C content yielding R^2 values of 0.67, 0.85, 0.98, 0.94, and 0.96, respectively.

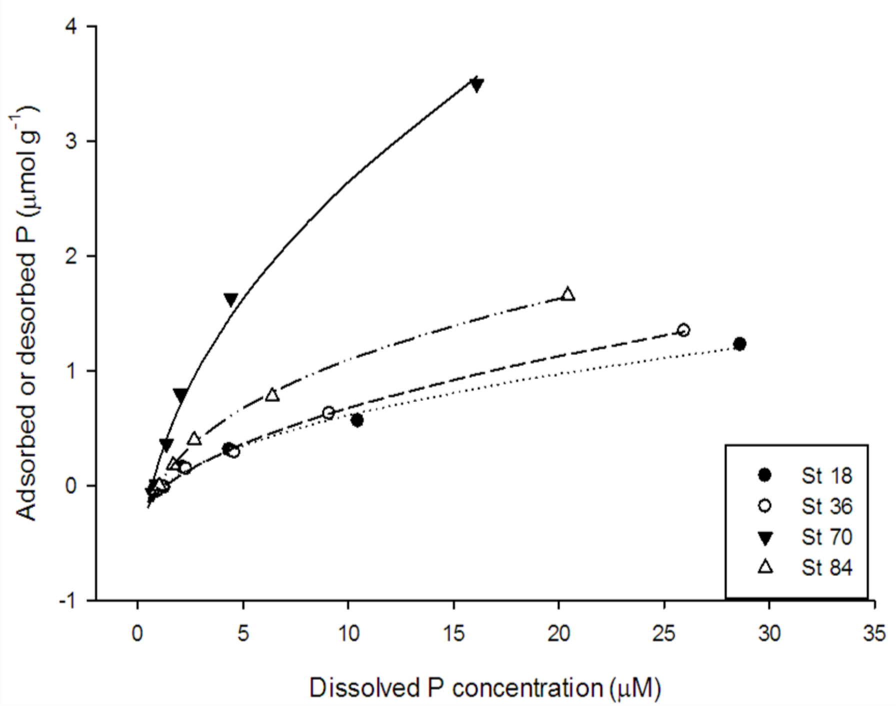

Figure 5. Sorption isotherms from the Balgzand sediments collected in June 2010 fitted using the Freundlich isotherm equation, modified according to the Metastable Adsorption Theory. All fits had a 0.93 < R^2 < 1.00.

Table 4. Estimated parameters using the modified Freundlich isotherm: *K_{sp}*, *m* and *β*, *NAP* (native adsorbed P in µmol g^{-1}), *EPC_0* (equilibrium concentration at which no adsorption or desorption occurs in µM), and *Q_{max}* (maximum sorption capacity in µmol g^{-1}). The later was estimated using the Langmuir isotherm. Data from March and September 2010 cruises and June 2010 field campaign to the Balgzand intertidal flat are presented.

	Station	K_{sp}	m	β	NAP	EPC_0	Q_{max}
Mar 2010	2	0.56	0.35	0.62	0.4	2.6	2.7
Mar 2010	5	0.33	−0.06	0.49	0.4	0.8	1.8
Mar 2010	11	0.95	0.39	0.49	0.3	1.3	1.9
Mar 2010	14	2.62	0.84	0.59	0.3	1.6	1.7
Mar 2010	17	0.23	0.06	0.68	0.2	1.3	2.7
Mar 2010	peat	1.90	−0.20	0.49	0.9	0.1	17.5
Sep 2010	2	1.02	0.48	0.61	0.3	1.5	2.7
Sep 2010	5	1.17	0.45	0.49	0.1	0.1	1.2
Sep 2010	6	1.46	0.38	0.90	0.7	1.0	43.9
Sep 2010	11	1.13	0.71	0.68	0.1	0.7	1.9
Jun 2010	BZ 18	1.01	0.35	0.44	0.4	1.2	1.8
Jun 2010	BZ 36	1.24	0.47	0.52	0.4	1.4	2.3
Jun 2010	BZ 70	2.16	0.23	0.46	1.1	0.7	5.6
Jun 2010	BZ 84	2.22	0.31	0.34	0.9	1.0	2.7

Comparing *EPC_0* with the porewater concentration of P provides an indication for the likelihood of adsorption or desorption. Plotting all combinations (Figure 6) shows that adsorption is favoured over desorption during most of the year, since the porewater concentrations exceeded the *EPC_0* values. This was especially clear during summer and for the intertidal stations, which agrees well with the estimated *Ksp* values (Table 4) showing maximum values during summer, especially for the intertidal stations. Only in March for stations 2, 14, and 17 and in September for station 11, desorption was clearly favoured, with the porewater concentrations much lower than the EPC_0. This is in accordance with the extraction results, which indicate a loss of P in the 0.46 M NaCl and 0.11 M NaDB extractable pools between February/March and September for stations 2, 5, 6, 11, and 17 (Figure 4). The strong likelihood of adsorption observed for the intertidal stations, however, may be somewhat overestimated due to the timing of sampling. Samples were taken during low tide when the diffusive exchange of P between the sediment and the water column is halted. Porewater concentrations of P may temporally increase to levels exceeding the EPC_0, favouring adsorption. During periods of immersion, the diffusion of dissolved P to the water column may result in a rapid release of the P sorbed during emersion. Thus, the sorption/desorption of P for intertidal sediments may be more dynamic and phased with the tides. Even though sorption experiments may provide an indication of the saturation status of sediments and the likelihood of adsorption or desorption, a quantification of seasonal release requires information on the sediment P content, as provided by the sequential extractions.

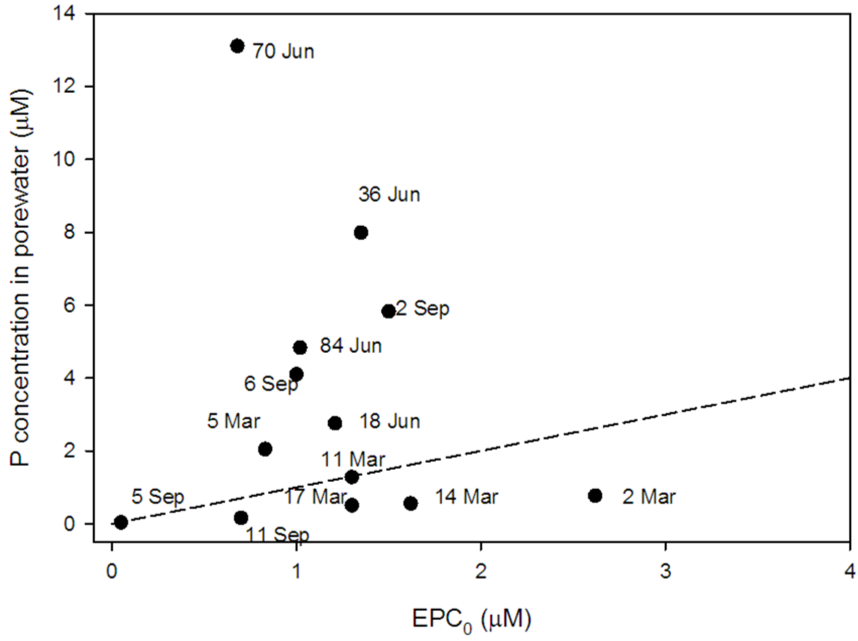

Figure 6. *EPC$_0$* calculated from the sorption isotherms versus the porewater concentration of dissolved P. The dashed line indicates when *EPC$_0$* is equal to the porewater concentration. Dots below the line suggest desorption, while dots above the line indicate adsorption.

3.4 Relationships between P fractions and sediment characteristics

The principal component analysis (PCA) suggested the use of 2 components, explaining 78 and 79% of the observed variance for the surface and deepest layer. For the surface layer, the total extractable and the bioavailable inorganic P showed a strong negative relationship with median grain size, indicating that larger grain sizes correlated with lower sediment P content (Figure 7). For the deeper layer, however, this relationship was almost absent. Both P pools showed a positive relationship with the specific surface area of the sediment for both the surface and deeper layers, indicating that sediment grain size is a major key explaining the distribution and content of sediment P. This has been observed in other studies (Rao and Berner 1997; Andrieux-Loyer and Aminot 2001) and directly related with the presence of a large sorbed P fraction, dependent on the surface area available for sorption. Since smaller grain size particles will have larger areas for the same volume, retention of P is expected to be higher. Therefore, grain size distribution was used as a master variable to extrapolate P content to other areas of the western Wadden Sea that were not sampled. Weak positive relationships were also observed for sorting, organic C content, and the porewater concentrations of NH_4^+ and P (Figure 7). The scores of the stations in the first 2 components show that stations 6 and 16 were clearly different from the others. As these stations have much higher silt contents this strongly suggests that principal component 1 is largely dominated by grain size. On the other hand, principal component 2 seems to be related with sorting or organic C content.

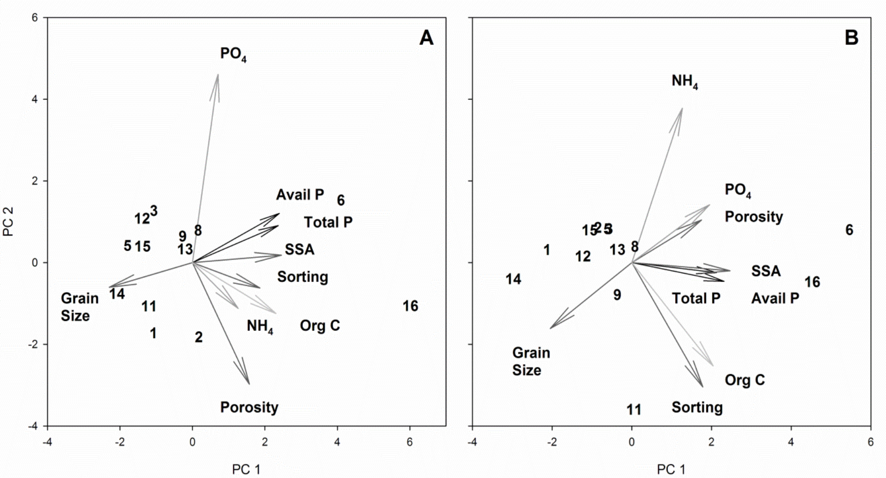

Figure 7. Results from the Principal Component Analysis using the data from April 2009 cruise, when the largest number of stations was sampled. A) shows data from the surface layer (0–0.25 cm) and B) presents data from the deepest layer (5–9 cm). Vectors indicate the relationships between the parameters along 2 principal components. Vectors pointing in opposite directions indicate a negative relation and vectors pointing in the same direction indicate a positive relation. Vectors making an angle of 90° show no relation between them, and are, therefore, independent. The numbers indicate the scores of each station.

3.5 Sediment P budget and the seasonal release of P

The calculation of sediment P budgets was based on the strong negative relationship observed for the bioavailable inorganic P content and median grain size (see chapter 3.4 and Figure 7). Budgets were calculated for the periods of maximum and minimum P content of the sediment, i.e. February/March and November and an estimate of P release by the sediment was calculated from their difference assuming that it was due to release to the overlying water and not to exchange between the pools. Another assumption was that no seasonal changes in the sediment grain size occurred due to flocculation/aggregation and deposition under lower energetic conditions in summer (Chang et al. 2006). However, uptake of P by benthic primary producers may also occur, which will act as a filter and limit the release of P to the overlying water. Since no measurements on the organic P content were made this hypothesis cannot be ruled out. Station 6 showed a large increase in the 0.5 M HCl extractable P towards spring and summer (Figure 4), which may indicate apatite formation fuelled by P release from the inorganic bioavailable pool (Figure 3). Nevertheless, the contribution from the area with fine grained sediments to the total budget is minor so the potential bias was assumed to be insignificant.

For the entire western Wadden Sea, the bioavailable inorganic P pool in the surface 9 cm of the sediment amounted to 1.0 x 10^8 moles of P (3222 ton) in February/March and to 0.6 x 10^8 moles of P (1897 ton) in November. The content was integrated over a 9 cm depth layer, which approximates the global average mixing depth for bioturbated sediments (Boudreau 1998) and applies to all stations but 6. In the sediments, the activity of macrofauna often results in a homogenization of the sediment, resulting in a layer of variable depth with similar composition. In addition to bioturbation and bioirrigation, advective mixing induced by tidal currents and wave action may also affect the release of P. The exchange between porewater and the overlying water is increased, promoting the release of P, but also reducing the effect of anoxia by the pumping of oxygenated porewater to higher depths, which results in the oxidation of Fe (Aller and Aller 1998; Huettel et al. 1998). Nevertheless, the budgets are considered conservative since topography was not taken into account when calculating the surface areas used to extrapolate the P content. This will result in an underestimation of the surface area and, consequently, in an underestimation of the budget. The seasonal variation in the 0.46 M NaCl and 0.11 M NaDB extractable pools suggested a period of sediment loading with P during autumn and winter, followed by a period of release during spring and summer (Figure 4). Since the sediment P content between February/March and November proved to be statistically different ($p < 0.04$ using a t-test) the difference was used to estimate an annual release of 0.4 x 10^8 moles of P (1325 ton) for the entire basin. This corresponds to a release of 0.4–1.8 µmol g^{-1} which is comparable with the values of 0.1–1.2 µmol g^{-1} obtained by van Raaphorst and Kloosterhuis (1994). The area with a mean grain size <60 µm accounted for 118 mmol m^{-2} whereas the area with a mean grain size >60 µm accounted for 60 mmol m^{-2}. The fine grained sediments only covered 2% of the total western Wadden Sea area, but nevertheless accounted for 10 and 13% of the total sediment P content in spring and fall, respectively. However, in terms of release its contribution was limited to ~5%. Despite the large reservoir of P, the release to the overlying water may not be as efficient in the fine grained area as in other areas with larger grain size, presumably due to a subdued biological and physical mixing of sediments in these depositional areas or a higher sorption capacity resulting from the higher Fe content (Table 3) and increased specific surface area (Table 4). Assuming a C:P ratio of 106, the estimated release of P can sustain a primary production of ~80 g C m^{-2}, which is well within the range given by de Jonge et al. (1993) of 45–150 g C m^{-2} y^{-1}, who considered a sediment layer of 12 cm. This accounts for ~40 % of the annual production of 200 g C m^{-2} y^{-1} for 2004 (Philippart et al. 2007). For reasons previously discussed, the budget is to be considered conservative, the more as it does not account for the rapid mineralization of organic matter which is supplied to the sediment during spring and summer. This may substantially increase the contribution of sediments in replenishing the water column with P.

Conclusions

Sediment P content and EPC_0 values, indicating the equilibrium concentration for sorption, were low, indicating that the sediments are lightly loaded with P. An exception was a depositional area characterized by grain size <60 µm. In addition, most sediment P was in a non-bioavailable form, presumably bound to Ca or Al compounds or in the form of refractory organic P. Nevertheless, the bioavailable inorganic P, corresponding largely to Fe bound P, represented 12–42% of the total extractable pool. The relatively high Fe/P ratios suggest that binding was mainly through sorption, instead of co-precipitation of Fe-P minerals. The bioavailable inorganic pool showed a clear seasonal variation, with a period of loading in autumn/winter and a period of release in spring/summer. This pattern is likely related with a more intense mineralization and consequent oxygen demand in the warmer months, which results in the reductive dissolution of Fe oxides and a decrease in the sorption capacity. The results suggest that, at present, P release from the sediment depends mainly on the annual recycling of organic material and not on desorption of P stored in the sediment during the past period of high freshwater loading. A sediment P budget was estimated for the western Wadden Sea for the months of February/March and November, when the contents were maximum and minimum, respectively. The difference yielded a conservative annual release with the potential to fuel 40% of present day primary productivity.

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Chapter 4

Sediment-water exchange of nutrients in the Marsdiep basin, western Wadden Sea: phosphorus limitation induced by a controlled release?

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In revision for *Continental Shelf Research*

Abstract

To quantify the release of inorganic phosphorus from the sediments and assess its contribution to present primary production, a basin-wide study of the Marsdiep (western Wadden Sea, The Netherlands) was performed. Two distinct sedimentary zones were identified: a depositional area characterized by a high content of silt and organic carbon and the majority of the area, composed of fine/medium sand and a low organic carbon content. The sediment-water exchange was higher in the fine grained area and based on a relationship found between the release of inorganic phosphorus and the silt content, a total annual release of 1.0 x 10^7 mol P was estimated for the whole Marsdiep basin. A spatial variability in the processes controlling the nutrient release was found. The exchange in the depositional area resulted mainly from molecular diffusive transport, with mineralization and sorption determining the concentration of inorganic phosphorus in the porewater. For the coarser sediment stations the activity of macrofauna clearly enhanced the fluxes. Given the relative demand of nutrients (N:P:Si) for phytoplankton growth, the release was phosphorus deficient during most of the year. Nevertheless, it increased from February until September, in parallel with the increase in temperature and light, thus having the potential to fuel primary production during their seasonal growth period. In terms of absolute values, our results show that the present exchange, enhanced by the activity of macrofauna has the potential to fuel a significant fraction of modern levels of primary productivity.

1. Introduction

The Wadden Sea is a shallow sea situated along the Dutch, German, and Danish coast. It consists of a series of tidal basins that are seaward bound by barrier islands and connected to the adjacent North Sea by tidal inlets. Its westernmost basin, the Marsdiep, has been subject to many studies on biological productivity, from primary productivity up to the level of fish and birds. The potential carrying capacity of the basin is set to a large degree by the advection and regeneration of nutrients, supporting the primary production that forms the food source for higher trophic levels. Nutrients are supplied mainly by freshwater discharge from Lake IJssel (van Raaphorst and de Jonge 2004), through the tidal exchange with the coastal North Sea (Postma 1954; de Jonge 1997), and in the case of nitrogen (N), by dry and wet atmospheric deposition (Hertel et al. 2002). These nutrients may be supplied in a dissolved state and be directly available for primary production or as particulate biogenic debris requiring solubilization prior to uptake by primary producers.

Several authors have highlighted the increase in nutrient loading during the 20th century and the impact on primary productivity and phytoplankton biomass (e.g. Postma and Rommets 1970; de Jonge and Postma 1974; Cadée 1986; Cadée and Hegeman 1993; van Beusekom et al. 2001). A historic reconstruction from about 1930 onwards showed a 4–6 times increase in N and phosphorus (P) loading until mid 1980s (van Raaphorst and Jonge 2004). In parallel, the rates of annual primary production, first documented in the 1970s, increased at least 3-fold from ca 150 g C m^{-2} up to 375 g C m^{-2} in the mid 1990s (Cadée and Hegeman 2002). The correlation between the inorganic P loading from Lake IJssel and primary production in the Marsdiep tidal inlet, as observed by de Jonge et al. (1993), would support the idea that P availability controls primary productivity in this basin. In an effort to counter eutrophication, measures were taken to reduce the loadings of N and especially P, resulting in a reduction by 45% for N and 75% for P by 2006 (OSPAR comission 2010). Despite a clear reduction as reflected in winter nutrient stocks of N and P since mid 1980s, annual primary production did not decline concomitantly, but remained high until the late 1990s. Annual primary production rates decreased only after 1994 to values around 200 g C m^{-2} in 2000 (Cadée and Hegeman 2002). Apparently, the availability of the limiting element for primary production, presumably P, was not substantially affected as to instantly lower the annual rates of primary production, which again stirred the debate on what factors and mechanisms control the productivity in the western Wadden Sea (van Beusekom and de Jonge 2002; Colijn and Cadée 2003; Philippart et al. 2007; Ly et al. 2014).

The view of the Wadden Sea as a net heterotrophic environment (Postma 1954; de Jonge and Postma 1974; Hoppema 1991; van Beusekom et al. 1999; van Beusekom and de Jonge 2002) then assumes a particular importance. The mineralization of organic matter imported from the North Sea adds to the nutrient regeneration from locally produced biogenic debris and may buffer the availability of P while loadings are reduced. In shallow coastal seas, the sediments are usually quantitatively important in the mineralization of biogenic debris. Following mineralization, nutrients are released to the water column or retained in the sediment. For the specific case of phosphate (PO_4), retention is accomplished by several mechanisms and occurs on various time scales. Long-term to permanent retention is often related to the burial of precipitates of PO_4 with calcium (Ca) or iron (Fe) (Ruttenberg and Berner 1993; Hyacinthe and Van Cappellen 2004) or to the burial of refractory organic matter, whereas short-term retention on a scale of months occurs by adsorption onto Fe and manganese (Mn) oxides (Krom and Berner 1980; Sundby et al. 1992; Slomp et al. 1996).The production of benthic biomass, from bacteria to macrofauna, also retains PO_4 for variable time periods. The release of PO_4 to the overlying water is generally viewed as the net balance of mineralization and temporary retention by sorption to the sediment. These two antagonistic processes may modulate the extent and seasonal timing of the release, resulting in an efficient supply of nutrients to primary producers in critical periods of the year; a more intense mineralization, typical of spring and summer, when temperatures and organic matter supply are higher, coincides with a lower sorption capacity of the sediment, due to the reductive dissolution of Fe oxides in the degradation of organic material (Krom and Berner 1980). The actual sediment-water exchange, however, is more complex and results from the combined effect of nutrient availability in the porewater and transport, whether diffusive and controlled by the concentration gradient between sediment and water or advective as driven by waves, bottom currents, groundwater discharge, and macrofauna irrigation (Krantzberg 1985; Huettel et al. 1998).

