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

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Abstract

At present, phosphorus (P) is seen as the main limiting nutrient for phytoplankton growth in the western Wadden Sea. Six cruises were performed for water sampling at selected stations covering a full tidal cycle for later determination of dissolved and particulate nutrient concentrations. The major P sources were identified on a seasonal basis, by comparing the contribution of freshwater discharge and sediment release, calculated in a previous study, 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. This was observed in early spring and was followed by a later increase in the nutrient concentrations in spring–summer. The low concentrations found for the freshwater and seawater end-members for this period ruled out their importance as nutrient sources, suggesting that this increase resulted mainly from internal recycling in the Wadden Sea. Even though P limitation was observed during most the year, a potential seasonal change in the limiting nutrient, from P to silica, was observed. The comparison between P supply to the Wadden Sea by freshwater discharge and sediment release showed a much higher contribution of the latter, especially in April–November. To our knowledge, this is the first study clearly presenting internal recycling as the main nutrient source to the western Wadden Sea in spring–autumn, instead of freshwater discharge or the North Sea.

Keywords: Nutrients, mineralization, Wadden Sea, primary production, sorption, freshwater discharge

1. Introduction

The Wadden Sea is a shallow coastal sea, separated from the North Sea by a chain of barrier islands, stretching for 600 km 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 secondary (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 matter from the North Sea has since long received considerable attention as to explain the high productivity and heterotrophic status of this 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 1950's until the 1980's the loading of nitrogen (N) and phosphorus (P) increased by a factor of 12 and 10, respectively, 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 1950's 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 (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-1950's (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 up to 100, suggesting severe P limitation on the primary production (van Raaphorst and de Jonge 2004; Philippart et al. 2007; Ly et al. 2014). Despite the decrease in nutrient loadings, high levels of biomass primary productivity were maintained and only since the 2000's a significant decrease was observed in biomass during the autumn blooms and in production, to present day values of ~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). The 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 was 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 were compared on a seasonal scale. In addition to dissolved nutrients, the concentration and composition of suspended particulate matter and chlorophyll *a* content were considered. This 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.

2. Methods

2.1 Study site

The Marsdiep Basin, the westernmost tidal basin of the Wadden Sea, covers an area of about 700 km^2, ~580 km^2 of which are 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/d. The tidal residual transport ranges 1–3 × 10^3 m^3 s^{-1} (Ridderinkhof et al. 2002; Nauw et al. 2014). Because of freshwater discharge from Lake IJssel and other minor sources, the area behaves like an estuary, covering a salinity range from 0.7 (near the sluices) to 30 (near the tidal inlets), with a flushing time of the discharged water of 5.5 days (van Aken 2008; Nauw et al. 2014; this study). On average, the water in this basin is composed of ~85% North Sea seawater, with a 15% admixture of Lake IJssel water (de Jonge et al. 1996) and the bulk of the sediment and particulate matter supply mainly originates from the North Sea (Oost and de Boer 1994). The suspended particulate matter concentrations are relatively high ranging 10–30 mg l^{-1} (Nauw et al. 2014; Philippart et al. 2013), resulting in light penetration depths of 0.1–0.5 m (Hommerson et al. 2009; Loebl et al. 2009). Therefore, benthic photosynthesis is unlikely in the subtidal domain. The Marsdiep Basin is largely composed of sandy sediments with a variable silt (particle size <63 µm) content (1–10%). Finer-grained sediments, with silt contents up to 72%, represent only 2% of the basin and are found adjacent to the coast (Leote et al. 2014). Most sediment P is in a non-easily exchangeable form, with the bioavailable fraction corresponding to ~1/3 of the total sediment P pool (Leote et al. 2014).

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 (~13 h) whereas station 16, located in Lake IJssel was sampled only once per cruise. Sampling campaigns were carried out on the 20–24th April and 2–7th November 2009, and on the 15–17th February, 22–26th March, 3–7th May, and 6–10th September 2010 for stations 2, 5, and 11. Because of logistic and weather constraints, stations 6 and 17 were not sampled in March 2010 and April 2009, respectively. Station 14 was only sampled in April 2009 and March 2010, while station 16 was sampled in April 2009 and March, May, and September 2010. All stations were sampled within the same week. For each station, water samples were collected every hour with a Niskin bottle from the side of the ship at three 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 matter

To determine the total suspended matter (TSM), particulate total C, N, and P, organic C, and chlorophyll *a* contents, 100–300 ml of water 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 until analysis, while the extraction for total particulate P started immediately after filtration. The chlorophyll *a* contents were only determined in 2010, while the TSM, and particulate C, N, and P were sampled from November 2009 on.

2.3 Analytical procedures

All analyses on dissolved nutrients were performed on a TRAACS 800 Segmented Continuous Flow Analyzer. NO_x ($NO_3 + NO_2$) and NH_4 were analyzed according to Grasshoff et al. (1999) and Helder and de Vries (1979) with detection limits of 0.04 and 0.07 µM and precisions of 0.02 and 0.03 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 analyses of TDN and TDP followed the NIOZ nutrient lab in-house method based on Schreurs and Nijsse (2000) and Nijsse and Spronk (2000), with a detection limit and precision of 0.03 µM. All analyses had an accuracy within the 95% confidence interval assigned for the reference materials used, as confirmed in the intercomparison rounds of Quasimeme and MRI Japan (Aoyama et al. 2010). The concentration of dissolved organic N (DON) was determined as the difference between

TDN and $NO_3 + NO_2 + NH_4$, while the dissolved organic P (DOP) was calculated as TDP minus PO_4. The TSM concentration 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 detection limits of 2.5 and 4.8 wt %, a precision of 9.7 and 2.7%, and an accuracy of 0.4 and 1.0% for N and C, respectively. The organic C was determined following the same procedure after removal of the carbonates with 2 M HCl. The total particulate P content was determined according to the persulfate oxidation method from Valderrama (1981), improved to a digestion time of 90 min by G. Kramer and K. Bakker (NIOZ nutrient lab). Chlorophyll *a* was analyzed in a High Performance Liquid Chromatographer (HPLC) after extraction in a 90% acetone medium (Jeffrey et al. 1997).

2.4 Data analyses

2.4.1 Statistical significance

The significance of the seasonal differences in the concentrations of dissolved and particulate nutrients, TSM, and chlorophyll a was assessed by a Student t-test in Excel (Microsoft ©), assuming a two-tailed distribution and an unequal variance.

