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Seasonal cycling of phosphorus in the southern bight of the North Sea

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Abstract

We have investigated the seasonal cycle of nutrients and the phosphorus speciation, i.e. dissolved inorganic and organic phosphorus (DIP and DOP) and particulate inorganic and organic phosphorus (PIP and POP), for 10 stations in the Belgian coastal zone. The Belgian part of the southern North Sea is strongly influenced by the river plumes of the Rhine, Meuse and Scheldt. In winter, high nutrient concentrations are observed, whereas in April–May these have all been consumed during the spring bloom and silica or phosphorus limitation develops. The phosphate concentrations increase rapidly again in summer-fall, whereas nitrate and silicate return to their winter values much later. This shows the efficient phosphorus recycling that takes place in the water column. The DOP concentration exhibits two peaks during a seasonal cycle: one in April–May when the phosphate concentration is at its lowest and a second one in fall when the POP content decreases. This indicates two periods of increased phosphorus recycling activity. The seasonal cycle of the DOP is different from that of dissolved organic nitrogen (DON).

1. Introduction

The southern bight of the North Sea receives nutrients from domestic, industrial and agricultural wastewater discharge, river inputs and atmospheric deposition. Most of these nutrients are linked to anthropogenic activities that have significantly increased the riverine flux of nitrogen (N) and phosphorus (P) to the coastal zones of the North Sea (North Sea Task Force, 1993). The flux of another major nutrient, dissolved silicate, has remained relatively constant because its major land source is through chemical weathering of silicate minerals. As a consequence, the nutrient ratios in the riverine flux to the coastal zone have drastically changed. This results in a concomitant modification of phytoplankton species composition and thus of the coastal ecosystem. For example, a reduced importance of the diatom bloom and the frequent occurrence of

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massive *Phaeocystis* blooms have been observed (Lancelot et al., 1987).

Turner et al. (2003a, b) reviewed data for dissolved inorganic nitrogen, dissolved inorganic phosphate and dissolved silicate in the world's largest rivers in order to predict future aquatic nutrient limitations assuming the predicted increase in fertilizer use (which has a N:P ratio of 26). The authors found that the coastal areas in northern Europe are most likely to have both P and Si limitation. At the international conference on the protection of the North Sea (London, 1987), all countries surrounding the North Sea agreed on reducing the anthropogenic input of nutrients by 50% between 1985 and 1995 for areas where nutrients cause pollution. As a result of the active reduction of P in wastewaters, the riverine P inputs have declined steadily, whereas this is much less the case for N (Behrendt et al., 2000). Recently, Skogen et al. (2004) ran model scenarios for the years of 1988 and 1989 with reduced nutrient inputs from the rivers to the North Sea. Simulation results indicated that a 50% decrease in the loads of N and P would lead to a decline in the primary production by 10–30% in the southern North Sea. A reduction only in the P load has shown that the primary production in the southern North Sea is limited by P, while N is limiting in the northern North Sea.

Philippart et al. (2000) showed that the phytoplankton community changed drastically in the eutrophic Marsdiep (westernmost inlet of the Wadden Sea) both between 1976 and 1978 and again between 1987 and 1988, whereas it was stable before (1974–1976), in-between (1978–1987) and thereafter (1988–1994). These major changes coincide with changes in absolute and relative (TN:TP) nutrient concentrations. In 1977, the system shifted from a phosphorus-controlled situation, towards a nitrogen-controlled environment, and re-shifted towards P control in 1987–1988. This coincidence implies a strong relationship between N:P ratios and the phytoplankton community structure. Phosphate concentrations dropped a little further since 1992 in the Marsdiep and since 1994 (until 2000) a decrease in primary productivity, chlorophyll *a* concentration and *Phaeocystis* cell numbers was observed (Cadée and Hegeman, 2002). These are the first signs of de-eutrophication.

The Belgian coastal zone is greatly influenced by the rivers Rhine, Meuse and the

Scheldt (Van Bennekom and Wetsteijn, 1990; Lacroix et al., 2004). As observed generally in the North Sea, the phosphorus flux decreased more in recent years than the nitrogen flux from the Scheldt to the Belgian coastal zone. The maximal annual total nitrogen load was reported to be 34 kt in 1993 and the annual phosphate (PO_4) load supplied by the river Scheldt to the Belgian coast was at average 1 kt between 1990 and 1993, whereas about 2 kt were supplied in the 1980s (Lenhart, 1996). Two major phytoplankton communities, the diatoms and *Phaeocystis*, dominate the nutrient removal in the Belgian coastal zone during the spring bloom. Tungaraza et al. (2003) measured the nutrient concentrations at station 330 (51°26 N, 2°48 E) in the Belgian coastal zone between late winter and early summer in 1996 and 1997. They found that the PO_4 concentrations ranged from 0.1 to 3.4 μM and 0.3 to 1.7 μM in 1996 and in 1997, respectively, and did not show pronounced seasonal patterns. Silicate and nitrate, on the other hand, showed clear seasonal variations with the lowest concentrations observed at the end of spring and during summer. Rousseau et al. (2002), however, did observe a seasonal pattern in the phosphate concentrations at station 330 in 1995. The PO_4 concentration started to decrease between February and March with the onset of the early-spring diatom bloom. In the second half of May, the decline in the *Phaeocystis* and *Rhizosolania* spp. bloom corresponded to the lowest DIN (3.3 μM), $Si(OH)_4$ (0.9 μM) and PO_4 (0.03 μM) concentrations recorded during spring. The lowest seasonal pCO_2values coincide with the *Phaeocystis* bloom and the lowest nutrient levels (Gypens et al., 2004).