For reasons of accessibility, geochemical studies in the western Wadden Sea have been mostly confined to its intertidal areas. These areas harbor macrobenthic communities that are important for the bio-deposition and burial of organic rich sediments and are therefore believed to represent areas of enhanced metabolic activity and nutrient regeneration. As a consequence, the subtidal domain has been underexposed and its contribution to overall mineralization of organic matter in the basin is unknown. Given the present limitation of PO_4 on phytoplankton productivity in the western Wadden Sea (Philippart et al. 2000; Ly et al. 2014), this paper aims to estimate the annual release of PO_4 from subtidal sediments in the Marsdiep basin and the identification of the main processes affecting the sediment-water exchange.

2. Materials and methods

2.1 Study Site

The Marsdiep basin, in the western Wadden Sea (Figure 1), covers approximately 700 km^2 and has a relatively low average depth of 3.3 m (Oost and de Boer 1994). Approximately 8% of the area is intertidal (Compton et al. 2013), with a mean tidal range in Den Helder of 1.37 m. Per tide approximately 1% of the total water volume is exchanged with the North Sea which yields a residence time of 5–15 days for the water mass, depending on meteorological conditions, neap-spring tidal phase and distance from the North Sea (Nauw et al. 2014). Freshwater enters the basin directly at an average daily rate of ca 400 $m^3\ s^{-1}$ at the sluices of Kornwerderzand and Den Oever, which control the discharge from Lake IJssel. Indirectly, freshwater is also added by exchange with the coastal North Sea that receives freshwater from the rivers Rhine, Meuse, and Scheldt. Some minor contributions are made from the harbors of Harlingen and Den Helder. This admixture of fresh water results in salinity extremes from close to 0 near the sluices up to 32 in the Marsdiep tidal inlet (van Aken 2008). An estimated 98% of western Wadden Sea sediments is composed of sand (app. 100–500 µm), leaving only 2% covered with finer grained particles (<70 µm). The fine grained sediments are largely confined to the intertidal margins of the basin and to a subtidal depositional area near the Afsluitdijk, which separates the western Wadden Sea from the freshwater Lake IJssel (Leote et al. 2014). Active benthic macrofauna, such as mussels (*Mytilus edulis*), jackknife clams (*Ensis sp.*), cockles (*Cerastoderma edule*), sandgapers (*Mya arenaria*), small gastropods (*Hydrobia sp.*), and polychaetes (*Nereis sp.*, etc), are present throughout the western Wadden Sea, their distribution presumably being mainly governed by median grain size, microphytobenthic biomass, hydrodynamic regime, and exposure time (Beukema et al. 2002; Compton et al. 2013).

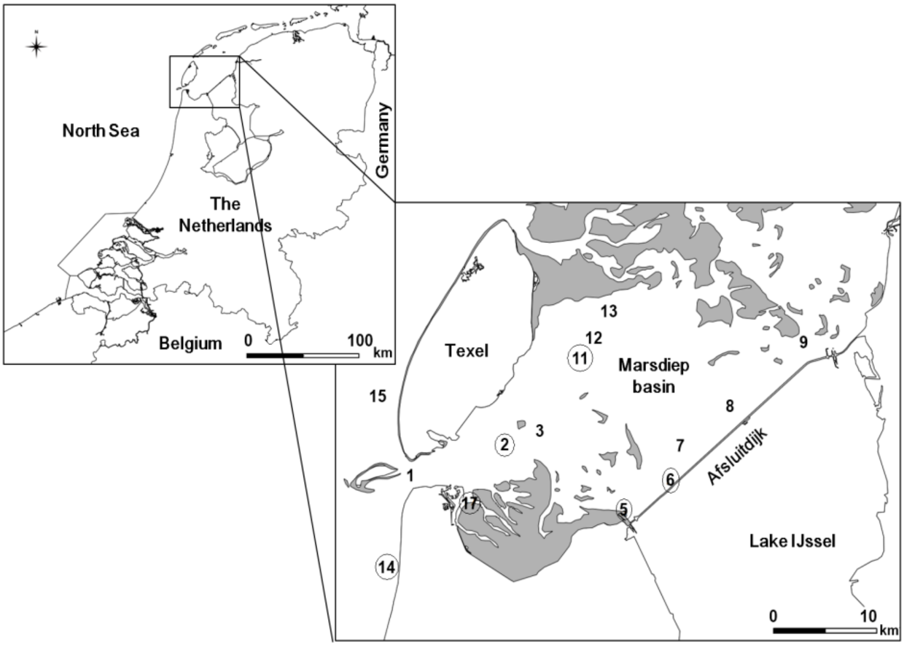


Figure 1. Location of the Marsdiep basin, western Wadden Sea. The stations that were seasonally sampled (2, 5, 6, 11, 14, and 17) are identified with a circle.

2.2 Sampling scheme

For a pilot study in April 2009, 13 stations restricted to the subtidal domain were initially selected based on location and mapped grain size distribution (Rijkswaterstaat). These stations were characterized with respect to sediment properties and porewater profiles of PO_4, NH_4, and Si. A subset of 6 stations was selected for seasonal surveys on the basis of station position relative to freshwater sources and tidal inlet, sediment grain size, sediment organic carbon content, and basic porewater chemistry. The seasonal surveys were conducted with RV Navicula in November 2009, February, March, May, and September 2010. During low tide, a Barnett-Watson multicorer was deployed to collect 8 small sediment cores (i.d. 6 cm) and 4 large cores (i.d. 10 cm). Only the cores devoid of a gas phase, indicating leakage due to percolation, and with clear overlying waters were selected for further processing. The cores were immediately transported to the laboratory at in situ temperature. The smaller cores were processed for porewater and solid phase sampling while the larger cores were incubated to measure the sediment-water exchange of dissolved nutrients and to record oxygen micro profiles.

2.3 Porewater and solid phase sampling

Six to 10 cores (i.d. 6 cm) were sliced in the following depth intervals: 0–0.25, 0.25–0.5, 0.5–0.75, 0.75–1, 1–1.5, 1.5–2, 2–2.5, 2.5–3, 3–4, 4–5, 5–6, 6–7, 7–9, 9–11, 11–13, 13–15, 15–17, 17–19, 19–21, and 21–23 cm. Porewater was extracted and filtered (0.2 µm pore diameter Acrodisc filter, Supor® membrane) by centrifugation (2000 rpm for 12 minutes) at in situ temperature. Samples were stored in pony vials at −20°C for NH_4 analysis. The samples for PO_4 and Si analysis were stored at 4°C after acidification with 5 N HCl suprapure (2 µl/ml of sample) to keep Fe in solution and avoid precipitation with PO_4. For DIC analysis the samples were poisoned with $HgCl_2$ and stored in glass vials at 4°C. After porewater extraction, the solid phase was stored frozen in BD Falcon^{TM} Tubes and freeze dried for grain size, total C, N, and organic C content determination. Three additional cores were processed for the determination of porosity.

2.4 Sediment-water exchange measurements

To determine the sediment-water exchange of dissolved nutrients, 3–4 cores (i.d. 10 cm) per station were left in darkness at in situ temperature for 1–2 h. After equilibration, the overlying water was carefully siphoned off and replaced by 470 ml of filtered bottom water from the sampling location. The cores were left open and the overlying water was gently mixed by a magnetic stirrer to avoid the formation of a concentration gradient. Eight ml aliquots were taken with a syringe every 30 to 45 min for a maximum period of 4 h and filtered immediately (0.2 µm pore diameter Acrodisc filter, Supor® membrane). The sampled volume was not replaced, but corrected for in the flux calculations. Samples were taken for the determination of NO_x, NH_4, Si, and PO_4 concentrations. NO_x samples were stored at −20°C in pony vials, while NH_4, Si, and PO_4 samples were stored as described above. Since the incubations were performed in open cores, allowing equilibration with the atmosphere, no samples for DIC were taken.

2.5 Oxygen profiling

Oxygen micro profiles were recorded using custom made Clark type microelectrodes furnished with an internal guard electrode (Revsbech 1989). The profiles were recorded at a vertical resolution of 100 µm with a computerized micromanipulator. The signal was calibrated at in situ temperature using the oxygen concentration in the overlying water (air saturation) and anoxic conditions deeper in the sediment (zero concentration). Two to 8 profiles were recorded for each station.

2.6 Analytical procedures

All dissolved nutrient analyses were performed on a TRAACS 800 Segmented Continuous Flow Analyzer. For NO_x and NH_4 analysis the methods of Grasshoff et al. (1983) and Helder and de Vries (1979) were followed, yielding a precision and detection limit of 0.02 and 0.04 µM and 0.03 and 0.07 µM, respectively. PO_4, Si, and DIC were analyzed according to the methods of Murphy and Riley (1962), Strickland and Parsons (1968), and Stoll et al. (2001) with detection limits of 0.007, 0.03, and 2 µM and a precision of 0.002, 0.016, and 2 µM, respectively. Total C and N were determined on freeze dried and ground sediment using a Thermo-Interscience Flash EA1112 Series Elemental Analyzer, based on the method of Verardo et al. (1990) with a detection limit of 100 ppm and a precision of 0.3%. Organic C was analyzed following the same procedure after removal of carbonates with 2 M HCl. Carbonate ($CaCO_3$) content was estimated as the difference between total and organic C. Porosity was determined by weight loss of sediment slices of known volume after freeze drying. The sediment grain size distribution was determined on freeze-dried sediments using a Coulter LS230 particle counter. Sediment samples were freeze-dried for 48 h and then homogenized with a mortar and pestle. Homogenized samples, including $CaCO_3$ and organic matter, were suspended in degassed Milli-Q water and shaken vigorously with a vortex mixer for 30 s prior to determining the grain size in 126 size classes (from 0.04 to 2000 µm). After conversion to the Krumbein phi scale, the particle sorting index was calculated according to Buchanan (1984).

2.7 Calculations

In addition to measuring the sediment-water exchange of nutrients by the whole core incubation technique, the solute exchange was predicted from the porewater profiles following two different methods. Fick's first law of diffusion was applied to predict the exchange from the maximum concentration gradient observed in the porewater profile: $J = \emptyset D_s (dC/dx)$, where J corresponds to the diffusive flux in µmol cm^{-2} s^{-1}, $\emptyset$ to the porosity, D_s to the molecular diffusion coefficient corrected for sediment tortuosity in cm^2 s^{-1}, C to the nutrient concentration in µM and x to depth in cm. D_s was calculated from the molecular diffusion coefficient (D_{sw}) according to Iversen and Jørgensen (1992): $D_s = D_{sw} / (1 + n\ (1 - ø))$, with n = 2 for all stations except station 6 (n = 3). The second approach to predict the sediment-water exchange from porewater profiles involved the application of an analytical transport-reaction model including "non-local exchange" to account for the effect of bioirrigation. The model was developed by Kristensen and Hansen (1999) and adapted to simultaneously fit PO_4, NH_4, and DIC profiles from a single reaction rate of organic matter mineralization and stoichiometric ratios for C/N and C/P. This model assumes two different zones in the sediment: a top layer where the concentration profile is governed by mineralization, molecular diffusion, and bioirrigation and a layer below with molecular diffusion as the single mode of transport and mineralization. Even though bioirrigation may enhance the volume of porewater exchanged with the overlying water, the mass exchange of a nutrient is limited by its production rate in the sediment. Therefore, assuming a constant vertical reaction rate, the sediment-water exchange could be calculated as: $J = ø\ R\ L$, where R corresponds to the reaction rate of the nutrient and L corresponds to the sediment depth where the concentration gradient $dC/dx = 0$ (i.e. production is very low or absent).

Oxygen fluxes at the sediment-water interface were predicted from the concentration profiles by applying the PROFILE software (Berg et al. 1998). A concentration and flux of zero at the bottom of the profile were used as boundary conditions and the expression of Iversen and Jørgensen (1992) was used to correct the molecular diffusion coefficient for sediment tortuosity.

Based on an inverse relationship found between the predicted fluxes and silt content, the sediment-water exchange measured for our stations could be extrapolated for the entire Marsdiep basin. A map of grain size distribution per class intervals (0–60, 60–120, 120–180, 180–240, 240–300, >300 µm) was available from the Rijkswaterstaat and was used to discriminate and calculate the areas of the high (0–120 µm) and low silt content (>120 µm) zones. Basin wide estimates of the sediment-water exchange were calculated for the months of April, May, September, and November. An annual budget was calculated assuming that the fluxes in January, February, and March were similar to April; June and July to May; August and October to September and December to November.

3. Results and Discussion

3.1 Pilot study

In April 2009 a pilot study was conducted to characterize 13 subtidal stations situated across the basin including the adjacent North Sea coastal stretch near the tidal inlet (Figure 1). Based on sediment properties and porewater composition, a subset of 5 stations was selected to continue a seasonal study on the release of dissolved inorganic phosphorus (PO_4) in the Marsdiep basin.

Table 1 provides an overview of some basic sediment properties for an initial characterization of the subtidal sediments. The values presented were averaged for the top 10 cm of sediment and based on 15 depth intervals. Granulometric analyses revealed a wide and rather continuous distribution of the average median grain size across the basin. Most stations felt in the range from 200–400 µm and qualify as medium sand (Wentworth 1922). Station 6, located near the Afsluitdijk, showed a small median grain size of about 65 µm, whereas maximum values of 550 µm were observed for station 11, located on the banks of one of the major subtidal channels. Above a median grain size of 189 µm, the silt content appeared limited to ca 10 wt% and independent of the median grain size. Oppositely, for station 6, the silt content increased to values of over 50%. The observed range in median grain size for the Marsdiep subtidal domain (490 µm) was substantially wider than the range that has been reported for the intertidal domain of the Marsdiep basin (234 µm, Compton et al. 2013). This may reflect an extended range in subtidal hydrodynamic action, generated by tides and meteorological conditions. Winnowing in high-energy areas such as the ebb-tidal delta and tidal channels and deposition of fines in subtidal areas of subdued hydrodynamic energy, may create various compositions of the sediment fractions including biogenic debris. As a consequence, the sediments near the inlet and in the coastal North Sea appeared to be well to moderately sorted, whereas the sediments from the more interior stations were poorly sorted.

The sediment organic C content covaried with the sediment silt content, which suggests a similar settling behavior or coalescence of these two fractions (Figure 2). The majority of stations felt in the range between 0.04 and 0.2 wt%, with stations located in the coastal North Sea (14, 15) and near the tidal inlet (12, 1) showing the lowest contents. A maximum value of 1.1 wt% was observed for station 6. These values are in the lower range for coastal sediments, but correspond well to values found for the adjacent southern North Sea (Slomp et al. 1996; 1998).

Table 1. General sediment characteristics from the stations sampled during the pilot study. Values given are averaged for the first 10 cm depth and based on 15 sampled intervals. Values of exchangeable P were taken from Leote et al. (2014).

St	Depth (m)	Median grain size (µm)	<63 µm (%)	Sorting	C_{org} (wt%)	Exch. P (µmol g^{-1})	Porosity (v/v)
1	36	255.1 ± 4.8	0.9 ± 1.6	0.55	0.06 ± 0.03	0.28 ± 0.15	0.37 ± 0.17
2	2.8	242.1 ± 6.4	4.0 ± 2.6	0.77	0.09 ± 0.07	0.66 ± 0.08	0.38 ± 0.05
3	2.4	224 ± 7.1	2.7 ± 0.4	0.64	0.07 ± 0.01	0.73 ± 0.19	0.36 ± 0.13
5	6.2	385.7 ± 98.3	3.5 ± 3	0.54	0.13 ± 0.09	0.53 ± 0.11	0.38 ± 0.12
6	2.6	65.5 ± 20.5	51.9 ± 12.8	1.95	1.11 ± 0.51	5.39 ± 2.15	0.61 ± 0.11
7		136.1 ± 39.9	30 ± 20			1.85 ± 0.91	
8	6.1	352.5 ± 57	4.4 ± 1.1	1.23	0.11 ± 0.04	1.67 ± 0.19	0.37 ± 0.13
9	9.6	293.6 ± 16.9	8.4 ± 2.6	1.63	0.16 ± 0.06	1.03 ± 0.25	0.35 ± 0.05
11	10.5	553.3 ± 157.2	9.8 ± 6.3	1.42	0.61 ± 0.51	0.44 ± 0.26	0.35 ± 0.04
12	2.6	277.4 ± 11.5	2.4 ± 0.4	1.17	0.06 ± 0.01	0.65 ± 0.1	0.33 ± 0.11
13	2.6	243.3 ± 32.9	5.3 ± 1.7	1.69	0.19 ± 0.09	0.86 ± 0.33	0.4 ± 0.1
14	12.5	327 ± 12.8	1.3 ± 1.5	0.83	0.04 ± 0.02	0.16 ± 0.07	0.32 ± 0.15
15	8.9	189.1 ± 6.7	1.7 ± 1.2	0.55	0.05 ± 0.01	0.47 ± 0.12	0.37 ± 0.08
16	5.1	75.5 ± 37.6	47.6 ± 21.4	2.63	4.26 ± 3.45	10.4 ± 7.48	0.72 ± 0.11

The mineralization of sediment organic C and inorganic biogenic debris strongly affects sediment geochemistry as reflected in the porewater concentration profiles of mineralization products. Excluding station 6, the concentrations of PO_4 and silicic acid (Si) were below 15 µM and 150 µM, respectively, suggesting low rates of mineralization and opal dissolution. Station 6 however, showed maximum concentrations of 550 µM PO_4 at 14 cm depth and 800 µM Si from 2.5 cm downward. The inventories of dissolved inorganic N (DIN = $NH_4 + NO_3 + NO_2$), PO_4, and Si for the porewater down to 10 cm depth confirmed the deviant conditions for station 6 as these values exceed those for other subtidal stations by 1–3 orders of magnitude. This difference was larger for PO_4 than for the other solutes, suggesting different processes controlling the porewater concentrations.

This pilot study revealed considerable differences in general sediment characteristics and geochemistry, most notably between station 6 and the remaining subtidal stations. Station 6 represents a deposition area called “de Vlieter” adjacent to a causeway (Afsluitdijk, Figure 1). The closure of this causeway in 1932, now separating the Lake IJssel from the Wadden Sea, created a convergence area, resulting in the accumulation of fine sediments including organic matter. ^{210}Pb-dating suggested fast sedimentation with maximum rates of 0.5 m yr^{-1} and mean rates of 1–2 mm yr^{-1} (Berger et al. 1987; Oost and de Boer 1994). The sediment cores from station 6 revealed a well defined interface between oxidized (yellow/orange colored) and reduced (dark grey/black colored) sediments. This suggests the absence of macrofauna activity or other processes that may physically disrupt the sediment surface and contrasts with the coarser sediment stations were no clear interface could be visually identified. Therefore, the results from station 6, representing the deposition area, will often be contrasted with stations 2, 5, 11, and 14 selected for the seasonal surveys. Station 17, located in the drainage channel of one of the main intertidal flats of the western Wadden Sea, the Balgzand, was included later in the seasonal surveys and also falls in the coarser sediment category.

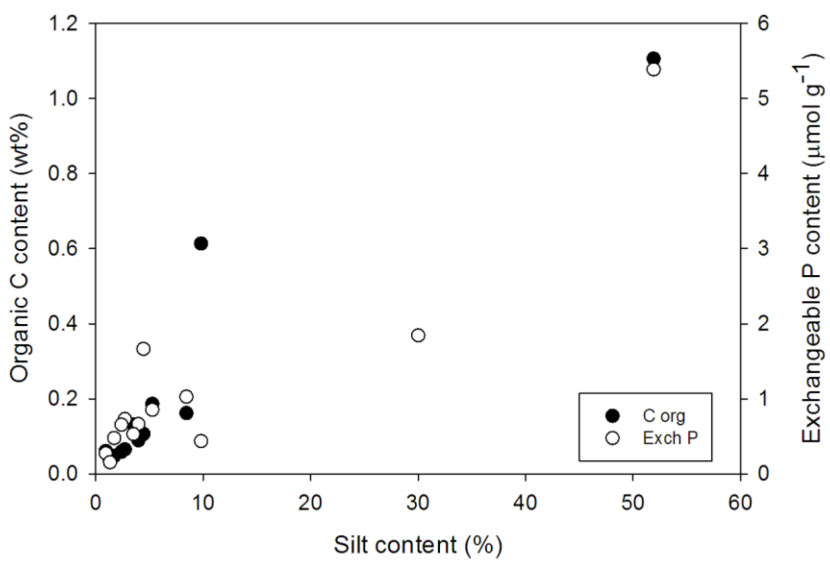


Figure 2. Content of silt versus organic C and exchangeable P contents (from Leote et al. 2014). Note the approximate linear relationship between silt content and organic C/exchangeable P.

