Leote, C. & Epping, E. (2015). Sediment–water exchange of nutrients in the Marsdiep basin, western Wadden Sea: Phosphorus limitation induced by a controlled release? Continental Shelf Research, 92, 44–58

Published version: dx.doi.org/10.1016/j.csr.2014.11.007

Link NIOZ Repository: www.vliz.be/nl/imis?module=ref&refid=245303

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

Catarina Leote *, Eric Epping

Royal Netherlands Institute for Sea Research (NIOZ) – Division Texel, PO box 59, 1790 AB Den Burg, Texel, The Netherlands

***Corresponding author: catarina.leote@nioz.nl**

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 a small grain size 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 depositional area and based on a relationship found between the release of inorganic phosphorus and the silt content, a total annual release of 1.0x10^7 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 the recent levels of primary productivity.

Keywords: Wadden Sea, phosphate, mineralization, sorption, sediment-water exchange, bioirrigation

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 especially in the form of particulate matter (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 1980’s (van Raaphorst and de Jonge 2004). In parallel, the rates of annual primary production, first documented in the 1970's, increased at least 3-fold from ca 150 g C m^{-2} up to 520 g C m^{-2} in 1981/1982 (de Jonge 1997; 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. (1993b), would support the idea that P availability controls primary productivity in this basin. In addition, during most of the time, the inorganic N:P ratio of the discharged freshwater was above the Redfield ratio for phytoplankton growth of 16 (de Jonge 1997). 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), which further increased the N:P ratio of the discharge (Raaphorst and de Jonge 2004). Despite a clear reduction as reflected in winter nutrient stocks of N and P since mid 1980's, annual primary production did not decline concomitantly, but remained high until the late 1990's. 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 (e.g., N, light conditions) control the productivity in the western Wadden Sea (de Jonge and de Jong 2002; 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 sediment 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. Assuming the sediment as a main source of nutrients to the pelagic western Wadden Sea, the presence of processes that retain PO_4, such as sorption, may control its release and contribute to its low availability. 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. Based on Redfield stoichiometry, an estimation of the primary production fuelled by sediment nutrient release is also given.

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 directus*), cockles (*Cerastoderma edule*), sandgapers (*Mya arenaria*), small gastropods (*Hydrobia sp.*) and polychaetes (*Arenicola marina, Oligochaeta sp.*), 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).

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 hours. 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 stirrer to avoid the formation of a concentration gradient. Eight ml aliquots were taken with a syringe every 30 to 45 minutes for a maximum period of 4 hours 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 −20ºC 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 hours 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 seconds 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, 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: $J = ø D_s (dC/dx)$, where J corresponds to the diffusive flux in µmol cm^{-2} s^{-1}, $ø$ 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 Jorgensen (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 (J. Cremer, Institute for Marine Resources and Ecosystem Studies, original data Rijkswaterstaat) 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 tidal deltas and tidal channels and deposition of fines in subtidal areas of reduced 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).

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. Even though the porewater concentrations reflect the balance between production and transport, the fact that these stations had a relatively low organic C content and that these values were obtained deeper in the sediment, where diffusion is the main transport process, suggests 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 dike causeway (Afsluitdijk, Figure 1). The completion of this dike 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.

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.

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 concentrations of exchangeable P were also one order of magnitude higher with an average value of 7.13 μmol g^{-1}. The stations with coarser sediments showed similar contents of total C, total N and exchangeable P, with values between 0.34–0.60 and 0.01–0.03 wt% and 0.21–0.62 μmol g^{-1}, 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 directus)*, gastropods (*Hydrobia sp*.) and small polychaetes was reduced or absent at station 6, but actively present in all stations with coarser sediment. In particular, station 2 presented a large community of *jackknife clams*, 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.

3.2.2 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 (Figure 3). 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, and the ^{210}Pb dating performed by Berger et al. (1987) further confirm this idea. The transport of solutes in the sediment is then mainly governed by molecular diffusion.

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, a single calculation method or model assuming the same set of processes cannot be successfully applied to all stations in the prediction of the sediment-water exchange based on the porewater concentration profiles. For an estimation of the release that takes into account this biogeochemical variability, the use of different calculation methods is required.

3.2.3 Sediment-water exchange

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

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, considering its apparent diffusion-controlled sediment-water exchange. 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.

The seasonality in the predicted sediment-water exchange using both the Kristensen&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, ranging between $-1.8\text{x}10^{-3}$ and -0.74, -2.5 and -51.8, -0.5 and -4.6, and -0.2 and -1.3 mmol m^{-2} d^{-1} for PO_4, DIC, NH_4 and Si, respectively. Fluxes were lowest in February, increasing towards September and decreasing again in November for PO_4, DIC and Si. The NH_4 fluxes increased until November. The predicted fluxes for the coarser sediment stations were by 2 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. Stations 2, 11, 14 and 17 showed much lower fluxes, usually higher between April and September. The fluxes ranged between $-2.8\text{x}10^{-3}$ and $-2.7\text{x}10^{-5}$, -0.33 and $1.4\text{x}10^{-3}$, -0.22 and $-6.2\text{x}10^{-5}$, and -0.05 and 0.01 mmol m^{-2} d^{-1}, for PO_4, DIC, NH_4 and Si, respectively.

Summarizing, the predicted sediment-water exchange was, in general, higher between April and September. Station 6 showed the clearest pattern, 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 were measured with whole-core incubations under 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. 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, −1.63 and 0.05, and −20.65 and 0.19 mmol m^{-2} d^{-1} for NH_4, PO_4, and Si, respectively, and mostly towards the overlying water. 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. 1993a; 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.

3.3 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). The import of organic material from the North

Sea, whose cycle of phytoplankton growth is similar, may also be relevant (Cadée 1978). 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).

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 (de Jonge et al. 1993; 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 1.81×10^{-4} mmol $g^{-1}d^{-1}$ (82% retention) compared with a rate of 7.57×10^{-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).

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 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 responsible for this mismatch, as outlined in section 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). 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 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.

3.4 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. Only the release of inorganic P (PO_4) was considered because the sediment-

water exchange of dissolved organic P (DOP) was, in general, much smaller than the release of PO_4. In addition, even though DOP can be used as nutrient source, it is not immediately available to all primary producers. For the measured sediment-water exchange, the ratios were usually higher than the Redfield-Brzezinski 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 identified PO_4 as a limiting nutrient, especially at present (de Jonge 1990; 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). This may be directly linked with the increase in the PO_4 concentrations found in the water column in late spring and summer by previous studies (Grunwald et al. 2010; Beusekom and de Jonge 2012) and may point to the absence of P limitation in summer.

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&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 $1.0x10^7$ 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. (1993a) based on flux measurements under oxic conditions and lower than the 78 g C m^{-2} y^{-1} estimated by Leote et al. (2014) 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 and is in line with the 100 g C m^{-2} y^{-1} found by de Jonge et al. (1993) for the contribution of the bioavailable pool estimated by incubations of sediment in a bacterial culture, to determine PO_4 consumption, and the value estimated by Leote et

al. (2014). These results also agree with the findings of van Beusekom et al. (1999), who, based on carbon budgets, concluded that only about 50% of remineralization occurs in the sediment in the shallow Wadden Sea. Therefore, approximately 100 g C m^{-2} y^{-1} of the total primary production of 200 g C m^{-2} y^{-1} may be fuelled by remineralization in the sediments, while the remaining may be fuelled by PO_4 recycled in the water column or from other sources. 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. The nutrient supply by sediment release may be even more relevant in the eastern Wadden Sea, which has a higher accumulation of fine particles and organic matter (Chang et al. 2006).This confirms the importance of the sediments in the recycling of nutrients, particularly in shallow coastal environments.