These studies, however, focussed mainly on the role of nitrogen, silicon and carbon in the Belgian coastal zone and the only phosphorus species measured was PO_4. Little research has been devoted to the phosphorus cycle in the Belgian coastal zone, while this element is an important and potentially limiting nutrient. Also with the changing N:P ratio of the riverine fluxes, recent data are required to assess the present nutrient situation of the ecosystem. In this context, we visited during one year (from August 2002 to December 2003) 10 stations located on the Belgian Continental Shelf. Particular attention is given to the speciation of phosphorus, as in the past usually only

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PO_4 was measured and little is known about the role of dissolved organic phosphorus compounds in eutrophied aquatic systems.

2. Materials and methods

2.1. Study site and sampling methods

The study area comprised the Belgian coastal zone of the southern North Sea (Fig. 1). This part of the North Sea is highly influenced by the eutrophied river Scheldt and oceanic water flowing from the Atlantic through the Channel into the North Sea. The 10 stations can be grouped along three near shore-offshore transects: one located close to the mouth of the Scheldt (stations 700, B07, 710 and 780), a second one near the city of Oostende (stations 130, 230 and 330) and a third most southern transect near Nieuwpoort (stations 120, 215 and ZG02). Surface waters were collected with Niskin bottles from 1 m water depth during almost monthly surveys with the *RV Zeeleeuw* in the Belgian coastal zone (Table 1 and Fig. 1). Samples were filtered for dissolved phosphorus speciation, nitrogen speciation and dissolved silicate determination. The particulate phase was collected on filters for the measurement of chlorophyll *a*, suspended matter, carbon and phosphorus species.

2.2. Chlorophyll *a* and particulate organic carbon

Chlorophyll *a* was determined on GF/F filters after filtration of 250 ml seawater under low suction, following the fluorometric method of Yentsch and Menzel (1963). Filters were immediately put in small tubes, wrapped in aluminium foil and stored at −20°C until analysis. For analysis the filters were extracted with 90% acetone at −20°C for 24 h. Samples were centrifuged (10 min, 5500 rpm) and the fluorescence of the extract was measured on a Shimadzu RF-150 fluorometer, using an excitation wavelength of 430 nm and an emission wavelength of 663 nm. The fluorescence was calibrated with a stock solution of pure chlorophyll *a* (Merck).

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Particulate organic carbon (POC) measurements were performed on particulate matter collected by filtration of seawater on precombusted (4 h, 500°C) GF/F filters. POC was measured using a Fisions NA-1500 elemental analyser after carbonate removal from the filters by strong acid fumes overnight. Certified reference materials were used for the calibration.

2.3. Dissolved Si and N species and dissolved organic carbon

Water samples for silicate were taken in plastic bottles and filtered on a plastic filtration set. Dissolved silicate was measured following the method of Grasshoff et al. (1983). Nitrate, nitrite and ammonium were determined colorimetrically. Nitrate and nitrite were analysed with a Technicon Autoanalyzer system following Grasshoff et al. (1983). Ammonium was measured with the indophenol blue technique according to Koroleff (1969). The dissolved organic nitrogen (DON) was determined as the difference between total dissolved nitrogen and the dissolved inorganic nitrogen (nitrate, nitrite and ammonium). Total dissolved nitrogen was measured by wet oxidation in alkaline persulphate (120°C, 30 min) (Grasshoff et al., 1983). The dissolved organic carbon (DOC) was determined with a Shimadzu TOC-5000 analyser using the widely accepted high-temperature catalytic oxidation (HTCO) technique (Sugimura and Suzuki, 1988; Suzuki, 1993).

2.4. Phosphorus speciation

Dissolved phosphorus species were determined after filtration through precombusted (4 h, 500°C) GF/F filters, which were used for the particulate phosphorus speciation. Soluble reactive phosphorus, hereafter phosphate, was measured according to the method of Grasshoff et al. (1983). Dissolved inorganic phosphorus (DIP) was determined as phosphate after digestion with 9N H_2SO_4 (120°C, 30 min). DIP comprises phosphate and polyphosphates, although hydrolysis of acid-labile organic phosphorus compounds may also contribute to this parameter. Polyphosphate was determined as the difference between DIP and phosphate. Total dissolved phosphorus (TDP) was measured by wet oxidation in acid persulphate (120°C, 30 min) (Grasshoff et al., 1983). Dissolved organic phosphorus was subsequently calculated as the difference between TDP and phosphate as upper estimate and the difference between TDP and DIP as lower estimate. Filters for the total particulate phosphorus (TPP) determination were combusted at 500°C for 1.5 h with $MgSO_4$ and subsequently extracted in 1N HCl for 24 h (Solorzano and Sharp, 1980). Filters for particulate inorganic phosphorus (PIP) were extracted in 1N HCl for 24 h. Particulate organic phosphorus (POP) was calculated as the difference between TPP and PIP. The unfiltered water sample was in addition digested by wet oxidation in acid persulphate, which gives the total phosphorus.

