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Spatial and temporal trends in nutrient concentrations in the Belgian Continental area of the North Sea during the period 1993–2000

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Abstract

Statistical analysis of nutrient data obtained during 8 years of monitoring indicated strong seasonal and spatial variability, with highest concentrations in winter and significantly higher concentrations (on average >2 times higher) in the salinity zone $S < 33$ than in the salinity zone $S \geq 33$. In the North Sea ammonium concentrations significantly decreased from 1995 on (47% in zone $S < 33$ and 64% in zone $S \geq 33$), while for nitrate no significant decrease was observed in the zone $S \geq 33$. Despite a drastic reduction (50%) in the riverine inputs of phosphorus to the North Sea during the last decade, phosphate concentrations decreased only slightly in the zone $S < 33$ (<20%). This observation was somewhat similar to what happened with nitrate. Phosphate concentrations were generally low (mean: 0.75 μM; maximum: 2.4 μM) compared to the other dissolved nutrients. Mean nitrate concentrations were about 18 μM but some extreme concentrations, up to 140 μM were observed. Finally, the dissolved organic nitrogen (DON) content represented a major fraction of the total dissolved nitrogen (TDN) (median of 72% for all data), especially in the zone $S \geq 33$, but no significant spatial differences in the DON concentrations were found in the Belgian area of the North Sea.

Keywords: nutrients; DIN; DON; seasonality; spatial variability; Belgian Continental zone; North Sea

1. Introduction

The North Sea is one of the most studied continental shelf seas in the world (Howarth et al., 1994). Geographically it can be considered as an open sea since exchange of water mass with the Atlantic Ocean occurs at the southern as well as the northern ends. The North Sea is characterised as an area with high productivity receiving high input of nutrients from the North Atlantic Ocean. Since the North Sea is surrounded by industrialised and densely populated areas, it also receives high amounts of anthropogenic nutrients via direct wastewater discharge, river runoff and atmospheric deposition (Radach et al., 1990; Brion et al., 2004). Total inputs of N and P to the North Sea are 8870 ± 4860 kT N y^{-1} and 494 ± 279 kT P y^{-1}. The major contributors are the waters flowing from the NW Atlantic (70 ± 40% for N and 87 ± 50% for P), atmospheric deposition (18 ± 8% for N) and the estuaries (9 ± 3% for N and 8 ± 2% for P) (Brion et al., 2004). These inputs can influence the ecological functioning of the North Sea.

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Although nutrients are involved in various biological processes, they are of special importance as they regulate primary productivity in freshwater and marine systems (Laane et al., 1993). High nutrient concentrations can cause eutrophication, which leads to a higher biomass in the system with dramatic consequences (e.g. oxygen depletion) for the water quality (Richardson and Jørgensen, 1996). The Southern Bight of the North Sea is a marine coastal ecosystem where eutrophication has been observed. Due to the increased nutrient inputs, elevated nutrient concentrations have been observed over the years in the coastal zones of the Southern Bight of the North Sea (Van Bennekom and Wetsteijn, 1990; Laane et al., 1993; Jickells, 1998). The most obvious changes in nutrient concentrations and in primary productivity have taken place in the continental coastal waters, but effects have also been seen further away from the major nutrient sources (Soiland and Skogen, 2000). To combat eutrophication and with the aim to achieve a healthy marine environment, the North Sea States made commitments to reduce the input of nutrients in the sea by 50% between 1985 and 1995, but for nitrogen this target was not achieved (OSPARCOM, 2000). The nutrient status of the North Sea has been studied for many years, focusing on the one hand on the increase in concentrations in the coastal zones and on the other hand on seasonal as well as spatial trends onshore and offshore (Postma, 1978; Baeyens et al., 1984; Mommaerts et al., 1984; Brockmann et al., 1988; Laane et al., 1993; Prandle et al., 1997). Several investigations have dealt with the effects of river input on the coastal zone's ecosystem of the North Sea (Van Bennekom and Wetsteijn, 1990; Lenhart et al., 1997).

The main objectives of this study are to (1) identify spatial and seasonal trends in nutrient concentrations in the Belgian Continental zone and (2) investigate the impact of the reduction in nutrient loads from rivers on their levels in this studied area of the Southern Bight of the North Sea.

2. Material and methods

2.1. Study area

Attention is focussed on the Belgian continental shelf of the Southern Bight of the North Sea, a part of the North Sea which is strongly influenced by the English Channel as well as by the rivers Thames, Scheldt and Rhine. A total of 23 stations (Fig. 1) were sampled for nutrients on a regular basis during 8 years (30 cruises) and covering all seasons to determine spatial and temporal fluctuations. Fourteen stations had a sampling frequency of ≥ 20, while the other 9 (all additional stations in the Scheldt plume) had a much lower sampling frequency (mean: 8) as they were introduced much later into the sampling program. The study area is characterised by a water depth less than 30 m, is tide influenced and is well mixed all year round. To describe the spatial and temporal nutrient distribution, a salinity based separation of the data was performed, resulting in a subdivision of the study area into two salinity zones ($S < 33$ and $S \geq 33$) which overlap for 9 of the 23 stations. Distinction between these two areas was made because of the existence of strong salinity gradients perpendicular to the coast due to the freshwater supply by rivers and because the different nutrient concentrations are generally higher in low salinity waters where they are influenced by human activities. For the Belgian area the zone $S < 33$ is strongly influenced by the Scheldt outflow and by coastal inputs. The mixing of estuary water (salinity 28) and seawater (salinity 35) results in a fraction of estuary water of 28.6% at a salinity of 33. The zone $S < 33$ is characterised by a mean salinity of 31.6 and the range is 26.6–32.9. Zone $S \geq 33$ mainly consists of water originating from the English Channel and the salinity in this zone varies from 33.0 to 35.2 with a mean of 34.2.

2.2. Sampling

Sampling cruises for the collection of data were performed aboard the research vessel RV Belgica by the Management Unit of the North Sea Mathematical Models (MUMM) and the Vrije Universiteit Brussel (VUB) during the period 1993–2000. Seawater was sampled from the research vessel RV Belgica with a Niskin bottle at 3 m depth for ammonium, $NO_x^- =$ nitrate + nitrite (referred to as nitrate), phosphate, silicate (referred to as Si) and dissolved organic nitrogen (DON) (data available from 1997 on). Samples for NO_x^-, silicate and DON were stored in acid rinsed polyethylene bottles, after filtration on sterile 0.45 μm cellulose-acetate syringe filters and immediately stored at −20 °C or 4 °C (silicate) until analysis. For phosphate determination, borosilicate glass bottles were used and the samples were stored at 4 °C. Samples for ammonium are collected in acid rinsed Scott bottles and immediately analysed aboard. Additional parameters such as salinity, temperature and oxygen are continuously measured on board the research vessel during each cruise by MUMM with a CTD-probe.