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, with sorption clearly limiting the release of PO_4 in winter for the fine-grained area (and possibly for the other stations). Even though, bioirrigation may increase sediment retention by sorption due to the increase of the oxic layer area, our results were not conclusive. 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 $1.0x10^7$ 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.

Acknowledgments

This research was funded by the Portuguese Foundation for Science and Technology (FCT) through the PhD grant SFRH/BD/38856/2007 to CL and by the IN PLACE project. The authors would like to gratefully acknowledge Sharyn Crayford and Lieke Mulder for the help during the cruises and sample processing. The crews from the RV Navicula and RV Stern and the IN PLACE team are also acknowledged for their support. A thank you note is also due to Jan van Ooijen, Karel Bakker, Sharyn Crayford and Evaline van Weerlee for all nutrient analysis performed by the NIOZ Nutrient Lab. The comments of Victor de Jonge, an anonymous reviewer and the editor greatly improved this manuscript.

References

Aller R (1994) Bioturbation and Remineralization of Sedimentary Organic Matter: Effects of Redox Oscillation. *Chemical Geology* 114: 331–45

Aller RC and Aller JY (1998) The Effect of Biogenic Irrigation Intensity and Solute Exchange on Diagenetic Reaction Rates in Marine Sediments. *Journal of Marine Research* 56 (4): 905–36 doi:10.1357/002224098321667413

Asmus RM, Sprung M and Asmus H (2000) Nutrient Fluxes in Intertidal Communities of a South European Lagoon (Ria Formosa) - Similarities and Differences with a Northern Wadden Sea Bay (Sylt-Romo Bay). *Hydrobiologia* 436: 217–35

Balzer W (1984) Organic Matter Degradation and Biogenic Element Cycling in a Nearshore Sediment (Kiel Bight). *Limnology and Oceanography* 29 (6): 1231–46

Berg P, Risgaard-Petersen N and Risgaard S (1998) Interpretation of Measured Concentration Profiles in Sediment Porewater. *Limnology and Oceanography* 43 (7): 1500–1510

Berger GW, Eisma D and van Bennekom AJ (1987) 210Pb-Derived Sedimentation in the Vlieter, a Recently Filled-in Tidal Channel in the Wadden Sea. *Netherlands Journal of Sea Research* 21 (4): 287–94

Beukema JJ, Cadée GC and Dekker R (2002) Zoobenthic Biomass Limited by Phytoplankton Abundance: Evidence from Parallel Changes in Two Long-Term Data Series in the Wadden Sea. *Journal of Sea Research* 48 (2): 111–25 doi:10.1016/S1385-1101(02)00162-4

Boudreau BP (1998) Mean Mixed Depth of Sediments: The Wherefore and the Why. *Limnology and Oceanography* 43 (3): 524–26

Brzezinski MA (1985) The Si:C:N ratio of marine diatoms: interspecific variability and the effect of some environmental variables. *J Phycol* 21: 347–357

Buchanan JB (1984) Sediment Analysis. In N.A. Holme and A.D. McIntyre (ed), Methods for the Study of Marine Benthos. 2nd edition. Blackwell Scientific Publications, Oxford, England. p. 41–65

Cadée GC (1978) On the origin of organic matter accumulating on tidal flats of Balgzand, Dutch Wadden Sea. *Aquatic Ecology* 12 (2): 145–150

Cadée GC (1986) Recurrent and Changing Seasonal Patterns in Phytoplankton of the Westernmost Inlet of the Dutch Wadden Sea from 1969 to 1985. *Marine Biology* 93: 281–89

Cadée GC and Hegeman J (1993) Persisting High Levels of Primary Production at Declining Phosphate Concentrations in the Dutch Coastal Area (Marsdiep). *Netherlands Journal of Sea Research* 31 (2): 147–52

Cadée GC and Hegeman J (2002) Phytoplankton in the Marsdiep at the End of the 20th Century; 30 Years Monitoring Biomass, Primary Production, and Phaeocystis Blooms. *Journal of Sea Research* 48 (2): 97–110 doi:10.1016/S1385-1101(02)00161-2

Canfield DE, Jørgensen BB, Fossing H, Glud R, Gundersen J, Ramsing NB, Thamdrup B, Hansen JW, Nielsen LP and Hall POJ (1993) Pathways of Organic Carbon Oxidation in Three Continental Margin Sediments. *Marine Geology* 113 (1–2): 27–40. doi:10.1016/0025-3227(93)90147-N

Chang TS, Joerdel O, Flemming BW, Bartholomä A (2006) The role of particle aggregation/disaggregation in muddy sediment dynamics and seasonal sediment turnover in a back-barrier tidal basin, East Frisian Wadden Sea, southern North Sea. *Marine Geology* 235: 49–61

Colijn F and Cadée GC (2003) Is Phytoplankton Growth in the Wadden Sea Light or Nitrogen Limited?. *Journal of Sea Research* 49: 83–93

Compton TJ, Holthuijsen S, Koolhaas A, Dekinga A, ten Horn J, Smith J, Galama Y, et al. (2013) Distinctly Variable Mudscapes: Distribution Gradients of Intertidal Macrofauna across the Dutch Wadden Sea. *Journal of Sea Research* 82: 103–16 doi:10.1016/j.seares.2013.02.002

Crosby SA, Butler EI, Whitfield M, Glasson DR and Millward GE (1981) Phosphate Adsorption onto Iron Oxyhydroxides at Natural Concentrations. *Environmental Technology* 2 (8): 371–78

de Jonge VN and de Jong DJ (2002) 'Global Change' Impact of Inter-Annual Variation in Water Discharge as a Driving Factor to Dredging and Spoil Disposal in the River Rhine System and of Turbidity in the Wadden Sea. *Estuarine, Coastal and Shelf Science* 55: 969–991

de Jonge VN (1997) High Remaining Productivity in the Dutch Western Wadden Sea despite Decreasing Nutrient Inputs from Riverine Sources. *Marine Pollution Bulletin* 34 (6): 427–36

de Jonge VN, Engelkes MM and Bakker JF (1993a) Bio-Availability of Phosphorus in Sediments of the Western Dutch Wadden Sea. *Hydrobiologia* 253: 151–63

de Jonge VN, Essink K and Boddeke R (1993b) The Dutch Wadden Sea: A Changed Ecosystem. *Hydrobiologia* 265: 45–71

de Jonge VN (1990) Response of the Dutch Wadden Sea ecosystem to phosphorus discharges from the River Rhine. In DS McLusky, VN de Jonge and J Pomfret (ed), North Sea-Estuaries Interactions. *Hydrobiologia* 195: 49–62

de Jonge VN and Postma H (1974) Phosphorus Compounds in the Dutch Wadden Sea. *Netherlands Journal of Sea Research* 8 (2–3): 139–53 doi:10.1016/0077-7579(74)90014-3de Vries I, Duin RNM, Peeters JCH, Los FJ, Bokhorst M and Laane RWPM (1998) Patterns and Trends in Nutrients and Phytoplankton in Dutch Coastal Waters: Comparison of Time-Series Analysis, Ecological Model