2.4.2 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. For the Marsdiep Tidal Basin, such mixing diagrams were compiled for each cruise with the concentrations of dissolved nutrients (NO_3, NH_4, PO_4, and Si) plotted against salinity. A negative relationship between salinity and dissolved nutrient concentration implied that the freshwater end-member was the main source of the nutrient for this tidal basin, whilst a positive relationship indicated that the oceanic end-member was the main source. The occurrence of a concave relation or the presence of lower concentrations at intermediate salinities indicated a loss of that nutrient within the tidal basin (e.g. denitrification or sedimentation). Oppositely, a convex relationship or higher concentrations at intermediate salinities indicated production or additional sources within the tidal basin (e.g. mineralization or local input).

2.4.3 Quantification of the P sources

A comparison was made between the relative importance to the pelagic P concentrations of freshwater discharge and release from the sediments. To do so, the monthly freshwater P discharge from the Lake IJssel sluices and the harbour of Den Helder was estimated and compared with the monthly sediment P release for the Marsdiep Basin according to Leote and Epping (2015). The discharge from Lake IJssel was calculated by multiplying the summed sluice debits in Den Oever and Kornwerderzand (Figure 1) by the PO_4 concentrations from Lake IJssel (station Vrouwezand) using data from the Rijkswaterstaat Waterbase (live.waterbase.nl). 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 Vrouwezand, which was assumed valid for the period between samplings. The PO_4 concentration of the freshwater discharging in Den Helder was assumed to correspond to the concentrations from the 1950s (Postma 1954), which agree well with the present concentrations from Lake Ijssel. The freshwater discharge was calculated between January 2009 and December 2010, so that the monthly discharge corresponded to an average value for the two years. Values for sediment nutrient release were taken from Leote and Epping (2015) who estimated the PO_4 release for the entire Marsdiep Basin based on a relationship found between the silt content and the sediment-water exchange for the same stations presented in this study. The sediment-water exchange was estimated based on porewater profiles of nutrient concentration using Fick’s Law and correcting for the effect of macrofauna activity. No benthic microphotosynthetic communities were detected, since oxygen microprofiles under different light intensities did not change with increased light availability (data not shown).

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, DON, and DOP) were, in general, similar for all depths, with the exception of station 5, close to the freshwater sluices of Den Oever (Figure 1), indicating a well-mixed water column with stratification only near the sluices or following a major freshwater discharge. The average NO_3 concentrations ranged 2–192 µM, while NH_4 had a much smaller variation (0.2–17 µM) (Figure 2). PO_4 varied between 0 and 1 µM, while Si reached a maximum of 76 µM and a minimum 0 µM. The DOP concentrations ranged 0–0.5 µM, while DON ranged 6–41 µM.

3.1.2 Seasonal pattern

A clear seasonal pattern was observed (Figure 2). For Si, PO_4, and NH_4, a dramatic decrease in concentrations was observed in February–April, when nutrient depletion was observed for all stations except 5 and 16 (located close to and in Lake IJssel, respectively), followed by an increase in May, especially for NH_4 and PO_4. A second drop in the concentrations was observed in September for PO_4 and NH_4 and in November for Si. This similar seasonal trend may point to common sources and sinks for these three nutrients. Oppositely, NO_3 concentrations decreased throughout the year for all Wadden Sea stations, suggesting different sources and sinks. The DOP and DON concentrations increased in February–April, followed by a decrease until November. The DON showed more spatial variation than the DOP, with higher concentrations for stations 5 and 16, clearly associated with freshwater. The seasonal trends of inorganic and organic nutrients were opposite, with higher concentrations of organic nutrients (DOP, DON) in parallel with a decrease in the inorganic nutrients (PO_4, NH_4). The concentration differences between months were always significant ($p < 0.01$), with the exception of April–May for NO_3 ($p = 0.53$), March–April for Si ($p = 0.03$), and March–April for NH_4 ($p = 0.62$).

3.1.3 Mixing diagrams

Regarding NO_3, Lake IJssel was clearly a source for the Marsdiep Basin in February–May, with a near conservative behaviour in February and May and net removal in March and probably in April (Figure 3). In September–November, the concentrations in Lake IJssel and the Wadden Sea decreased substantially to close to zero and the North Sea became a minor source of NO_3. The NH_4 concentration was always lower in the freshwater end-member. Therefore, the elevated concentrations along the salinity gradient likely resulted from production/regeneration within the Wadden Sea, most prominent in May, but also evident in February, September, and November. The PO_4 concentration was also always lower in Lake IJssel, except in May. In February, an approximately conservative behaviour was observed, with the North Sea as the source. In March–April, the concentrations were very low, while in May, the concentrations for the intermediate salinities were clearly above the predicted, indicating PO_4 production, while in September–November they were below, suggesting consumption or eventual adsorption to Fe oxyhydroxides from surface sediments. Si concentration was mostly higher in the freshwater end-member. In February, Si showed a conservative behaviour, while in March the concentrations decreased, with consumption at intermediate salinities. In April–May, all concentrations were close to zero, with a slight increase at the intermediate salinities in May. In

September, the concentrations were below the predicted with Lake IJssel as the source, while in November, the concentrations levelled off between the freshwater and seawater end-members.

3.2 Particulate matter

3.2.1 Measured values

The concentration of TSM varied between 15 and 120 mg l^{-1} (Figure 4). The total and organic C contents ranged 6–25 wt % and 1–21 wt %, respectively, with the highest values for Lake IJssel in March–September. The total N content was much lower, 0.5–3 wt %, while the total particulate P ranged 14–69 µmol g^{-1}, being higher in Lake IJssel in March and September, respectively. The organic C/total P ratio provides additional information concerning the composition of particulate P, i.e. biogenic- or terrigenous/mineral- associated. During our sampling period, it ranged 38–841, mostly above the Redfield ratio (C:P = 106:1), being higher in February in Den Oever and in March and May in Lake IJssel.

3.2.2 Seasonal pattern

Like the dissolved nutrients, the TSM, total C, N, P, organic C, and organic P/total C ratio showed a clear seasonal variation (Figure 4). The TSM concentration and standard deviation was lower in February–March, increasing in May–September and decreasing in November. The contents of total and organic C, total N, and especially the particulate P showed a comparable seasonal pattern. The organic C/total P ratio showed an opposite seasonal profile, with higher values in February–March, decreasing in May–September and slightly increasing in November. The differences in concentrations between the months were always significant ($p < 0.01$), with the exception of February–March and May–September for both TSM and total P ($p = 0.95$ and 0.92 for TSM; $p = 0.07$ and 0.08 for total P, respectively).

3.2.3 Chlorophyll a

The average chlorophyll *a* concentrations varied between ~4 µg l^{-1} in February and 84 µg l^{-1} in September (Figure 5). The concentrations and respective standard deviations were lower in February and May and higher in March and September, especially for the surface samples, with lower values for the mid column and bottom depths (data not shown). The spatial variation was also higher in March and September. The seasonal differences observed were statistically significant ($p < 0.01$).