3.2 Seasonal surveys

3.2.1 Sediment characteristics

The physical and chemical characteristics of the sediment, averaged for the first 10 cm depth, showed no major seasonal differences throughout the year, even though, in general, higher values were obtained between March and September for the C and N contents. For a comparison between stations, average values including all seasons are given in Table 2.

Table 2. General sediment characteristics from the stations sampled seasonally. Values given are averaged for the first 10 cm depth and based on 15 sampled intervals.

St	Median grain size (μm)	Porosity	N_{tot} (wt%)	C_{tot} (wt%)	C_{org} (wt%)	$CaCO_3$ (wt%)	C_{org}/N_{tot}
2	233.4 ± 8.9	0.41 ± 0.03	0.01 ± 4e−3	0.35 ± 0.08	0.10 ± 0.003	0.26 ± 0.06	9.2 ± 1.3
5	396.0 ± 42.4	0.39 ± 0.04	0.02 ± 0.01	0.42 ± 0.08	0.16 ± 0.04	0.26 ± 0.05	9.7 ± 1.4
6	45.3 ± 11.3	0.72 ± 0.09	0.23 ± 0.08	3.97 ± 0.81	2.00 ± 0.55	1.97 ± 0.28	10.2 ± 0.7
11	310.2 ± 112.5	0.38 ± 0.02	0.03 ± 0.02	0.60 ± 0.34	0.43 ± 0.31	0.17 ± 0.08	15.2 ± 2.7
14	323.0 ± 1.3	0.33 ± 0.02	0.01 ± 1e−3	0.34 ± 0.05	0.06 ± 0.01	0.28 ± 0.04	10.9 ± 0.5
17	220.0 ± 18.4	0.34 ± 0.03	0.01 ± 4e−4	0.35 ± 0.08	0.04 ± 0.01	0.30 ± 0.07	8.1 ± 1.1

Station 6 clearly showed the smallest median grain size of 45 μm, corresponding to fine silt (Wentworth 1922), and the highest porosity, with an average value of 0.72. Oppositely, stations 2, 5, 11, 14, and 17 had larger median grain sizes, corresponding to fine/medium sand with values between 220 (for station 17) and 396 μm (for station 5). Porosity was higher in the top layers decreasing to uniform downcore values of 0.33–0.41.

The sediment contents of total C, total N, organic C, and $CaCO_3$ for station 6 were one order of magnitude higher than for the other stations, with average values throughout the year of 3.97, 0.23, 2.00, and 1.97 wt%, respectively, evidencing a higher content of organic material and carbonate. The stations with coarser sediments showed similar contents of total C and total N, with values between 0.34–0.60 and 0.01–0.03 wt%, respectively. The content of organic C showed some spatial variation. Stations 14 and 17, located in the coastal North Sea and near the tidal inlet, presented the lowest contents of 0.06 and 0.04 wt% and were the stations with the lowest content of organic material. The organic C contents for stations 2, 5, and 11 were higher between 0.10 and 0.43 wt%. In spite of the observed spatial variation, the contents measured for the western Wadden Sea were within the range found for coastal sediments of similar grain size such as the North Sea, German Bight, Skagerrak, and bay of Brest (van Raaphorst et al. 1990; Slomp et al. 1996; 1998; Tallberg et al. 2008). The ratio of particulate organic C/total N was quite similar for all stations, varying between 8.1 (station 17) and 10.9 (station 14). Even though it exceeds the Redfield ratio for the average composition of phytoplankton and may indicate a preferential degradation of N relative to C or the presence of terrestrial biogenic material, it is within the range found for other coastal environments with oceanic phytoplankton as the main source of organic material (Martens et al. 1978; Krom and Berner 1981). Station 11, however, had a higher ratio of 15.2, presumably due to the admixture of peat formed during geological sea level lows (Louchouarn et al. 1997; Ruttenberg and Goni 1997). The carbonate content showed little variation among stations varying between 0.17 (station 11) and 0.30 wt% (station 17), which is relatively low in comparison with the North Sea (Slomp 1996).

Benthic macrofauna including jackknife clams (*Ensis minor)*, gastropods (*Hydrobia sp*.), and small polychaetes was reduced or absent in station 6, but actively present in all stations with coarser sediment. In particular, station 2 presented a large community of *Ensis minor*, while the remaining stations had mainly small gastropods and polychaetes. A clear impact of their activity on the sediment structure was observed i.e. the frequent disruption of the sediment's surface and the absence of a well defined redox interface.

The differences in abiotic and biotic sediment composition between station 6 and the other stations were reflected in the porewater chemistry as well. These differences were not restricted to the levels of maximum concentrations, as outlined in the pilot study, but also in the curvature of the profiles, indicating different modes of transport.

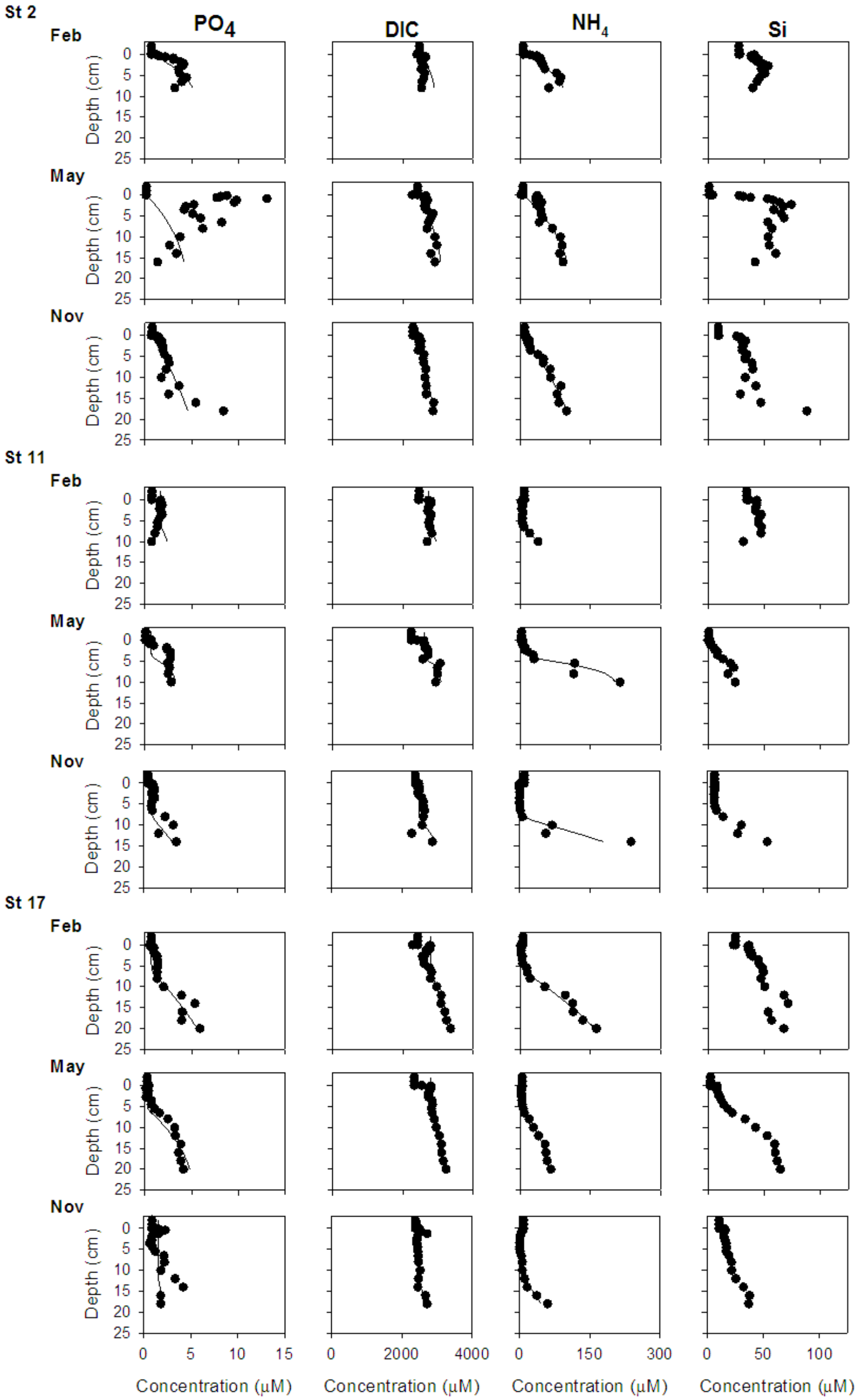
3.1.2 Porewater profiles

As already observed in the pilot study, station 6 clearly showed the highest concentrations of dissolved nutrients in the sediment throughout the year, with maximum values of 1100 µM for PO_4, 60000 µM for DIC, 6000 µM for NH_4, and

1300 µM for Si. Among the coarser sediment stations, station 5 had the highest concentrations, reaching maximum values of 300 µM for PO_4, 15000 µM for DIC, 1500 µM for NH_4, and 600 µM for Si. The other stations only reached maximum values of 20, 4000, 500, and 200 µM for PO_4, DIC, NH_4, and Si. The highest concentrations were measured between April and September.

In addition to the different concentration ranges observed between station 6 and the other stations, the shape of the porewater profiles was also clearly different, especially immediately below the sediment-water interface.

For station 6, the shape of the concentration profiles was quite similar for porewater PO_4, DIC, NH_4, and Si, with low concentrations at the surface followed by a sharp increase immediately below the sediment-water interface (Figure 3). The concentrations of DIC and NH_4 kept increasing slowly below 20 cm depth while PO_4 and Si reached an approximately constant concentration below 5–10 cm depth. For all nutrients, the concentration gradient below the interface increased in May, when temperature and organic matter availability were higher. Since Si is only moderately sensitive to sorption and its production in the sediment depends not on mineralization, like PO_4, DIC, and NH_4, but on a well defined dissolution rate (Loucaides 2009), it can be considered as a “conservative tracer”. The relative linearity observed in the profiles, and especially for Si, with a steady gradient between the overlying water and the maximum concentration deeper in the sediment, suggests the absence of physical disturbance of the sediment structure. The lack of macrofauna and the well defined redox interface observed close to the surface further confirm this idea. The transport of solutes in the sediment is then mainly governed by molecular diffusion.


St 2
Feb
May
Nov
St 11
Feb
May
Nov
St 17
Feb
May
Nov
PO4
DIC
NH4
Si
Depth (cm)
0
5
10
15
20
25
0
5
10
15
0
2000
4000
0
150
300
0
50
100
Concentration (µM)
Concentration (µM)
Concentration (µM)
Concentration (µM)

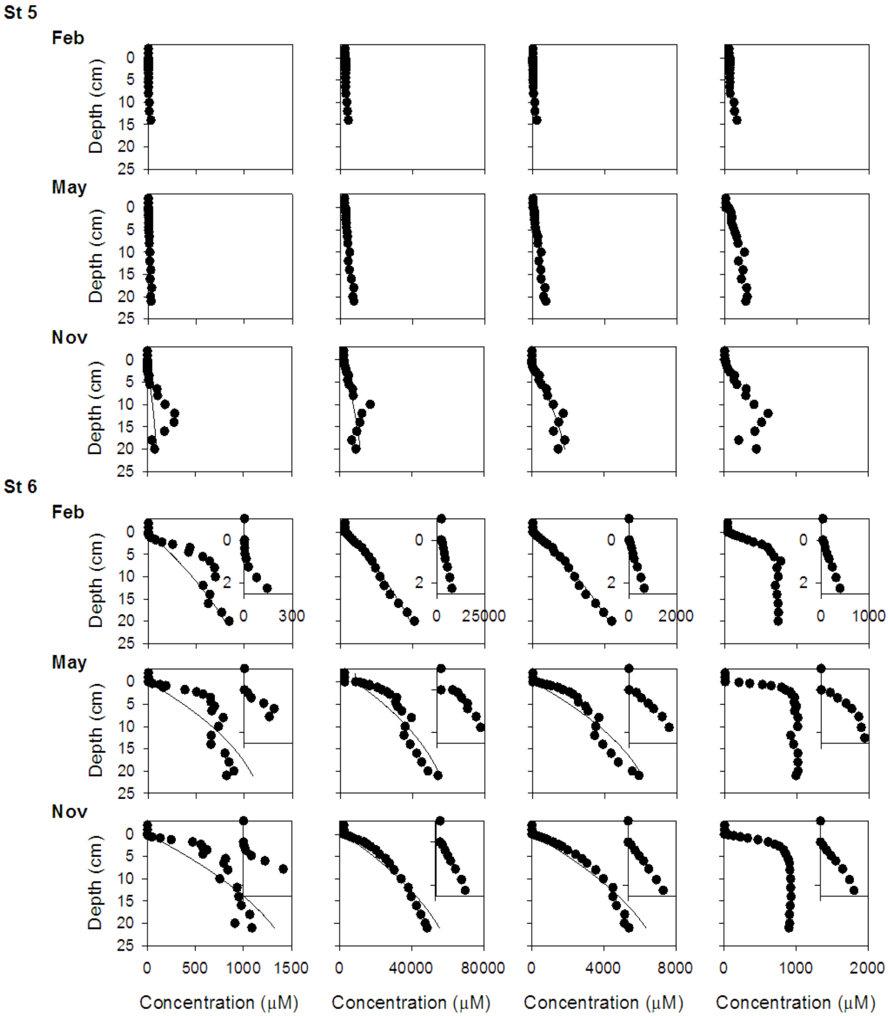


Figure 3. Porewater profiles of PO_4, DIC, NH_4, and Si concentration for stations 2, 11, 17, 5, and 6 in February 2010, May 2010, and November 2009. The small insets on station 6 correspond to a detailed view of the concentrations in the top 2 cm of the profile. The lines indicate the fitted profile using the adapted model of Kristensen and Hansen (1999) for PO_4, DIC, and NH_4. Note the evidence of bioirrigation in stations 11, 17, and 5 and of sorption in station 6 in February and November.

The coarser sediment stations also showed lower concentrations near the sediment-water interface, increasing downcore (Figure 3). However, for most cases, instead of a steep increase below the sediment-water interface, a layer of variable depth and constant low concentration, often similar to the overlying water, was observed for all nutrients. In addition, the shape of the concentration profiles was more erratic (see station 2 in Figure 3). Unlike station 6, no consistent seasonal pattern could be observed in the porewater profiles. The presence of this layer of constant concentration down to a similar depth in the profiles of all nutrients suggests that a transport and not a reaction process is the responsible for this shape, since Si, as mentioned above, is not directly affected by the same chemical reactions as DIC, PO_4, and NH_4. Consequently, diffusion only cannot explain the profiles obtained for the coarser sediment stations. The presence of active macrofauna in these stations and the absence of a well defined redox interface suggests bioirrigation as a main transport process at the top layer of the sediment, leveling off the porewater concentrations in relation to the overlying water, as observed in our profiles.

Different processes seem to be affecting the distribution of nutrients in the porewater and are possibly controlling the release to the overlying water. Therefore, no single method based on the porewater concentration profiles can be successfully applied to all stations in the prediction of the sediment-water exchange.

3.1.3 Sediment-water exchange

The sediment-water exchange was predicted using two different methods, the Fick's law and the Kristensen and Hansen approach, in an attempt to overcome the spatial differences in the porewater profiles outlined in the previous chapter.

In a diffusion controlled exchange, the exchange rate is proportional to the concentration gradient and Fick's law can be used in the calculations. This is immediately valid for station 6, using the concentration gradient at the interface. However, for the coarser sediment stations, the maximum concentration gradient, observed below the top bioirrigated layer (Figure 3), was used, based on the premise that the transfer of mass to the overlying water depends on the supply of solute to the bioirrigated zone. Bioirrigation will accelerate the exchange in the top layer but the limiting factor for the mass transfer is the nutrient production rate in the sediment and the diffusive transport from below to the interface between the bioirrigated and non-bioirrigated layer. To better account for the effect of bioirrigation in the top layer, the second method involved the adaptation of the model developed by Kristensen and Hansen (1999), to simultaneously fit the profiles of DIC, PO_4, and NH_4, allowing for a better estimation of the reaction rates and bioirrigation intensity and depth. Since the production of Si in the sediment cannot be coupled with the production of DIC, PO_4, and NH_4, the sediment-water exchange of Si was only predicted using the Fick's law approach. However, the similarity observed between the predicted fluxes of DIC, PO_4, and NH_4 using both methods (Figure 4) gives us confidence that the Fick's law approach can be considered a reliable method for the calculation of the exchange with the overlying water.

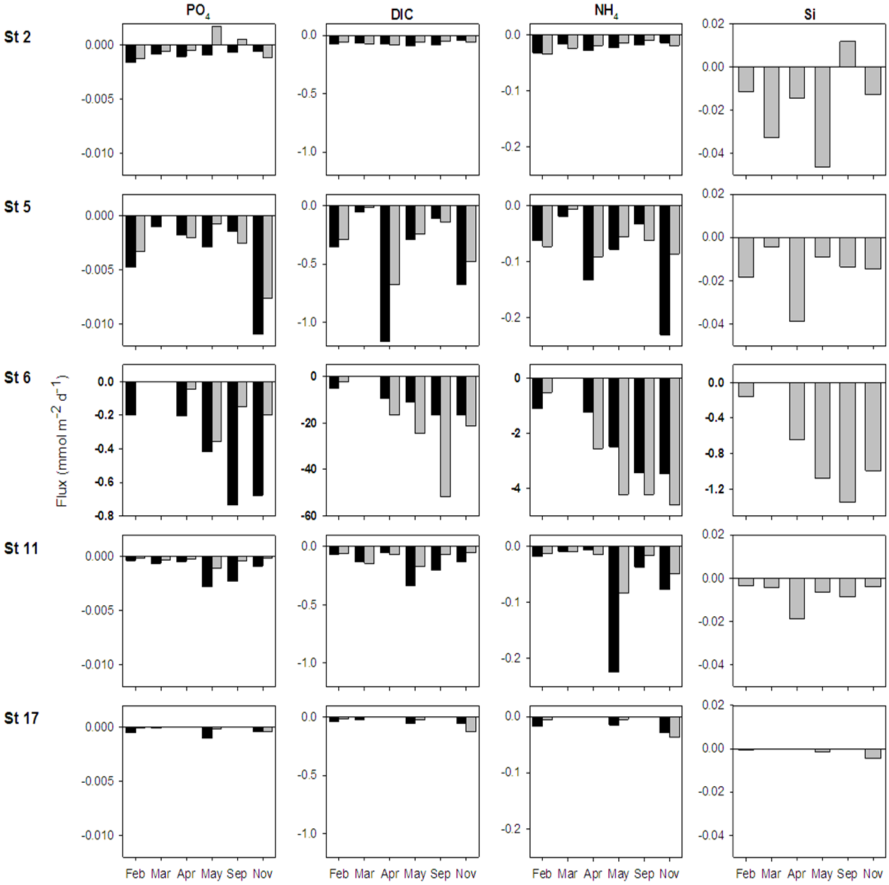


Figure 4. Sediment-water exchange of PO_4, DIC, and NH_4 for stations 2, 5, 6, 11, and 17. Note the different scale for station 6. The black bars indicate the fluxes predicted by the Kristensen and Hansen approach while the grey bars show the flux predicted according to the Fick's law approach.

