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A seasonal study of particulate organic matter composition and quality along an offshore transect in the Southern North Sea.

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Abstract

We investigated temporal differences in particulate organic matter (POM) composition and quality in the water column and sediment at three stations along a transect from the coast via Oyster Grounds to Dogger Bank within the southern North Sea, using a multiproxy approach covering a wide spectrum of organic matter (OM) degradation states. Results of pigments and phospholipid-derived fatty acids showed distinct OM composition and quality differences in these stations, as well as seasonal variations. Major events, such as a late fall bloom at Dogger Bank and a spring bloom at Oyster Grounds and the Coastal Station were highlighted and the semi-depositional status of Oyster Grounds was confirmed. The OM composition and quality were relatively constant in the upper 10 cm of the sediment at all stations. Finally, this study highlights the importance of lateral and vertical transport processes in seasonal

variations in the biogeochemical carbon cycle in this area and the intense pre-depositional processing before eventual burial in coastal settings.

Keywords: Particulate Organic Matter; biogeochemistry; biomarkers; seasonal variations; OM quality; North Sea.

1. Introduction

The North Sea is a shelf system separating the United Kingdom from the European mainland. Up to fourteen water masses have been identified in this shelf system (NSTF, 1993), making the North Sea a complex and interesting area to investigate as the circulation and the distribution of these water masses influence the primary productivity and transport of living and non-living material (OSPAR Commission, 2000). Eisma and Kalf (1987) reported that these water masses are organised in a generally strong anti-clockwise circulating tidal motion, responsible for the transport of water and material. Waterborne transport of material in the southern North Sea has been well documented (Otto *et al.*, 1990; De Haas, 1997; Dauwe and Middelburg, 1998). For instance, OM produced in the southern part of the North Sea is transported northwards with residual tidal currents, where it meets with OM transported from and produced in the north. Then the OM moves, via the frontal systems and the German Bight to the Skagerrak area (Otto *et al.*, 1990), before eventually being accumulated in the Skagerrak, the depositional area of the North Sea (de Haas and van Weering, 1997; Dauwe and Middelburg, 1998). Some accumulation can also occur in areas such as the Oyster Grounds and the German Bight, considered as semi-depositional areas (Otto *et al.*, 1990). Dauwe and Middelburg (1998) reported that during this transport, the labile organic matter, which undergoes repetitive cycles of sedimentation and resuspension, becomes more refractory.

Although the North Sea is a well-studied area, previous studies on OM cycling focused either on organic matter degradation via quantification of sediment-water exchanges (Boon *et al.*, 1998; Provoost *et al.*, 2013), or on OM transport across and within specific sites (*e.g.* Kattegat and Skagerrak – de Haas and van Weering, 1999; Oyster Grounds – van Raaphorst *et al.*, 1998). Dauwe and Middelburg (1998) were the first to clearly document the compositional consequences of the repetitive deposition-resuspension cycles of OM, a process called OM spiralling, during OM transport from the main primary production area in the Southern Bight to the main deposition area in the Skagerrak. In a recent study covering a set of stations along this main OM transport route, Le Guitton *et al.* (2015) showed how spiralling of particles leaves a clear imprint on the biogeochemical composition of water-column and sedimentary OM. Whereas this previous study focused on large scale spatial patterns during one single period, a clear temporal signal is also expected, *e.g.* linked to seasonal primary production, or to rough weather conditions which will modify the erosion-deposition cycle. High wind velocities, often found from December to March (Gerritsen *et al.*, 2001), are known to be one of the driving forces in the large-scale transport and the sedimentation and erosion processes. A recent study of Davis *et al.* (2014) in the Celtic Sea showed that a storm could induce changes in the stoichiometry of OM. Understanding such temporal changes is of importance in a system where the turnover rate of water is about a year (Otto *et al.*, 1990) or even less (Breton *et al.*, 1992).

We investigated the seasonal variation of POM composition and quality, in terms of degradation state, at three nearby stations located on the so-called Terschelling transect in the southern North Sea. Suspended particulate matter and surface sediments from 0 to 10 cm deep were analysed at various levels of the ‘biomarkers pyramid’ (see Bianchi and Canuel, 2001, Le Guitton *et al.*, 2015) at three different periods of the year: November, February and May. Linking the biochemical composition to calculated indicators of organic matter quality,

our results are discussed in terms of seasonal variations both in SPM and down to 10 cm in the sediments.