3.2.4 Tidal variation

In addition to the seasonal pattern, a tidal pattern was observed for the concentrations of particulate matter in the water column. Taking station 17, located in the Balgzand tidal flat, as an example, in February–March, the TSM concentration was very low and similar for all depths, with no significant variation during the tidal cycle (Figure 6). However, in May–September, the concentrations increased approximately after maximum tidal current speed (i.e. between high and low tide), especially at the bottom, suggesting resuspension of deposited material. A similar pattern was observed for chlorophyll *a*, indicating that part of the resuspended material corresponded to fresh organic matter. The plots of the concentration of chlorophyll *a* versus the TSM were highly correlated, with chlorophyll *a* representing a larger fraction of the TSM in March–September.

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 (Cadée and Hegeman 1993; Loebl et al. 2007; van Beusekom et al. 2009). This is based on the assumption that the concentrations of dissolved and particulate nutrients and chlorophyll *a* did not differ greatly between 2009 and 2010, since we use a combination of data from both years. Even though this is not ideal, studies on the seasonal variation of nutrients, turbidity, salinity, and chlorophyll a suggest this is a fair assumption (Cadée and Hegeman 2002; van Beusekom and de Jonge 2002; Colijn and Cadée 2003; Kuipers and van Noort 2008; van Aken 2008; Philippart et al. 2000; 2010; 2013). In February, the concentrations of inorganic nutrients were within the highest measured (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 behaviour (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 no conservative behaviour. The higher concentrations of chlorophyll *a* for station 5 (close to a freshwater sluice) suggest the occurrence of an earlier phytoplankton bloom in Lake IJssel 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 chlorophyll *a* concentrations (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 in the Wadden Sea levelled 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 was organic, corroborate this idea. Moreover, a first phytoplankton bloom in early March is in line with previous studies (Cadée 1986; Cadée and Hegeman 1993; Philippart et al. 2000; Kuipers and van Noort 2008; Philippart et al. 2010). After the initial bloom, nutrient depletion likely limited the growth of primary producers, as apparently seen in May, with a decrease in the concentrations of chlorophyll *a* and particulate organic C and total N (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 primary producers 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 compensated for the biological uptake. Even though part of the measured chlorophyll a might correspond to resuspended benthic microalgae, most is likely of pelagic origin, since the high turbidity limits benthic primary production to intertidal areas, which cover only 8% of the Marsdiep Basin (Compton et al. 2013). 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, as also observed for the East Frisian Wadden Sea (Grunwald et al 2010), the same did not apply to PO_4 and NH_4 likely due to an earlier phytoplankton bloom in Lake IJssel, as mentioned above. 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 winter availability of NH_4 and PO_4 in the Wadden Sea 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 the Marsdiep in March resulted in a high demand for NH_4, PO_4, and Si in both end-members and the Wadden Sea, with the concentrations of dissolved inorganic nutrients dropping to extremely low values after conversion to particulate organic material. However, the degradation of the dead phytoplankton cells can replenish the water column with dissolved nutrients (van Beusekom and de Jonge 2012), as evidenced by the increase in DON and DOP concentrations in April (Figure 2). This 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). This drop in PO_4 and Si concentrations in spring, followed by an increase towards summer has been observed for other basins of the Wadden Sea, namely the East Frisian Wadden Sea, close to Spiekeroog Island (Grunwald et al 2010; Beck and Brumsack 2012). For the List Tidal Basin, northern Wadden Sea, Loebl et al (2007) and van Beusekom et al (2009) have also reported an increase in the PO_4 concentrations in early summer, after the first bloom; however, the Si and NH_4 concentrations remained relatively low until autumn. Similarly, higher DOP concentrations during spring and summer, an opposite behaviour between DOP and PO_4, and a positive relationship between DOP and chlorophyll *a* have also been reported for the Dutch Wadden Sea and Sylt-Rømø area (van Beusekom and de Jonge 2012). In May, comparing the increase in the NH_4, PO_4, and Si concentrations 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, this increase 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 compared to NH_4 and PO_4, since the 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 Leote and Epping (2015) 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 favourable oxidizer after oxygen, its consumption is expected to increase in this period, mainly via denitrification. Annual sediment denitrification rates of 110 mmol N m^{-2} have been reported for the western Wadden Sea (Kieskamp et al.1991), while a total N loss within the basin of 4 mmol N m^{-2} d^{-1} was reported by Philippart et al. (2000). This explains why NO_3 concentrations were independent of chlorophyll *a*, continuously decreasing from February until September, i.e. from the lowest to the highest temperature, with no increase in May–September, since consumption by denitrification prevented its accumulation in the water column. Other Wadden Sea regions, such as the East Frisian Wadden Sea also showed a later increase in NO_3 concentrations when compared to the other inorganic nutrients (Grunwald et al 2010; Beck and Brumsack 2012).

The conclusions above match well with the previous findings of Leote and Epping (2015), who found a higher oxygen consumption in late spring. The same authors also found increasing sediment-water exchange rates for dissolved inorganic carbon between March and September. Since dissolved inorganic carbon is an end product of mineralization, its higher release rates further confirm a higher mineralization during this period, at least in the sediment, with release rates ranging between 0 (in winter) and 52 mmol m^{-2} d^{-1} (in late summer).

The shallowness of the western Wadden Sea suggests a major role of the sediments in nutrient regeneration with a 70% efficiency in the recycling of organic P compounds reported by van Raaphorst et al. (1988). In addition, resuspension, due to tidal currents and wind-driven waves, 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 TSM concentrations measured for the western Wadden Sea were slightly higher than the reported by van Beusekom (2005) and Reynhout (2002) in February, March, and November, when no major differences were observed during a tidal cycle (Figures 4 and 6). However, in May and September, the concentrations were much higher, increasing to 205 mg l^{-1} after the maximum tidal current speeds and especially for the bottom samples (Figure 6), suggesting resuspension of the deposited material (Postma 1961). A certain time lag was observed between the expected maximum current speed and the maximum TSM concentrations, similarly to Lunau et al. (2006). These increased TSM concentrations at higher current speeds have already been observed in the Wadden Sea and specifically in the Marsdiep Basin (Hommerson et al. 2009; Nauw et al. 2014). The concentrations of chlorophyll *a* followed a similar pattern (Figure 5), indicating that part of the resuspended material was fresh organic material, in agreement with the high organic C/total P ratio found throughout the year (Figure 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, as observed by Hommerson et al. (2009). This suggests that higher the TSM concentrations did not result from increased current speeds but might be attributed to the increased availability of easily resuspendable material i.e. an observed fluffy layer of deposited fresh organic material instead of a well-defined interface of clay/sand particles (Pempkowiak et al. 2005). 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 a larger surface area of the organic matter to a well-oxygenated environment (Ståhlberg et al. 2006).