The seasonality in the predicted sediment-water exchange using both the Kristensen and Hansen and the Fick's law approach is illustrated in Figure 4 for PO_4, DIC, NH_4, and Si and for stations 2, 5, 6, 11, and 17. Defining positive fluxes as uptake by the sediment and negative fluxes as release to the overlying water, station 6 always released PO_4, DIC, NH_4, and Si to the overlying water. The predicted exchange for this station was up to two orders of magnitude higher than for the other stations. Fluxes were lowest in February, increasing towards September and decreasing again in November for PO_4, DIC, and Si. The NH_4 fluxes showed an increase until November. For PO_4, the predicted exchange according to the Kristensen and Hansen approach was higher than the predicted using the Fick's law approach, with fluxes ranging between -1.8×10^{-3} and -0.74 mmol m^{-2} d^{-1}. For DIC and NH_4, the flux according to the Fick's law approach was slightly higher than the Kristensen and Hansen's ranging between -2.5 and -51.8 mmol m^{-2} d^{-1} and -0.5 and -4.6 mmol m^{-2} d^{-1}, respectively. The Si exchange according to the Fick's law approach ranged between -0.2 and -1.3 mmol m^{-2} d^{-1}. The predicted fluxes of PO_4, DIC, NH_4, and Si for the coarser sediment stations were by two orders of magnitude lower than for station 6, but still directed mainly towards the overlying water. Station 5 showed the highest exchange rates, possibly due to its location close to the Afsluitdijk sluice, thereby receiving a large input of fresh organic material from Lake IJssel. The predicted PO_4 exchange for station 5 varied between -0.01 and app. 0 mmol m^{-2} d^{-1}, being higher in February and November. DIC, NH_4, and Si fluxes showed an increase from February until April, after which a decrease was observed, followed by higher values in November. Values varied between -1.16 and -0.01 mmol m^{-2} d^{-1} for DIC, -0.23 and -7.4×10^{-3} mmol m^{-2} d^{-1} for NH_4, and -0.04 and -4.5×10^{-3} mmol m^{-2} d^{-1} for Si. Stations 2, 11, 14, and 17 showed much lower fluxes, usually higher between April and September. For these stations, PO_4 exchange varied between -2.8×10^{-3} and -2.7×10^{-5} mmol m^{-2} d^{-1}, DIC ranged between -0.33 and 1.4×10^{-3} mmol m^{-2} d^{-1}, NH_4 showed values between -0.22 and -6.2×10^{-5} mmol m^{-2} d^{-1}, while Si ranged between -0.05 and 0.01 mmol m^{-2} d^{-1}. Summarizing, the predicted sediment-water exchange was, in general, higher between April and November. Station 6 showed the clearest pattern, with an increase in the fluxes from February until September/November, while the remaining stations showed a more erratic behavior for the predicted exchange. Both methods provide a conservative estimation of the exchange by assuming a similar reaction rate in the top and deeper layers, which may not be the case, due to a higher availability of labile organic material closer to the surface.

Nevertheless, the absence of a defined redox boundary suggests significant reworking of the sediment by macrofauna, so that a good supply of fresh organic material to the deeper layers is a fair assumption.

In addition to the predicted sediment-water exchange, the fluxes have also been measured with whole-core incubations in dark conditions. The measured fluxes of PO_4, NH_4, and Si were sometimes more than one order of magnitude higher than the predicted, except for station 6 (Table 3). For the fine grained station 6, the exchange was higher in May and within the same order of magnitude of the predicted fluxes with maximum values of −0.31, −15.39, and −6.45 mmol m^{-2} d^{-1} for PO_4, DIC, and Si. This agreement supports the idea that molecular diffusion was the dominant transport process involved in the exchange of nutrients across the sediment-water interface at this station. For the coarser sediment stations, the highest discrepancies between predicted and measured fluxes were observed for stations 2 and 5, which showed high densities of macrofauna. In spite of the evidence of macrofauna activity in the porewater profiles of stations 11, 14, and 17 the concentrations in the sediment were quite low and similar to the overlying water, resulting in low fluxes and a small difference between the measured and the predicted exchange. Like the predicted fluxes, the measured exchange was higher in May and September, ranging between −25.17 and 0.02 mmol m^{-2} d^{-1} for NH_4, −1.63 and 0.05 mmol m^{-2} d^{-1} for PO_4, and −20.65 and 0.19 mmol m^{-2} d^{-1} for Si. The measured exchange was mostly towards the overlying water, even though uptake by the sediment was sometimes observed. However, the precipitation of fresh Fe oxides in the overlying water, following the release of reduced Fe(II) from the sediment, was visually observed for station 6 and might be true for the other stations, under high mineralization rates. Phosphate, and to a smaller extent NH_4 and Si can adsorb to these colloidal oxides and be removed from the dissolved fraction, resulting in apparent uptake by the sediment (Crosby et al. 1981; Sundby et al. 1986).

The disparity between the measured and predicted sediment-water exchange has been reported elsewhere (Balzer 1984; Hall et al. 1996; Slomp et al. 1998) and, in spite of the large temporal and spatial variation, our results are comparable with values obtained for similar coastal environments (Balzer 1984; van Raaphorst et al. 1990; Mortensen et al. 1993; Hall et al. 1996; Asmus et al. 2000; Serpa et al. 2007). For the particular case of sediment PO_4 release in the Wadden Sea, our fluxes were often lower than previously reported values ranging between −0.2 and 0.036 mmol

m^{-2} d^{-1} for oxic incubations, in situ measurements, and modeling results (van Raaphorst et al. 1988; de Jonge et al. 1993; van Raaphorst and Kloosterhuis 1994).

Given the much higher nutrient concentrations in the porewater, a significantly higher release would be expected for station 6. Nevertheless, the measured fluxes for this station were not clearly distinct from the other stations, suggesting processes, other than diffusion and mineralization, to control the release of nutrients to the water column.

Table 3. Measured sediment-water exchange with whole-core incubations in dark conditions. Positive fluxes represent uptake by the sediment while negatives fluxes represent release to the overlying water. Dissolved inorganic nitrogen (DIN) refers to release of $NO_3 + NO_2 + NH_4$. Missing values in the ratios correspond to uptake by the sediment.

	Measured fluxes ($\text{mmol m}^{-2}\ \text{d}^{-1}$)					
	NH_4	Si	PO_4	DIN/PO_4	DIN/Si	Si/PO_4
Station 2						
Feb 2010	0.02	−0.34	−0.01	52.97	1.70	31.12
Mar 2010	−1.75	−0.51	−0.07	23.64	3.46	6.83
May 2010	−3.18	−4.86	−0.21	14.98	0.66	22.65
Sep 2010	−25.17	−13.44	−1.63	15.57	1.89	8.22
Station 5						
Feb 2010	−0.24	−1.54	−0.03	69.47	1.55	44.72
Mar 2010	−1.19	−2.67	−0.02	95.96	0.62	155.62
May 2010	−6.07	−5.47	−0.09	74.83	1.20	62.32
Sep 2010	−13.54	−20.65	−0.14	95.27	0.66	143.79
Station 6						
Feb 2010	−1.82	−0.36	−0.01	135.67	5.37	25.28
Mar 2010	--	--	--	--	--	--
May 2010	−15.39	−6.45	−0.31	49.57	2.40	20.64
Sep 2010	−7.10	−2.49	0.03	--	2.91	--
Station 11						
Feb 2010	0.07	−0.05	4e−3	--	6.04	--
Mar 2010	0.08	0.06	3e−3	--	--	--
May 2010	0.40	0.17	0.02	--	--	--
Sep 2010	0.35	−0.24	0.05	--	0.32	--

Station 14						
Feb 2010	--	--	--	--	--	--
Mar 2010	−0.04	−0.01	−0.01	4.94	2.97	1.67
May 2010	--	--	--	--	--	--
Sep 2010	--	--	--	--	--	--
Station 17						
Feb 2010	0.03	−0.15	4e−4	--	2.32	--
Mar 2010	−0.03	−0.09	−0.03	1.01	0.33	3.10
May 2010	0.67	0.19	0.03	--	--	--
Sep 2010	--	--	--	--	--	--

3.2 Controls on sediment nutrient release

The sediment release of DIC and NH_4, both end-products of the degradation of organic matter, can be used as an indicator of the mineralization intensity. The consumption of oxygen can be used in a similar way, as it accounts for both the aerobic mineralization of organic material and the re-oxidation of reduced electron acceptors, used as an alternative in the absence of oxygen (Canfield et al. 1993).

Oxygen consumption varied between 3.11 and 70.64 mmol m^{-2} d^{-1} with stations 2, 5, and 6 showing the highest fluxes (Figure 5). Both the oxygen consumption and the content of organic C in the sediment were, in general, higher in spring and summer (Figure 5), suggesting a higher mineralization rate in this period, directly related with the cycle of phytoplankton growth in the Western Wadden sea and following deposition in the sediment (Cadée and Hegeman 1993). Consequently, in spring and summer the nutrient concentrations in the porewater increase in relation to the overlying water and expectedly induce a higher release (Slomp et al. 1993).

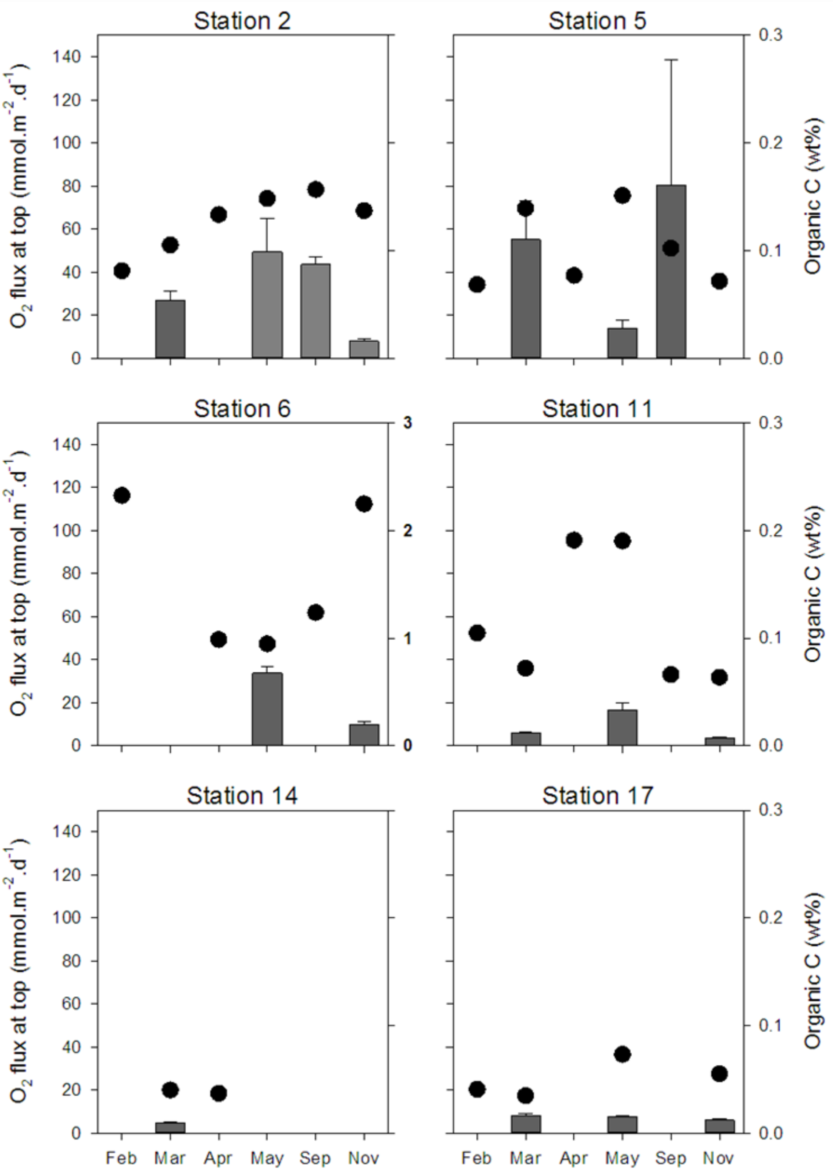


Figure 5. Oxygen exchange at the sediment-water interface (bars) with positive exchange corresponding to uptake by the sediment and organic C content (dots). Note the different scale for organic C content for station 6. A higher oxygen consumption was observed in spring in accordance with a higher organic C content.

This was observed for station 6, with steeper concentration gradients in the porewater profiles at the sediment-water interface (Figure 3) and a higher release of DIC and NH_4 (Figure 4) between May and November. However, the porewater PO_4 profiles showed an additional feature, with a layer of constant and low concentration right below the interface (Figure 3). This layer extended deeper in the sediment in February and April, was practically absent in May and increased again in September and November. Only PO_4, more prone to sorption than DIC, NH_4 or Si, showed this behavior, suggesting that sorption may be controlling the availability of PO_4 in the porewater (Tuominen et al. 1997; Rahnemaie et al. 2007). Supporting this idea is the fact that this station has a high Fe content (up to 280 µmol g^{-1}) and a large Fe bound PO_4 pool (Leote et al. 2014). The retention of PO_4 in the sediment can be assessed by comparing the maximum gradient in the porewater profile, corresponding to the maximum production rate, and the gradient at the interface, which provides the exchange rate with the overlying water. The retention was higher in February in line with the low exchange obtained for this period, since 99% of the PO_4 produced in the sediment was retained in the upper layer at a maximum sorption depth of 1.25 cm (Table 4). Oppositely, in May only 50% of the PO_4 diffusing upward was retained, within a layer of 0.35 cm, likely due to the reductive dissolution of Fe oxides, used as electron acceptors in the degradation of organic matter (Krom and Berner 1981; Sundby et al. 1992). A comparison between May and September shows a higher retention in September, with a specific sorption rate of 1.81 x 10^{-4} mmol g^{-1} d^{-1} (82% retention) compared with a rate of 7.57 x 10^{-5} mmol g^{-1} d^{-1} (50% retention) in May. This explains the lower release in September, in spite of the higher mineralization rate, according to the release of DIC and NH_4 (Figure 4). Summarizing, nutrient release from station 6 depends on the degradation of organic material, higher in the end of spring and summer, and on diffusion as the main transport process. For the specific case of PO_4, sorption affects the availability in the porewater, with strong retention in autumn and winter. The combined effect of a higher mineralization and lower sorption capacity in May resulted in the highest sediment-water exchange for this period (Grunwald et al. 2010).

Table 4. Sorption parameters from station 6: oxygen penetration depth, rate of PO_4 retained and relative retention, maximum sorption depth, and specific sorption rate.

Month	O_2 penetration depth (cm)		PO_4 retained (mmol m^{-2} d^{-1})	PO_4 retained (%)	Sorption depth (cm)	Specific sorption (mmol g^{-1} d^{-1})
	mean	stdev				
Feb 2010	n.a.	n.a.	0.12	98.5	1.25	1.37e−5
Apr 2009	n.a.	n.a.	0.34	89.4	0.80	6.02e−5
May 2010	0.14	4e−4	0.19	49.7	0.35	7.57e−5
Sep 2010	n.a.	n.a.	0.51	81.6	0.40	1.81e−4
Nov 2009	0.31	2e−2	0.56	87.7	0.55	1.45e−4

Nevertheless, for the coarser sediment stations, this mineralization/sorption approach is not applicable. The seasonal variation of the release was more erratic, without a clear increase between in spring and summer, as observed for station 6. As an example, PO_4 and NH_4 showed a decreasing release throughout the year for station 2, while for station 5, the release of PO_4 was lower between March and September. Additionally, there was a clear mismatch between the measured and predicted exchange with the overlying water (Figure 4 and Table 3) indicating that other processes may be involved. The layer of constant concentration below the sediment-water interface observed for all nutrients (Figure 3) suggests that bioirrigation may be the responsible for this mismatch, as outlined in chapter 3.1.2. The maximum depth for this layer in our profiles was of about 15 cm which agrees well with the 9.8 ± 4.5 cm found by Boudreau (1998) and the model of Kristensen and Hansen (1999), which considers a layer at the surface with bioirrigation as the transport process, yields a good fit of the DIC, NH_4, and PO_4 profiles (Figure 3), further confirming this hypothesis. The activity of macrofauna significantly affects the biogeochemistry of the sediment by mixing both solid and dissolved phase and accelerating the exchange between the oxic overlying water and sediment surface and the reduced deeper sediment (Aller and Aller 1998; Kristensen and Hansen 1999). The increased availability of electron acceptors and labile organic matter and induced redox oscillations is thought to stimulate microbial mineralization (Krantzberg 1985; Kristensen 1985; Aller 1994), while the 3-D mosaic of oxic-anoxic interfaces created by the movement of macrofauna increases the surface area in contact with the overlying water, which may facilitate the release but also increase the retention capacity of the sediment by increasing the oxic sorption layer (Krantzberg 1985; Kristensen 2000). By depending on the type of sediment, species composition, abundance, and size of the community, the effect of macrofauna activity on the sediment-water exchange shows a large spatial and temporal variability. Consequently, even though its effect on nutrient release is large, it is very difficult to predict, as seen in our measured fluxes (Figure 4).

Our results suggest that the sediment-water exchange was controlled by different processes throughout the year. In the depositional area, identified by station 6, sorption appears to limit the release during autumn and winter. In spring, however, following the first phytoplankton bloom, mineralization likely overrules sorption, by reducing the sediment's sorption capacity and dramatically increasing the concentrations in the porewater. In addition to sorption and mineralization, in the coarser sediment areas the activity of benthic macrofauna is also affecting nutrient release by stimulating the degradation of organic matter and enhancing the release rates, due to mixing and irrigation of the sediment. The action of these different processes results in a variable seasonal contribution of the sediments to pelagic nutrient concentrations.

3.3 Contribution of sediment nutrient release to primary production

The Redfield-Brzezinski ratio (Redfield et al. 1963; Brzezinski 1985) gives an estimation of the relative demand of DIN (= NO_3 + NO_2 + NH_4), Si, and PO_4 for phytoplankton growth and can be compared with the sediment-water exchange of DIN, Si, and PO_4 to assess the contribution of sediment release in meeting the needs of primary producers. For the measured sediment-water exchange, the ratios were usually higher than the Redfield ratio of 16:15:1 for DIN:Si:PO_4. Values ranged between 1.01–135.67, 0.32–6.04, and 1.67–155.62 for the DIN/PO_4, DIN/Si, and Si/PO_4 ratios (Table 3). The nutrient release was always PO_4 deficient for stations 5 and 6 and in February and May for station 2. Si deficiency was observed for station 2 in March and September and in March for station 14 (Figure 6). DIN deficiency was only observed for station 17 in March. A deficit in the release of PO_4, likely due to sorption, agrees well with literature on nutrient limitation in the water column for the western Wadden Sea, which identifies PO_4 as a limiting nutrient (Cadée 1986; Philippart and Cadée 2000; Ly et al. 2014). In March, following the spring phytoplankton bloom in the Wadden Sea (de Vries et al. 1998;

Kuipers and van Noort 2008), no PO_4 deficiency was observed for the fluxes from stations 2, 14, and 17, suggesting less retention as observed for station 6 (Table 4).

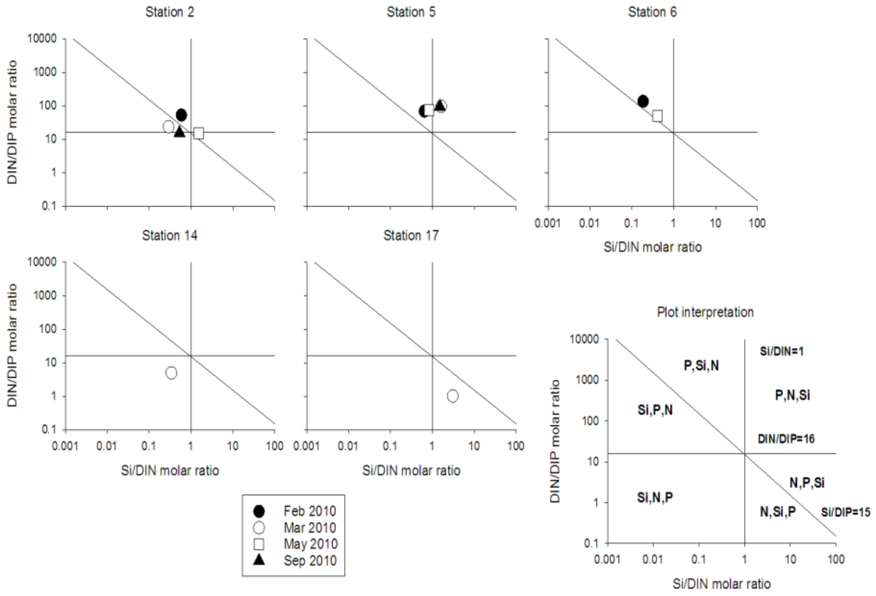


Figure 6. Nutrient limitation diagrams applied to the measured sediment-water exchange indicating a lower relative release of PO_4 and Si compared with DIN considering the demand for phytoplankton growth given by the Redfield-Brzezinski ratio (Rocha et al. 2002).