3. Results

3.1. Chlorophyll *a*, POC and DOC

The chlorophyll *a* concentration was low from September 2002 until February 2003 after which it increased at all stations (Fig. 2). Peak concentrations in chlorophyll *a* occurred at the end of March and of April 2003. The chlorophyll *a* concentration remained subsequently at a higher level from May to September 2003 compared to the values from September 2002 to February 2003. Finally, the chlorophyll *a* concentration returned to a lower level in December 2003. No data are available between September 2003 and December 2003.

The POC content of the suspended material exhibits a seasonal trend similar to the chlorophyll *a* concentration (Fig. 2). The POC content was relatively low between September 2002 and the end of March/April when it reached its maximum, subsequently it remained relatively high until September 2003 when it returned to its winter values. The highest POC contents are observed at the stations along the Nieuwpoort transect and the lowest at the stations near the mouth of the Scheldt. The measured

POC probably does not only represent the organic carbon in pelagic material but may also contain resuspended sediment especially in periods of stormy weather. The DOC values were determined for September and November 2002 and January, March, April, May and June 2003. The DOC concentration exhibits an increasing trend from its minimum in Novermber 2003 until April 2003, when it reaches its maximum value (Data not shown).

3.2. Dissolved Si and N species

The seasonal pattern in the silicate concentration showed the same trend for all stations (Fig. 3). The silicate concentration was the highest in the months of January and February and reached its lowest values in May. Two general trends can be observed. First, the maximal silicate concentrations observed in winter are higher at the stations on the Scheldt transect close to the mouth of the estuary (700, 710, 780 and B07; 35–48 μM $Si(OH)_4$), than those of the Nieuwpoort transect (120, 215, ZG02; 10–28μM $Si(OH)_4$), the most southwestern transect. The maximal silicate values at the stations of the Oostende transect (130, 230 and 330) lie in between (17–39 μM $Si(OH)_4$). Secondly, the dissolved silicate concentration decreases going from the near-shore to the offshore stations along each transect.

Nitrate is the predominant dissolved nitrogen species of the four N species measured (Fig. 3). The nitrate plus nitrite (hereafter referred to as nitrate) concentration at all stations increased after October 2002 and remained high from December 2002 to February/March 2003 after which it reached its lowest values in May 2003. Similar to the silicate concentration, the maximal nitrate concentrations are higher at stations located close to the mouth of the Scheldt estuary as compared to those along the Nieuwpoort transect. Along each transect, a trend of decreasing nitrate concentration going from the coast seaward is also apparent. The variation in the ammonium concentration with time is less pronounced than for nitrate, but again a minimum in the concentration occurs around April–May 2003 (Fig. 3). Differences in ammonium concentration between the stations are much less distinct than for the silicate and nitrate data. The DON concentrations are the highest in wintertime and start to decrease after March 2004 until they reach their minimum in July (Fig. 3). The DON seasonal patterns for the stations on the same transect are very similar.

3.3. Phosphorus species

Three dissolved P species were determined: phosphate (PO_4), polyphosphates and dissolved organic phosphorus (DOP). The polyphosphate concentration was always very low, generally less than 0.11 μM, and did not show any seasonal or spatial variation (data not shown). The seasonal pattern of the DOP concentration appears to contain two maxima: one around May 2003 and a second one at a higher concentration around August-September 2003 (Fig. 4). The DOP concentration was similar for all stations and usually low compared to the PO_4 concentration, although the DOP concentration exceeded the PO_4 concentration at all stations in the months of April and May 2003. The PO_4 concentration at the different stations shows the decreasing trend along a transect going from the coast to the open sea (Fig. 4). However, the differences in concentration are not as pronounced as observed for the silicate and the nitrate concentrations. At the stations of the Nieuwpoort transect (120, 215 and ZG02) and station 330, the strongest decline in PO_4 concentrations was observed between February and March 2003, whereas the other stations showed a strong decline between March and April 2003. The lowest values for the PO_4 concentration were measured in April at the following stations: 120, 130, 700, 710, 780 and B07, whereas the lowest values at stations 215, 230 and 330 were measured in May 2003. No data are available for station ZG02 in April 2003. The PO_4 concentrations increase in the fall, from August onwards for most stations, reaching the winter values again, in contrast to the seasonal patterns observed for silicate and nitrate.

The POP contents are high when the PO_4 concentrations are low in spring (Fig. 4). The highest values of POP content are observed at the stations further away from the mouth of the Scheldt estuary in contrast to the concentrations of the dissolved nutrients phosphate, nitrate and silicate. The PIP contents at the stations of the “Scheldt” transect are very similar to those of POP as well as the seasonal trend (data not shown). However, at the stations of the other two transects the PIP content is similar to the POP content in the wintertime, but PIP content does not increase in spring as the POP content does.

4. Discussion

4.1. Spatial trends

The spatial distributions of the major nutrients in the Belgian coastal zone result from the mixing of relatively low nutrient-high salinity North Atlantic water flowing northeastward through the Channel into the North Sea with high nutrient freshwater which is discharged from the rivers Rhine, Meuse and Scheldt. The freshwater flows clockwise southwestward along the Dutch and Belgian coast before it mixes with the northeastward flowing Channel water (Lacroix et al., 2004). This water circulation pattern is reflected in the winter nutrient concentrations at the different stations: high nutrient concentrations at the stations on the Scheldt transect as well as the coastal stations 120 and 130, which are located in the Rhine/Meuse and Scheldt plumes and lower nutrient concentrations at the other stations. Basically, it gives a wintertime nutrient gradient in the nearshore-offshore direction and in the northeast-southwest direction.