4.4 Nutrient availability and potential relation with 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). Recent findings for the Marsdiep Basin on the absence of trends in light conditions during the last 40 years (Philippart et al. 2013) and the occurrence of P limitation during spring blooms using various techniques (Ly et al. 2014) strongly suggest the structuring role of P on phytoplankton growth in this area for the recent years. 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 (Ly et al. 2014), 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 (Egge and Asknes 1992). The growth of flagellates and *Phaeocystis* spp. was then favoured since they do not require Si, as shown by Ly et al. (2014) for the Marsdiep Basin in 2010 and for the List Tidal Basin (Loebl et al. 2007). In addition, *Phaeocystis* spp. can use DOP 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). In September, Si seemed to no longer be the limiting nutrient (P-Si-N or P-N-Si limitation) and the drop in Si concentrations in November suggested a secondary diatom bloom, consistent with the findings of Cadée (1986).

4.5 Sources of P to the western Wadden Sea

Since P was identified as the limiting nutrient during most of the year, in agreement with recent literature (Philippart et al. 2007; Kuipers and van Noort 2008; Ly et al. 2014), we will only compare its different sources 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; Philippart et al. 2000; van Raaphorst and Jonge 2004). Postma (1954) suggested that the high PO_4 concentrations in spring–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, with the concentrations of NH_4, PO_4, and Si increasing at intermediate salinities in May, while the lower concentrations for Lake IJssel and the North Sea (Figure 3) make them improbable major sources of inorganic P. Besides, the discharge of freshwater was low during this period with usually <25% of freshwater in the water column composition. A comparison between PO_4 release from the sediments and freshwater discharge from Den Helder and the Afsluitdijk sluices, which correspond to app. 60% of the discharged water into the western Wadden Sea (Ridderinkhof 1988; van Raaphorst and van der Veer 1990), showed a much higher contribution of sediment release to the water column loading, throughout the year and especially for May–November (Figure 8). A similar low contribution of freshwater in terms of nutrient supply has also been found for the East Frisian Wadden Sea (Grunwald et al 2010). In addition, the contribution of mineralization within the Wadden Sea is likely underestimated, since it is based on a conservative estimate of sediment release using porewater profiles of nutrient concentrations (Leote and Epping 2015) and does not include mineralization or desorption in the water column, potentially enhanced by resuspension. No bias in the fluxes due to microphytobenthos activity (Sundbäck et al. 1991) was expected, given the reduced light penetration depth for the Marsdiep Basin. In addition, flux overestimation due to advection-driven fluxes is also not likely considering the relatively poor sorting of our stations, in spite of their high sand content, meaning that the sediment was well-compacted (Leote and Epping 2015). However, the contribution from submarine groundwater discharge is unknown for this area but has been reported for other regions of the Wadden Sea (e.g., East Frisian Wadden Sea) as having an impact on some nutrient concentrations in the water column (Riedel et al 2010; Moore et al 2011). Even though we have no data to assess its contribution, we expect it to be low when compared to the East Frisian Wadden Sea, considering the smaller intertidal area of the Marsdiep Basin and the low hydraulic gradient generated by the land adjacent to the Marsdiep Basin (Moore et al 2011; Compton et al 2013). 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, likely of both autochthonous and allochthonous origin, seems to be the main source of PO_4 to the western Wadden Sea, largely fuelling primary production during spring and summer.

Conclusions

In this study, we presented updated dissolved and particulate nutrient information for the Marsdiep Basin collected over full tidal cycles. Regarding seasonality, the concentrations of dissolved nutrients in the western Wadden Sea were closely linked to the growth of primary producers with a negative relationship between the concentrations of chlorophyll *a* and the major inorganic nutrients. Phosphorus limitation, according to the Redfield ratio, was observed during most of the year, even though Si was also limiting in late spring. Recycling of fresh organic material resulting from the first phytoplankton bloom in spring seemed to be the major source of inorganic nutrients in late spring–summer, since the low concentrations measured for the North Sea and Lake IJssel made them unlikely sources for that 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. In addition, sediment resuspension was observed in spring–summer, potentially further favouring sediment nutrient release. This is in contrast with most previous work, where freshwater discharge was seen as the main source of nutrients to the Marsdiep Basin.

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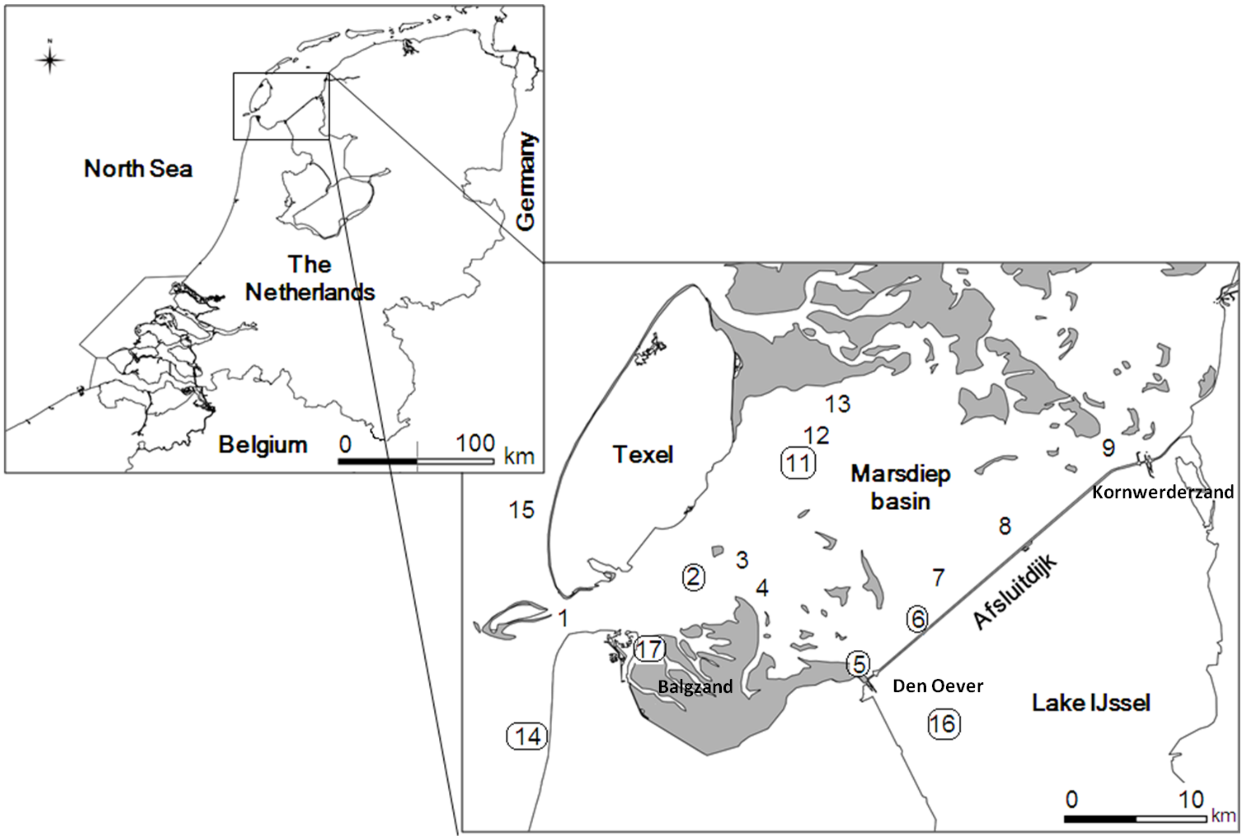