Simulation, and Mesocosm Experiments. *ICES Journal of Marine Science: Journal Du Conseil* 55 (4): 620–634 doi:10.1006/jmsc.1998.0399

Grasshoff K, Ehrhardt M and Kremling K (1999) Methods of Seawater Analysis, 3rd Ed. Wiley-VCH, Weinheim, Germany

Grunwald M, Dellwig O, Kohlmeier C, Kowalski N, Beck M, Badewien TH, Kotzur S, Liebezeit G and Brumsack H-J (2010) Nutrient Dynamics in a Back Barrier Tidal Basin of the Southern North Sea: Time-Series, Model Simulations, and Budget Estimates. *Journal of Sea Research* 64 (3): 199–212 doi:10.1016/j.seares.2010.02.008

Hall, POJ, Hulth S, Hulthe G, Landen A and Tengberg A (1996) Benthic Nutrient Fluxes on a Basin-Wide Scale in the Skagerrak (north-Eastern North Sea). *Journal of Sea Research* 35 (1–3): 123–37

Helder W and de Vries RTP (1979) An Automatic Phenol-hypochlorite Method for the Determination of Ammonia in Sea- and Brackish Waters. *Netherlands Journal of Sea Research* 13 (1): 154–160

Hertel O, Skjøth CA, Frohn LM, Vignati E, Frydendall J, de Leeuw G, Schwarz U and Reis S (2002) Assessment of the Atmospheric Nitrogen and Sulphur Inputs into the North Sea Using a Lagrangian Model. *Physics and Chemistry of the Earth, Parts A/B/C* 27 (35): 1507–15 doi:10.1016/S1474-7065(02)00153-5

Hoppema JMJ (1991) The Oxygen Budget of the Western Wadden Sea, The Netherlands. *Estuarine, Coastal and Shelf Science* 32 (5): 483–502 doi:10.1016/0272-7714(91)90036-B

Huettel M, Ziebis W, Forster S and Luther III GW (1998) Advective Transport Affecting Metal and Nutrient Distributions and Interfacial Fluxes in Permeable Sediments. *Geochimica et Cosmochimica Acta* 62 (4): 613–31

Hyacinthe C and Van Cappellen P (2004) An Authigenic Iron Phosphate Phase in Estuarine Sediments: Composition, Formation and Chemical Reactivity. *Marine Chemistry* 91 (1–4): 227–51 doi:10.1016/j.marchem.2004.04.006

Iversen N and Jørgensen BB (1992) Diffusion coefficients of sulfate and methane in marine sediments: Influence of porosity. *Geochimica et Cosmochimica Acta* 57: 571–578

Krantzberg G (1985) The Influence of Bioturbation on Physical, Chemical and Biological Parameters in Aquatic Environments: A Review. *Environmental Pollution* 39 (Series A): 99–122

Kristensen E (1985) Oxygen and Inorganic Nitrogen Exchange in a Nereis Virens (Polychaeta) Bioturbated Sediment-Water System. *Journal of Coastal Research* 1 (2): 109–16

———. (2000) Organic Matter Diagenesis at the Oxic/anoxic Interface in Coastal Marine Sediments, with Emphasis on the Role of Burrowing Animals. *Hydrobiologia* 426: 1–24

Kristensen E and Hansen K (1999) Transport of Carbon Dioxide and Ammonium in Bioturbated (Nereis Diversicolor) Coastal, Marine Sediments. *Biogeochemistry* 45: 147–68

Krom MD and Berner RA (1980) Adsorption of Phosphate in Anoxic Marine Sediments. *Limnology and Oceanography* 25 (5): 797–806

———. (1981) The Diagenesis of Phosphorus in a Nearshore Marine Sediment. *Geochimica et Cosmochimica Acta* 45: 207–16

Kuipers BR and van Noort GJ (2008) Towards a Natural Wadden Sea?. *Journal of Sea Research* 60 (1–2): 44–53 doi:16/j.seares.2008.04.002

Leote C, Mulder L and Epping E (2014) A Budget of Bioavailable Inorganic Phosphorus in the Sediment for the Western Wadden Sea. *Journal of Sea Research* 87: 79–90

Loucaides S (2009). Dissolution of Biogenic Silica: Roles of pH, Salinity, Pressure, Electrical Charging and Reverse Weathering. Utrecht University

Louchouarn P, Lucotte M, Duchemin E and de Vernal A (1997) Early Diagenetic Processes in Recent Sediments of the Gulf of St-Lawrence: Phosphorus, Carbon and Iron Burial Rates. *Marine Geology* 139: 181–200

Ly J, Philippart CJM and Kromkamp JC (2014) Phosphorus Limitation during a Phytoplankton Spring Bloom in the Western Dutch Wadden Sea. *Journal of Sea Research* 88 (April): 109–20 doi:10.1016/j.seares.2013.12.010

Martens CS, Berner RA and Rosenfeld JK (1978) Interstitial Water Chemistry of Anoxic Long Island Sound Sediments. 2. Nutrient Regeneration and Phosphate Removal. *Limnology and Oceanography* 23 (4): 605–17

Mortensen PB, Jensen HS, Rasmussen E and Thamdrup B (1993) Seasonal Variation in P-Pools, Porewater SRP and P-Release in a Coastal Marine Sediment. *Hydrobiologia* 253: 101–102

Murphy J and Riley JP (1962) A Modified Single Solution Method for the Determination of Phosphate in Natural Waters. *Analytica Chimica Acta* 27: 31–36

Nauw JJ, Merckelbach LM, Ridderinkhof H and van Aken HM (2014) Long-Term Ferry-Based Observations of the Suspended Sediment Fluxes through the Marsdiep Inlet Using Acoustic Doppler Current Profilers. *Journal of Sea Research.* 87: 17–29

Oost AP and de Boer PL (1994) Sedimentology and Development of Barrier Islands, Ebb-Tidal Deltas, Inlets and Backbarrier Areas of the Dutch Wadden Sea. *Senckenbergiana Maritima* 24 (1/6): 65–115

OSPAR comission. (2010) RID 2008 Data Report. Compilation of National Reports. National Reports on Riverine Inputs and Direct Discharges to Convention Waters during 2008. Gothenburg: OSPAR - Convention for the Protection of the Marine Environment of the North-East Atlantic

Philippart CJM, Beukema JJ, Cadée GC, Dekker R, Goedhart PW, van Iperen JM, Leopold MF and Herman PMJ (2007) Impacts of Nutrient Reduction on Coastal Communities. *Ecosystems* doi:10.1007/s10021-006-9006-7

Philippart CJM, Cadée GC, Van Raaphorst W and Riegman R (2000) Long-Term Phytoplankton-Nutrient Interactions in a Shallow Coastal Area: Algal Community Structure, Nutrient Budgets and Denitrification Potencial. *Limnology and Oceanography* 45 (1): 131–44

Philippart CJM and Cadée GC (2000) Was Total Primary Production in the Western Wadden Sea Stimulated by Nitrogen Loading?. *Helgoland Marine Research* 54: 55–62

Postma H (1954) Hydrography of the Dutch Wadden Sea. PhD, University of Groningen

Postma H and Rommets JW (1970) Primary Production in the Wadden Sea. *Netherlands Journal of Sea Research* 4 (4): 470–93 doi:10.1016/0077-7579(70)90009-8

Rahnemaie R, Hiemstra T and Van Riemsdijk WH (2007) Carbonate Adsorption on Goethite in Competition with Phosphate. *Journal of Colloid and Interface Science* 315: 415–25