The lack of a spatial trend in the concentrations of both the DOP and DON at any time suggests that they are produced at sea in the Belgian coastal zone in contrast to the phosphate and nitrate where a concentration gradient going from the northeast towards the southwest indicates the strong influence of the rivers Rhine/Meuse and Scheldt on their winter concentrations. This is also reflected in the DOP and PO_4 concentration versus salinity plots (Fig. 5) where the wintertime PO_4 concentration is dominated by conservative mixing, in contrast to the wintertime DOP concentration.

The intensity of the spring bloom, as reflected by the chlorophyll *a* data (Fig. 2), seems to be evenly distributed over the Belgian coastal zone. There are two pronounced peak values, namely the peak values of station 230 and station B07 at the end of April 2003. General trends as seen in the nutrient distribution, however, are not apparent for chlorophyll *a*. The spatial distribution of the particulate organic carbon and phosphorus contents indicates an increasing trend going from the northeast to the southwest (Figs. 2 and 4). This trend is caused by the dilution of organic-rich pelagic material with relatively organic-poor resuspended sediment at the more turbid stations near the mouth of the Scheldt estuary. It is further supported by the higher suspended matter concentration at the stations on the Scheldt transect and the similar POP concentration at all stations, when expressed in μmol P/l seawater (not shown).

4.2. Seasonal trends in phosphate concentration

Besides the minimum in PO_4 concentration in spring, another minimum is observed in October 2002, which is not accompanied by an increase in POP content or chlorophyll *a* concentration. This minimum is caused by the relative higher contribution of high salinity-low nutrient water from the Channel. Phosphate concentration versus salinity plots for the different months indicate a more or less conservative behaviour in the winter months (October 2002, November 2002, December 2002, January 2003 and December 2003), whereas the biological activity determines the phosphate concentration in spring-summer and summer-fall (Fig. 5).

The largest decrease in the major nutrient concentrations occurs between the end of February and the end of April 2003 coinciding with the largest increase in chlorophyll *a* concentration and particulate organic carbon content (Figs. 2–4). For the northeastern stations (700, 710, 780, B07, 130 and 230) the largest decline in nutrients occurs between the end of March and the end of April 2003, whereas for the southwestern stations the major decrease occurs one month earlier. At the end of the summer the dissolved Si, PO_4 and DIN concentrations increase again when their supply exceeds their consumption. In contrast to the dissolved Si and DIN, the PO_4 concentrations reach their pre-bloom levels again already in the fall. This difference in the seasonal evolution of P versus N and Si was also noted in a compilation of nutrient data from

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1993–2000 in the same area (De Galan et al., in press). Thus, the rate of regeneration and/or supply of phosphorus is higher than that for dissolved Si and DIN in the Belgian coastal zone. One source of these nutrients is river run-off from the Rhine/Meuse and Scheldt. It is not likely that river run-off would deliver more phosphate than nitrate in fall, because nitrate concentrations tend to increase as river flow increases, whereas phosphate concentrations tend to decrease (Balls, 1992; 1994). Another source for nitrogen is atmospheric input, but for phosphorus this is negligible in the North Sea (Brion et al., 2004). Both atmospheric and riverine input would deliver more nitrogen than phosphorus and are therefore not likely to cause the earlier replenishment of phosphate as compared to nitrate in the Belgian coastal zone. In the southern bight of the North Sea, the oceanic/riverine inflow rates of phosphate, nitrate and silicate are insufficient to support their seasonal cycle and therefore internal recycling is required (Prandle et al., 1997). Since the supply of phosphate to the Belgian coastal zone is not higher than that of silicate and nitrate, the difference can be attributed to the internal cycling. Preferential regeneration of P over N and C has already been demonstrated both in the hydrolysis of dissolved organic matter (e.g. Hopkinson et al., 1997; Clark et al., 1998; Vidal et al., 1999) and in the remineralisation of particulate organic matter (Bishop et al., 1977; Garber, 1984; Martin et al., 1987).

4.3. Phosphate being the first limiting nutrient

In estuaries and plume zones, turbidity can cause light limitation of primary production, while nutrient levels remain high. In the Thames plume for example, minimal concentrations of nitrate and phosphate were ca. 7 μM and 1 μM, respectively, but silicate concentrations were strongly depleted in summer and spring, presumably by diatom growth (Sanders et al., 2001). The authors hypothesized that the limited development of non-siliceous organisms, in spite of high residual levels of nitrate and phosphate, was due to a more intense light limitation of non-siliceous compared to diatom growth. Primary production was also strongly regulated by irradiance and nutrients in the Wadden Sea (Colijn and Cadée, 2003). Model results from the Humber estuary indicate that in the plume area the primary production is controlled by light limitation between October and March and by nutrient availability during the rest of the year (Allen, 1997). Typical nitrate and phosphate half saturation constants for coastal phytoplankton populations are ca. 1–2 μM nitrate and 0.1–0.5 μM phosphate and typical half saturation constants for coastal diatom populations are ca. 1–2 μM silicate (Fisher et al., 1988). In our study area, the lowest nutrient concentrations recorded for the individual stations range from <0.01 to 0.13 μM PO_4, from 0.27 to 1.53 μM $Si(OH)_4$ and from 0.37 to 5.48 μM NO_3. The first nutrient to drop below its half saturation constant is phosphate, then silicate and later nitrate, although not at all stations. The consumption of nutrients resulting in such low levels indicates that it is the nutrient that limits the primary production at the time of the phytoplankton bloom and not the light intensity.