The relationship found between the silt content and the exchangeable P content (Figure 2) (Leote et al. 2014), was also observed for the PO_4 sediment-water exchange predicted according to the Kristensen and Hansen approach, with higher fluxes associated with a higher silt content. An extrapolation of the exchange for the Marsdiep basin, assuming a high silt content area (identified by grain sizes between 0 and 120 µm) and a lower silt content area (with grain sizes >120 µm) (Table 1), for each sampled month, showed an increase from February (1.3×10^4 mol d^{-1}) until September (4.4×10^4 mol d^{-1}), followed by a decrease in November (Figure 7). This higher sediment release in spring and summer has the potential to fuel primary production in this area and particularly the second phytoplankton bloom (Cadée 1986; Philippart et al. 2000). The total release of PO_4

over one year was estimated in 1.0 x 10^7 moles (321 ton of P) for the Marsdiep basin. Using the Redfield-Brzezinski ratio and assuming PO_4 as the limiting nutrient, the annual release from the sediments had the potential to contribute to a primary production of 19 C m^{-2} y^{-1}, which is close to the 15 g C m^{-2} y^{-1} obtained by de Jonge et al. (1993) based on diffusive fluxes under oxic conditions and lower than the 78 g C m^{-2} y^{-1} estimated by Leote et al. (2013) based on the seasonal difference in the exchangeable PO_4 pool in the sediment. The contribution of sediment PO_4 release to primary production estimated by this study seems to be of minor importance when compared with the latest estimates of 200 g C m^{-2} y^{-1} (Philippart et al. 2007). Nonetheless, a significant difference between the predicted and the measured fluxes was found, confirming that our budget represents a conservative estimate of PO_4 release. The surface area used in the calculations is also smaller than the real one, since topography and 3-D structures induced by bioturbation were not included. In addition, for the flux calculations it was assumed that PO_4 production in the bioirrigated layer was similar to the measured in the deeper layers which may not be true due to the increased availability of organic matter and electron acceptors induced by biological mixing. The activity of macrofauna and physical mixing induced by waves and bottom currents are known to enhance nutrient release up to 5-fold (Webb and Theodor 1972; Huettel et al. 1998; Kristensen and Hansen 1999), while the mismatch between our measured and predicted fluxes indicates a 3–800 times underestimation of the PO_4 exchange. A 5 times higher release would contribute to a primary production of 95 g C m^{-2} y^{-1}, which corresponds to approximately half of the current primary production. The release of PO_4 from the western Wadden Sea sediments has then the potential to fuel a very significant fraction of present primary production, given the PO_4 limitation.

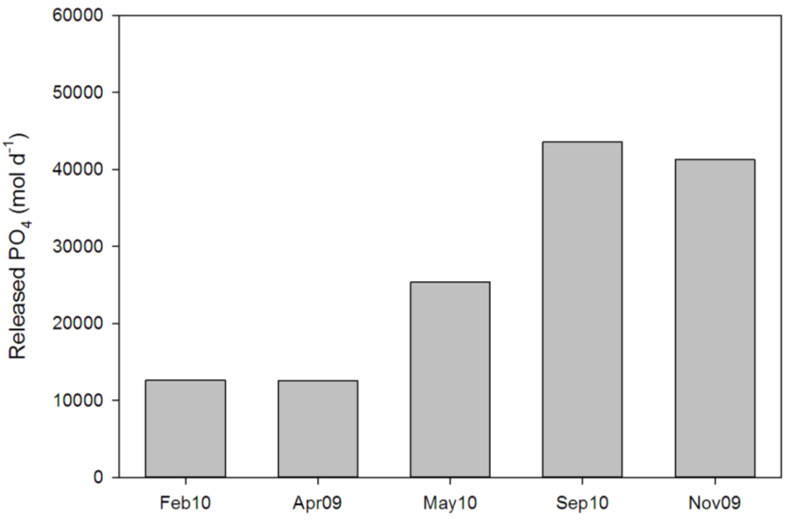


Figure 7. Phosphate release (in moles per day) for the months of February 2010, April 2009, May and September 2010 and November 2009 extrapolated for the Marsdiep basin.

Conclusions

Two distinct areas were identified in the western Wadden Sea regarding their characteristics. A depositional zone characterized by fine-grained sediment and a high content of organic material and the majority of the area, characterized by coarser sandy sediments and low organic matter content. Porewater concentrations of DIC, Si, NH_4, and PO_4 were also much higher in the fine-grained area, resulting in a higher sediment-water exchange. The shape of the porewater profiles, together with the clear seasonal pattern and similarity between the measured and predicted sediment-water fluxes suggests that PO_4 exchange in the depositional area was mainly controlled by mineralization and sorption, with a retention in the sediment >88% in February, April, and November. Oppositely, the coarser sediment stations clearly showed higher measured than predicted fluxes and a layer of constant concentration below the sediment's surface for all nutrients, challenging the view of a mineralization/sorption controlled release. The presence of macrofauna in these stations suggests that bioirrigation is enhancing the exchange. The release of nutrients was deficient in PO_4 during most of the year relative to the demand by phytoplankton. An increase in the exchange was observed from February until September, potentially supplying primary producers with nutrients during the blooming season. The annual PO_4 release for the western Wadden Sea sediments was estimated in 1.0 x 10^7 mol, based on the predicted exchange, which has the potential to fuel a primary production of 19 g C m^{-2} y^{-1}. Since it represents a conservative estimation, with the real fluxes expected to be several fold higher, a 5-times higher release from the sediments, based on literature, has the potential to sustain a significant fraction of present day productivity.

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Chapter 5

Nutrients in the western Wadden Sea: freshwater input vs internal recycling

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Abstract

The major phosphorus sources to the western Wadden Sea were identified on a seasonal basis, by comparing the contributions of freshwater discharge and sediment release to the concentrations in the water column. A close relationship was found between the pelagic concentrations of dissolved inorganic nutrients and chlorophyll *a*, with a concomitant decrease in nutrients and increase in chlorophyll *a*. This was observed in early spring and was followed by a later increase in the nutrient concentrations in spring and summer. The low concentrations found for the freshwater and seawater end-members for this period rule out their importance as nutrient sources and suggest that the increase resulted mainly from internal recycling in the Wadden Sea. This may include mineralization of autochthonous and allochthonous organic material in the water column/sediment and desorption of nutrients stored in the sediments over winter. Resuspension of deposited material due to tidal currents seems to be a common feature in the Wadden Sea, potentially enhancing mineralization and sediment release. Even though phosphorus limitation was observed during most the year, a seasonal change in the limiting nutrient was observed, which may have implications in the species composition of the phytoplankton community. The comparison between phosphorus supply to the Wadden Sea by freshwater discharge and sediment release showed a much higher contribution of sediment release, especially between April and November.

1. Introduction

The Wadden Sea is a shallow coastal sea, separated from the North Sea by a chain of barrier islands, stretching from the Netherlands to Denmark. It represents a complex system of intertidal flats and gullies creating a highly diverse ecosystem of high biological productivity (Beukema 2002). The primary supply of nutrients to its westernmost area, the Marsdiep basin, occurs via direct freshwater discharge from the adjacent Lake IJssel, and indirectly via the coastal bound residual flow of Rhine and Scheldt river waters admixed with North Sea water. The atmospheric contribution to the overall nutrient input through wet and dry deposition is considered of secondary importance (van Raaphorst et al. 2000). Nutrients are supplied in dissolved and particulate organic and inorganic form, where the form dominating the input depends on the element and stage of the seasonal productivity cycle. Especially the input of particulate organic nutrients as organic matter from the North Sea has since long received considerable attention as to explain the high productivity and heterotrophic status of the basin (Postma 1954; van Beusekom and de Jonge 2002; van Beusekom 2005).

Similar to many European coastal waters, the western Wadden Sea experienced a major increase in the nutrient loading from freshwater sources. From the 1950s until the 1980s the loading of nitrogen (N) and phosphorus (P) increased by a factor of 12 and 10 due to anthropogenic activities (van Raaphorst and de Jonge 2004). The increase in nutrient supply and presumably availability was paralleled by a rise in primary production from an estimated 20 g C m^{-2} y^{-1} prior to the 1950s up to 520 g C m^{-2} y^{-1} in 1986 supporting the view of a strict and causal relationship between freshwater discharge and primary production in the western Wadden Sea (de Jonge 1990). Restrictive policies in nutrient riverine discharge to the coastal zone resulted in a reduction of the loadings to values close to the pre−1950s (de Jonge 1997; Colijn and van Beusekom 2005), followed by a proportional response in the nutrient concentrations in the Wadden Sea (de Vries et al. 1998; Kuipers and van Noort 2008). This was particularly effective for P resulting in dissolved N/P ratios as high as 100, which suggests severe P limitation on the primary production in the western Wadden Sea (van Raaphorst and de Jonge 2004). Despite the decrease in nutrient loadings, high levels of primary productivity were maintained and only since the 2000s a significant decrease was observed to present day values of ca 200 g C m^{-2} y^{-1} (de Jonge 1990; Cadée and Hegeman 1993; de Jonge et al. 1996; van Beusekom 2005; Kuipers and van Noort

2008). This lag in productivity with decreased nutrient loading is generally attributed to the temporal storage of nutrients, notably P, in the sediment and controlled exchange with the overlying water, dampening the decrease in freshwater loading.

The goal of this study is to understand the interaction between phytoplankton growth and nutrient availability in the water column and to identify the main seasonal nutrient, and especially P, sources to primary producers in the modern western Wadden Sea. Assumed as the main nutrient sources to the study area, the contributions of freshwater discharge and sediment release to the pelagic P concentrations are compared on a seasonal scale.

2. Methods

2.1 Study Site

The Marsdiep basin, in the western Wadden Sea covers an area of about 700 km^2, approximately 580 km^2 of which is covered by tidal channels (Dastgheib 2007) (Figure 1). The basin, with an average depth of 3.3 m, is subject to a mesotidal regime, with a mean tidal range of 1.37 m and a tidal frequency of 1.92 tides per day. A daily tidal exchange of 3.6×10^7 m^3, amounting to approximately 1% of the total water volume, yields an average water residence time of 5–15 days (Ridderinkhof 1988; Nauw et al. 2013). Due to freshwater discharge from Lake IJssel and other minor sources, the study area behaves like an estuary, covering a salinity range from 15 (near the sluices) to 32 (near the tidal inlets) (van Aken 2008). On average, the water in this basin is composed of ca 85% North Sea seawater, with a 15% admixture of Lake IJssel water (de Jonge et al. 1996). The bulk of the sediment and particulate matter supply mainly originate from the North Sea (Oost and de Boer 1994). The Marsdiep basin is largely composed of sandy sediments with a variable silt content (1–73%), where most P in the sediments is in a non easily exchangeable form, with the bioavailable fraction corresponding to approximately 1/3 of the total sediment P pool (Leote et al. 2014).

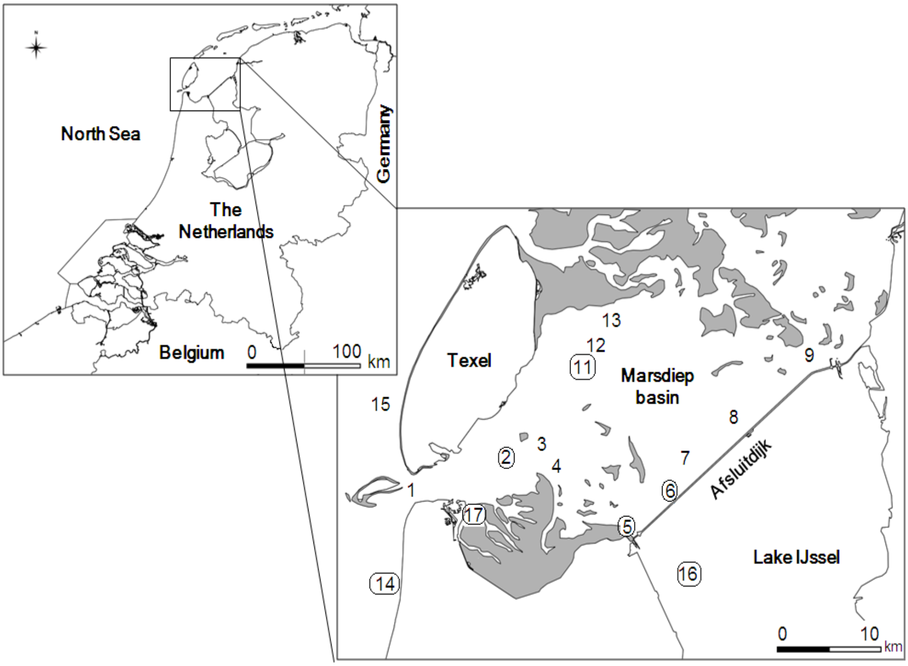

Figure 1. Map of the western Wadden Sea with the sampling locations in the Wadden Sea (1–13, 17), North Sea (14, 15), and Lake IJssel (16). The stations marked with a circle were seasonally sampled.

2.2 Sampling scheme

Sixteen stations were selected to cover the Marsdiep tidal basin and the freshwater (Lake IJssel) and seawater (North Sea) end-members (Figure 1). Six stations (2, 5, 6, 11, 14, and 17) were seasonally sampled during a full tidal cycle (app. 13h) whereas station 16, located in Lake IJssel was sampled only once per cruise. Sampling campaigns were carried out in April and November 2009, February, March, May, and September 2010. For each station, water samples were collected every hour with a Niskin bottle from the side of the ship at 3 depths: surface, mid column, and bottom. Each sampling event was preceded by CTD (conductivity, temperature, and depth) profiling to retrieve information on the tidal stage locally.

2.2.1 Dissolved nutrients

Water samples were collected with a syringe and filtered (0.2 μm pore diameter Acrodisc filter, Supor® membrane) for later analysis of NO_3, NO_2, NH_4, total dissolved nitrogen (TDN), Si, PO_4, and total dissolved phosphorus (TDP). Samples were stored in pony vials at −20°C for NO_3, NO_2, NH_4, TDN, and TDP and at 4°C for PO_4 and Si.

2.2.2 Particulate material

To determine the total suspended matter (TSM), particulate total C, N, and P, organic C, and chlorophyll *a* contents, 100–300 ml of water sample were collected every 2 h and filtered using pre-ashed (500°C for 4 h) Whatman GF/F filters. Filters for the analysis of TSM, total C, total N, organic C, and chlorophyll *a* content were stored at −20°C, while the extraction for total particulate P started immediately after filtration.

2.3 Analytical procedures

All analyses on dissolved nutrients were performed on a TRAACS 800 Segmented Continuous Flow Analyzer. NO_3 + NO_2 and NH_4 were analyzed according to the methods of Grasshoff et al. (1983) and Helder and de Vries (1979) with a precision and detection limit of 0.021 and 0.04 µM and 0.03 and 0.07 µM, respectively. PO_4 and Si were analyzed according to the methods of Murphy and Riley (1962) and Strickland and Parsons (1968), with detection limits of 0.007 and 0.03 µM and a precision of 0.002 and 0.016 µM, respectively. The analysis of TDN and TDP followed a method based on Schreurs and Nijsse (2000) and Nijsse and Spronk (2000) adapted by K. Bakker (NIOZ nutrient lab), with a detection limit and precision of 0.03 µM. The concentration of dissolved organic N was determined as the difference between TDN and NO_3 + NO_2 + NH_4, while dissolved organic P was calculated as TDP minus PO_4. The concentration of total suspended matter was determined by subtracting the filter weight from the weight of the freeze dried filter with sample. The contents of total particulate C and N were measured on the filters using a Thermo-Interscience Flash EA1112 Series Elemental Analyzer according to Verardo et al. (1990), with a detection limit of 100 ppm and a precision of 0.3%. Organic C was determined following the same procedure after removal of the carbonates with 2 M HCl. Total particulate P content was determined according to the persulfate oxidation method described by Valderrama (1981) as improved by G. Kramer and K. Bakker (NIOZ nutrient lab) to a digestion time of 90 min. Chlorophyll *a* was analyzed in a High Performance Liquid Chromatographer (HPLC) after extraction in a 90% acetone medium (Jeffrey et al. 1997).

2.4 Calculations

A comparison was made between the contribution to the pelagic P concentrations of freshwater discharge and release from the sediments. To do so, it was estimated how much P was discharged monthly from the Lake IJssel sluices and the harbor in Den Helder and how much P was released monthly from the sediments of the Marsdiep basin. The discharge from Lake IJssel was calculated by multiplying the sluice debits in Den Oever and Kornwerderzand by the PO_4 concentrations from Lake IJssel (station Vrouwenzand) using data from the Rijkswaterstaat Waterbase. The database provided one daily debit value (in $m^3 s^{-1}$), which was assumed to be valid for 24 h. The debit in Den Helder was assumed to be 1/20 of the total debit from Lake IJssel based on van Raaphorst and van der Veer (1990). The database provided one monthly PO_4 concentration value for station Vrouwenzand, which was assumed to be valid for the period between samplings. The PO_4 concentration of the freshwater discharging in Den Helder was assumed to correspond to the concentrations measured in the 1950s (Postma 1954). The freshwater discharge was calculated between January 2009 and December 2010, so that the monthly discharge corresponds to an average value for the two years. Values for sediment nutrient release were taken from Chapter 4.

3. Results

3.1 Dissolved nutrients

3.1.1 Measured values

The concentrations of the major dissolved nutrients (NO_3, NH_4, PO_4, Si, organic N, and organic P) were, in general, similar for all depths, with the exception of station 5. This indicates a well mixed water column with stratification only occurring nearby the freshwater sluices or following a major freshwater discharge event. The seasonal variation in the nutrient concentrations, averaged for a complete tidal cycle and including all depths is shown in Figure 2. NO_3 concentrations ranged between 2 µM for station 11 and 192 µM for station 16, in Lake IJssel. NH_4 showed a much smaller seasonal amplitude than NO_3, reaching a minimum of 0.2 µM for station 14 in the North Sea and a maximum of 17 µM for station 5, close to a freshwater sluice. PO_4 concentrations varied between 0 µM for station 16 and 1 µM for station 17, situated in the main channel of the Balgzand tidal flat. Si concentrations went up to a maximum of 76 µM for station 16, with a minimum value of 0 µM measured for station 6. The concentrations of dissolved organic P varied between 0 µM for station 16 and 0.5 µM for stations 5 and 16, while organic N varied between 6 µM for station 14 and 41 µM for station 5. A clear seasonal pattern was observed for all dissolved nutrients.

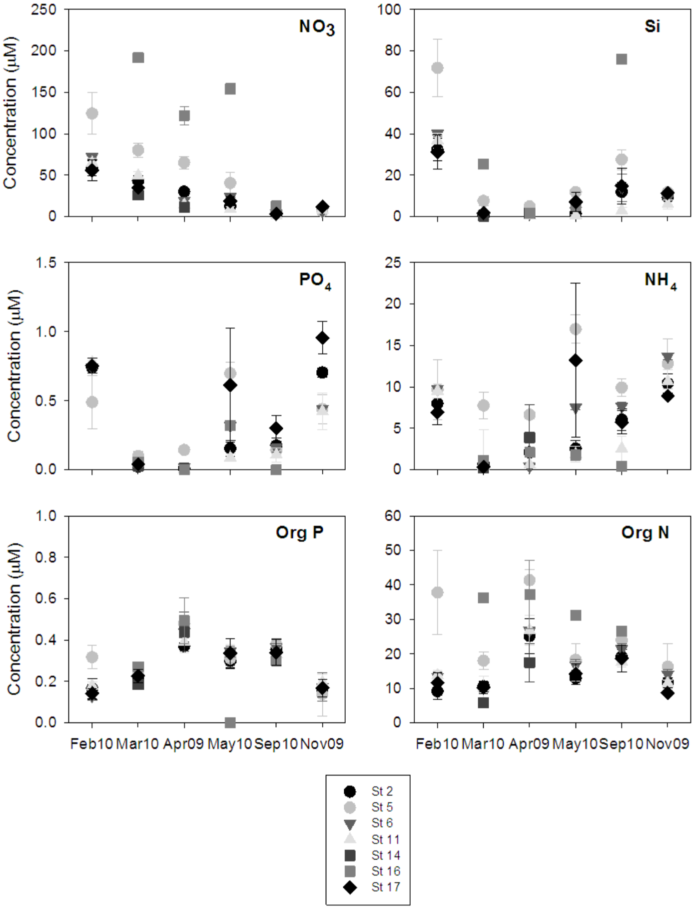

Figure 2. Seasonal variation of the concentrations in the water column of inorganic (NO_3, Si, PO_4, and NH_4) and organic (organic P and organic N) dissolved nutrients. Average values for all depths and for a full tidal cycle are presented with standard deviations.