2.3. Analytical methods

Determination of ammonium was based on the indophenol blue complex method (Koroleff, 1969) and the colour formation was measured spectrophotometrically after 24 h by using a 10 cm light path (DL = 0.05 μM; RSD = 5%). Nitrate, phosphate and silicate were analysed with a Technicon™ A-II model auto analyser. Nitrate determination was based on the

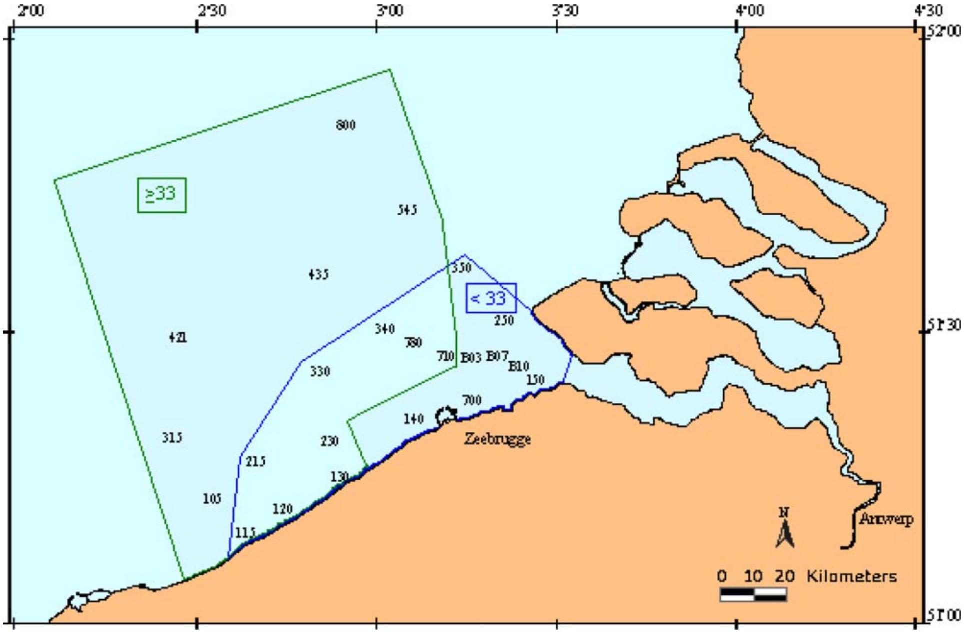

Fig. 1. Geographical location of the sampling stations in the Belgian area of the North Sea and location of the two areas, salinity zone S < 33 and zone S ≥ 33.

sulphanilamide colorimetric method while for phosphate and silicate the methods described by Koroleff (1983a,b) were used. Detection limits for nitrate, phosphate and silicate are 0.05 μM, 0.05 μM and 0.5 μM, respectively, and the precision is 3% for nitrate and phosphate and 6% for silicate determination. DON measurements were performed as described by Dafner et al. (1999) (DL = 3 μM, RSD = 3%). The laboratory participated on a regular basis in the Quasimeme intercomparison exercises for nutrients in seawater and in estuarine water with satisfactory results.

2.4. Statistical analysis

In order to describe the overall and seasonal variability in nutrients during the study period, robust statistical methods were used (Massart et al., 1997). Firstly, descriptive statistics was applied to the data set as a whole, and then to the seasonal data sets, obtained from a sea surface temperature based separation. This sea surface temperature approach resulted in a "seasonal" data set different from the one obtained based on astronomical seasons. When outliers in the data set were detected on the basis of the *Q*-test (Massart et al., 1997), they were removed from the data set. A cusum analysis, i.e. the cumulative sum of the difference between the observed values and the overall mean, was applied to the nutrient data in order to detect patterns of change amongst the randomness. This was achieved in the area S < 33 as well as the S ≥ 33 area. In order to ensure the use of representative values for seasonal and trend analysis, the median rather than the mean values were used. In addition, box-plot profiles were created and a cusum analysis on the median monthly concentration was performed to identify the start and the duration of the vegetative season and to make an estimation of the corresponding nutrient consumption during the bloom period.

3. Results

Detailed descriptive statistics of the studied nutrient concentrations in terms of their overall concentrations as well as their seasonal profiles is summarised in Table 1. Seasonal variations exist for all nutrients, except for DON, and they all follow a similar seasonal evolution pattern: high levels in winter, an important drop in spring, low values in summer and a gradual increase in autumn, sometimes interrupted by a smaller autumn phytoplankton bloom, although, exceptions to this general trend can be observed (ex. ammonium highest in summer). Normality tests (Kolmogorov Smirnov test) on the data sets of zone S < 33 and zone S ≥ 33 (median concentrations were used) indicate that nutrients in both zones are distributed normally at the 99% level of confidence. Hence, a paired *t*-test was used to determine if a significant difference between both zones exists. In addition, a pooled standard deviation was calculated to test the equality of variances. For all inorganic nutrients, the paired *t*-test showed significant differences between zone S < 33 and zone S ≥ 33 at a confidence level of 99% with significant higher concentrations in the former. The values obtained for the pooled standard deviations also indicated a significant

Table 1
Descriptive statistics for the different nutrients studied during a seasonal cycle (values are expressed in μM)

	n	Mean	Stdev	Median	IQR	Min	Max
Ammonium							
Spring	91	2.56	3.66	0.82	2.28	<DL (0.05)	17.5
Summer	113	3.85	3.04	3.49	5.22	0.08	11.8
Autumn	46	2.42	1.93	2.13	2.42	0.07	9.84
Winter	120	3.28	2.85	2.73	3.51	0.07	12.6
All data	370	3.17	3.08	2.28	3.89	<DL (0.05)	17.5
Nitrate							
Spring	98	11.6	19.1	1.74	15.0	0.10	95.6
Summer	113	10.5	10.2	6.58	17.5	0.11	41.0
Autumn	46	17.5	14.8	11.7	21.1	1.35	59.2
Winter	118	31.1	24.2	25.5	27.8	1.94	140
All data	375	18.1	20.4	11.7	23.9	0.10	140
DON							
Spring	44	21.7	11.2	17.9	12.6	<DL (3.0)	63.5
Summer	52	15.6	7.69	13.9	11.6	3.49	37.0
Autumn	12	19.4	7.58	17.3	7.40	8.43	37.8
Winter	16	20.4	10.4	18.4	11.4	<DL (3.0)	47.3
All data	124	18.7	9.72	17.2	10.6	<DL (3.0)	63.5
Phosphate							
Spring	95	0.27	0.25	0.17	0.22	<DL (0.05)	1.42
Summer	108	0.78	0.62	0.58	0.96	<DL (0.05)	2.38
Autumn	44	0.96	0.57	0.76	0.90	0.28	2.28
Winter	111	1.04	0.47	0.94	0.65	0.30	2.42
All data	358	0.75	0.58	0.63	0.85	<DL (0.05)	2.42
Silicate							
Spring	77	3.47	3.00	2.64	3.15	<DL (0.5)	14.8
Summer	92	6.32	5.79	4.53	7.93	<DL (0.5)	27.8
Autumn	44	10.4	6.72	7.94	10.6	2.08	26.8
Winter	116	12.4	8.96	9.82	13.3	1.01	39.7
All data	329	8.33	7.65	5.87	8.90	<DL (0.5)	39.7

difference in variance at the 99% significance level between both areas for all inorganic nutrients. Details of the data analysis are given in Table 2. Cusum analysis shows that only for ammonium a significant decrease at the 99% significance level was observed in the $S < 33$ and the $S \geq 33$ areas during the past 8 years. For all the other nutrients the weak changes are not significant.

Significant changes in nutrient concentrations were identified at the end of March corresponding with the start of the spring phytoplankton bloom and during autumn in both salinity areas (Fig. 2). These differences are at least a factor 2 for DIN and Si and even a factor 4 for phosphate in zone $S < 33$. In zone $S \geq 33$ this difference is a factor 2 for Si and a factor 4 for phosphate while for DIN a difference factor of at least 5.5 is observed. A small difference in the length of the growing season exists between both zones and between nutrients. Although nutrient concentrations sometimes reached limiting values at certain periods of the year, they were never exhausted in both areas.