Redfield AC, Ketchum BH and Richards F (1963) The influence of organisms in the composition of seawater. In: Hill MN (ed) The sea, Vol II. Wiley, New York, p 26–77

Revsbech NP (1989) An Oxygen Microsensor with a Guard Electrode. *Limnology and Oceanography* 34 (2): 474–78

Rocha C, Galvão H and Barbosa A (2002) Role of Transient Silicon Limitation in the Development of Cyanobacteria Blooms in the Guadiana Estuary, South-Western Iberia. *Marine Ecology Progress Series* 228: 35–45

Ruttenberg KC and Berner RA (1993) Authigenic Apatite Formation and Burial in Sediments from Non-Upwelling, Continental Margin Environments. *Geochimica et Cosmochimica Acta* 57: 991–1007

Ruttenberg KC and Goni MA (1997) Phosphorus Distribution, C:N:P Ratios and delta13Coc in Arctic, Temperate and Tropical Coastal Sediments: Tools for Characterizing Bulk Sedimentary Organic Matter. *Marine Geology* 139: 123–45

Serpa D, Falcão M, Duarte P, Fonseca LC and Vale C (2007) Evaluation of Ammonium and Phosphate Release from Intertidal and Subtidal Sediments of a Shallow Coastal Lagoon (Ria Formosa - Portugal): A Modelling Approach. *Biogeochemistry* 82: 291–304

Slomp CP, Malschaert JFP and Van Raaphorst W (1998) The Role of Adsorption in Sediment-Water Exchange of Phosphate in North Sea Continental Margin Sediments. *Limnology and Oceanography* 43 (5): 832–46

Slomp CP, Van Raaphorst W, Malschaert JFP, Kok A and Sandée AJJ (1993) The Effect of Deposition of Organic Matter on Phosphorus Dynamics in Experimental Marine Sediment Systems. *Hydrobiologia* 253: 83–98

Slomp C, Van der Gaast SJ and Van Raaphorst W (1996) Phosphorus Binding by Poorly Crystalline Iron Oxides in North Sea Sediments. *Marine Chemistry* 52: 55–73

Stoll MHC, Bakker K, Nobbe GH and Haese RR (2001) Continuous-Flow Analysis of Dissolved Inorganic Carbon Content in Seawater. *Anal. Chem.* 73 (17): 4111–4116 doi:10.1021/ac010303r

Strickland JDH and Parsons TR (1968) A practical book of seawater analysis. Bulletin 167. Fisheries Research Board of Canada. Canada

Sundby B, Gobeil C, Silverberg N and Mucci A (1992) The Phosphorus Cycle in Coastal Marine Sediments. *Limnology and Oceanography* 37 (6): 1129–45

Sundby B, Anderson LG, Hall POJ, Iverfeldt Å, van der Loeff MMR and Westerlund SFG (1986) The Effect of Oxygen on Release and Uptake of Cobalt, Manganese, Iron and Phosphate at the Sediment-Water Interface. *Geochimica et Cosmochimica Acta* 50 (6): 1281–88 doi:10.1016/0016-7037(86)90411-4

Tallberg P, Treguer P, Beucher C and Corvaiser R (2008) Potentially Mobile Pools of Phosphorus and Silicon in Sediment from the Bay of Brest: Interactions and Implications for Phosphorus Dynamics. *Estuarine, Coastal and Shelf Science* 76: 85–94

Tuominen L, Hartikainen H, Kairesalo T and Tallberg P (1997) Increased Bioavailability of Sediment Phosphorus due to Silicate Enrichment. *Water Research* 32 (7): 2001–8

Van Aken HM (2008) Variability of the Salinity in the Western Wadden Sea on Tidal to Centennial Time Scales. *Journal of Sea Research* 59 (3): 121–32 doi:10.1016/j.seares.2007.11.001

van Beusekom JEE, Fock H, de Jong F, Diel-Christiansen S and Christiansen B (2001) Wadden Sea Specific Eutrophication Criteria. 14. Wadden Sea Ecosystem

van Beusekom JEE, Brockmann U, Hesse K-J, Hickel W, Poremba K and Tillman U (1999) The Importance of Sediments in the Trnsformation and Turnover of Nutrients and Organic Matter in the Wadden Sea and German Bight. *German Journal of Hydrography* 51 (2/3): 245–66

van Beusekom JEE and de Jonge VN (2012) Dissolved organic phosphorus: An indicator of organic matter turnover?. Estuarine, Coastal and Shelf Science 108: 29–36

van Beusekom JEE and de Jonge VN (2002) Long Term Changes in Wadden Sea Nutrient Cycles: Importance of Organic Matter from the North Sea. *Hydrobiologia* 475/476: 185–94

van Raaphorst W and de Jonge VN (2004) Reconstruction of the Total N and P Inputs from the Ijsselmeer into the Western Wadden Sea between 1935–1998. *Journal of Sea Research* 51: 109–31

van Raaphorst W and Kloosterhuis HT (1994) Phosphate Sorption in Superficial Intertidal Sediments. *Marine Chemistry* 48: 1–16

van Raaphorst W, Kloosterhuis HT, Cramer A and Bakker KJM (1990) Nutrient Early Diagenesis in the Sandy Sediments of the Dogger Bank Area, North Sea: Porewater Results. *Netherlands Journal of Sea Research* 26 (1): 25–52

van Raaphorst W, Ruardij P and Brinkman AG (1988) The Assessment of Benthic Phosphorus Regeneration in an Estuarine Ecosystem Model. *Netherlands Journal of Sea Research* 22 (1): 23–36

Verardo DJ, Froelich PN and McIntyre A (1990) Determination of organic carbon and nitrogen in sediments using the Carlo Erba Na-1500 analyzer. *Deep-Sea Res.*, 37: 157–165

Webb JE and Theodor JL (1972) Wave-Induced Circulation in Submerged Sands. *J. Mar. Biol. Ass.* 52: 903–14

Wentworth C (1922) A Scale of Grade and Class Terms for Clastic Sediments. *The Journal of Geology* 30: 377–92