3.1.2 Seasonal Variation

NO_3 showed a decreasing trend in concentrations from February until November for all Wadden Sea stations. However, the seasonal trend in the concentrations of Si, PO_4, and NH_4 was clearly different from NO_3, suggesting a difference in sources and sinks for NO_3 and the other nutrients. For Si, PO_4, and NH_4, a dramatic decrease in concentrations was observed between February and March, when nutrient depletion was observed for all stations except 5 and 16. The concentrations of Si and PO_4 remained low in April while NH_4 showed a small increase. In May, NH_4 and PO_4 concentrations increased approximately 3-fold, while Si showed only a minor increase. PO_4 and NH_4 concentrations decreased again in September, increasing in November. Oppositely, Si increased by a factor of 2 in September, decreasing again in November. This similarity in seasonal trend may point at common sources and sinks throughout the year for NH_4, PO_4, and Si. The concentrations of organic P and N increased from February until April and were followed by a decrease until November. Organic N showed more spatial variation than organic P, with clearly higher concentrations measured for stations 5 and 16 and, therefore, associated with freshwater. The seasonal trends of PO_4 and organic P and NH_4 and organic N showed an opposite behavior, with higher concentrations of organic nutrients in parallel with a decrease in the concentrations of inorganic nutrients.

3.1.3 Mixing diagrams

In estuarine systems, a plot of the nutrient concentration versus a conservative tracer such as salinity may provide information concerning the fate and origin of nutrients between the freshwater and seawater end-members. Such mixing diagrams for NO_3, NH_4, PO_4, and Si are shown in Figure 3 for all the cruises.

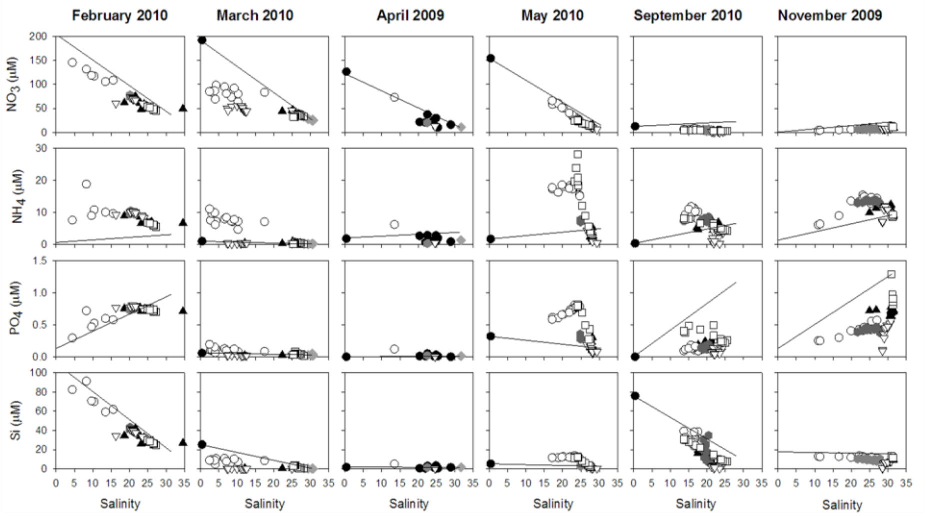

Figure 3. Mixing diagrams for the major inorganic nutrients (NO_3, NH_4, PO_4, and Si) plotted separately for each cruise. Surface values for all sampled stations are presented: station 2 (closed triangles), station 5 (open circles), station 6 (dark grey hexagons), station 11 (open triangles), station 14 (light grey rhombuses), station 16 (closed circles), and station 17 (open squares). The other stations sampled in April 2009 (1, 3, 4, 7–9, 12, 13, 15) are represented by closed circles. The line represents the predicted concentrations assuming mixing between the end members as the only process affecting the concentration distribution. End member concentrations were taken from the Rijkswaterstaat Waterbase.

Lake IJssel was clearly a source of NO_3 for the Marsdiep Basin from February until May, with a near conservative behavior observed in February and May and net removal of NO_3 during the months of March and April. In September and November, the concentrations from the freshwater end-member and the Wadden Sea decreased substantially to values close to zero and the North Sea became a minor source of NO_3. The concentration of NH_4 was always lower in Lake IJssel than in the Wadden Sea or North Sea. Therefore, the elevated concentrations observed along the salinity gradient likely resulted from production/regeneration within the Wadden Sea, which was most prominent in May, but also evident in February, September, and November. In March and April, the NH_4 concentration was very low along the entire salinity range, except for station 5 showing concentrations well above the conservative mixing line. Similar to NH_4, the concentration of PO_4 was always lower in Lake IJssel, except in May, when it was slightly higher than for the North Sea. In February, an approximately conservative behavior was observed, with the North Sea as the source. Nevertheless, the concentrations were slightly above the conservative mixing line for salinities under 22 and slightly below for salinities above 22. In March and April, the concentration was very low for both end-members with station 5 showing values slightly above the predicted by mixing. In May, the concentrations measured at intermediate salinities were clearly above the predicted line, indicating production, while in September and November they were below, suggesting consumption. Si concentration was always higher in the freshwater end-member. In February, Si concentrations showed a conservative behavior while in March the concentrations decreased with consumption at intermediate salinities. In April and May, the concentrations were close to zero in both end-members and the Wadden Sea, with a slight increase being observed at intermediate salinities in May. In September, an approximately conservative behavior was observed, even though the concentrations were slightly below the predicted values, with Lake IJssel as the source of Si. In November, concentrations decreased again leveling off between the freshwater and seawater end-members.

3.2 Particulate matter

3.2.1 Measured values

The concentration and composition of suspended particulate matter may provide information about the growth cycle of primary producers but also on the potential availability of nutrients following the degradation of the particulate material. The contents of total suspended matter, total C, N, and P and organic C were analyzed for 5 different cruises (Figure 4). The concentration of total suspended matter varied between 15 and 120 mg l^{-1}. The total C and organic C contents ranged 6–25 wt% and 1–21 wt%, respectively. The content of total N was much lower, between 0.5 and 3 wt%, while total particulate P ranged between 14 and 69 µmol g^{-1}. The ratio between the content of organic C and total P provides additional information concerning the composition of particulate P, i.e. biogenic or terrigenous/mineral associated. During our sampling period, it ranged between 15 and 325, most of the time reaching values below the Redfield ratio. Like the dissolved nutrients, the suspended particulate matter showed a clear seasonal variation.

3.2.2 Seasonal variation

The seasonal variation of the concentrations of total suspended matter, total C, N, and P and organic C and the ratio between organic C and total P, averaged for all depths and for a full tidal cycle are shown in Figure 4. The concentration of total suspended matter was low in February and March, with small standard deviations, followed by an increase in both average concentrations and standard deviations in May and September and a decrease in November. The contents of total C, total N, and organic C showed a comparable seasonal pattern, with lower values in February and a small increase in March, followed by a slight decrease in May. The highest contents were measured in September, after which they decreased in November. The content of total particulate P showed a seasonal trend similar to the total suspended matter with lower values and standard deviations in February and March, followed by an increase in May and September and a decrease in November. The organic C/total P ratio showed a seasonal profile opposite to the observed for the total suspended matter and total P contents, with higher values in February and especially March, followed by a decrease in May and September and a slight increase in November.

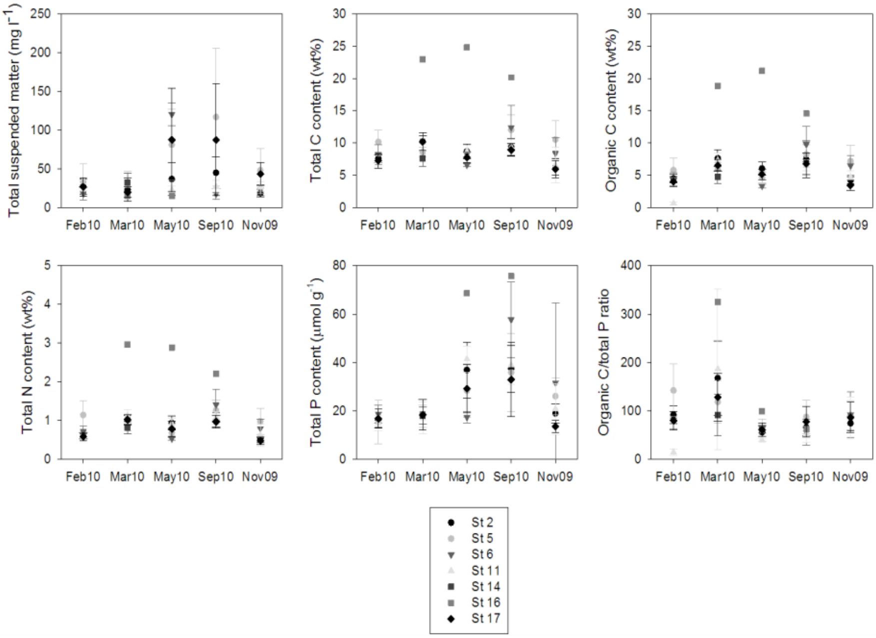

Figure 4. Seasonal variation of the concentration of total suspended matter, total C, organic C, total N, total P, and organic C/total P ratio in the water column for all seasonally sampled stations. Values presented correspond to an average for all depths and for a full tidal cycle with the respective standard deviations.

3.2.3 Chlorophyll a

Chlorophyll *a* was measured as an indicator of primary production at surface, mid column, and bottom depths in February, March, May, and September 2010 (Figure 5). Average values for all depths and a full tidal cycle varied between 4 µg l^{-1} in February and 84 µg l^{-1} in September. Concentrations and respective standard deviations were lower in February and May, with similar concentrations for all depths. The chlorophyll *a* concentration was higher in March and September, especially for the surface samples, with lower values measured at mid column and bottom depths (data not shown). Concomitantly with the higher concentrations, an increase in the standard deviations and spatial variation was observed.

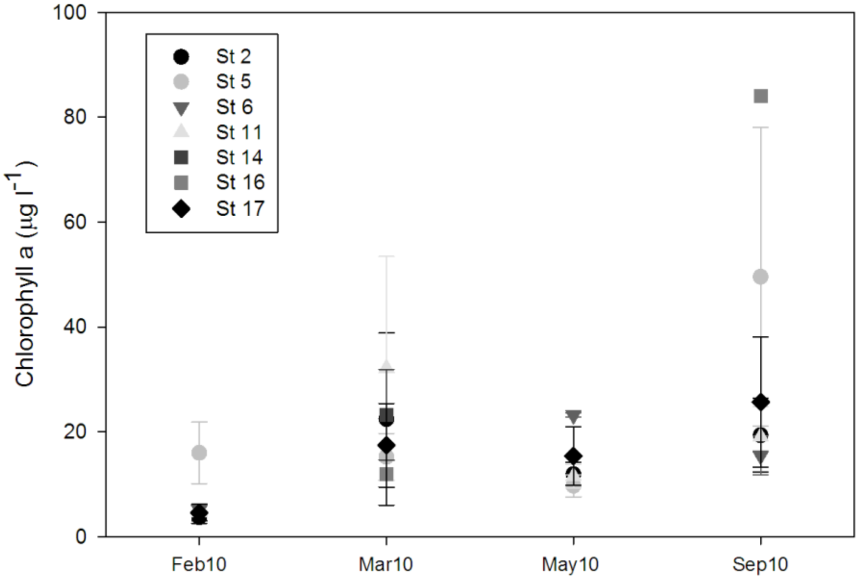

Figure 5. Seasonal variation of the concentrations of chlorophyll *a* in the water column for all the seasonally sampled stations. The plot includes the average values for all depths and for a full tidal cycle with the respective standard deviations.

3.2.4 Tidal variation

In addition to the seasonal pattern, a tidal pattern was observed for the concentrations of particulate matter and chlorophyll *a* in the water column. As an example, these are plotted for a full tidal cycle in Figure 6 for station 17 in February, March, May, and September 2010. In February and March, the content of total suspended matter was very low and similar for all sampled depths, with no significant variation during the tidal cycle. Oppositely, in May and September, values were much higher, with a clear increase during maximum tidal current speed (i.e. between high and low tide) and the highest concentrations measured at the bottom. This is a clear evidence of resuspension of the deposited material. The concentrations of chlorophyll *a* showed a similar pattern to the total suspended matter, with lower concentrations, similar contents for the different depths and a very small variation with the tide height in February. Nevertheless, in March, and particularly May and September, the concentrations were higher, especially during the periods of maximum current speed and for the bottom samples, suggesting that part of the resuspended material corresponded to fresh organic matter. The plots of the concentration of chlorophyll *a* versus the total suspended matter show a high correlation between both, with chlorophyll *a* representing a larger fraction of the total suspended matter between March and September.

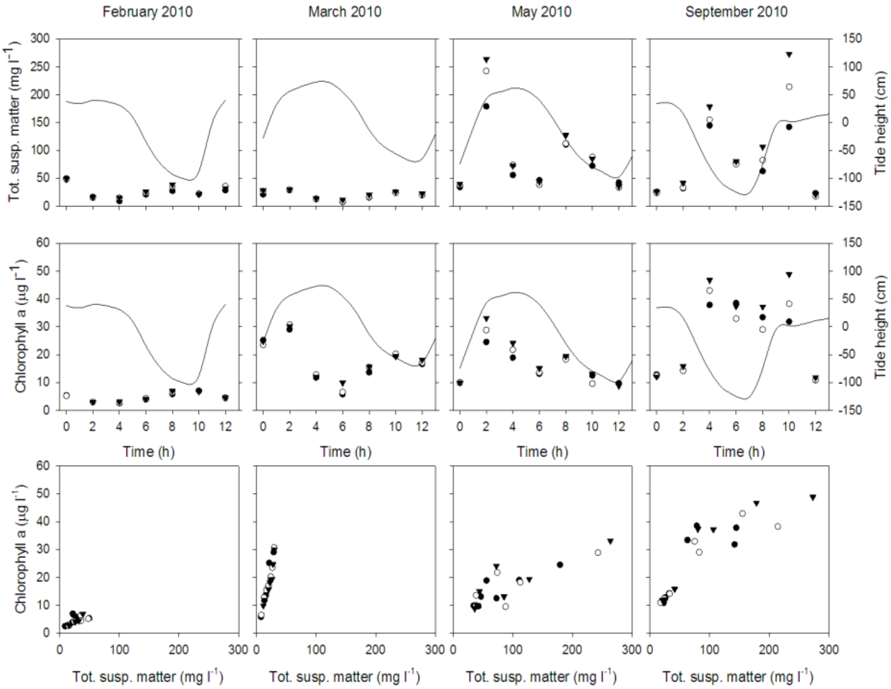

Figure 6. Total suspended matter and chlorophyll *a* concentrations plotted for a full tidal cycle and chlorophyll *a* versus total suspended matter concentrations. Values presented are for station 17 for surface (closed circles), mid (open circles), and bottom (closed triangles) depth.

4. Discussion

4.1 Nutrient concentrations linked to primary production

Throughout the year, a clear relationship between the concentrations of chlorophyll *a* and the major inorganic and organic nutrients was observed in the Wadden Sea and Lake IJssel (Loebl et al. 2007; van Beusekom et al. 2009). In February, the concentrations of inorganic nutrients were within the highest measured throughout the year (Figure 2). Lake IJssel was clearly the source of NO_3 and Si, according to the mixing diagrams, with the concentrations at intermediate salinities resulting from mixing between the two end-members, i.e. conservative behavior (Figure 3). However, this did not seem to be the case for PO_4 and NH_4, which showed very low concentrations in the freshwater end-member and did not behave conservatively. The higher concentrations of chlorophyll *a* measured for station 5, close to a freshwater sluice, suggest the occurrence of an earlier phytoplankton bloom in the lake consuming PO_4 and NH_4, in agreement with previous studies (Cadée 1986; de Vries et al. 1998). Later in March and April, the increase in the concentrations of chlorophyll *a* (Figure 5) was coupled with depletion in the water column of NH_4, PO_4, and Si, the most important nutrients for phytoplankton growth (Crouzet et al. 1999) (Figure 2), suggesting a first phytoplankton bloom in the western Wadden Sea between February and March. Consumption overcame production/supply and the nutrient concentrations in the freshwater and seawater end-members and the Wadden Sea leveled off. The higher contents of organic C and total N in the particulate matter (Figure 4), indicating that a large fraction of the suspended material is organic, corroborate this idea. Moreover, a first phytoplankton bloom in early March is in line with previous studies for the Wadden Sea (Cadée 1986; Cadée and Hegeman 1993; Philippart et al. 2000; Kuipers and van Noort 2008). After the initial bloom, nutrient depletion likely limited the growth of phytoplankton, as apparently seen in May, with a decrease in the concentrations of chlorophyll *a* and organic C and total N in the particulate material (Figures 4 and 5). In May, the increase in the concentrations of PO_4, NH_4, and Si indicates that the supply of nutrients, probably from mineralization of organic material, exceeded the consumption by primary producers (Figures 2 and 3). The growth of phytoplankton was no longer limited by the availability of nutrients, allowing for a second bloom in September, evidenced by the concomitant increase in the concentrations of chlorophyll *a*, total C, total N, and organic C concentrations, and decrease in the concentrations of NH_4, PO_4, and

Si (Figures 2, 4, and 5). Nutrients were apparently available in the water column throughout summer, indicating that, in spite of a relatively high primary production during that period, the supply of nutrients was enough to compensate for the uptake by phytoplankton. This suggests mineralization as an important responsible for nutrient replenishment in the water column, since the high temperatures and availability of labile organic material, promote a higher degradation rate during summer.

4.2 Internal recycling and sediment release as a source of nutrients to the water column

The mixing diagrams (Figure 3) support the idea of mineralization in the Wadden Sea as an important source of NH_4, PO_4, and Si to the water column, especially in spring and summer. As mentioned above, even though freshwater appeared to be the source of NO_3 and Si to the western Wadden Sea in winter, the same did not apply to PO_4 and NH_4 likely due to an earlier phytoplankton bloom in the lake. In addition, retention of NH_4 and PO_4 by sorption in the sediments may be more efficient in freshwater than in seawater, due to the reduced presence of competing ions (Caraco et al. 1989; Hawke et al. 1989). Instead, the availability of NH_4 and PO_4 in the Wadden Sea in winter seemed to result from internal “production”, whether by slow degradation of refractory organic matter and/or desorption of nutrients stored over winter in the sediments (van Raaphorst et al 1988; van Raaphorst and Kloosterhuis 1994; de Vries et al. 1998; Leote et al. 2013). The first phytoplankton bloom, in March, resulted in a high demand for NH_4, PO_4, and Si in both end-members and the Wadden Sea. As a consequence, the concentrations of dissolved inorganic nutrients dropped significantly to extremely low values after being converted in particulate organic material. However, the following degradation of the dead phytoplankton cells can replenish the water column with dissolved nutrients (van Beusekom and de Jonge 2012). In April, the increase in the concentrations of dissolved organic N and P (Figure 2) indicates an initial degradation of the organic material, with nutrients becoming available to heterotrophs or autotrophs after external oxidation or microbial degradation (Nausch and Nausch 2006; 2007). In May, comparing the increase in the concentrations of NH_4, PO_4, and Si in the water column with the mixing diagrams (Figure 3) it becomes clear that neither Lake IJssel nor the North Sea were the main nutrient sources. Instead, the increase in the concentrations was only observed at intermediate salinities, suggesting that mineralization within the

Wadden Sea, enhanced by the increased availability of fresh organic matter and higher temperatures, was the main nutrient source (van Beusekom et al. 2009). Silicate showed a less marked increase in the concentrations in comparison to NH_4 and PO_4, since dissolution of biogenic Si requires an initial degradation of the organic coating of diatom frustules (Van Cappellen and Qiu 1997) and can be delayed by aggregation of the diatom cells (Loucaides 2009), unlike NH_4 and PO_4. The rapid availability of fresh organic material and consequent reduced oxygen availability in the sediments, as presented in Chapter 4 for this period, likely resulted in an increased demand for electron acceptors to be used in the oxidation of organic matter. Since NO_3 is the next most favorable oxidizer after oxygen, its consumption is expected to increase in this period. This explains why NO_3 concentrations were independent of chlorophyll *a*, showing a continuous decrease from February until September, from the lowest to the highest temperature, and no increase in May–September, since connsumption via denitrification at intermediate salinities, i.e. within the Wadden Sea, prevented its accumulation in the water column.

The shallowness of the western Wadden Sea suggests a major role of the sediments in nutrient regeneration (Grunwald et al. 2010) with a 70% efficiency in the recycling of organic P compounds reported by van Raaphorst et al. (1988). In addition, resuspension may enhance the release of nutrients by disruption of the sediment-water interface and desorption from sediment particles due to changing equilibrium conditions (Leote et al. 2013).