3.1. Ammonium

Concerning ammonium, the most reduced N compound, the majority of the area was marked by relatively low concentrations with a mean of 3.17 μM but high concentrations up to 17.5 μM have been measured (Table 1). The seasonal pattern indicates lowest concentrations in spring due to the development of the phytoplankton bloom as a result of increasing sunlight and temperature. The growth of phytoplankton was accompanied with the consumption of the available nutrients and ammonium was preferentially used by phytoplankton before nitrate due to the higher energy requirements for nitrate uptake. Ammonium concentrations increased towards summer due to the high remineralisation rate of the particulate material after the bloom period. At the end of summer these concentrations slightly decreased again, due to a second phytoplankton bloom, and stayed rather constant during autumn and winter. Somewhat surprisingly the maximum value of all seasons was found in spring

Table 2
Statistic results for the data analysis (t-test and F-test) for zone $S < 33$ and zone $S \geq 33$ (median data are used)

	Ammonium		Nitrate		DON		Phosphate		Silicate	
	$S < 33$	$S \geq 33$	$S < 33$	$S \geq 33$	$S < 33$	$S \geq 33$	$S < 33$	$S \geq 33$	$S < 33$	$S \geq 33$
t-test: paired two sample for means, $\alpha = 0.01$										
Mean	4.18	1.68	32.8	7.35	20.9	15.2	1.18	0.44	13.7	4.68
Variance	9.51	2.31	319	48.1	42.5	15.4	0.38	0.08	81.8	13.8
Observations	30	30	30	30	11	11	28	28	26	26
Pearson correlation	0.69		0.72		0.18		0.75		0.71	
Hypothesized mean difference	0		0		0		0		0	
df	29		29		10		27		25	
t stat	5.91		10.18		2.75		8.71		6.59	
P ($T \leq t$) two-tail	2.05 E-06		4.43 E-11		0.021		2.55 E-09		6.60 E-07	
t critical two-tail	2.76		2.76		3.17		2.77		2.79	
F-test: two-sample for variances, $\alpha = 0.01$ (pooled stdev)										
Pooled variance	4.82	5.31	245	51.7	112	22.3	0.26	0.45	17.2	17.8
F	4.11		6.65		2.71		4.93		5.92	
P ($F \leq f$) one-tail	0.00014		1.06 E -06		0.066		4.13 E -05		1.61 E -05	
F critical one-tail	2.42		2.42		4.85		2.49		2.60	

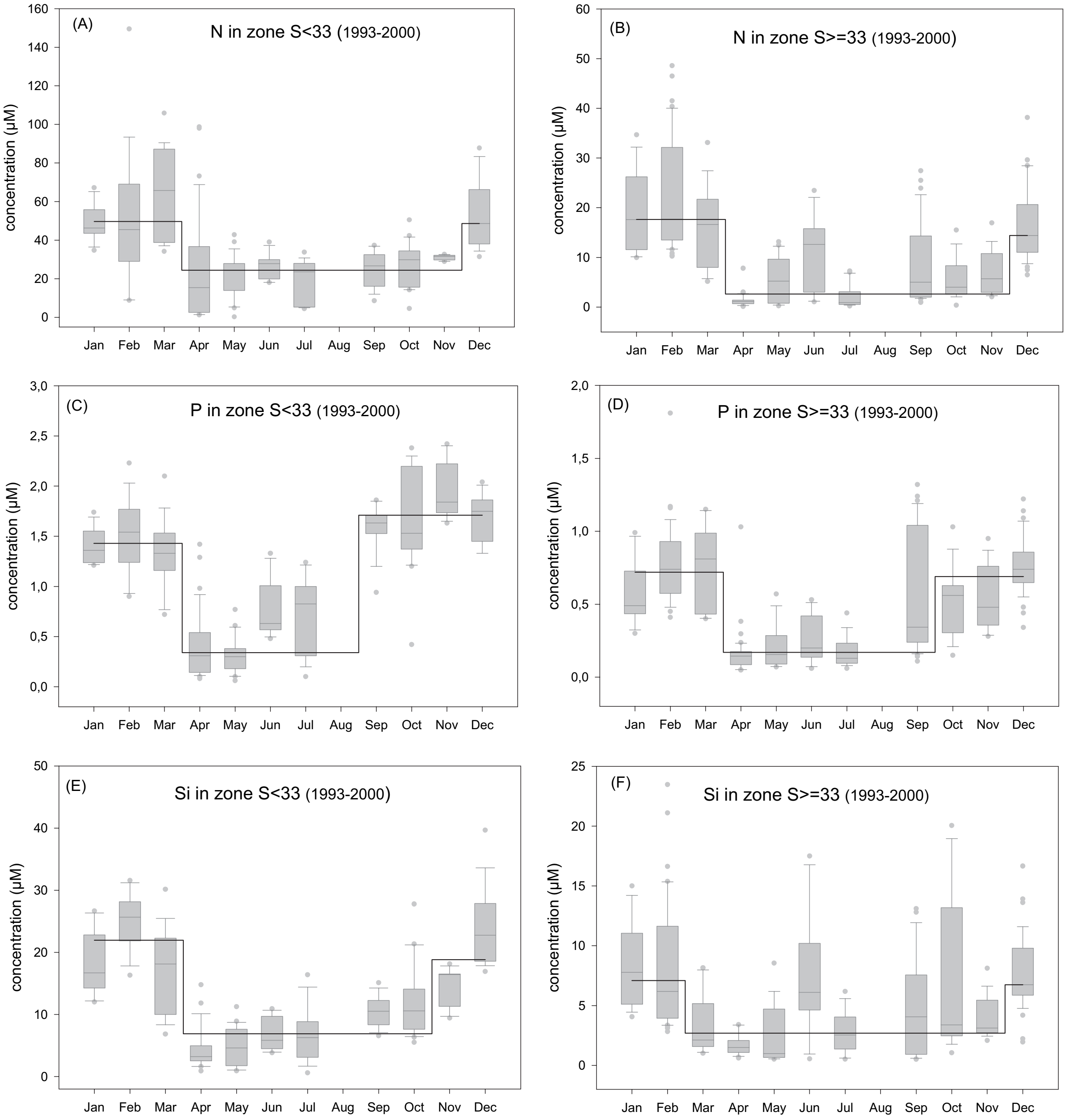

Fig. 2. Monthly box-plot for the seasonal variation in DIN (A, B), phosphate (C, D) and silicate (E, F) concentrations (μM) in zone S < 33 (A, C, E) and zone S ≥ 33 (B, D, F). Black line represents the significant variation in the median concentration obtained from a cusum analysis.

although the lowest mean value was also observed in that season. Only few sampling points in spring have high concentrations as proved by comparing the median value of 0.82 μM with the mean concentration of 2.56 μM.

From Fig. 3 and Table 2 it is obvious that there was a significant difference ($t = 5.91$; $p[\leq T_{\mathrm{crit}\ 99\%}] < 0.001$) in ammonium concentrations between the two studied areas. The overall mean concentration was 4.18 μM in zone S < 33, while this was only 1.68 μM in zone S ≥ 33. Another important feature is that the ammonium concentrations show a distinct evolution during the last 8 years. Ammonium concentrations during the first part of the study period were rather high in both areas (6.26 μM in zone S < 33 and 3.16 μM in zone S ≥ 33) and even slightly increased, but this short period was followed by an important decrease which started at the end of 1994. The critical test value obtained from the cusum test even indicates that the observed decrease is significant at the 99% significance level for both areas. A reduction of 47% in zone S < 33 was obtained and in zone S ≥ 33 this reduction even amounted to 64%.

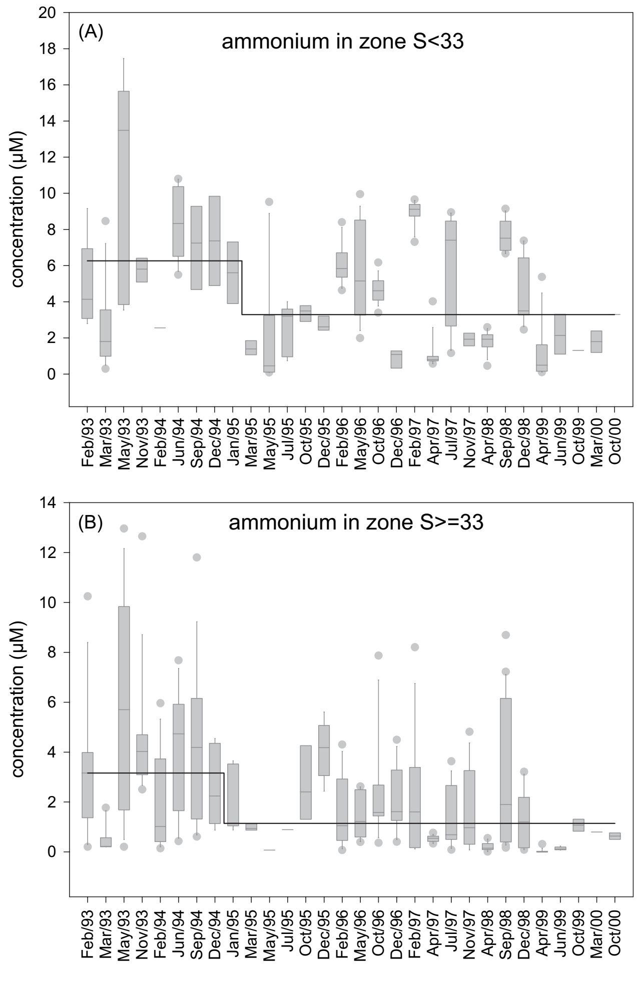

Fig. 3. Box-plot for the variation in ammonium concentration (µM) from 1993 to 2000 in zone S < 33 (A) and zone S ≥ 33 (B). Black line represents the significant variation in the median concentration before and after the change as obtained from a cusum analysis.