We have compiled a table in attempt to give an indication of what the limiting nutrient for phytoplankton growth can be (Table 2). The concentrations of ΣDIN, phosphate and silicate are given in the month when they are the lowest for the individual stations. For some stations, all three nutrients reach their lowest levels in the same month; then only the data of that month are listed and the N:P, Si:P and Si:N ratios are given. When N:P and Si:P are larger than 16, phosphate is likely to be the limiting nutrient. In the case where Si:P<16 and Si:N<1, then silicate is likely to be the limiting nutrient (for diatom growth). When N:P<16 and Si:N>1, nitrogen would be the limiting element. Note that for the four stations near the mouth of the estuary (700, 710, 780 and B07) and station 130, the phytoplankton is first P limited but then becomes Si limited. The stations that are least influenced by the river plumes (ZG02 and 330) are likely to be P limited for phytoplankton growth. Phosphorus limitation of primary production during the early spring bloom was also observed in the Gironde plume (Herbland et al., 1998; Labry et al., 2002), whereas the winter bloom was initiated by light availability (Labry et al., 2001). At no time is the phytoplankton community limited by inorganic nitrogen in the Belgian coastal zone. Also when the N:P ratios are calculated using total dissolved N and P concentrations, e.g. including dissolved organic nitrogen and phosphorus, P is limiting. This is because the DON concentration is more than 16 times that of

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DOP in the months considered. DON always constitutes a large fraction of the total dissolved nitrogen, in contrast to DOP that becomes an important fraction only when the phosphate levels are low. DON representing a major fraction of the total dissolved nitrogen was also reported by De Galan et al. (2004), but a seasonal trend in the DON concentrations was not observed, possibly due to a too low sampling frequency.

4.4. DOP and phosphorus cycling

DOP is an important source of biologically available phosphorus for both bacteria and phytoplankton in marine ecosystems, when the PO_4 concentration is low (Orrett and Karl, 1987; Björkman and Karl, 1994). DOP is not readily available to phytoplankton and bacteria, but it can be utilized as phosphorus source by means of hydrolytic enzymes: the non-specific alkaline phosphatase (Perry, 1972) and 5′-nucleotidase (Ammerman and Azam, 1985; Flynn et al., 1986). Alkaline phosphatase is induced by low PO_4 concentrations and cleaves the $-PO_4$ moiety from organic phosphorus compounds after which the cell can assimilate the PO_4. Van Boekel and Veldhuis (1990) have shown that alkaline phosphatase synthesis in *Phaeocystis* sp. is controlled by the external phosphate concentration and that the threshold concentration for derepression is ca 0.5 μM. Unlike alkaline phosphatase, 5'-nucleotidase recognizes the carbon moiety of nucleotides and is not inhibited at high PO_4 levels.

The wintertime DOP concentrations in the Belgian coastal zone (Fig. 5) are comparable to those reported for the oligotrophic North Pacific Subtropical Gyre (~0.2 μM; Church et al., 2002), the oligotrophic central Atlantic Ocean (0.1–0.3 μM; Vidal et al., 1999) and the northeastern continental shelf of the USA (~0.2 μM; Hopkinson et al., 1997). The elevated DOP concentrations in the Belgian coastal zone are of similar magnitude to those reported for surface waters along the north coast of Australia (Mulholland et al., 2002) and the Southern California Bight (Ammerman and Azam, 1991). DOP concentrations of ~0.2 μM are reported for the Baltic Sea, but higher DOP values of 0.35–0.75 μM were measured in cyanobacterial blooms (Nausch et al., 2004).

When the PO_4 concentration is low, a significant fraction of the dissolved P is present in the form of DOP. Between March and July, when the PO_4 concentration is at its lowest level (Fig. 4), phytoplankton and bacteria may have to turn to DOP as their phosphorus source. In general, it is assumed that elevated dissolved organic matter (DOM) concentrations in surface waters result from enhanced DOM production associated with primary production (Duursma, 1961). This may be due to DOM excretion from cells (Lancelot, 1979), viral mediated cell lysis (Furhman and Shuttle, 1993), sloppy feeding by zooplankton (Eppley et al., 1981) or from particle solubilization (Smith et al., 1992). The seasonal trend in DOP shows 2 periods of elevated concentrations (Fig. 4). The first period is in April for the most southwestern stations and in May for the most northeastern stations. This period of elevated DOP concentration coincides with the lowest PO_4 concentration and the highest chlorophyll *a* concentration and POP content, and therefore corresponds most likely to the period of elevated primary production. The second period of elevated DOP concentration occurs in August-September when the POP content is decreasing strongly and the PO_4 concentration rises again. In this period, the organic phosphorus contained in cells is released upon their lysis and degraded, and the DOP is presumably further remineralised into phosphate. Turk et al. (1992) have demonstrated that bacterial biomass grazed by protozoa plays an important role in the cycling of P, due to the ejection of the consumed bacterial DNA and the subsequent rapid DNA degradation and liberation of PO_4. Thus, the elevated DOP concentrations indicate two distinct periods of intensive P cycling. During the first period P is regenerated and sustains the bloom, and during the second period P is recycled as biomass is decaying.