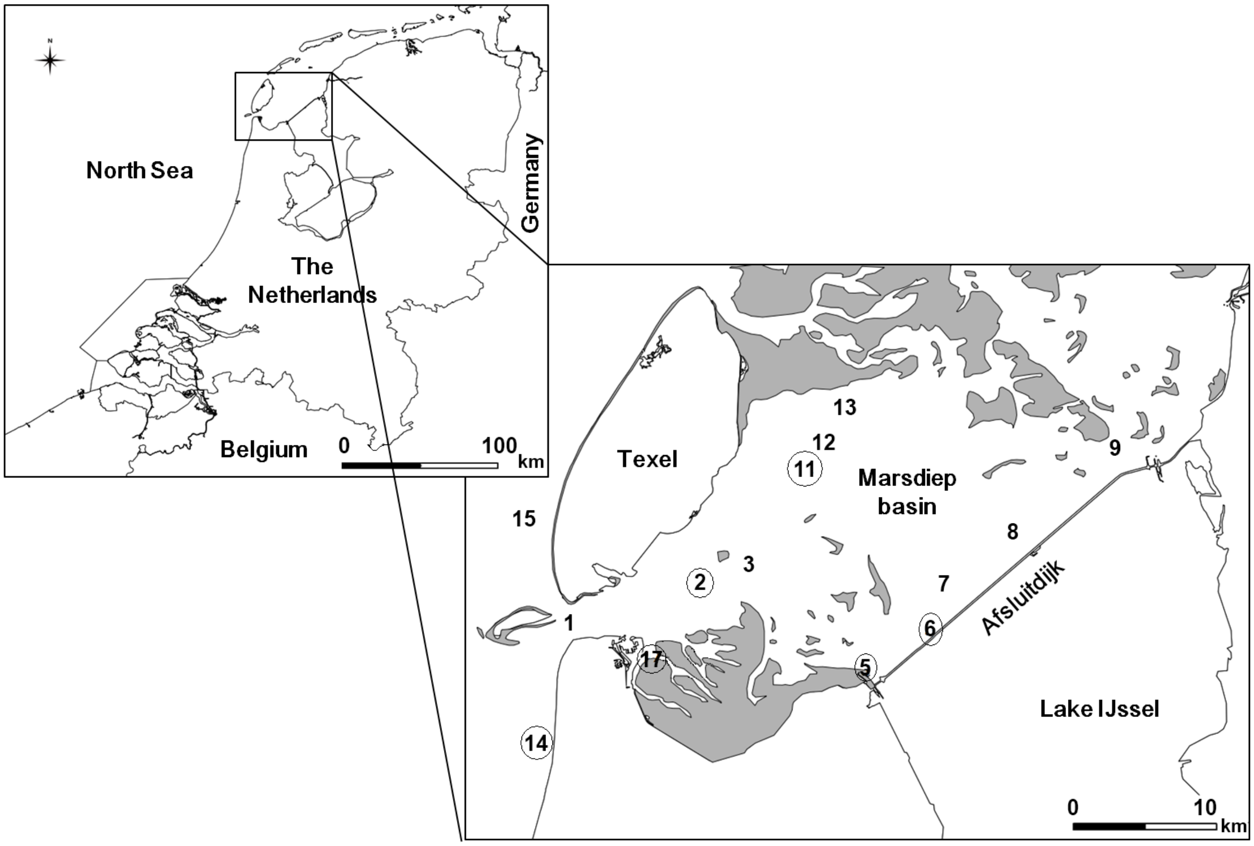


Figure 1 Location of the Marsdiep basin, western Wadden Sea. The stations that were seasonally sampled (2, 5, 6, 11, 14 and 17) are identified with a circle.

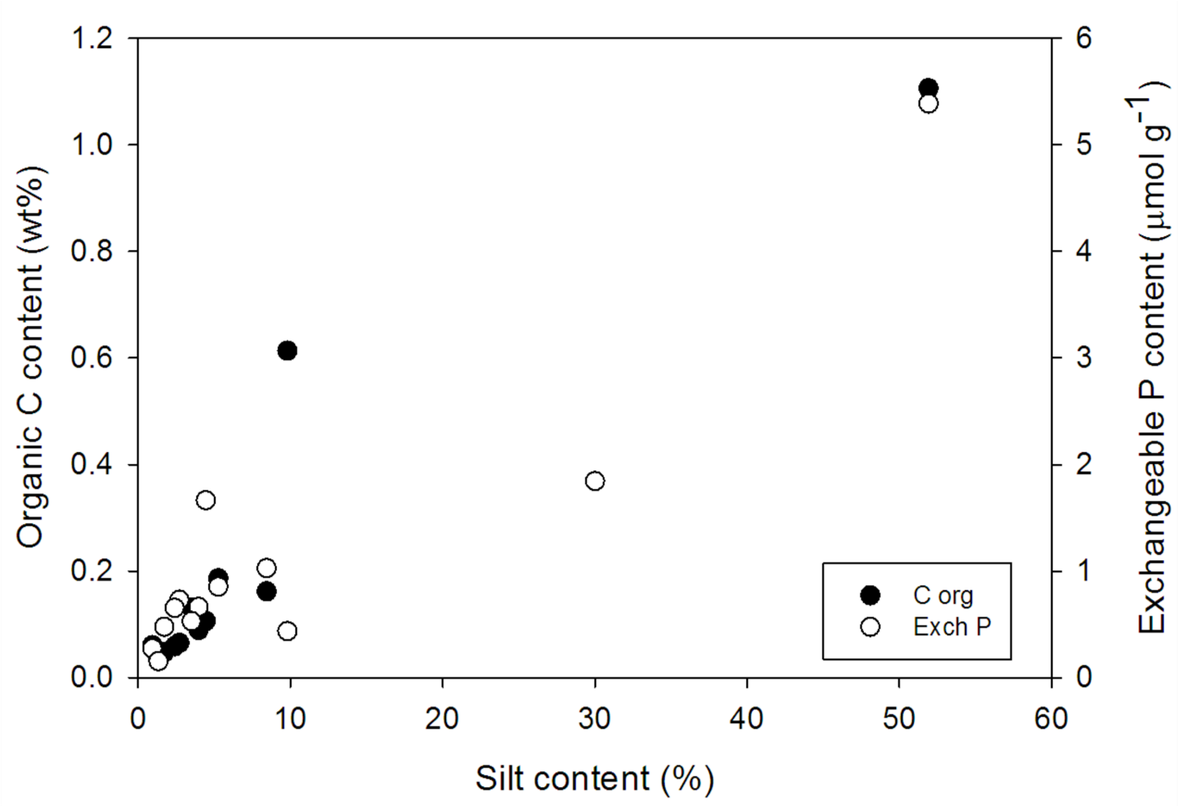
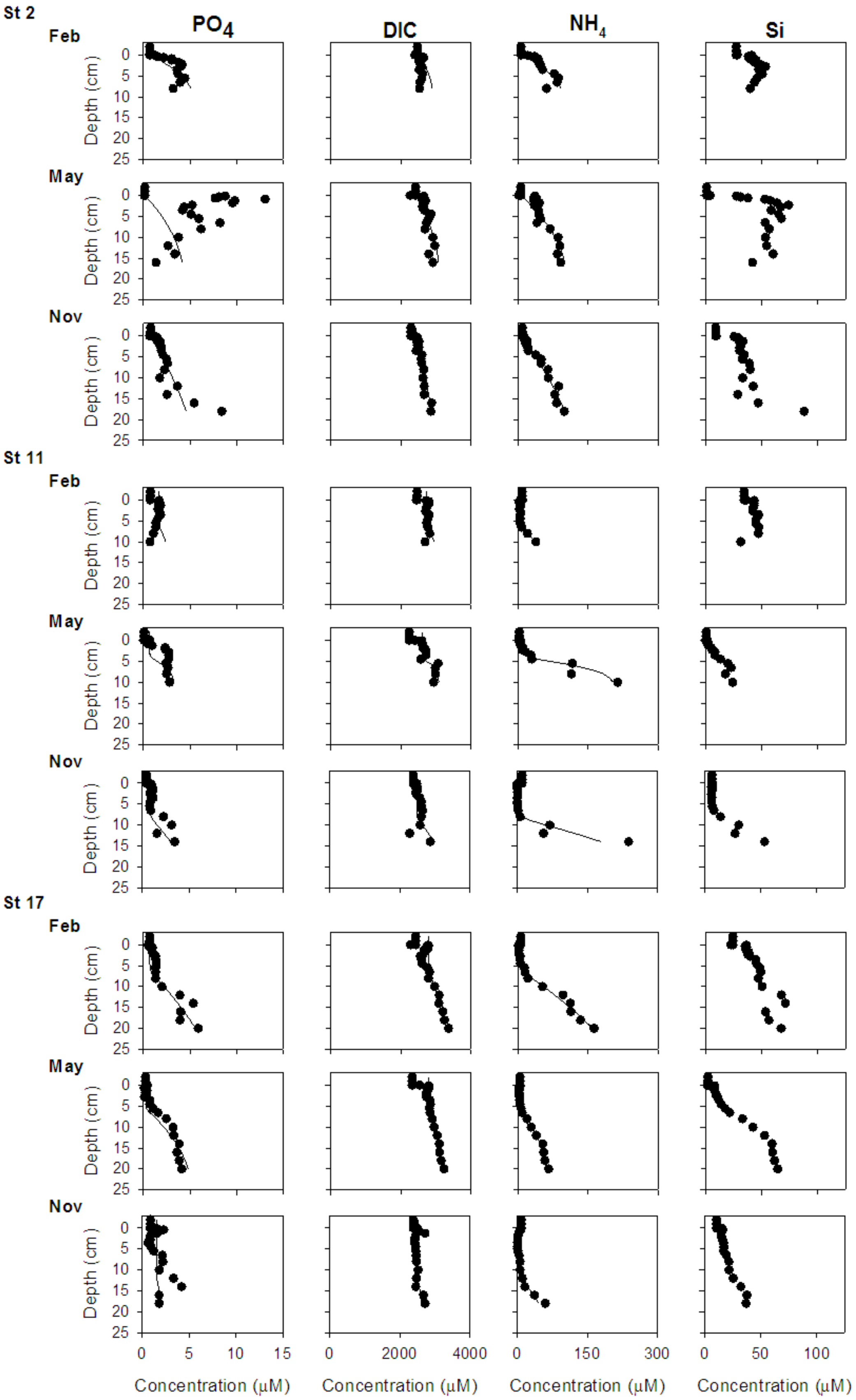