3.2. Nitrate

From the different dissolved inorganic nutrients studied, the dominant compound in the Belgian area of the North Sea is nitrate. It is also the compound, which showed the highest variability of all dissolved nutrients. Nitrate concentrations were almost always higher than 20 µM independent of the season for marine stations directly under influence of the Scheldt. The stations close to the coastal plume also exhibited relatively high nitrate concentrations but concentrations decreased slowly towards the west. The mean winter stock observed in this study was around 30 µM and this stock decreased strongly with the spring phytoplankton bloom (up to 160 mg N m^{-2} d^{-1} end of the 1970s (Baeyens et al., 1984)) and the utilization of the available nitrate was extended until the end of summer. After this, concentrations built up during autumn and winter. In brief, mean nitrate was around 11 µM in spring and summer and started to increase to 17 µM in autumn.

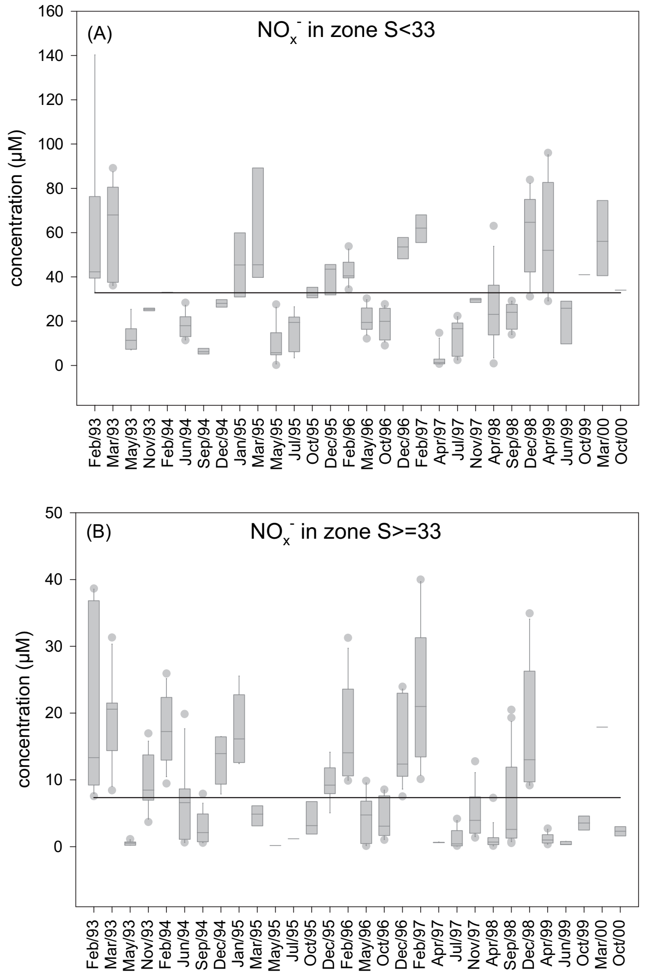

Fig. 4. Box-plot for the variation in NO_x^- concentration (µM) from 1993 to 2000 in zone S < 33 (A) and zone S ≥ 33 (B). Black line represents the median concentration for the whole period.

Nitrate concentration and variation in zone S < 33 and zone S ≥ 33 was clearly not identical (Fig. 4). Statistical comparison showed significant differences in terms of concentrations as well as in terms of variances (Table 2). In the zone S ≥ 33 mean nitrate value for the whole study period was 7.35 µM while in the zone S < 33 the mean nitrate concentration was more than 4 times higher (32.8 µM). These relatively high nitrate concentrations in zone S < 33 are mainly due to the Scheldt river input. The nitrate concentration at the mouth amounts to 53.5 µM. In addition, differences between the mean concentrations of both areas were most perceptible during winter period.

Trend analysis on the nitrate data set 1993–2000 indicates that in the zone S < 33 an initial increase (beginning of 1993) was immediately followed by a slight decline or levelling off in nitrate concentrations until 1998, after which again a slight increase is observed. The zone S ≥ 33 is marked by a complete absence of any trend. The weak decrease for nitrate is not significant at the 95% significance level.

3.3. Dissolved inorganic nitrogen

The seasonal profile for DIN given in Fig. 2 indicates that a significant decrease of 25.2 μM DIN in zone $S < 33$ and of 15.0 μM DIN in zone $S \geq 33$ was observed at the end of March indicative of the start of the spring phytoplankton bloom. After this significant drop, DIN concentration stayed rather constant for a long period (till the end of November) and was then followed by a significant increase. In December, the DIN concentration was restored to a value of 48.7 μM in zone $S < 33$ and to a value of 14.4 μM in zone $S \geq 33$. This important change in DIN corresponds to a total consumption of 5.3 g N m^{-2} in zone $S < 33$ (mean depth 15 m) and of 4.2 g N m^{-2} in zone $S \geq 33$ (mean depth 20 m) averaged over the period April–November.

3.4. Dissolved organic nitrogen

The DON concentrations in this study, measured since July 1997, did not show a clear seasonal trend (Table 1 and Fig. 5). DON concentrations varied between DL (3 μM) and 63.5 μM for the entire area, although 80% of the data had DON concentrations lower than 25 μM. The spatial variability for DON was also poor. Slight differences, although not statistically significant (Table 2), were observed between the zone $S < 33$ and the zone $S \geq 33$ with mean concentrations of 20.9 ± 6.5 μM and 15.2 ± 3.9 μM, respectively. A reversal of the general pattern of slightly higher concentrations in zone $S < 33$ compared to zone $S \geq 33$ was not valid in October 1999 and March 2000 and could be indicative of a declining trend in DON concentrations in zone $S < 33$, but this assumption should be taken with care as it concerned only two sampling campaigns and few sampling points.

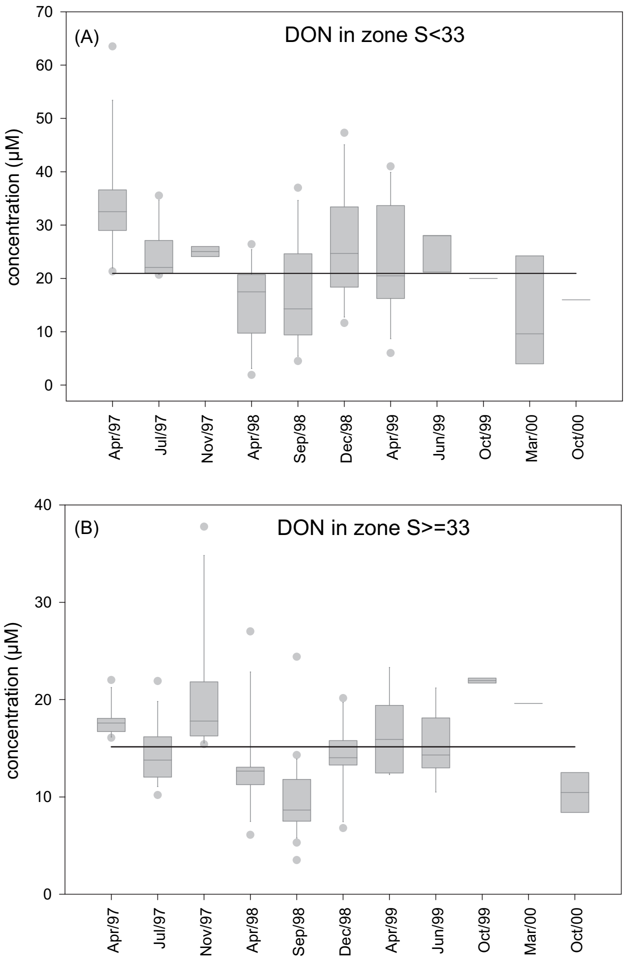

Fig. 5. Box-plot for the variation in DON concentration (μM) from 1993 to 2000 in zone $S < 33$ (A) and zone $S \geq 33$ (B). Black line represents the median concentration for the whole study period.