4.3 Resuspension as an enhancer of mineralization

The concentrations of total suspended matter measured for the western Wadden Sea were slightly higher than the values reported by van Beusekom (2005) and Reynhout (2002) in February, March, and November, when no major differences during a full tidal cycle were observed (Figures 4 and 6). However, in May and September, the concentrations were much higher, increasing up to 205 mg l^{-1} at maximum tidal current and especially in the bottom (Figure 6), suggesting resuspension of the deposited material (Postma 1961). The concentrations of chlorophyll *a* followed a similar pattern (Figure 6), indicating that part of the resuspended material was fresh organic material. Nevertheless, in May and September the organic C/total P ratio was lower than the Redfield ratio (Figure 4), suggesting a non biogenic supply of P, such as silt particles loaded with sorbed PO_4. Even though bottom currents are potentially higher in winter, when wind induced mixing is stronger (Reynhout 2002), the higher concentrations of suspended material were observed in spring and summer. This may be due not to increased current speed but to increased availability of easily resuspendable material i.e. presence of a fluffy layer of fresh organic material instead of a well defined interface of clay/sand particles. The resuspension of this organic rich material (Figure 4) may have important implications in the regeneration of nutrients by increasing mineralization in the water column, due to exposure of the organic matter to a well oxygenated environment.

4.4 Nutrient availability and composition of the phytoplankton community

Irradiance and nutrient (N, P, and Si) availability are the main controls of phytoplankton growth in the Wadden Sea, even though debate remains concerning the limiting factor (de Jonge et al. 1996; Philippart and Cadée 2000; Colijn and Cadée 2003; Colijn and van Beusekom 2005). Due to different nutritional needs, the proportional availability of nutrients will determine the species composition of the phytoplankton community. Based on Redfield stoichiometry, PO_4 was apparently the limiting nutrient during most of the year (Figure 7) as found by Philippart et al. (2007) and Kuipers and van Noort (2008). A P-Si-N limitation was observed in the end of winter allowing the growth of diatoms, as evidenced by the depletion of Si observed in March. However, in spring, Si became the limiting nutrient, with concentrations often below 2 µM, a threshold value for dinoflagellate growth to take over diatoms (Grunwald et al. 2010). The growth of flagellates and *Phaeocystis* was then favored, since they do not require Si. In addition, *Phaeocystis* can use organic P as a source of P (Schoemann et al. 2005; Verity et al. 2007), giving it an advantage in April, when NH_4 but no PO_4 was available (Figure 2). The drop in Si concentrations in November , again under P-Si-N or P-N-Si limitation, suggests a secondary diatom bloom, consistent with the findings of Cadée (1986).

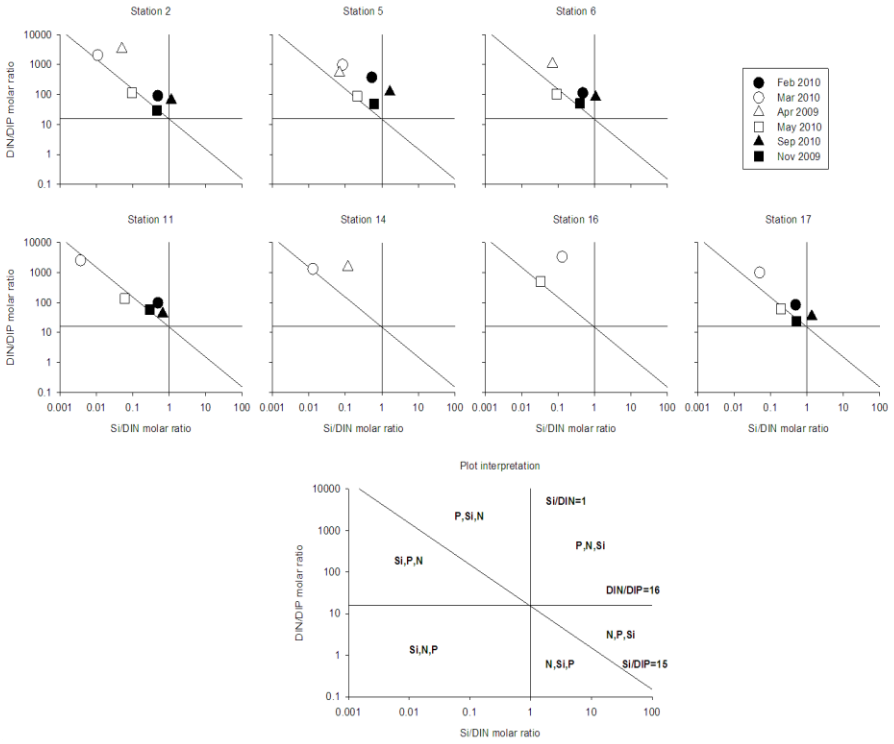

Figure 7. Diagrams based on Redfield-Brzezinski ratio showing the major nutrient (N, P, Si) limitation (Rocha et al. 2002) throughout the year and plotted separately for each seasonally sampled station.

4.5 Sources of P to the western Wadden Sea

The main source of PO_4 to the western Wadden Sea remains unclear, with the North Sea, Lake IJssel, and internal recycling as the main candidates (de Jonge 1990; van Raaphorst and van der Veer 1990; de Jonge et al. 1996; de Jonge 1997; van Raaphorst and Jonge 2004). Postma (1954) suggested that the high PO_4 concentrations observed in spring and summer in the study area result from the mineralization of particulate organic matter from the North Sea. In agreement, our results confirm the importance of mineralization within the Wadden Sea: in May, the concentrations of NH_4, PO_4, and Si increased at intermediate salinities with the lower concentrations observed for Lake IJssel and the North Sea (Figure 3) making those unlikely major sources of inorganic P. Besides, the discharge of freshwater was low during this period with usually less than 25% of freshwater in the composition of the water column. A comparison between PO_4 release from the sediments and freshwater discharge from Den Helder and the Afsluitdijk sluices, which correspond to ~60% of the discharged water into the western Wadden Sea (Ridderinkhof 1988; van Raaphorst and van der Veer 1990), shows a much higher contribution of sediment release in terms of loading to the water column, throughout the year and especially between May and November (Figure 8). In addition, the contribution of mineralization within the Wadden Sea is likely underestimated, since it is based on a conservative estimate of sediment release from Chapter 4 and doesn't include mineralization or desorption in the water column, potentially enhanced by resuspension. Concluding, in spite of the past large contribution of freshwater discharge in terms of PO_4 loading (van Raaphorst and van der Veer 1990; van Raaphorst and Jonge 2004), at present, internal recycling of organic material seems to be the main source of PO_4 in the western Wadden Sea, largely fuelling primary production during spring and summer.

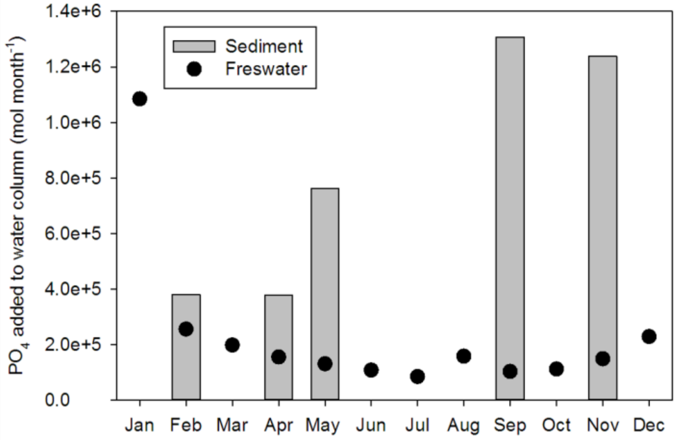

Figure 8. Comparison between the contribution of freshwater (Rijkswaterstaat Waterbase, assuming discharge from Den Oever, Kornwerderzand, and Den Helder) and sediment release (Chapter 4) in terms of loading of PO_4 to the western Wadden Sea.

Conclusions

The concentrations of dissolved nutrients in the western Wadden Sea were closely linked to the growth of primary producers with a negative relationship observed between chlorophyll *a* and the concentrations of the major inorganic nutrients. Mineralization of the fresh organic material resulting from the first phytoplankton bloom in spring seemed to be the major source of inorganic nutrients during late spring and summer. Sediment resuspension, observed in spring and summer, may enhance mineralization and desorption in the water column, and favor nutrient release from the sediments. The slower recycling of Si resulted in Si-P-N limitation in late spring and unfavored growth of diatoms during this period. A comparison between PO_4 loading to the Wadden Sea by freshwater discharge and sediment release revealed a much higher contribution of sediment release during the whole year. The relatively low concentrations measured for the North Sea during this period also made it an unlikely source of nutrients to the Wadden Sea. Internal recycling of autochthonous and allochthonous organic material in the sediments and water column appears to be the main source of inorganic nutrients sustaining primary production.

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SUMMARY

In marine ecosystems, primary producers are the basis of the food chain by assimilating inorganic nutrients, incorporating them in their biomass and supplying the heterotrophic food chain with organic material. Several nutrients are required for their growth. Phosphorus (P), nitrogen (N), and silica are the most important. Since atmospheric N can be assimilated by cyanobacteria, and P and silica depend on continental rock weathering, the later, and especially P, since not all species require silica for their growth, are often the limiting nutrients in marine ecosystems.

In addition to the continental supply via freshwater and groundwater discharge, the availability of inorganic P for phytoplankton growth depends on the mineralization (oxidation) of organic material by microbial communities, in both the water column and the sediments. When mineralization takes place in the water column, P becomes readily available for primary producers. On the other hand, after mineralization in the sediments, P can be released back to the overlying water or be retained for a period of time, ranging from hours to permanent. Short-term retention is mostly associated with sorption to Fe and Mn oxides while the precipitation of authigenic minerals, such as apatite, represents long-term to permanent storage. In shallow environments, most organic material will be degraded in the sediments because of the short settling times. In coastal environments, the study of P availability requires then a careful understanding of the processes controlling the sediment release and storage.

In the modern western Wadden Sea, the high dissolved N/P ratio allied to a phytoplankton community typical from P deficient environments, suggests a P limitation on the growth of phytoplankton. The study of P cycling is then vital for the understanding of the western Wadden Sea ecosystem and was, therefore, the goal of this thesis.

Since sorption is one of the main processes controlling the concentrations of P in the porewater, this thesis started with several pilot studies of P sorption to marine sediments **(Chapter 2)**. The distribution between the adsorbed and dissolved phase depends on the electrochemical characteristics of the sediment particles, the concentration of dissolved P, the fraction of P adsorption in the sediment and the concentration of dissolved compounds that also exhibit an

affinity for sorption, acting as potential competitors for the sorption sites. Isotherms, expressions describing the distribution between the solid and dissolved phases, are used to describe the sorption equilibrium, and are obtained via incubations of sediment at different concentrations of dissolved P. A kinetic model was developed to reproduce the sorption equilibrium and extrapolate the dissolved and adsorbed concentrations to one year. Isotherms are assumed to be typical for a certain temperature, pressure, and medium composition, and independent of the concentration of sorbent, i.e. sediment particles, in this case. However, we found a particle concentration effect, with higher sorption densities and steeper isotherms at lower concentrations of sorbent, even after extrapolation to near equilibrium conditions. This effect may have induced significant bias in previous work if results of incubations performed at relatively low particle concentrations were extrapolated for natural conditions, where the particle concentrations are higher. In addition, the comparison of values from separate studies is no longer valid, since differences in the sorption equilibrium may result not only from different sediment/solution characteristics but also from the use of different particle concentrations in the incubations. The use of a Freundlich isotherm, modified according to the Metastable Equilibrium Adsorption Theory, accounted well for our incubations at different particle concentrations.

Since only a fraction of the total sediment P pool can be exchanged with the water column, the different sediment P pools present in the western Wadden Sea were quantified. Sequential extractions allow the identification of different functional reservoirs of P in the sediment. In **chapter 3**, sequential extractions were used to discriminate between the easily exchangeable (0.46 M NaCl extractable), the redox sensitive (0.11 M NaDB extractable), the Al bound, organic and remaining Fe bound (0.1 M NaOH extractable), the Ca bound (0.5 M HCl extractable), and the refractory organic (1 M HCl extractable) P pools. Most P was in a non-bioavailable form, with the exchangeable fraction corresponding to 12–42% of the total extractable pool. Based on an inverse relationship found between median grain size and sediment P content, the exchangeable P pool for the entire western Wadden Sea was quantified for the periods of maximum and minimum content, in February/March and November, respectively. This suggested storage in the sediment in winter/early spring and release in spring/summer. The estimated release, based on the difference between maximum and minimum content, of had the potential to fuel approximately 40% of present primary production, assuming an annual value of 200 g C m^{-2}.

The previous chapter assessed the sediment release of P stored over winter. However, part of the P resulting from organic matter oxidation will not be retained in the sediment and instead be quickly released to the overlying water. Thus, to have a more realistic estimation of the total release, additional measurements were needed. In **chapter 4**, an estimation of the annual release of P from the sediments was given for the western Wadden Sea basin, based on porewater profiles and incubation measurements. The content of organic C and grain size distribution divided the sampled area in two distinct zones: a smaller depositional area characterized by high silt and organic C content and the remaining, composed of fine/medium sand with a low organic C content. The porewater concentrations and the sediment-water exchange, estimated using the porewater profiles, were also much higher for the fine grained area. However, no clear difference between the two zones was observed for the sediment-water exchange measured with whole-core incubations. The porewater nutrient profiles, sediment oxygen consumption, and visual observation of the sediment stratification in the collected cores suggest that the porewater concentrations of P in the depositional area result mainly from the balance between mineralization and sorption with diffusion as the main transport process involved in the release. For the coarser grain size area there was a clear enhancement of the fluxes due to bioirrigation and the effect of sorption was less clear. The sediment-water exchange estimated using the porewater profiles could be related with the grain size distribution, with higher fluxes associated with finer grain sizes. This allowed the estimation of a total annual P release of 2.2×10^7 mol for the western Wadden Sea basin. The release increased from February until September, meaning that P is likely released to the water column in critical periods of the year regarding phytoplankton growth. The measured nutrient release from the sediment was P deficient during most of the year, considering the phytoplankton demand given by the Redfield-Brzezinski ratio.

In addition to sediment release, freshwater discharge is usually recognized as an important P source to the western Wadden Sea, being particularly significant in the past. **Chapter 5** relates the nutrient concentrations in the water column with the concentrations of chlorophyll *a*, used as an indicator for primary production. The present P release from the sediment is also compared with the P supply by freshwater discharge, to identify the major source of P to the western Wadden Sea. The concentrations of nutrients in the water column were closely related with chlorophyll *a*, with the concentrations of inorganic nutrients decreasing while chlorophyll *a* increases, in line with the occurrence of a first phytoplankton bloom in the beginning of spring. Later in spring, the concentrations of inorganic nutrients increased again in the water column at intermediate salinities, which appeared to result from nutrient recycling within the Wadden Sea, given the low concentrations in the freshwater and seawater end-members. This may include mineralization in the water column and especially release from the sediments of both mineralized and stored P. However, the resuspension of deposited material, observed at maximum tidal current speed, may have enhanced the pelagic degradation of organic material. Phosphorus limitation, according to the Redfield-Brzezinski ratio, was observed during most of the year in the water column, even though an apparent silica limitation in the end of spring may have limited the growth and the species composition of the phytoplankton community in this period. A comparison between the P added to the western Wadden Sea basin by freshwater discharge and sediment release showed a much higher contribution from the sediments especially between April and November.

The release of P from the sediments depends on processes such as mineralization and storage, mainly through sorption. Both are affected by factors such as temperature, pH, redox conditions, grain size, etc, resulting in a high temporal and spatial variation. Therefore, in addition to a seasonal study it becomes essential to cover the spatial heterogeneity. This becomes particularly relevant in areas such as the Wadden Sea, where approximately 1/3 of the area is intertidal. The extrapolation to intertidal environments using data mainly from subtidal areas is far from straightforward. In addition to the cyclic emerged/submerged conditions, which complicate the sediment-water exchange, the presence of active benthic phytoplanktonic communities has potentially large implications on the storage/sorption of P and deserves further study. Benthic photosynthesis strongly alters the conditions in the sediment surface layer by consuming carbon dioxide (CO_2) and thereby strongly increasing the pH from about 7 up to 10 and by increasing both oxygen concentrations and penetration depth several fold. The availability of oxygen has large implications on the precipitation/dissolution of Fe and Mn oxides and consequently on the availability of sorption sites, while a higher pH represents increased sorption competition due to the higher concentrations of hydroxyl ions (OH^-). Further research to better understand how benthic photosynthesis may affect the retention/release of P in the sediment and to better integrate P release from intertidal areas in the budget for the western Wadden Sea basin is necessary.

SAMENVATTING

Het fytoplankton staat aan de basis van de voedselketen in mariene ecosystemen. Als fotoautotrofe organismen assimileren zij (an-)organische voedingsstoffen bij de vorming van hun biomassa en voorzien hiermee de heterotrofe organismen van organisch materiaal. Fosfor (P), stikstof (N) en silicium (Si) zijn de belangrijkste voedingsstoffen voor hun groei. Omdat atmosferisch stikstofgas gefixeerd kan worden door o.a. cyanobacteriën en niet al het fytoplankton Si nodig heeft voor groei, vormt P vaak de beperking voor de aanwas van biomassa van het fytoplankton en daarmee voor de hoeveelheid voedsel die mogelijk beschikbaar kan komen voor de gehele voedselketen.

De beschikbaarheid van anorganisch P voor het mariene fytoplankton is niet slechts afhankelijk van terrestrische aanvoer via rivieren en grondwaterstroming, maar ook van de afbraak van organisch materiaal (OM) door microbiële gemeenschappen in de waterkolom en de zeebodem. Bij de afbraak in de waterkolom komt het organisch gebonden P gemakkelijk beschikbaar voor het fytoplankton. Wordt het organisch materiaal in de bodem afgebroken, dan vloeit een deel van het vrijgemaakte P terug naar de waterkolom terwijl het restant voor korte of langere tijd kan worden vastgelegd in de bodem. Bij het vastleggen op een tijdschaal van uren speelt de sorptie van P aan ijzer- en mangaanoxiden een belangrijke rol, terwijl het neerslaan van authigene, P-houdende mineralen zoals apatiet, vaak leidt tot quasi-permanente verwijdering. In ondiepe systemen vindt een belangrijk deel van de OM-mineralisatie plaats in het sediment en daarom moet een studie naar fosfaatbeschikbaarheid in kustgebieden zich met name richten op de processen die sturend zijn voor de opslag en afgifte in en door sedimenten.

Momenteel wordt in de westelijke Waddenzee een hoge N/P-ratio van voedingsstoffen waargenomen, evenals een fytoplanktongemeenschap die kenmerkend is voor P beperkte systemen. Dit suggereert dat P beperkend is voor de groei van het fytoplankton en daarmee voor de draagkracht van dit deel van de Waddenzee. Een studie naar de P-stromen is daarom essentieel voor een beter begrip van de westelijke Waddenzee en vormt het onderwerp van dit proefschrift.

De sorptie van P aan vaste materialen van de bodem bepaalt in belangrijke mate de concentratie van P in het poriewater en daarom is dit werk begonnen met een studie naar het sorptiegedrag van P aan mariene sedimenten **(Hoofdstuk 2)**. De verdeling van P tussen de opgeloste en geadsorbeerde fase wordt bepaald door electrochemische karakteristieken van de sedimentdeeltjes, de concentratie opgelost P, de bezettingsgraad van het sediment met P en de concentratie van opgeloste verbindingen die eveneens sorptie-affiniteit voor het sediment vertonen. De evenwichtsverdeling tussen de opgeloste en vaste fase over een bereik van P concentraties kan mathematisch worden beschreven met een zgn. sorptie-isotherm. De sorptiekarakteristieken van een sediment kunnen worden bepaald door de parameters van deze vergelijking te schatten aan de hand van experimentele incubaties waarbij een hoeveelheid sediment volgens een constante verhouding wordt geïncubeerd in medium met verschillende initiële opgeloste P concentraties. Een kinetisch model werd ontwikkeld om het experimentele sorptie-evenwicht te reproduceren en te simuleren na een fictieve incubatie van één jaar. Isothermen worden geacht karakteristiek te zijn voor een zekere temperatuur, druk en medium samenstelling en onafhankelijk te zijn van de verhouding sediment:medium ratio. In onze experimenten zagen we echter een duidelijk effect van de sediment:medium ratio op de sorptie-isotherm; hogere sorptiedichtheden en steilere isothermen werden waargenomen bij lagere sediment:water verhoudingen, zelfs als de experimentele gegevens werden geëxtrapoleerd naar evenwichtscondities. Dit zogenaamde ‘particle concentration effect’ kan een wezenlijke invloed hebben gehad op de uitkomsten van eerdere studies indien experimentele resultaten die verkregen zijn bij relatief geringe sediment:medium ratios zijn geëxtrapoleerd naar natuurlijke condities waarvoor veel hogere sediment:medium ratios gelden. Bovendien is een vergelijking van uitkomsten tussen verschillende studies niet meer mogelijk omdat de waargenomen sorptie-evenwichten niet slechts afhankelijk zijn van verschillen in sediment- en oplossingskarakteristieken, maar ook nog eens van de gekozen sediment:medium verhouding tijdens de experimenten. Om het effect van sediment:medium ratio in onze studie uit te sluiten is gebruik gemaakt van een Freundlich isotherm die is aangepast op basis van de ‘Metastable Equilibrium Adsorption Theory’. Deze aangepaste isotherm bleek zeer geschikt om incubaties bij verschillende sediment:medium verhoudingen te beschrijven.