Figure 1. Map of the western Wadden Sea with the sampling locations in the Wadden Sea (1–13, 17), North Sea (14, 15), and Lake IJssel (16). The stations marked with a circle were seasonally sampled

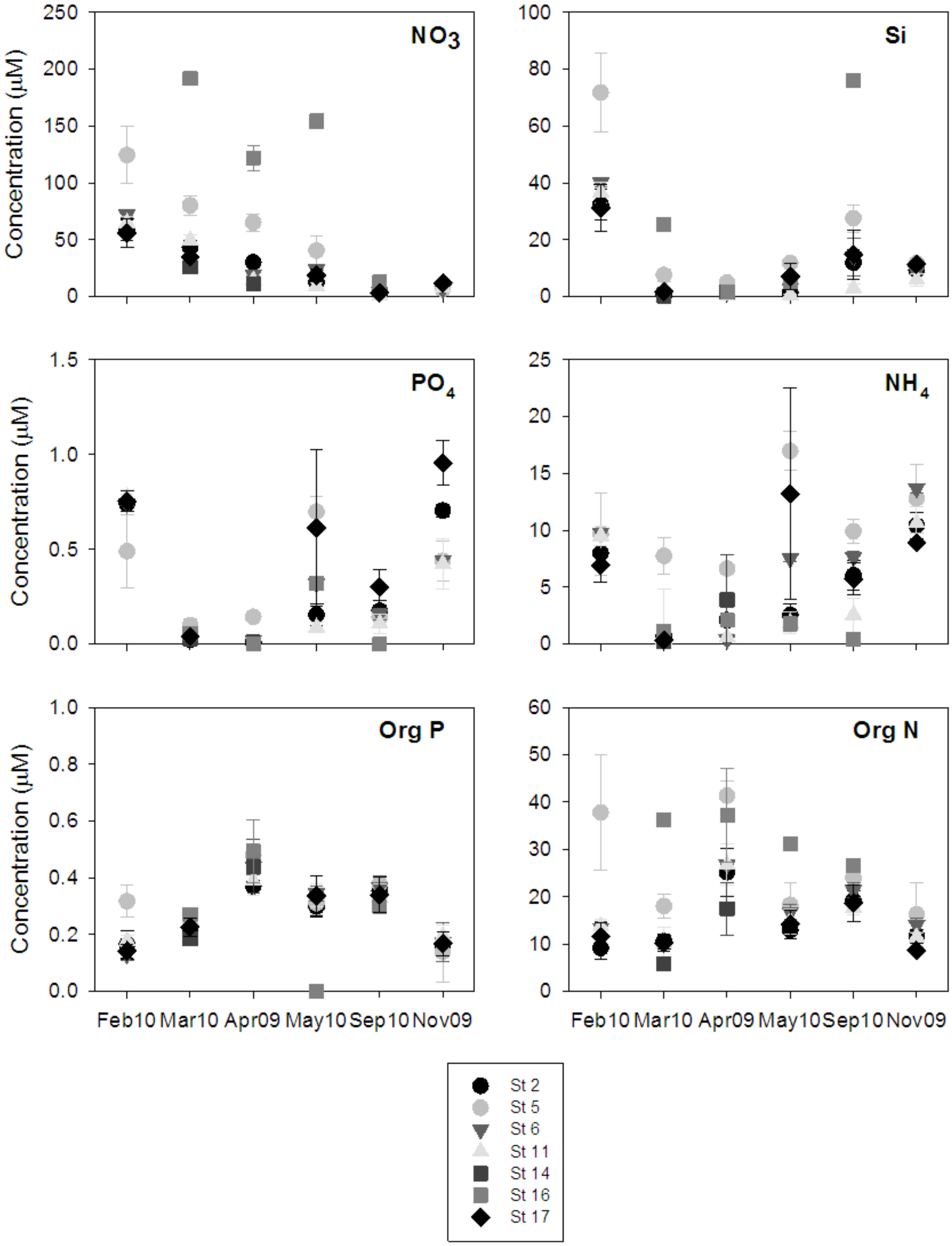

Figure 2. Seasonal variation of the concentrations in the water column of inorganic (NO_3, Si, PO_4, and NH_4) and organic (DOP and DON) dissolved nutrients, including measurements from 2009 and 2010. Average values for all depths and for a full tidal cycle are presented with standard deviations