According to Bronk (2002), the most important fraction of the total dissolved nitrogen pool consists of DON, averaging 60–69%. In the Belgian waters a mean DON fraction of 64.3 ± 27.7% (Table 3) was observed which corresponds very well with this mean value. This occurred in the period when biological activity was at a maximum, thus the available dissolved inorganic nutrients are consumed and this production increases the DON pool considerably. Some pronounced differences concerning the DON fraction existed between the stations in zone $S \geq 33$ and the stations in the other zone. An important difference was the fact that the DON fraction was much higher in zone $S \geq 33$. Seventy-five percent of the data in that area had values higher than 70% DON while in the zone $S < 33$ this was only 23% of the data. The lowest observed fraction value in the zone $S \geq 33$ was 22.7% DON while in zone $S < 33$ 15% of the data showed values lower than 22.7%. On a seasonal time scale, the DON fraction was most important between April and June except in 2000, especially in zone $S \geq 33$. This was the period when biological activity was at a maximum, the available dissolved inorganic nutrients were consumed and thus production increased the DON pool considerably. Another important feature observed in zone $S < 33$ (Fig. 6) was that the organic fraction of the TDN showed a declining trend in time accompanied with an increase in the

Table 3
Data analysis for the DON fraction (%) in zone $S < 33$, zone $S \geq 33$ and the entire Belgian Continental Plate

% DON of TDN pool	Zone $S < 33$	Zone $S \geq 33$	All data (BCP)
n	53	71	124
Mean	46.9	77.3	64.3
Standard deviation	25.8	21.4	27.7
Median	38.8	86.1	73.7
25% quartile	27.7	70.6	37.3
75% quartile	64.2	93.3	90.6
Minimum	10.7	22.7	10.7
Maximum	95.6	98.3	98.3

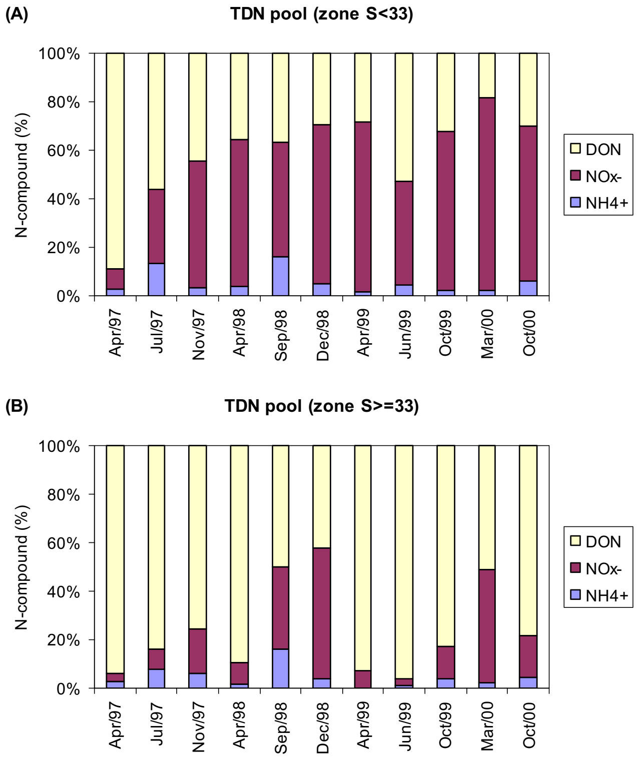

Fig. 6. Temporal evolution of the different fractions (DIN and DON) of the TDN pool expressed in % in zone $S < 33$ (A) and zone $S \geq 33$ (B) from 1993 to 2000.

inorganic nitrate fraction. This decreasing trend of DON fraction was not perceptible in zone $S \geq 33$.

3.5. Phosphate

Phosphate concentrations were generally low all over the year (mean: 0.75 μM) with highest values observed in autumn and winter and lowest in spring (Table 1). Distinct differences in terms of concentrations were observed between both zones (Fig. 7). In zone $S \geq 33$, mean phosphate was 0.44 ± 0.28 μM, while in zone $S < 33$, phosphate was at least 2 times higher (1.18 ± 0.62 μM). The *t*-test (Table 2) shows that the higher concentrations in zone $S < 33$ relative to those in the other zone were statistically significant. Fig. 2 indicates that in early spring (end of March) a decrease in phosphate was observed of 1.09 μM and of 0.55 μM in zone $S < 33$ and zone $S \geq 33$, respectively. This corresponds with the consumption of 506 mg P m^{-2} in zone $S < 33$ and of 341 mg P m^{-2} in zone $S \geq 33$. Phosphate concentrations started to increase again at the end of August in zone $S < 33$ to a median value of 1.7 μM and at the end of September in zone $S \geq 33$ to a value of 0.69 μM; this was much earlier than for DIN and silicate. These phosphate consumption rates together with those calculated for DIN result in an N:P assimilation ratio of 10.4 in zone $S < 33$ and of 12.35 in zone $S \geq 33$.

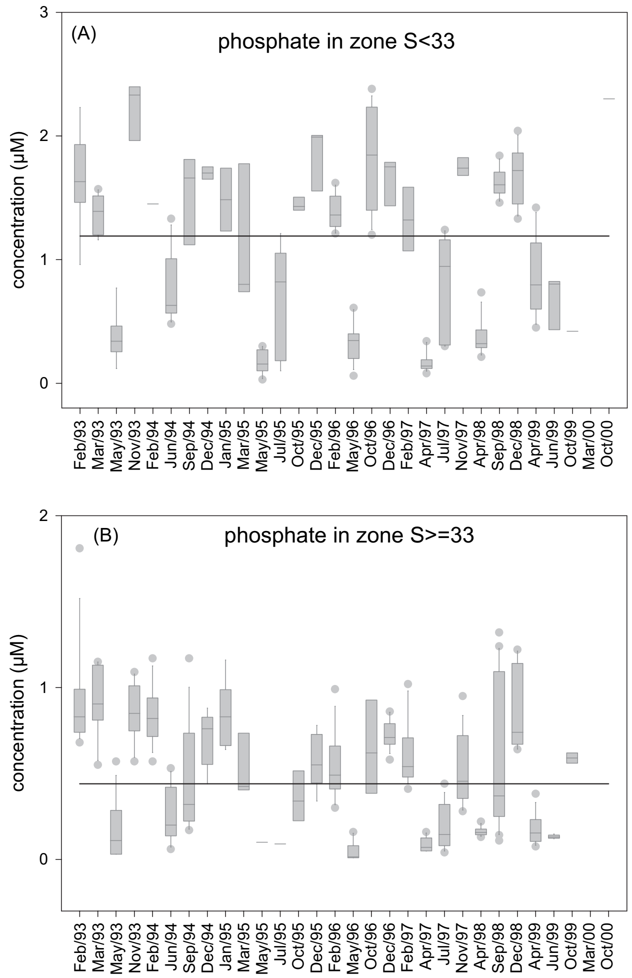

Fig. 7. Box-plot for the variation in phosphate concentration (μM) from 1993 to 2000 in zone $S < 33$ (A) and zone $S \geq 33$ (B). Black line represents the median concentration for the whole study period.