5. Conclusions

Nutrient and P speciation data obtained by monthly cruises during one complete year were presented for 10 stations in Belgian coastal zone. Spatial and seasonal trends were studied. The rivers Rhine/Meuse and Scheldt have a strong influence on the distribution of inorganic nutrients, but not on that of the DOP and DON.

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At most stations, PO_4 is the first nutrient to decrease below its half-saturation value during the bloom period, thereafter $Si(OH)_4$ and subsequently NO_3. The low nutrient levels indicate that phytoplankton growth is limited by the nutrient and not by the light availability during the bloom. The elemental ratios of N, P and Si suggest that either P or Si limitation of phytoplankton growth could develop, and for the stations on the Scheldt transect first P and later Si limitation. The rate of regeneration of PO_4 is much faster than that of NO_3 and $Si(OH)_4$ so that PO_4 reaches again its wintertime concentrations often in August/September already.

The DOP concentration is elevated at the time of the lowest PO_4 concentration and highest primary production as is also frequently observed for the DOC concentration, but not for DON at our stations. A second period of elevated DOP concentration occurs during the decline of the bloom when POP is degraded and PO_4 levels are restored. Thus, elevated DOP concentrations are indicative for intensive internal cycling of P. Phosphorus regeneration is an important process in the southern bight of the North Sea, which allows phytoplankton growth even at very low PO_4 levels.

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Table 1. Sampling locations and dates.

Station name	Latitude	Longitude	Sampling dates
Nieuwpoort Transect			23 August 2003
120	51°11.1	2°42.0	27 September 2003
215	51°16.5	2°36.8	29 October 2003
ZG02	51°20.0	2°30.0	21 November 2003
			23 December 2003
Oostende Transect			20 January 2004
130	51°16.2	2°54.2	26 February 2004
230	51°18.4	2°51.0	31 March 2004
330	51°26.0	2°48.5	25 April 2004
			26 May 2004
Scheldt Transect			30 June 2004
700	51°22.6	3°13.2	31 July 2004
710	51°26.5	3°08.3	28 August 2004
780	51°28.3	3°03.5	26 September 2004
B07	51°25.9	3°17.9	9 December 2004

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Table 2. Lowest nutrient concentrations observed, N:P, Si:P and Si:N ratios and possible limiting nutrient for each station.

Station	Date	ΣDIN (μM)	DIP (μM)	Si (μM)	N:P ratio	Si:P ratio	Si:N ratio	Limiting nutrient
120	April 2003	14.05	**0.07**	0.92	211	14	0.1	Si
	May 2003	**0.78**	0.19	**0.41**	4	2	0.5	Si
215	May 2003	0.66	<0.01	0.36	>66	>36	0.5	P
ZG02	May 2003	0.73	0.02	0.36	35	17	0.5	P
130	April 2003	16.87	**0.07**	3.63	253	54	0.2	P
	May 2003	**0.60**	0.10	**0.46**	6	5	0.8	Si
230	May 2003	0.37	0.04	0.36	9	9	1.0	?
330	May 2003	1.31	0.01	0.27	116	24	0.2	P
700	April 2003	**5.48**	**0.10**	3.72	53	36	0.7	P
	June 2003	16.37	0.57	**1.53**	29	3	0.1	Si
710	April 2003	1.51	**0.09**	2.27	18	27	1.5	P
	May 2003	1.15	0.13	0.55	9	4	0.5	Si
780	April 2003	3.76	**0.08**	1.95	50	26	0.5	P
	May 2003	**0.92**	0.08	**0.36**	11	4	0.4	Si
B07	April 2003	6.85	0.13	2.79	52	21	0.4	P
	June 2003	**3.30**	0.23	**1.06**	14	5	0.3	Si

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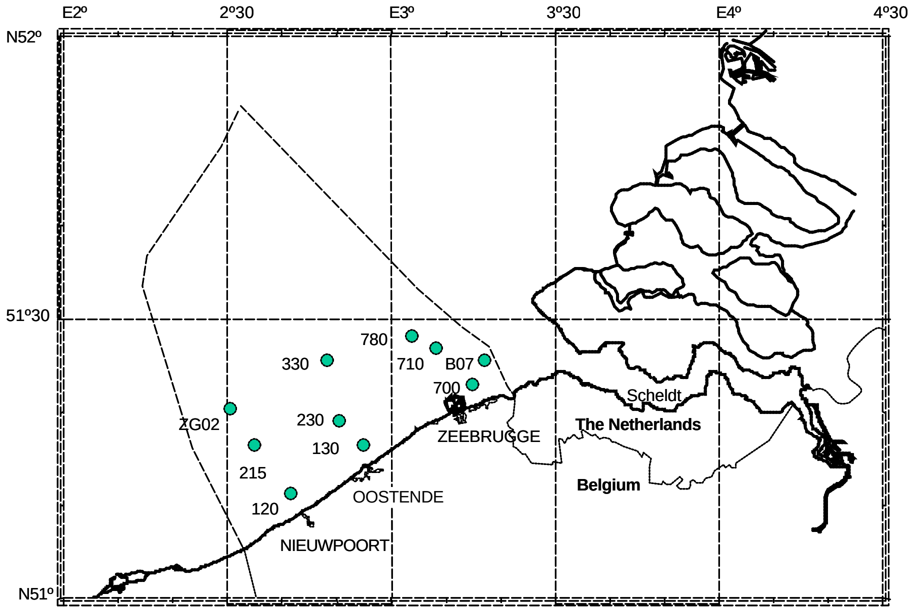

Fig. 1. Map of the Belgian coastal zone indicating the location of the ten stations.