Het totale reservoir van sedimentgebonden P is opgebouwd uit chemisch verschillende fracties. Omdat slechts een beperkte fractie uitgewisseld kan worden met het poriewater en vervolgens met de waterkolom, zijn de chemische fracties in sedimenten van de westelijke Waddenzee gekwantificeerd door sequentiële extracties uit te voeren. In **Hoofdstuk 3** wordt deze techniek gebruikt om onderscheid te maken tussen de ‘makkelijk uitwisselbare fractie’(0.46 M NaCl extraheerbaar), de ‘redoxgevoelige fractie’ (0.11 M NaDB extraheerbaar), de ‘Al gebonden, organische en overige Fe gebonden fractie’ (0.1 M NaOH extraheerbaar), de ‘Ca gebonden fractie’ (0.5 M HCl extraheerbaar) en de ‘refractair organische fractie’ (1 M HCl extraheerbaar). De uitwisselbare fractie bedroeg 12–42% van de totale extraheerbare hoeveelheid en het grootste deel van het sedimentgebonden P bleek dus niet beschikbaar voor biologische processen. Op basis van een empirisch vastgestelde relatie tussen mediane korrelgrootte en het P gehalte van het sediment kon uit een bekende korrelgrootteverdeling voor de westelijke Waddenzee de uitwisselbare fractie van P worden berekend voor dit bekken. Op basis van deze berekeningen lijkt er opslag van P plaats te vinden gedurende de herfst en winter en afgifte tijdens het voorjaar en de zomer. Het verschil tussen het maximale gehalte in Februari/Maart en de minimale waarde in November suggereert een afgifte van 4.0×10^7 mol P, hetgeen voldoende zou zijn om 40% van de jaarlijkse primaire productie te voeden, uitgaande van een jaarlijkse primaire productie van 200 g C m^{-2}.

In Hoofdstuk 3 wordt een schatting gemaakt van de P afgifte door het sediment gedurende de winter. Echter, een deel van het P dat vrijkomt bij de oxidatie van recent gesedimenteerd OM wordt niet vastgelegd in de bodem, maar wisselt snel uit met het bovenstaande water. Om een meer realistische schatting van de totale uitwisseling te kunnen maken zijn dus aanvullende metingen vereist. In **Hoofdstuk 4** wordt een schatting gemaakt van de totale jaarlijkse afgifte van P door het sediment van de westelijke Waddenzee op basis van poriewaterprofielen en van sedimentincubaties. De bemonsterde sedimenten vallen uiteen in twee clusters op basis van het gehalte aan organisch materiaal en de korrelgrootteverdeling van het sediment; een relatief klein depositiegebied met een hoog gehalte aan silt en organisch materiaal en het overige areaal, bestaand uit fijn tot middelfijn zand met een laag gehalte aan organisch materiaal. De concentraties van P in het poriewater en de daarop gebaseerde voorspellingen van de uitwisseling van P tussen het sediment en water waren beduidend hoger voor het rijke depositiegebied dan voor de zandige gebieden. Toch bleek er nauwelijks een verschil tussen de twee gebieden bij de metingen van de fluxen middels het incuberen van de sedimenten. De poriewaterprofielen van nutrienten, het zuurstofverbruik en het visuele waarneming van het sediment stratificatie in de verzamelde kernen suggereren dat de poriewaterconcentraties van P in het depositiegebied grotendeels worden bepaald door de balans tussen mineralisatie, sorptie en uitwisseling tussen het sediment en de waterkolom met moleculaire diffusie als belangrijkste transportmechanisme. In de zandige gebieden lijkt de uitwisseling tussen bodem en waterkolom te worden versterkt door bio-irrigatie, terwijl het effect van P sorptie aan het sediment minder duidelijk was. De voorspelde bodem-wateruitwisseling op basis van de poriewaterprofielen bleek te variëren met de korrelgrootte van het sediment; hogere fluxen waren geassocieerd met kleinere korrelgrootte. Op basis van de korrelgrootteverdeling voor de westelijke Waddenzee werd de totale jaarlijkse afgifte van P voor dit basin geschat op 2.2 x 10^7 mol. De afgifte nam toe van Februari tot September hetgeen dus samenvalt met de krtische periode voor de groei van fytoplankton. Gedurende het grootste deel van het jaar bleek de afgifte van voedingsstoffen door de bodem beperkt in P, ervan uitgaande dat de nutrientbehoefte van het fytoplankton overeenstemt met de Redfield-Brzezinski ratio.

Naast de afgifte van P door het sediment wordt zoetwaterlozing in het algemeen gezien als belangrijke bron van P voor de westelijke Waddenzee. In **Hoofdstuk 5** worden de concentraties van voedingsstoffen in de waterkolom in verband gebracht met de concentraties chlorofyl *a*, zijnde een maat voor de primaire productie. De huidige afgifte door het sediment is vervolgens vergeleken met de aanvoer via zoetwaterlozing om de belangrijkste P bron voor de wetselijke Waddenzee te kunnen identificeren. De concentraties van nutrienten bleek sterk gekoppeld aan de concentratie chlorofyl *a*, waarbij de concentraties anorganische voedingsstoffen afnamen met een toename in chlorofyl *a*, geheel in overeenstemming met het voorkomen van de eerste fytoplanktonbloei in het vroege voorjaar. Later in het voorjaar stegen de concentraties anorganische voedingsstoffen weer. Aangezien deze toename bij intermediaire zoutgehalten plaatsvond en de concentraties voedingsstoffen in het zoete en meest zoute bereik laag waren vond er kennelijk recycling van voedingsstoffen plaats binnen het basin. Deze recycling betreft de mineralisatie in de waterkolom, maar vooral ook de afgifte van gemineraliseerd en gebonden P door sedimenten. Echter, de opwerveling van reeds gesedimenteerd materiaal, zoals werd waargenomen bij maximale stroomsnelheden, zal de mineralisatie in de waterkolom hebben versterkt.

Uitgaande van de Redfield-Brzezinski ratio, lijkt de primaire productie in de waterkolom gedurende het grootste deel van het jaar beperkt door fosfor, hoewel ook silicium aan het eind van het voorjaar de groei kan hebben beperkt en zodoende de soortsamenstelling van de algenpopulatie kan hebben beïnvloed. Een kwantitatieve vergelijking van de bronnen laat zien dat de bijdrage van P door het sediment veel belangrijker is dan de aanvoer via zoetwater, met name tussen April en November.

De afgifte van P door sedimenten wordt bepaald door processen als mineralisatie van OM en vastlegging in het sediment, voornamelijk door sorptie. Beide processen zijn afhankelijk van factoren als temperatuur, pH, redoxcondities, korrelgrootte etc., hetgeen resulteert in hoge temporele en ruimtelijke variabiliteit. Daarom is het van belang om naast de seizoensafhankelijkheid, ook de ruimtelijke variatie te bepalen, vooral in een gebied als de Waddenzee dat voor ~1/3 uit getijdegebied bestaat. De vertaalslag vanuit het ‘subtidale domein’ naar het intergetijdengebied is allesbehalve eenvoudig. Het droogvallen en onderlopen van de gebieden door getijdewerking zal een sterke invloed hebben op de uitwisseling van voedingsstoffen tussen bodem en waterkolom, zowel in grootte als in fasering. Daarnaast kan een actieve populatie van benthische microalgen een groot effect hebben op de opslag/sorptie van P in het sediment. Benthische fotosynthese leidt tot sterke veranderingen in de chemische condities nabij het sediment-watergrensvlak. Door de opname van CO_2 en HCO_3^- kan de pH oplopen tot >9 en de productie van O_2 leidt tot verhoogde zuurstofconcentraties en grotere indringdiepte van zuurstof in de bodem. Deze verandering is van sterke invloed op het neerslaan en oplossen van Fe en Mn oxiden en daarmee op de beschikbaarheid van sorptieplaatsen. Tegelijkertijd zal de de toename in hydroxyl anionen (OH^-) bij pH verhoging de competitie om deze sorptieplaatsen verhevigen. Om het effect van benthische fotosynthese op afgifte en retentie van P in getijdesedimenten beter te begrijpen en om een kwantitatieve inschatting te kunnen maken voor de bijdrage van deze sedimenten aan het P budget voor de westelijke Waddenzee is verder onderzoek noodzakelijk.

SUMÁRIO

Nos ecossistemas marinhos, os produtores primários são a base da cadeia alimentar, ao assimilarem nutrientes inorgânicos e incorporá-los na sua biomassa, fornecendo assim matéria orgânica para a cadeia alimentar heterotrófica. Vários nutrientes são necessários para o seu crescimento, sendo o fósforo (P), o azoto (N) e a sílica os mais importantes. Como o N atmosférico pode ser assimilado por cianobactérias, enquanto que o P e a sílica dependem da meteorização e erosão das rochas continentais, os últimos, e em particular o P, já que nem todas as espécies necessitam de sílica para o seu crescimento, são frequentemente os nutrientes limitantes nos ecosistemas marinhos.

Além do fornecimento continental através das descargas dos rios e aquíferos, a disponibilidade de P inorgânico para o crescimento do fitoplâncton depende da mineralização (oxidação) de matéria orgânica por comunidades microbianas, tanto na coluna de água como nos sedimentos. Quando a mineralização ocorre na coluna de água, o P fica imediatamente disponível para os produtores primários. Contudo, após mineralização nos sedimentos, o P tanto pode ser libertado para a coluna de água como ficar retido por um período de tempo, que pode variar desde horas a permanente. A retenção por um curto período está geralmente associada à adsorção a óxidos de Fe e Mn, enquanto que a precipitação de minerais autigénicos, como a apatite, representa uma retenção longa ou permanente. Em ambientes pouco profundos, a maioria da matéria orgânica vai ser degradada nos sedimentos, devido às rápidas taxas de sedimentação. Deste modo, em ambientes costeiros, o estudo da disponibilidade de P requere uma compreensão cuidada dos processos que controlam a sua libertação e retenção nos sedimentos.

No actual Mar de Wadden Ocidental, o elevado rácio de N/P dissolvido aliado a uma comunidade fitoplanctónica típica de ambientes deficientes em P, sugere uma limitação de P no crescimento do fitoplâncton. O estudo do ciclo do P é assim vital para a compreensão do ecosistema do Mar de Wadden Ocidental e é, por essa razão, o objectivo desta tese.

Sendo a adsorção um dos processos principais que controlam as concentrações de P na água intersticial, esta tese começou com vários estudos-piloto da adsorção de P em sedimentos marinhos **(Capítulo 2)**. A distribuição entre as fases adsorvida e dissolvida depende das respectivas concentrações nessas duas fases e da presença de competidores pelos locais de adsorção. As isotérmicas são expressões que descrevem a distribuição entre as fases sólida e dissolvida e são usadas para descrever o equilíbrio de adsorção, sendo obtidas através de incubações de sedimento em diversas concentrações de P dissolvido. Foi desenvolvido um modelo cinético para reproduzir o equilíbrio de adsorção e extrapolar as concentrações nas fases dissolvida e adsorvida para um ano. As isotérmicas são consideradas características de uma dada temperatura, pressão e composição do meio e independentes da concentração de adsorvente, ou seja, das partículas de sedimento, neste caso. Contudo, foi encontrado um efeito da concentração de partículas, com densidades de adsorção mais elevadas e isotérmicas de maior declive na presença de concentrações mais baixas de sedimento, mesmo após extrapolação dos resultados para condições próximas do equilíbrio. Este efeito pode ter introduzido desvios significativos em trabalhos anteriores, caso os resultados obtidos através de incubações em concentrações relativamente baixas de sedimento tenham sido extrapolados para condições naturais, onde as concentrações de partículas são superiores. Além disso, a comparação de valores obtidos por diferentes estudos já náo é válida, já que as diferenças no equilíbrio de adsorção podem resultar não apenas das diferentes características do sedimento/solução, mas também do uso de diferentes concentrações de sedimento nas incubações. O uso de uma isotérmica de Freundlich, modificada de acordo com a Teoria da Adsorção de Equilíbrio Metastável, permitiu reproduzir bem as nossas incubações com diferentes concentrações de partículas.

Como apenas uma fracção do P nos sedimentos pode ser libertada para a coluna de água, as diferentes fracções presentes nos sedimentos do Mar de Wadden Ocidental foram quantificadas. As extrações sequenciais permitem a identificação de diferentes reservatórios funcionais de P no sedimento. No **Capítulo 3**, foram utilizadas extrações sequenciais para discriminar entre os reservatórios de P facilmente libertado (extraído em 0.46 M NaCl), sensível a reações de oxi-redução (extraído em 0.11 M NaDB), associado a Al, P orgânico e restante Fe (extraído em 0.1 M NaOH), associado a Ca (extraído em 0.5 M HCl) e orgânico refractário (extraído em 1 M HCl). A maior parte do P encontrava-se numa forma não facilmente bio-disponível, com a potencialmente bio-disponível a corresponder a 12–42% do reservatório total de P extraível. Com base na relação inversa encontrada entre a mediana do tamanho das partículas e o conteúdo em P, o reservatório de P potencialmente bio-disponível foi quantificado para o Mar de Wadden Ocidental, para os períodos de conteúdo máximo e mínimo, em Fevereiro/Março e Novembro, respectivamente, o que sugere retenção no sedimento no Inverno/início da Primavera e libertação na Primavera/Verão. A libertação, estimada com base na diferença entre os conteúdos máximo e mínimo, de 4.0×10^7 mol P teve o potencial de contribuir para aproximadamente 40% da produção primária actual, assumindo um valor de 200 g C m^{-2}.

O capítulo anterior avaliou a libertação do P retido durante o Inverno. Contudo, parte do P resultante da oxidação de matéria orgânica não vai ficar retido no sedimento, sendo rapidamente libertado para a coluna de água. Assim, uma estimativa mais realista da libertação total de P dos sedimentos requer medições adicionais. No **Capítulo 4** é feita uma estimativa anual da libertação de P dos sedimentos do Mar de Wadden Ocidental, baseada em perfis de concentração na água intersticial e incubações. O conteúdo em matéria orgânica e a granulometria dividiram a área de amostragem em duas zonas distintas: uma pequena zona de deposição, caracterizada por elevados conteúdos de silte e C orgânico e o restante, composto por areias finas/médias e um baixo conteúdo em C orgânico. As concentrações na água intersticial e as trocas sedimento-coluna de água, estimadas através dos perfis de água intersticial, foram também mais elevados na zona de baixa granulometria. Contudo, não foi observada nenhuma diferença clara entre as duas zonas no que respeita às trocas sedimento-coluna de água medidas através de incubações de cores. Os perfis de concentração de nutrientes na água intersticial, o consumo de oxigénio no sedimento e o aspecto visual sugerem que as concentrações de P na água intersticial da zona deposicional resultam essencialmente do balanço entre mineralização e adsorção, com a difusão como o principal processo de transporte envolvido na libertação. Na região de granulometria mais grosseira, houve um claro aumento dos fluxos devido a bioirrigação e o efeito da adsorção foi menos claro. A libertação de nutrientes do sedimento foi deficiente em P durante a maior parte do ano, de acordo com as necessidades do fitoplâncton definidas pelo rácio de Redfield-Brzezinski. As trocas sedimento-coluna de água estimadas através dos perfis de água intersticial foram relacionadas com a granulometria, com os fluxos mais elevados associados a granulometrias mais finas. Isto permitiu uma estimativa da libertação anual de P para a bacia do Mar de Wadden Ocidental de 2.2×10^7 mol. A libertação aumentou entre Fevereiro e Setembro, o que significa que o P é provavelmente libertado para a coluna de água em períodos críticos do ano no que respeita ao crescimento de fitoplâncton.

Além da libertação dos sedimentos, as descargas fluviais são geralmente identificadas como uma importante fonte de P para o Mar de Wadden Ocidental, tendo sido particularmente significativas no passado. O **Capítulo 5** relaciona as concentrações de nutrientes na coluna de água com as concentrações de clorofila a, utilizada como um indicador da produção primária. A actual libertação de P dos sedimentos foi também comparada com o fornecimento de P a partir de descargas fluviais, de modo a identificar a principal fonte de P para o Mar de Wadden Ocidental. As concentrações de nutrientes na coluna de água estiveram directamente relacionadas com a clorofila a, com as concentrações de nutrientes inorgânicos a diminuirem com o aumento da clorofila a, de acordo com a ocorrência de um primeiro bloom de fitoplâncton no início da Primavera. A meio da Primavera, as concentrações de nutrientes inorgânicos na coluna de água aumentaram novamente nas salinidades intermédias, o que pareceu resultar da regeneração de nutrientes no interior do Mar de Wadden, dadas as baixas concentrações obtidas nos extremos da água doce e salgada, podendo incluir mineralização na coluna de água e, principalmente, libertação de P mineralizado e retido nos sedimentos. Contudo, a resuspensão de material depositado observada nos máximos de velocidade de corrente tidal pode ter estimulado a degradação pelágica de material orgânico. De acordo com o rácio de Redfield-Brzezinski, o P foi o nutriente limitante na coluna de água durante a maior parte do ano, apesar de uma aparente limitação em silica no final da Primavera poder ter limitado o crescimento e a composição da comunidade fitoplanctónica nesse período. Uma comparação entre o P adicionado à bacia do Mar de Wadden Ocidental pelas descargas fluviais e pela libertação dos sedimentos mostrou uma muito maior contribuição dos sedimentos, principalmente entre Abril e Novembro.

A libertação de P dos sedimentos depende de processos como a mineralização e a retenção, principalmente por adsorção. Ambos são afectados por factores como a temperatura, o pH, as condições de oxi-redução, a granulometria, etc, resultando numa grande variação temporal e espacial. Assim, além de um estudo sazonal, torna-se essencial cobrir a heterogeneidade espacial. Isto torna-se particularmente relevante em áreas como o Mar de Wadden, onde aproximadamente 1/3 da área é intertidal. A extrapolação para ambientes intertidais utilizando dados de zonas subtidais está longe de ser linear, pois além das condições cíclicas de emersão/submersão, que complicam as trocas sedimento-coluna de água, a presença de comunidades fitobentónicas activas tem implicações potencialmente grandes na retenção/adsorção de P, e merece estudos futuros. A fotossíntese bentónica altera fortemente as condições na camada superficial do sedimento ao consumir dioxido de carbono (CO_2), e assim aumentar o pH de aproximadamente 7 até 10, e ao aumentar significativamente as concentrações de oxigénio e a profundidade de penetração do mesmo. A disponibilidade de oxigénio tem grandes implicações na precipitação/dissolução de óxidos de Fe e Mn e consequentemente na disponibilidade de locais de adsorção, enquanto que um pH mais elevado representa um aumento da competição pelos locais de adsorção devido ao aumento das concentrações do ião hidróxilo (OH^-). É assim necessária mais investigação para melhor compreender os efeitos da fotossíntese bentónica na retenção/libertação de P do sedimento e para integrar melhor a contribuição das áreas intertidais no balanço da bacia do Mar de Wadden.

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ABOUT THE AUTHOR

Catarina Maria de Freixo Leote was born on the 23rd of February 1983 in Lisboa, Portugal. After finishing high-school in 2001 she moved south to study Oceanography at the University of the Algarve in Faro. She finished her 5-year licentiate degree in 2007 with a final thesis on “Submarine Groundwater Discharge as a nitrate source to the Ria Formosa”. Between 2005 and 2007 she joined the research group of Dr. Carlos Rocha on sediment biogeochemistry at the University of the Algarve, studying submarine groundwater discharge in the Ria Formosa. During that period she also worked as a guide in a science museum (Centro Ciência Viva do Algarve) in Faro. In January 2008, she started her PhD at the Royal Netherlands Institute for Sea Research under the supervision of Dr. Eric Epping. Her work focused on the recycling and availability of phosphorus in the western Wadden Sea and resulted in this thesis.