On the other hand, considering the phosphate time-series of the data set (Fig. 7), it was noticed that phosphate concentrations changed only very slightly between 1993 and 1999. These small changes observed over time were without significance (95%), for the zone $S < 33$ as well as the zone $S \geq 33$.

3.6. Silicate

A clear seasonal trend in silicate is perceived from Table 1 and mean silicate concentration in the Belgian area was 8.3 ± 7.6 μM. Silicate distribution showed a clear heterogeneity with significantly higher ($t = 6.6$; $p[\leq T_{\text{crit } 99\%}] < 0.001$) concentrations in zone $S < 33$ ($\text{mean}_{(1993\text{–}2000)} = 13.7$ μM) relative to the values found in zone $S \geq 33$ ($\text{mean}_{(1993\text{–}2000)} = 4.68$ μM) of the Belgian waters (Table 2). Calculations for silicate consumption (Fig. 2) in the Belgian area indicate that in zone $S < 33$ the silicate concentration decreased at the end of March and this decrease amounted to

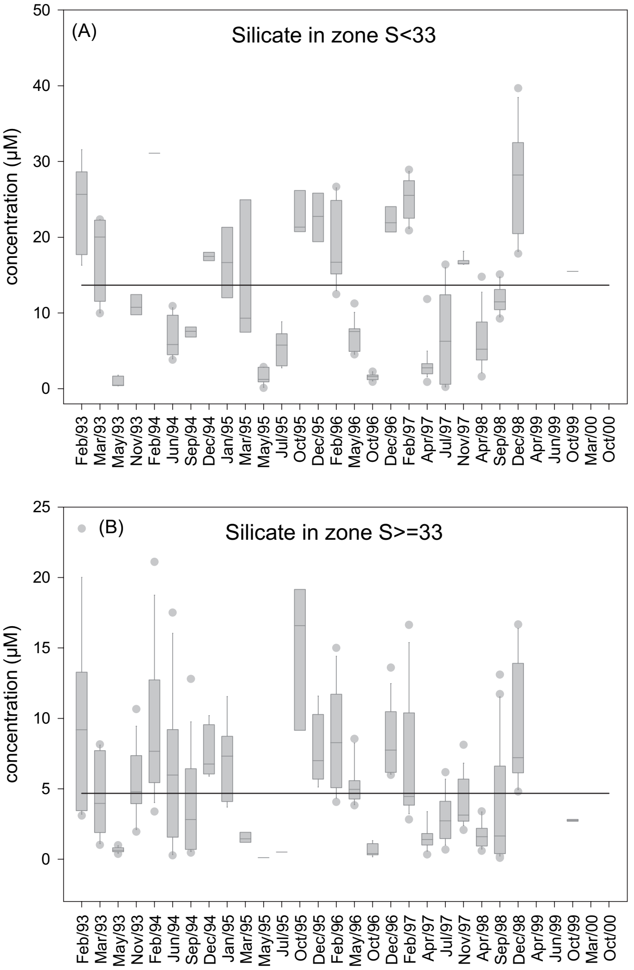

Fig. 8. Box-plot for the variation in silicate concentration (µM) from 1993 to 2000 in zone $S < 33$ (A) and zone $S \geq 33$ (B). Black line represents the median concentration for the whole study period.

15.1 µM (= 6.4 g Si m^{-2}). At the end of October silicate increased again to a value of 18.8 µM. In zone $S \geq 33$ diatoms started their primary production at the end of February accompanied with the use of 4.4 µM of silicate (= 2.5 g Si m^{-2}) and this consumed silicate was only restored from the end of November on.

The corresponding N:Si and P:Si ratios, as calculated from the consumption, are 0.83 and 0.08, respectively, in zone $S < 33$, and these ratios amount to values of 1.7 (N:Si) and 0.14 (P:Si) in zone $S \geq 33$. Nearly 80% of the silicate concentrations of the data set were lower than 12 µM. This may indeed indicate a slight decreasing trend in dissolved silicate to the system, which amounts in the present case to 0.17–0.28 µMy^{-1} between 1993 and 2000.

Analysis of the 1993–2000 time series for silicate did not show an apparent downward or upward trend of significant importance (at a significance level of 95%) in both areas (Fig. 8). In spite of this, a small decline in dissolved silicate was notable in the zone $S \geq 33$ since 1997.

4. Discussion

The Belgian coastal waters are characterised by high turbidity, which strongly limits primary production and hence causes spreading of the nutrient discharges from the estuaries to larger areas (Brockmann et al., 1988). This results in high nutrient concentrations (especially nitrate) for stations located in the coastal plume of the Scheldt. In addition, the water masses from the Channel are mixed with the highly polluted Scheldt water in front of the Belgian coast, thus enhancing the residence time of the water.

The ammonium concentrations found in the present work are in agreement with the values reported by Prandle et al. (1997) for a study conducted in 1988 and 1989. These authors found mean ammonium concentrations of 1.3 ± 1.0 µM covering the whole Southern North Sea area with largest values observed along the continental coast, particularly in the German Bight and the maximum concentration measured was 18 µM in November. Although ammonium concentrations were lowest in spring, the few sampling points that exhibited high concentrations in that period were stations which are geographically located in the Scheldt estuarine plume and which are thus strongly influenced by its discharge. The significant decrease in ammonium observed in the Belgian waters (Fig. 3) can be explained by the severe measures that have been taken by the different North Sea states in reducing the N loads from the rivers to the North Sea (4th Progress Report, 1995; OSPARCOM, 2000). Decrease in ammonium concentration is also partly due to the installation of sewage purification plants. Another explanation can be the better oxygen conditions measured in the Scheldt estuary during recent years (Van Damme, pers. comm.). Higher oxygen levels may enhance the transformation of ammonium to nitrate within the estuary, again resulting in lower ammonium loads to the North Sea.

The mean winter stock of nitrate (±30 µM), observed in this study, is in agreement with the mean winter concentration of 30–40 µM found in 1978–1979 by Baeyens et al. (1984) and Brockmann et al. (1988). These values also indicate that the winter stock value observed now is still the same as the one at the end of the 1970s. The seasonal changes found for nitrate are in agreement with the traditionally found seasonal cycle for nitrate or nutrients in seas, oceans and estuaries, whereby the primary productivity in spring and summer results in minima in nitrate concentrations, while a minimum in biological activity during winter leads to a maximum in nitrate concentrations (Baeyens et al., 1984; Brockmann et al., 1988; Prandle et al., 1997; Gentilhomme and Lizon, 1998). The significant fall in DIN (Fig. 2) at the start of the phytoplankton bloom in both zones is comparable with the findings of Baeyens et al. (1984). They found a DIN decrease of 21.4 µM during the phytoplankton bloom period (1 March–1 June) inside a coastal zone from direct DIN measurements at the end of the 1970s and they also observed spatial variations of DIN between onshore and offshore areas of the Belgian coast due to the Scheldt estuary with differences amounting from 9 to 25 μM-N depending on the season.

Trend analysis on existing nutrient data in different coastal zones has revealed that nutrient concentrations have increased in the coastal waters of the North Sea between 1930 and 1970 and that there is no obvious trend during the 1980s (Van Bennekom and Wetsteijn, 1990). The stabilisation of the DIN concentrations in the 1980s continues in the nineties as perceived by trend analysis on our nutrient data of 1993–2000.

The growing understanding of the role of DON in phytoplankton nutrition and ecology (Antia et al., 1991; Bronk et al., 1994) and the enhanced dissolved organic matter concentrations in seawater reported by Sugimura and Suzuki (1988), due to improved analytical methods, shed new light on the significance of the DON pool. According to estimates (Sharp, 1983), DON often represents a major proportion of total dissolved nitrogen in seawater.