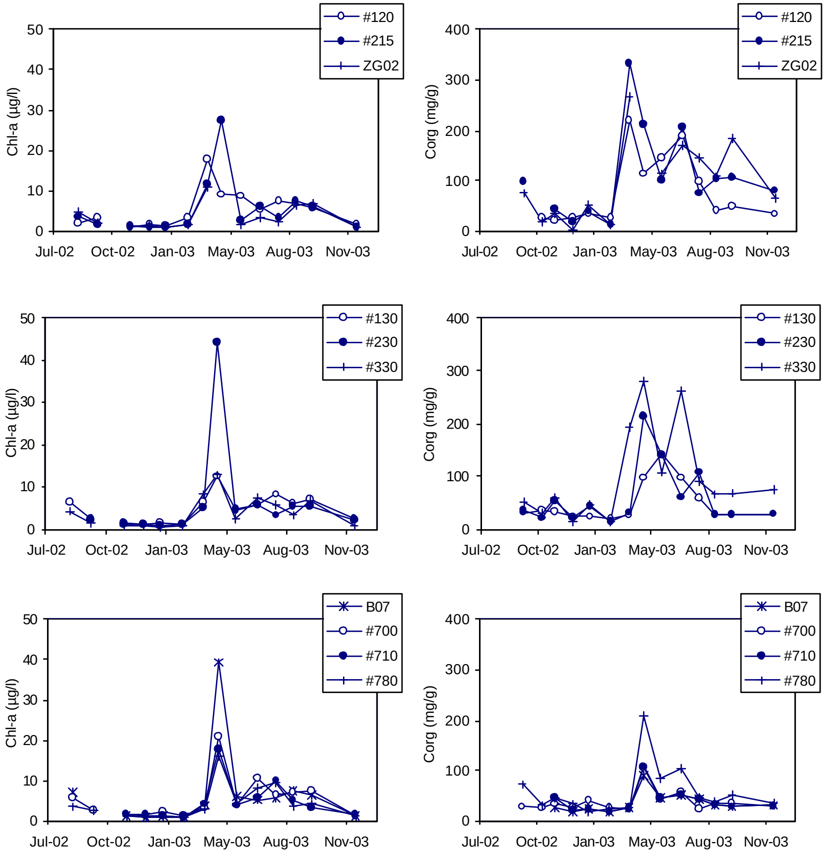

Fig. 2. Seasonal trend in the chlorophyll *a* concentration and in the particulate organic carbon content for the ten stations investigated. The stations are grouped per transect: on the Nieuwpoort transect stations 120, 215 and ZG02, on the Oostende transect stations 130, 230 and 330 and on the Scheldt transect stations B07, 700, 710 and 780.

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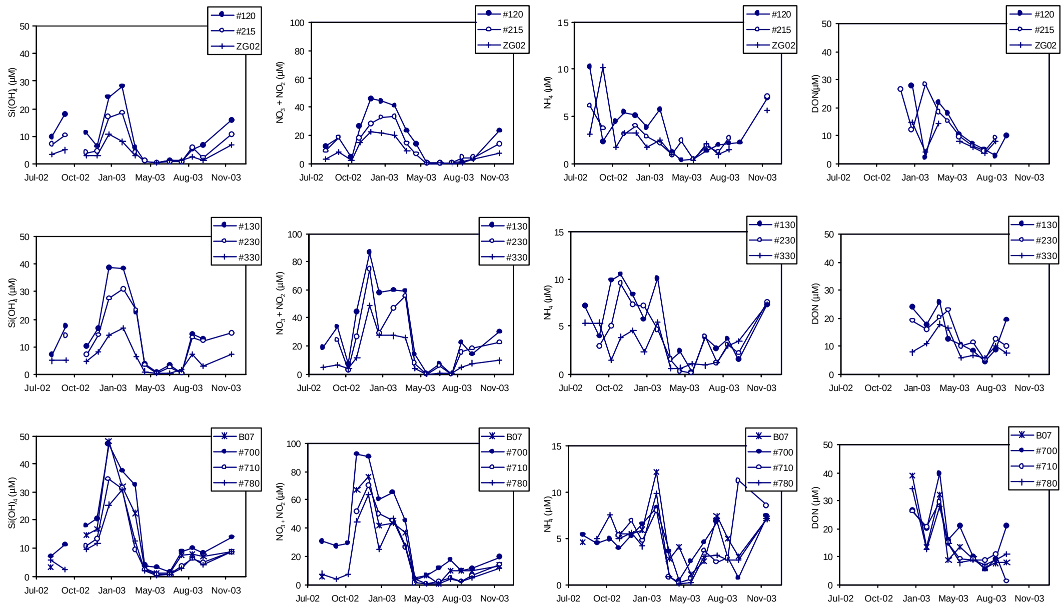

Fig. 3. The seasonal trend in the concentrations of silicate, nitrate, ammonium and dissolved organic nitrogen (DON) for the ten stations.