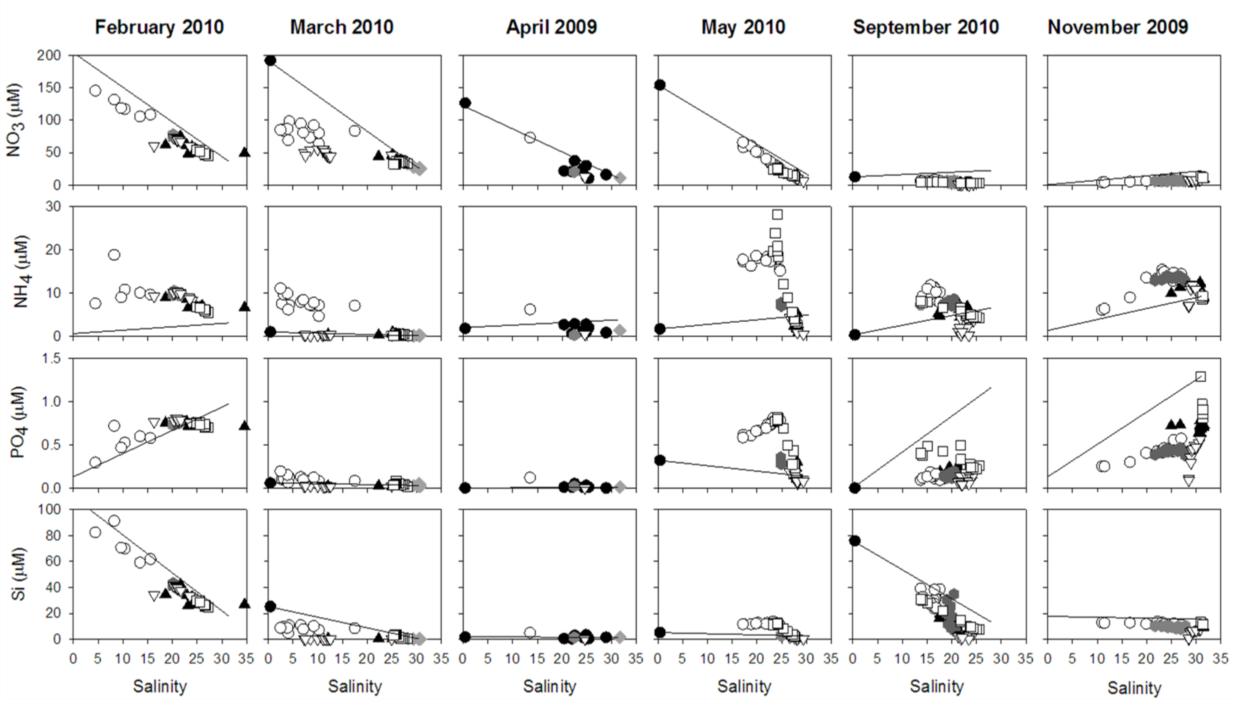

Figure 3. Mixing diagrams for the major inorganic nutrients (NO_3, NH_4, PO_4, and Si) plotted separately for each cruise. Surface values for all sampled stations are presented: station 2 (closed triangles), station 5 (open circles), station 6 (dark grey hexagons), station 11 (open triangles), station 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 eend members as the only process affecting the concentration distribution. The end member concentrations (North Sea and Lake IJssel) were taken from the Rijkswaterstaat Waterbase (live.waterbase.nl)

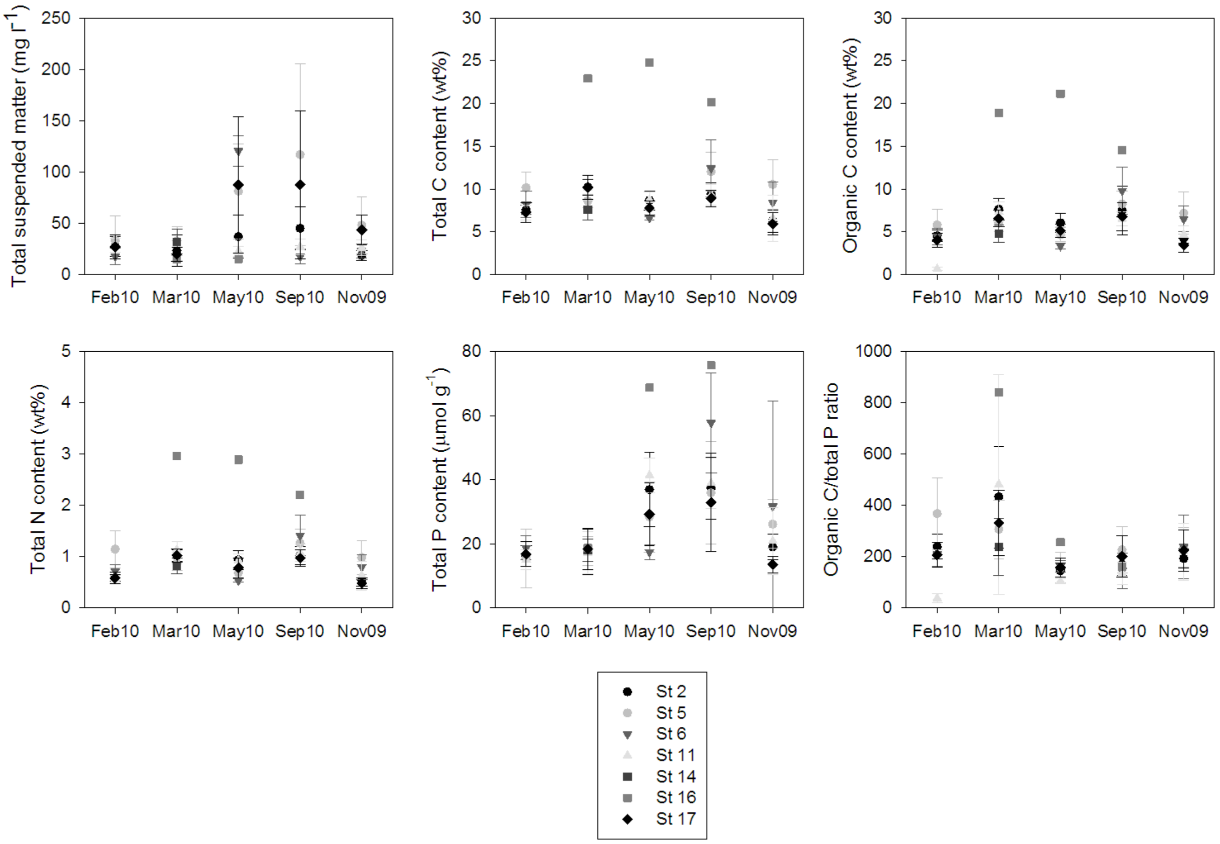

Figure 4. Seasonal variation of the concentration of total suspended matter (TSM), total C, organic C, total N, total P, and organic C/total P ratio in the water column for all seasonally sampled stations. Values presented correspond to an average for all depths and for a full tidal cycle with the respective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