Figure 2 Content of silt versus organic C and exchangeable P contents (from Leote et al. 2014). Note the approximate linear relationship between silt content and organic C/exchangeable P.


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)

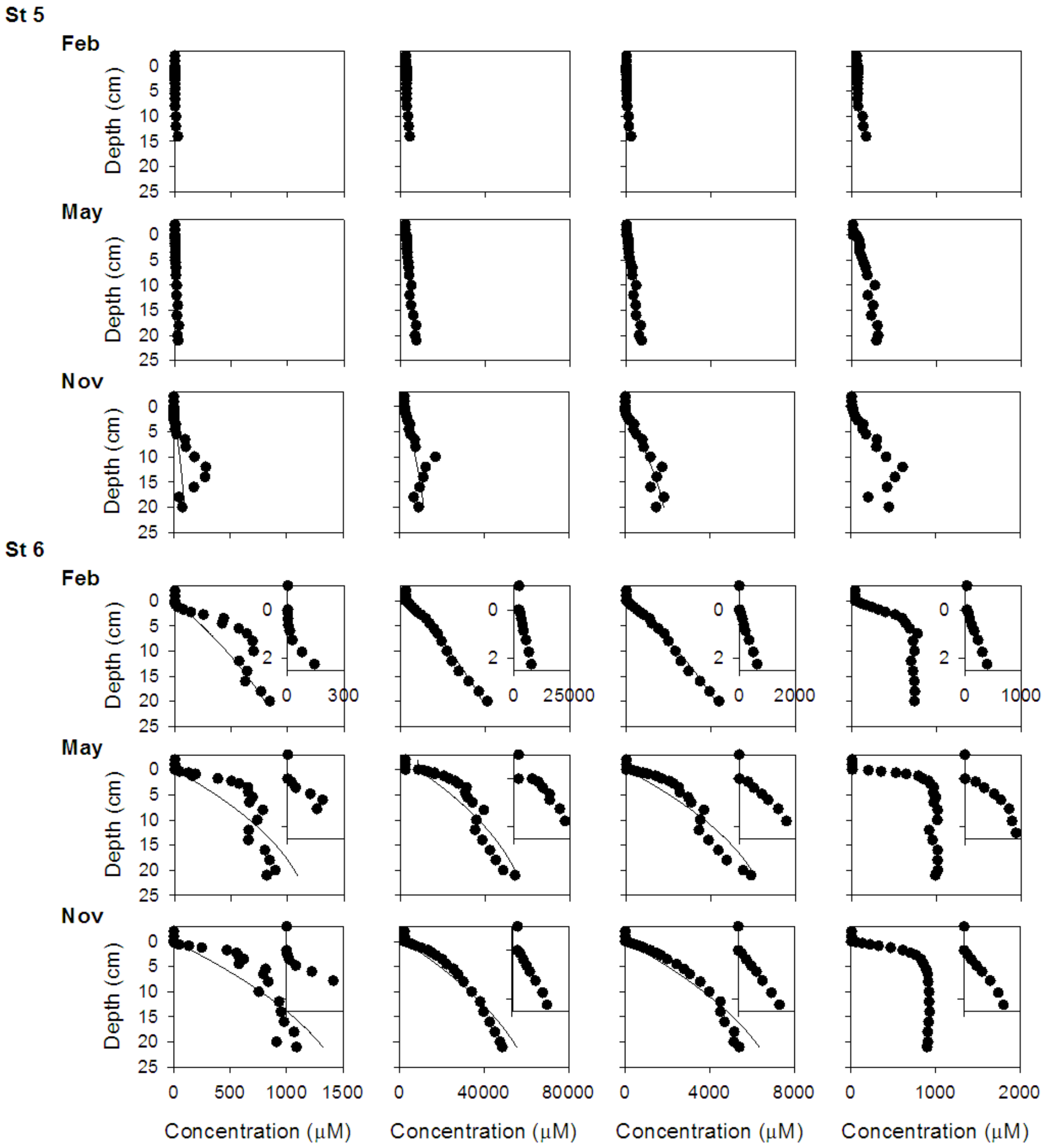


Figure 3 Porewater profiles of PO_4, DIC, NH_4 and Si concentration for stations 2, 11, 17, 5 and 6 in February 2010, May 2010 and November 2009. The small insets on station 6 correspond to a detailed view of the concentrations in the top 2 cm of the profile. The lines indicate the fitted profile using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