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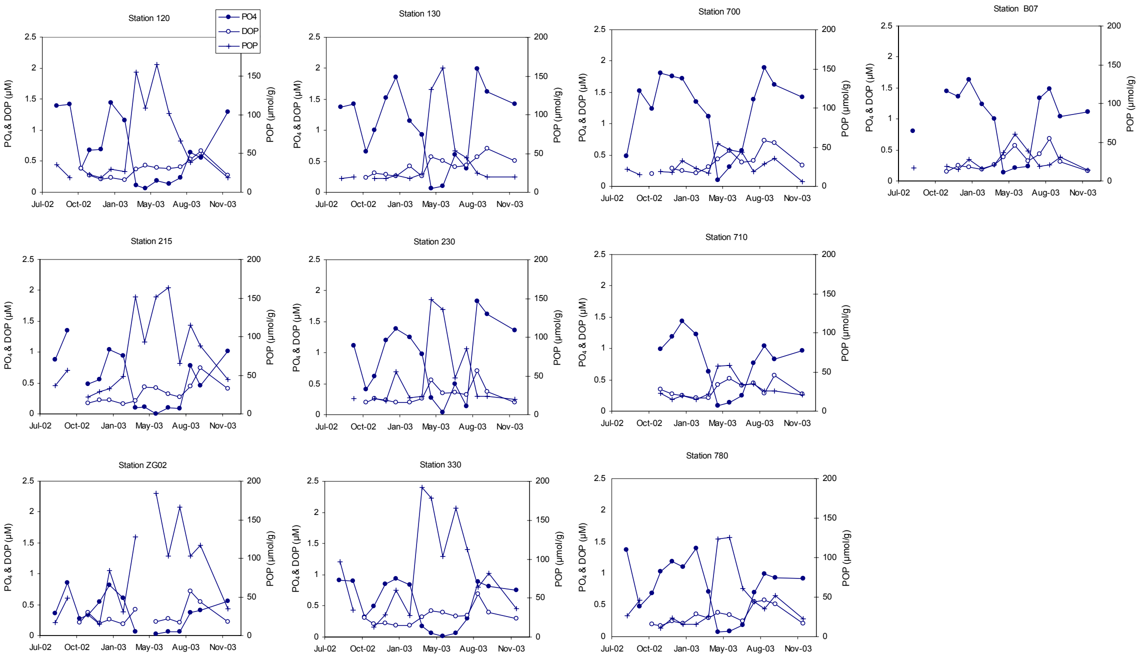

Fig. 4. Seasonal trends in the PO_4 and DOP concentrations and in the POP content for the Nieuwpoort transect (120, 215 and ZG02), Oostende transect (130, 230 and 330) and Scheldt transect (B07, 700, 710 and 780).

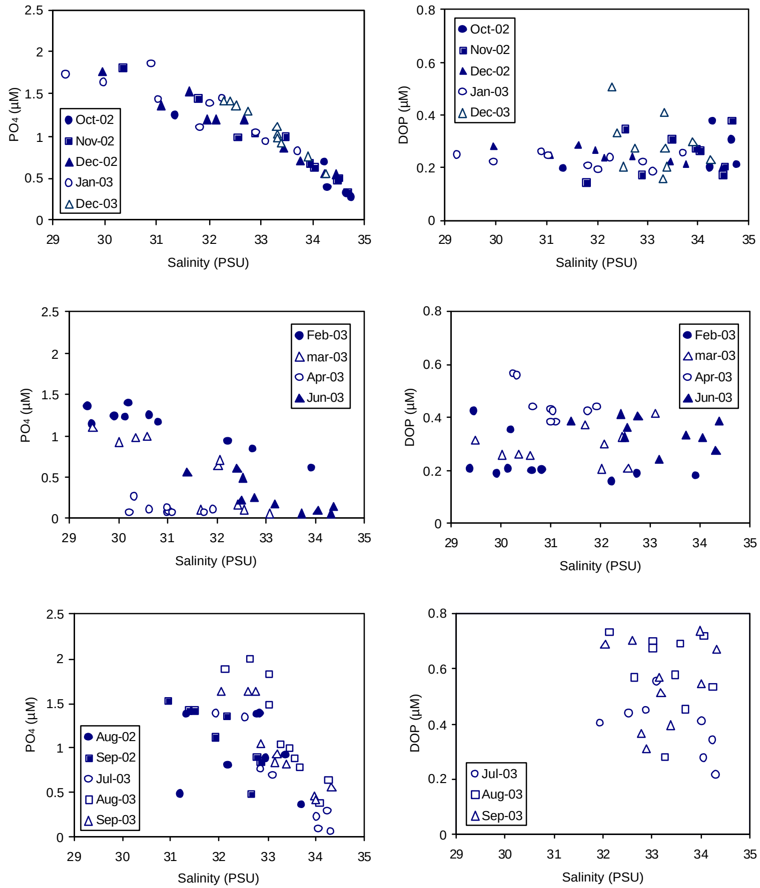

Fig. 5. The PO_4 and DOP concentrations versus salinity, data of all the stations in different months. For the month of May, no salinity data were available. DOP was not determined for the months of August and September 2002.

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