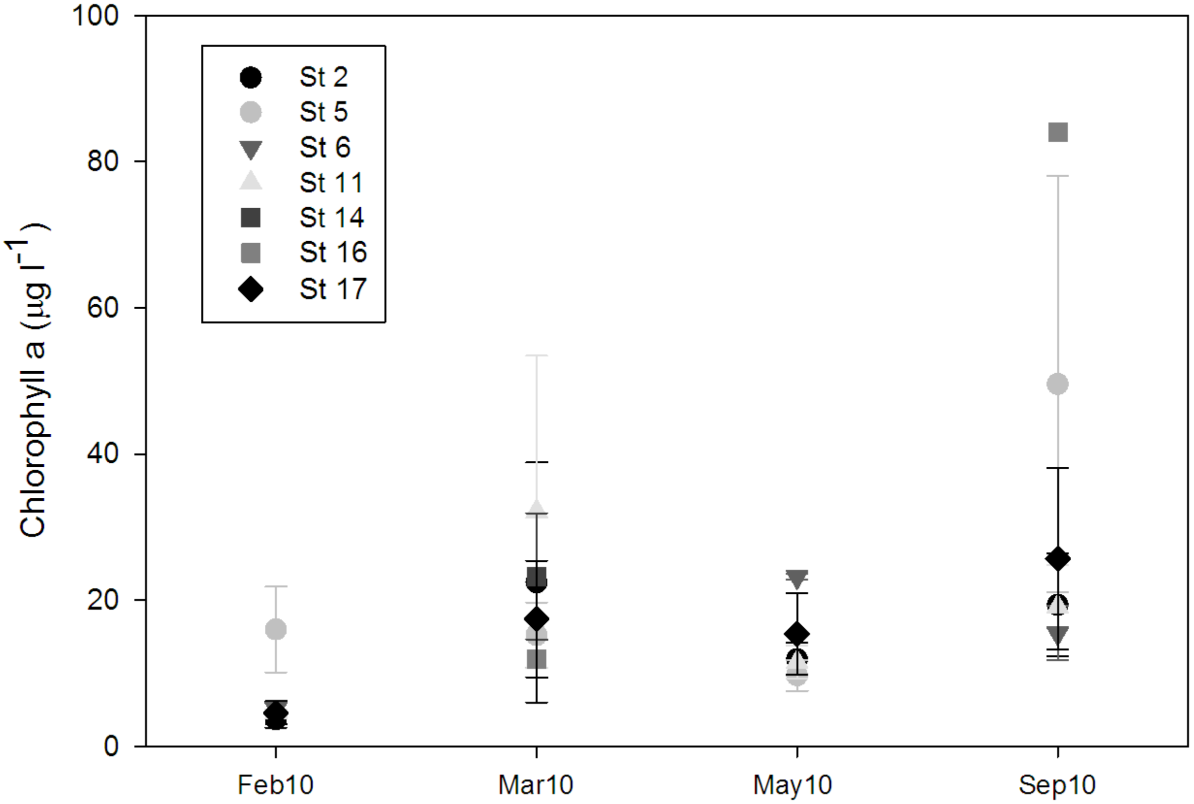

Figure 5. Seasonal variation in the concentrations of chlorophyll *a* in the water column for all the seasonally sampled stations. The plot includes the average values for all depths and for a full tidal cycle with the respective standard deviations

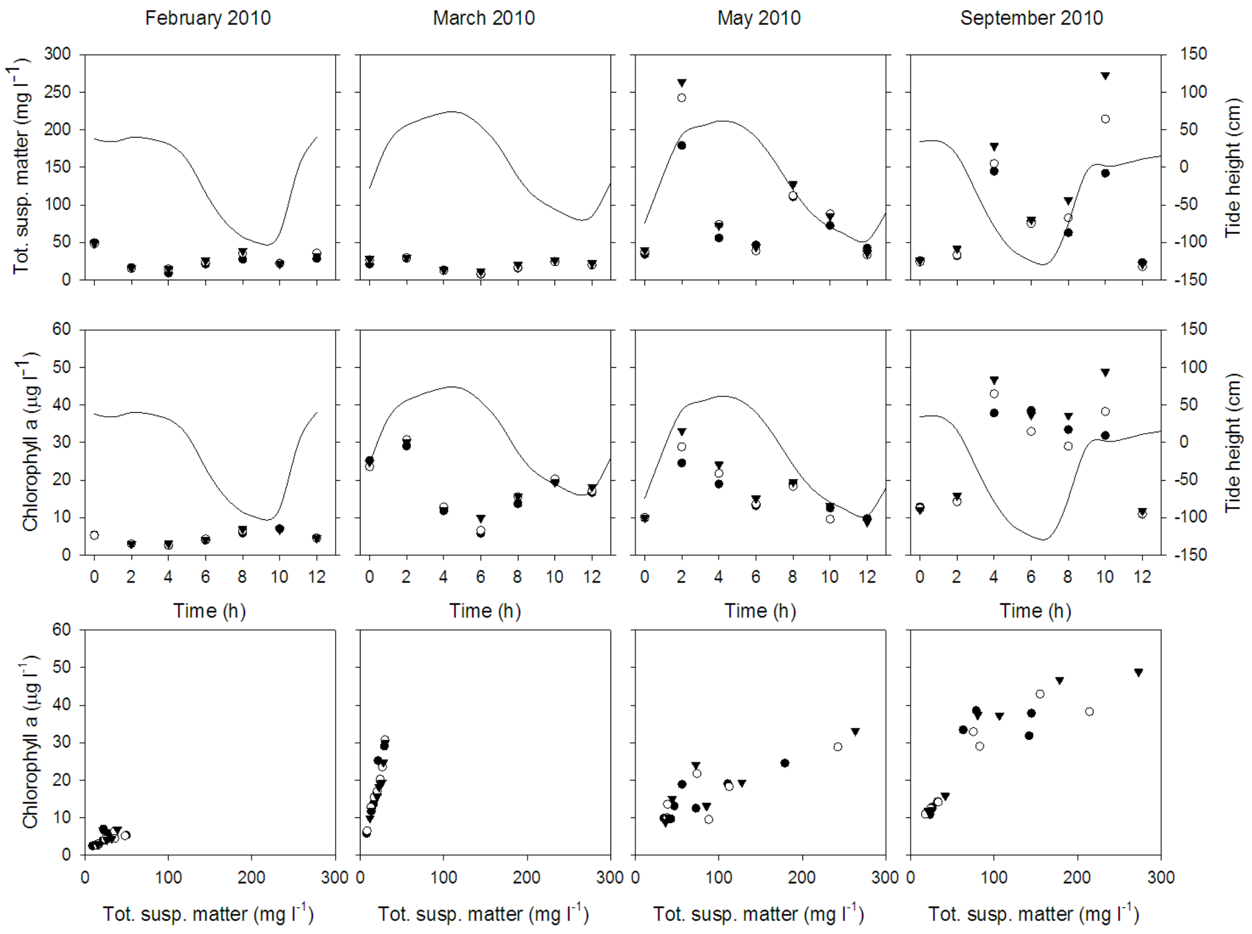

Figure 6. Total suspended matter (TSM) and chlorophyll *a* concentrations plotted for a full tidal cycle and chlorophyll *a* versus TSM concentrations. Values presented are for station 17 for surface (closed circles), mid (open circles), and bottom (closed triangles) depth. The line in the first two rows indicates the tide height