From different studies performed in a variety of areas, Bronk (2002) calculated a mean DON concentration for the coastal and continental shelf of 9.9 ± 8.1 μM and of 22.5 ± 17.3 μM for estuaries. Mean DON concentrations in this study fall within these ranges (Table 1). Although the existence of a seasonal cycle of DON has been indicated in the English Channel by long-term surveys (Butler et al., 1979), it was difficult to perceive a distinct seasonal trend in DON in the adjacent Belgian waters. Although seasonal variability in DON concentration is rather small, there is a tendency to find higher concentrations of DON in winter and lower ones in spring (except in April 1997), which is in contrast with the steady increase from January to August and the decline from August to December found by Butler et al. (1979). The 'absence' of a distinct seasonal trend in our data set can be due to (1) the too low sampling frequency (for example sampling every two months) whereby possible peaks are missed or (2) the fact that there is no seasonal trend at all for DON in the studied environment. Indeed, some areas, for instance the Santa Monica Bay and the BATS site in the Sargasso Sea, do not show a seasonal pattern (Hansell and Carlson, 2001). DON concentrations are rather similar for all stations and seasons and the DON pool in the North Sea is important and may not be neglected in biogeochemical studies as already stated before by some authors (Laws, 1984; Bronk et al., 1994).

As for many other nutrients, phosphorus loads have increased by approximately 2–8 times relative to the values at the turn of the century (Gerlach, 1988; Conley, 2000). From 1960 on, an important increase in phosphorus loads in the river Rhine was observed due to the introduction of phosphate-containing detergents (Van Bennekom and Wetsteijn, 1990; Ærtebjerg et al., 2001). The introduction of phosphate-free detergents and the construction and implementation of advanced sewage treatment plants in the middle of the 1980s have resulted in reduced P loads in a number of estuarine systems worldwide (Conley, 2000). Also in many estuaries and coastal areas of the North Sea, phosphorus concentrations have decreased (up to 50%) since the middle of the 1980s (4th Progress Report, 1995; Ærtebjerg et al., 2001). In 1978–1979, mean winter phosphate concentrations for the continental coastal areas from the Strait of Dover to the German Bight are around 1 μM for the French coastal zone; 3 μM in the Belgian coastal zone and 3–4 μM in the Dutch coastal zone (Brockmann et al., 1988). A decade later, mean phosphate value is 2.5 μM in Dutch waters (Laane, pers. comm.) while for the southern North Sea area mean phosphate values ranged from 0.3 to 0.75 μM with highest values occurring closest to the coast (Prandle et al., 1997). Comparing the mean winter phosphate concentration of 1.04 μM from our data set with the 3–4 μM measured at the end of the 1970s by Brockmann et al. (1988), confirms the findings of many research reports that from the 1980s on phosphate concentrations declined in the coastal areas of the Southern North Sea (Ærtebjerg et al., 2001). So, in spite of the decreasing trend observed in the 1980s in most of the coastal zones of the North Sea and a significant decrease of around 50% in the Dutch waters between 1990 and 1999 (Laane, pers. comm.), the Belgian waters do not exhibit a significant decrease in phosphate between 1993 and 2000.

Unlike nitrogen and phosphorus, inputs of dissolved silicate are largely unaffected by human activity, and originate primarily from the weathering of silicate rocks (Conley, 2000). Therefore, it is reasonable to assume that silicate concentrations have not changed through time (Gowen et al., 2002). A consequence of increased N and P inputs and a rather constant Si input is that N:Si and P:Si ratios of the receiving waters have been altered considerably (Jickells, 1998; Ragueneau et al., 2002). In this study the corresponding N:Si and P:Si ratios are 0.83 and 0.08, respectively, in zone $S < 33$, and 1.7 (N:Si) and 0.14 (P:Si) in zone $S \geq 33$. These ratios indicate an important limitation of silicate in the high salinity zone compared with the traditional Redfield ratio of 16:1:16 for N:P:Si. Therefore, enhanced primary productivity may exhaust silicate and this limitation of Si relative to N or P can occur more frequently (Conley et al., 1993), leading to shifts in the phytoplankton community from diatoms to non-siliceous algae, a feature that is commonly observed in the Southern Bight of the North Sea (Riegman et al., 1992; Jickells, 1998, Rousseau et al., 2002). Declining trends in dissolved silicon concentrations have been observed in many coastal environments, i.e. Adriatic Sea, Black Sea, Kattegat (Conley et al., 1993), and the German Bight of the North Sea (Radach et al., 1990). In some areas of the Baltic Sea, the dissolved silicate concentrations have decreased by 0.19–0.85 μM y^{-1} in the period 1968–1986 (Ærtebjerg et al., 2001). Data from the 1970s indicate that for years with a homogenous winter distribution, Si concentration was 5–6 μM in the entire central Southern Bight (Van Bennekom and Wetsteijn, 1990) and that mean dissolved silicate was around 12 μM in the Belgian coastal zone (station 330) in 1978–1979 (Brockmann et al., 1988). Nearly 80% of the silicate concentrations of our data set was lower than 12 μM. This may indeed indicate a slight decreasing trend in dissolved silicate to the system, which amounts in our case to 0.17–0.28 μM y^{-1} between 1993 and 2000. This reduction can be caused by an increased sedimentation of biogenic silica in the Southern Bight (definite burial) or in the estuarine system causing a lower supply to the coastal system. Retention of Si has also been observed by Conley et al. (1993), as diatoms are trapped in lakes and behind dams. In addition, the observed values are in good agreement with the silicate winter values of 10–20 μM stated by Ærtebjerg et al. (2001) for the Belgian zone for the period 1985 and 1998 and are in the same range of silicate concentrations observed in other regions. The lack of a silicate trend is consistent with the limited anthropogenic influence on riverine concentration of this nutrient as stated by Gowen et al. (2002) and is only influenced by weathering conditions and thus rainfall.

5. Conclusions

Nutrient concentrations in the Belgian area of the North Sea show clear seasonal and spatial differences. Highest nutrient concentrations are observed in winter months when biological activity is negligible, while lowest values are found at the end of spring coinciding with the development of the phytoplankton blooms. Significantly higher nutrient concentrations occur in the $S < 33$ area compared to the $S \geq 33$ area mainly due to the influence of river water discharge. According to the fourth North Sea Conference Progress Report (4th Progress Report, 1995) there has been a reduction of 50% in the riverine inputs of phosphorus between 1985 and 1995, while for nitrogen the 50% reduction objective has not been achieved. Although severe actions have been undertaken by the North Sea states to reduce the N and P loads from the rivers, these reductions are not reflected in the Belgian area. In general, nutrient concentrations (with the exception of ammonium) in the waters of both studied zones do not show a significant decreasing trend between 1993 and 2000.

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Reference

Ærtebjerg, G., Carstensen, J., Dahl, K., Hansen, J., Nygaard, K., Rygg, B., Sørensen, G., Severinsen, G., Casartelli, S., Schrimpf, W., Schiller, C., Druon, J.N., Künitzer, A., 2001. Eutrophication in Europe’s Coastal Waters. European Environment Agency. Topic report 7/2001; 115 pp. Available from: http://reports.eea.eu.int/topic_report_2001_7/en/tab_content_RLR.

Antia, N.J., Harrison, P.J., Oliveira, L., 1991. The role of dissolved organic nitrogen in phytoplankton nutrition, cell biology and ecology. Phycologia 30, 1–89.

Baeyens, W., Mommaerts, J.-P., Goeyens, L., Dehairs, F., Dedeurwaerder, H., Decadt, G., 1984. Dynamic patterns of dissolved nitrogen in the Southern Bight of the North Sea. Estuarine, Coastal and Shelf Science 18, 499–510.

Brion, N., Baeyens, W., De Galan, S., Elskens, M., Laane, R.W.P.M., 2004. The North Sea: source or sink for nitrogen and phosphorus to the Atlantic Ocean? Biogeochemistry 68, 277–296.

Brockmann, U., Billen, G., Gieskes, W.W.C., 1988. North Sea nutrients and eutrophication. In: Salomons, W., Bayne, B.L., Duursma, E.K., Forstner, U. (Eds.), North Sea Pollution. Springer Verlag, Berlin, pp. 348–389.