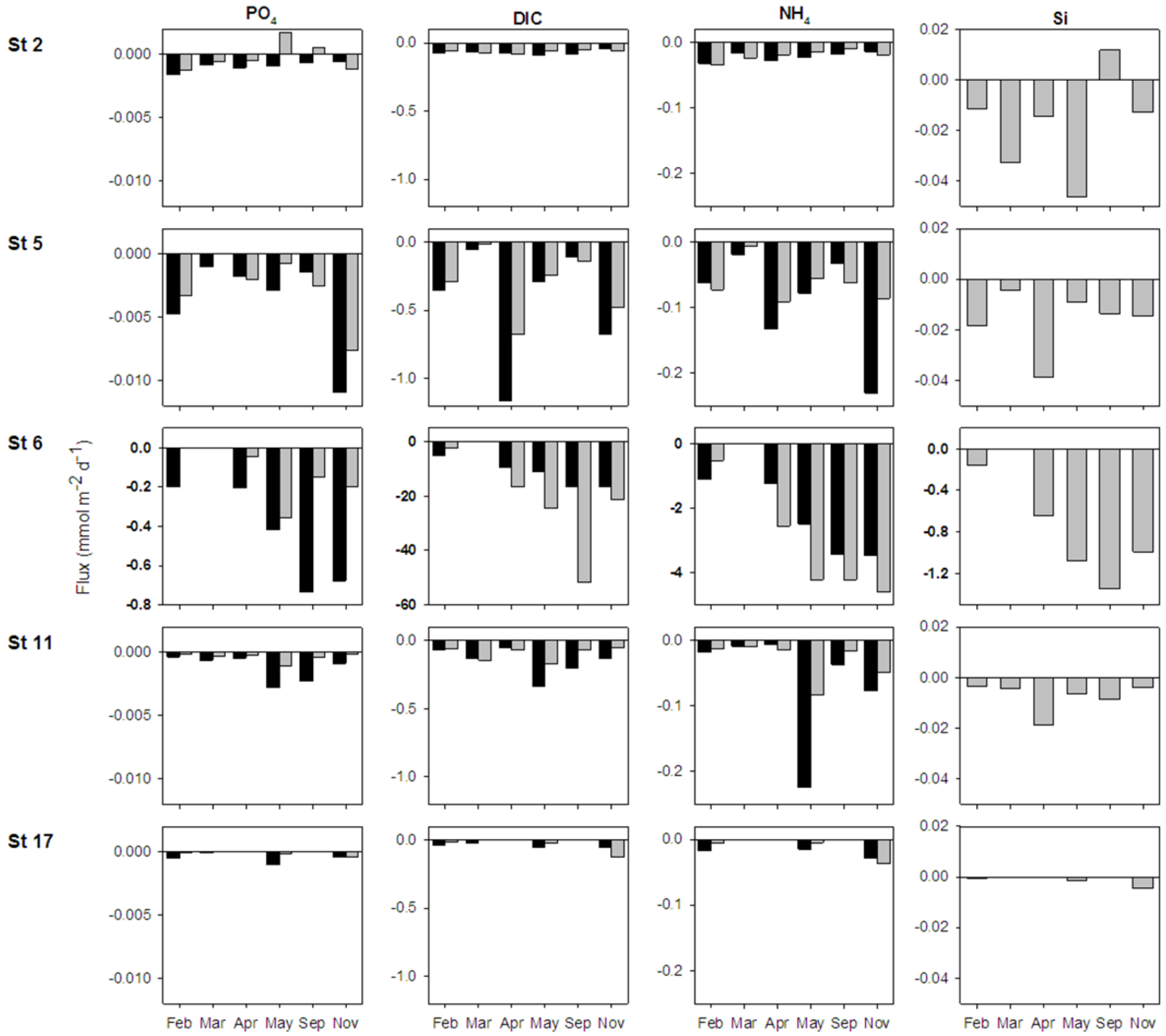


Figure 4 Sediment-water exchange of PO_4, DIC and NH_4 for stations 2, 5, 6, 11 and 17. Note the different scale for station 6. The black bars indicate the fluxes predicted by the Kristensen&Hansen approach while the grey bars show the flux predicted according to the Fick's law approach. Positive values indicate downward fluxes (i.e., into the sediment) and negative values indicate upward fluxes (i.e., from the sediment).

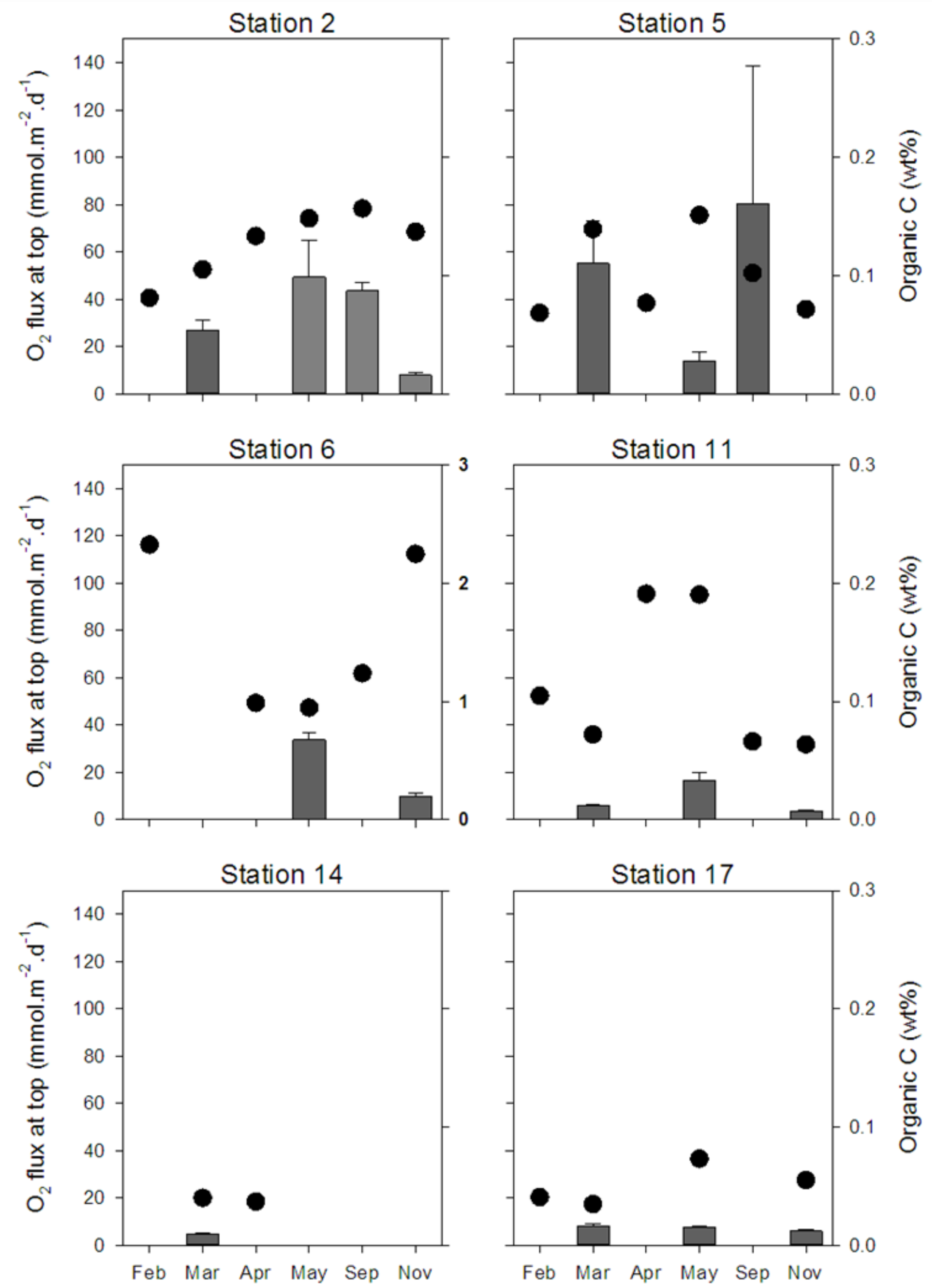


Figure 5 Oxygen exchange at the sediment-water interface (bars) with positive exchange corresponding to uptake by the sediment and organic C content (dots). Note the different scale for organic C content for station 6. A higher oxygen consumption was observed in spring in accordance with a higher organic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