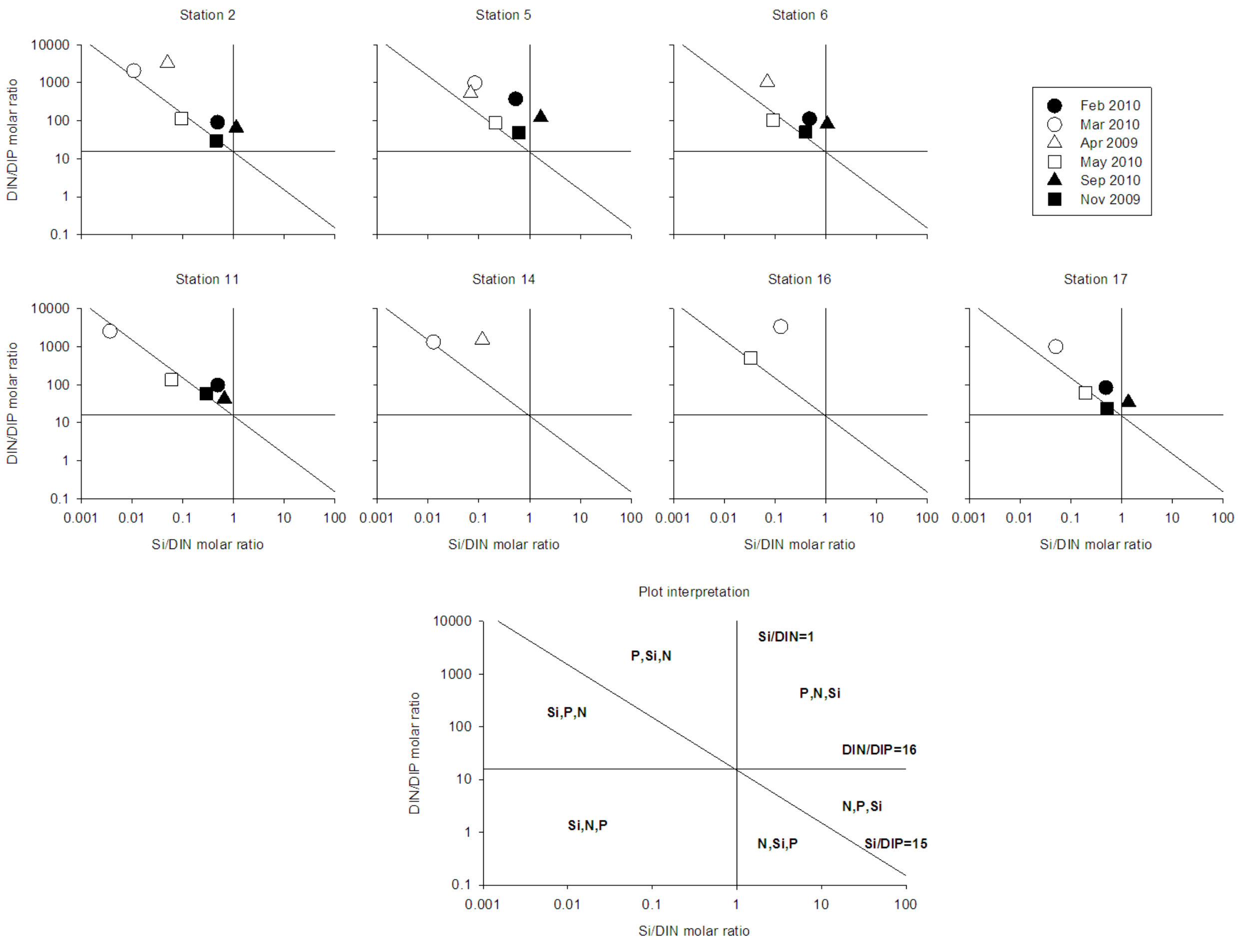

Figure 7. Diagrams based on the Redfield-Brzezinski ratio showing the major nutrient (N, P, Si) limitation (Rocha et al. 2002) throughout the year and plotted separately for each seasonally sampled station. Plotting the DIN/DIP against the Si/DIN molar ratios in the water column and comparing them with the Redfield-Brzezinski ratio allows the definition of "zones" of sequential nutrient limitation. The diagram below indicates those "zones" where, for example, in the lower left quadrant, Si is the main limiting nutrient, followed by N and P

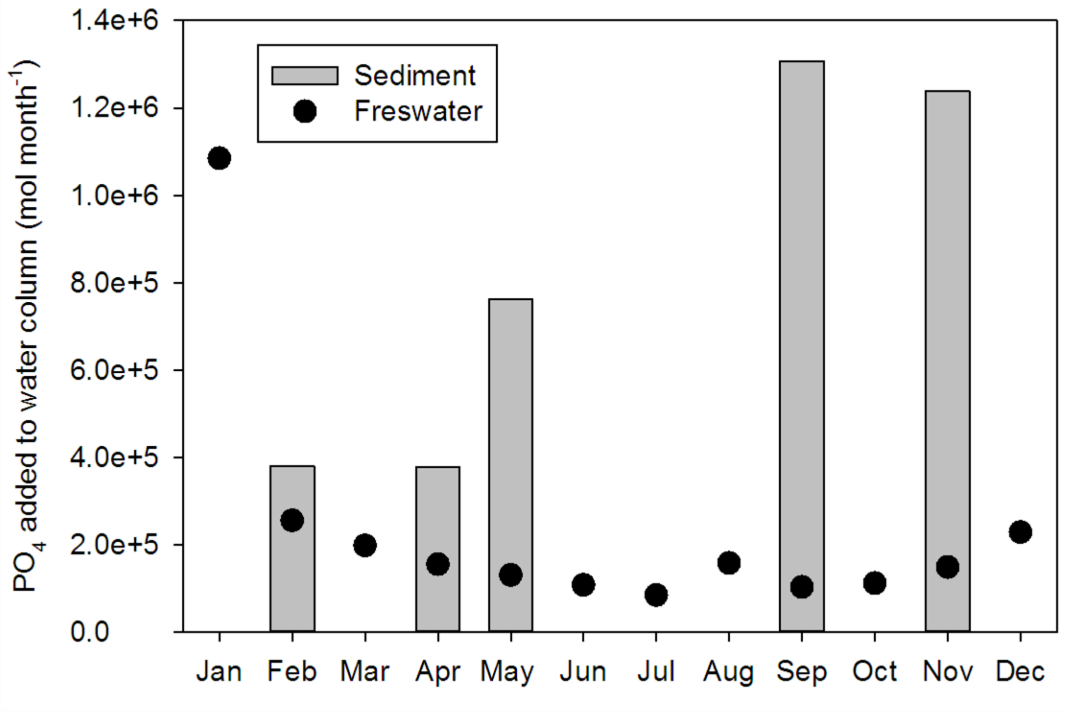

Figure 8. Comparison between the contribution of freshwater (Rijkswaterstaat Waterbase (live.waterbase.nl), assuming discharge from Den Oever, Kornwerderzand, and Den Helder) and sediment release (Leote and Epping 2015) in terms of PO$_4$ loading to the western Wadden Sea