Bronk, D.A., 2002. Dynamics of DON. In: Hansell, D.A., Carlson, C.A. (Eds.), Biogeochemistry of Marine Dissolved Organic Matter. Academic Press, San Diego, CA, pp. 153–247.

Bronk, D.A., Glibert, P.M., Ward, B.B., 1994. Nitrogen uptake, dissolved organic nitrogen release, and new production. Science 265, 1843–1846.

Butler, E.I., Knox, S., Liddicoat, M.I., 1979. The relationship between inorganic and organic nutrients in seawater. Journal of Marine Biology Assessment U.K. 59, 239–250.

Conley, D.J., 2000. Biogeochemical nutrient cycles and nutrient management strategies. Hydrobiologia 410, 87–96.

Conley, D.J., Schelske, C.L., Stoermer, E.F., 1993. Modification of the biogeochemical cycle of silica with eutrophication. Marine Ecology Progress Series 101, 179–192.

Dafner, E., De Galan, S., Goeyens, L., 1999. Microwave digestion of organic substances, a useful tool for dissolved organic nitrogen measurements. Water Research 33, 548–554.

Gentilhomme, V., Lizon, F., 1998. Seasonal cycle of nitrogen and phytoplankton biomass in a well-mixed coastal system (Eastern English Channel). Hydrobiologia 361, 191–199.

Gerlach, S.A., 1988. Nutrients – an overview. In: Newman, P.J., Agg, A.R. (Eds.), Environmental Protection of the North Sea. Heinemann, Oxford, pp. 147–175.

Gowen, R.J., Hydes, D.J., Mills, D.K., Stewart, B.M., Brown, J., Gibson, C.E., Shammon, T.M., Allen, M., Malcolm, S.J., 2002. Assessing trends in nutrient concentrations in coastal shelf seas:

a case study in the Irish Sea. Estuarine, Coastal and Shelf Science 54, 927–939, doi:10.1006/ecss.2001.0849.

Hansell, D.A., Carlson, C.A., 2001. Biogeochemistry of total organic carbon and nitrogen in the Sargasso Sea: control by convective overturn. Deep Sea Research II 48, 1649–1667.

Howarth, M.J., Dyer, K.R., Joint, I.R., Hydes, D.J., Purdie, D.A., Edmunds, H., Jones, J.E., Lowry, R.K., Moffat, T.J., Pomroy, A.J., Proctor, R., 1994. Seasonal cycles and their spatial variability. In: Charnock, H., Dyer, K.R., Huthnance, J.M., Liss, P.S., Simpson, J.H., Tett, P.B. (Eds.), Understanding the North Sea System. Chapman & Hall, London, pp. 5–25.

Jickells, T.D., 1998. Nutrient biogeochemistry of the coastal zone. Science 281, 217–222.

Koroleff, F., 1969. Direct determination of ammonia in natural waters as indophenol blue. Council Meeting Document - International Council for the Exploration of the Sea, pp. 19–22.

Koroleff, F., 1983a. Determination of silicon. In: Grasshoff, K., Ehrhardt, M., Kremling, K. (Eds.), Methods of Seawater Analysis. Verlag Chemie, Basel, pp. 174–183.

Koroleff, F., 1983b. Determination of phosphorus. In: Grasshoff, K., Ehrhardt, M., Kremling, K. (Eds.), Methods of Seawater Analysis. Verlag Chemie, Basel, pp. 125–139.

Laane, R.W.P.M., Groeneveld, G., De Vries, A., Van Bennekom, A.J., Sydow, J.S., 1993. Nutrients (P, N, Si) in the Channel and the Strait of Dover: seasonal and year to year variation, and fluxes to the North Sea. Oceanologica Acta 16, 607–616.

Laws, E., 1984. Isotope dilution models and the mystery of the vanishing N-15. Limnology and Oceanography 29, 379–386.

Lenhart, H.J., Radach, G., Ruardij, P., 1997. The effect of river input on the ecosystem dynamics in the continental coastal zone of the North Sea using ERSEM. Journal of Sea Research 38, 249–274.

Massart, D.L., Vandeginste, B.G.M., Buydens, L.M.C., De Jong, S., Lervi, P.J., Smeyers-Verbeke, J., 1997. In: Vandeginste, B.G.M., Puten, S.C. (Eds.), Handbook of Chemometrics and Qualimetrics: Part A. Elsevier, Amsterdam, 867 pp.

Mommaerts, J.P., Pichot, G., Ozer, J., Adam, Y., Baeyens, W., 1984. Nitrogen cycling and budget in Belgian coastal waters: North Sea areas with and without river inputs. Rapports et Proces Verbaux du Conseil International pour l'Exploration de la Mer 183, 57–69.

OSPARCOM, 2000. Quality Status Report 2000 Region II The Greater North Sea. OSPAR commission, London, 212 pp. Available from: http://www.ospar.org/.

Postma, H., 1978. The nutrient contents of North Sea water: changes in recent years, particularly in the Southern Bight. Rapports et Proces Verbaux du Conseil International pour l'Exploration de la Mer 172, 350–357.

Prandle, D., Hydes, D.J., Jarvis, J., McManus, J., 1997. The seasonal cycles of temperature, salinity, nutrients and suspended sediment in the Southern North Sea in 1988 and 1989. Estuarine, Coastal and Shelf Science 45, 669–680, doi:10.1006/ecss.1996.0227.

4th Progress Report, 1995. Fourth International conference on the Protection of the North Sea, Esbjerg, Denmark, 8–9 June 1995. Ministry of the Environment and Energy, Danish Environmental Protection Agency, Strandgade 29, DK-1401 Copenhagen, Denmark.

Radach, G., Berg, J., Hagmeier, E., 1990. Long-term changes in the annual cycles of meteorological, hydrographic, nutrient and phytoplankton time series at Helgoland and at LV ELBE 1 in the German Bight. Continental Shelf Research 19, 305–328.

Ragueneau, O., Chauvaud, L., Leynaert, A., Thouzeau, G., Paulet, Y.-M., Bonnet, S., Lorrain, A., Grall, J., Corvaisier, R., Le Hir, M., Jean, F., Clavier, J., 2002. Direct evidence of a biologically active coastal silicate pump: ecological implications. Limnology and Oceanography 47, 1849–1854.

Richardson, K., Jørgensen, B.B., 1996. Eutrophication: definition, history and effects. In: Jørgensen, B.B., Richardson, K. (Eds.), Eutrophication in Coastal Marine Ecosystems. Coastal and Estuarine Studies, vol. 52, pp. 1–19.

Riegman, R., Noordeloos, A.A.M., Cadée, G.C., 1992. Phaeocystis blooms and eutrophication of the continental coastal zones of the North Sea. Marine Biology 112, 479–484.

Rousseau, V., Leynaert, A., Daoud, N., Lancelot, C., 2002. Diatom succession, silicification and silicic acid availability in Belgian coastal waters (Southern North Sea). Marine Ecology Progress Series 236, 61–73.

Sharp, J.H., 1983. The distribution of dissolved inorganic and organic nitrogen in the sea. In: Carpenter, E.J., Capone, D.G. (Eds.), Nitrogen in the Marine Environment. Academic Press, San Diego, CA, pp. 1–35.

Soiland, H., Skogen, M.D., 2000. Validation of a three-dimensional biophysical model using nutrient observations in the North Sea. ICES Journal of Marine Science 57, 816–823.

Sugimura, Y., Suzuki, Y., 1988. A high temperature catalytic oxidation method of non volatile dissolved organic carbon in seawater by direct injection of liquid samples. Marine Chemistry 24, 105–131.

Van Bennekom, A.J., Wetsteijn, F.J., 1990. The winter distribution of nutrients in the Southern Bight of the North Sea (1961–1978) and in the estuaries of the Scheldt and the Rhine/Meuse. Netherlands Journal of Sea Research 25, 75–87.