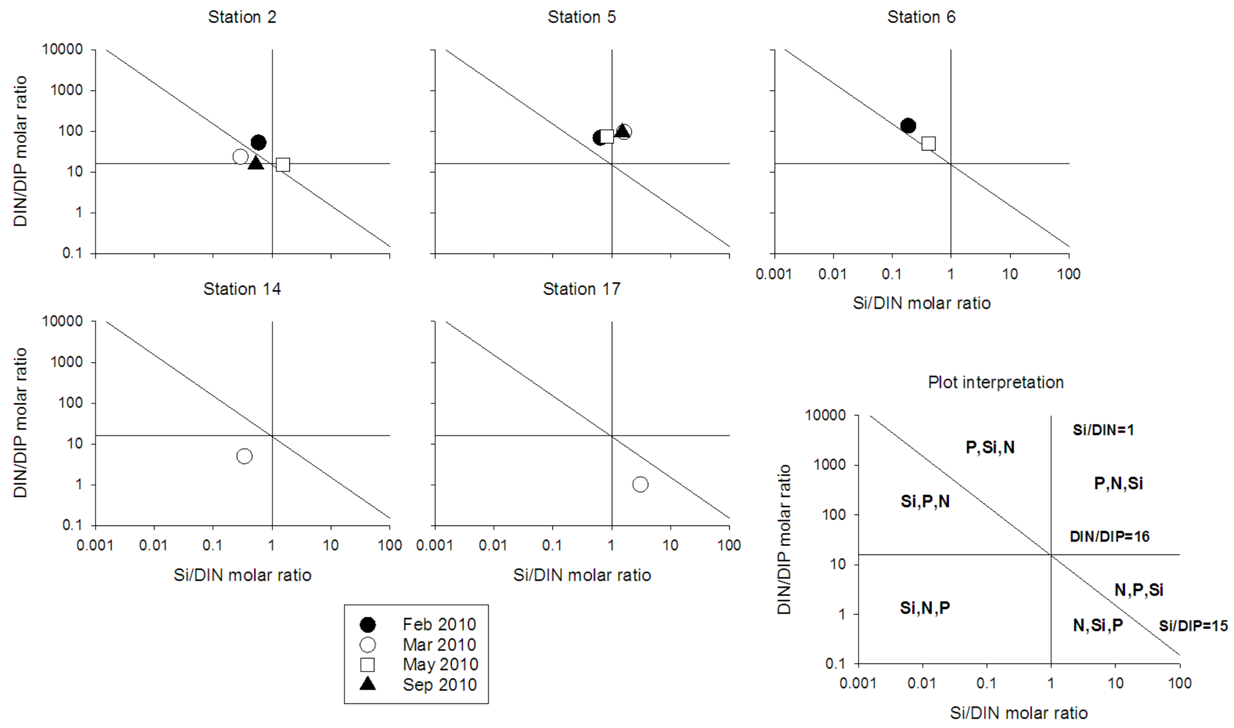


Figure 6 Nutrient limitation diagrams applied to the measured sediment-water exchange indicating a lower relative release of PO_4 and Si compared with DIN considering the demand for phytoplankton growth given by the Redfield-Brzezinski ratio (Rocha et al. 2002).

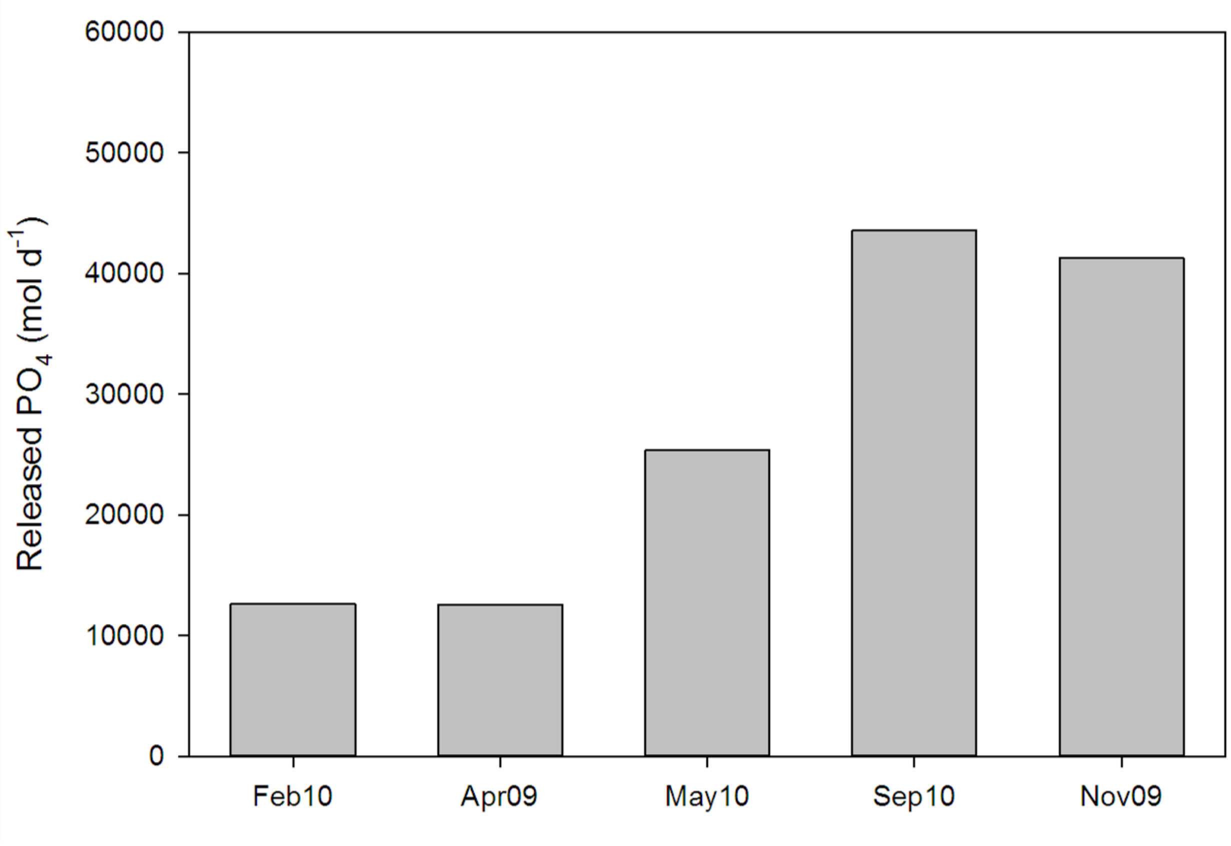


Figure 7 Phosphate release (in moles per day) for the months of February 2010, April 2009, May and September 2010 and November 2009 extrapolated for the Marsdiep basin.

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 taken from Leote et al. (2014).

Station	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

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. Values for exchangeable P are based on 8 sampled intervals and taken from Leote et al. (2014).

St	Median grain size (µm)	Porosity	N_{tot} (wt%)	C_{tot} (wt%)	C_{org} (wt%)	Exch. P (µmol g^{-1})	$CaCO_3$ (wt%)	C_{org}/N_{tot}
2	233.4±8.9	0.41±0.03	0.01±4e−3	0.35±0.08	0.10±.003	0.62±0.09	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	0.44±0.14	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	7.13±2.67	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	0.35±0.15	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	0.21±0.03	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	0.43±0.08	0.30±0.07	8.1±1.1

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 (mmol m^{-2} 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	**--**	**--**	**--**	**--**	**--**	**--**

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