2. Material and methods

2.1. Study area and samples collection

Three stations were sampled along the ‘Terschelling transect’ (Peeters and Peperzak, 1990), on board the R.V. *Pelagia* (Tab. 1, Fig. 1). The Dogger Bank and the Coastal Station, the most offshore (235 km) and onshore (4 km) stations of the Terschelling transect, respectively, are considered as non-depositional areas for POM (Fig. 1), while the station in between, Oyster Grounds (100 km), is a temporary depositional area for OM (De Haas, 1997) (Fig. 1); its waters are stratified in summer (Bale *et al.*, 2013). The Coastal Station is situated along the major OM transport route (De Haas *et al.*, 1997; Dauwe and Middelburg, 1998; Le Guitton *et al.*, 2015) (Fig. 1).

The samples were collected in November 2010, February and May 2011. The summer season could not be included due to logistic constraints. The ship’s non-toxic pumping device (Aquaflow) was used to collect water samples at 5 m depth. These samples were filtered to collect Suspended Particulate Matter (SPM) on GF/6 filters (1-3 μm pore size) for pigment analysis and 0.70 μm GF/F filters for bulk and PLFA analyses. Sediment was sampled using a multi-corer (Octopus type) with four cores of 100 mm diameter. The sediment cores were directly sliced onboard, per cm down to 10 cm deep, using a manual core slicer. This 10 cm deep record was chosen to investigate the mixed layer at each season for each station (Dauwe and Middelburg, 1998). Due to logistic constraints, full depth profiles for sediments could only be made for November and February. The SPM and SS samples were then stored at -20°C prior analyses, except for SPM and SS pigment samples, which were stored at -80°C.

Tab. 1. Main characteristics of the stations, and properties of the suspended particulate matter (SPM) and surface sediment (SS, section 0-1 cm) at Dogger Bank, Oyster Grounds and Coastal Station in November (N) 2010, February (F) and May (M) 2011.

		Dogger Bank (DB)			Oyster Grounds (OG)			Coastal Station (CS)		
Latitude	°N	55.17			54.13			53.4		
Longitude	°E	3.15			4.33			5.15		
Depth	m	30.8			49.0			9.4		
Depositional character		non-depositional			temporary depositional			non-depositional		
		N	F	M	N	F	M	N	F	M
Temperature of surface water ^a	°C	8.9	5.2	11.5	10.3	5.0	10.5	7.9 ^b	4.9 ^b	14.0 ^b
Temperature of bottom water ^a	°C	8.9	5.2	11.4	10.3	5.0	8.6			
Salinity ^a		34.6	34.8	34.8	34.5	34.4	34.4	31.7	30.1	32.2
SPM										
POC	mg-C.l ⁻¹	0.1	0.1	0.1	0.1	0.1	0.2	0.3	2.6	0.5
SS										
TOC	%wt	0.05	0.04	0.08	0.37	0.28	0.50	0.04	0.03	0.03
Porosity		0.3	0.3	0.3	0.4	0.4	0.4	0.3	0.3	0.3
Coarse sand	% 500-1000 µm	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Medium sand	% 250-500 µm	31.0	26.0	26.0	0.0	0.0	0.0	41.0	40.0	41.0
Fine sand	% 125-250 µm	62.6	70.8	68.1	22.5	19.1	22.4	57.7	57.9	58.0
Very fine sand	% 63-125 µm	6.4	3.5	5.5	48.0	65.7	49.0	0.9	1.7	0.8
Silt	% < 63 µm	0.0	0.0	0.0	29.8	15.6	29.0	0.0	0.0	0.0

^aData from Bale *et al.*, 2013.

^bAt CS, temperature was measured at mid-depth due to the shallow depth of the station.

POC = Particulate Organic Carbon, TOC = Total Organic Carbon

2.2. Analyses

The SPM and SS samples were analysed for organic carbon (OC), total nitrogen (TN), pigments and phospholipid derived fatty acids (PLFAs). For OC analysis, samples were acidified with 6 M HCl within Ag cups to remove inorganic carbon and analysed using a Carlo Elba elemental analyser NA-1500 (Nieuwenhuize *et al.*, 1994). Reproducibility is ~2 % for OC and N; detection limits are about 2 µg C and 0.4 µg N, respectively, related to about 0.02 and <0.01 wt% C and N for sediment samples. The pigments were extracted from SPM and SS samples and analyzed by reversed phase chromatography using the method described in Le Guitton *et al.* (2015) modified from Jeffrey *et al.* (1997). The PLFAs were extracted

from SPM and SS samples using the method described in Boschker *et al.* (1999) modified from Bligh and Dyer (1959).

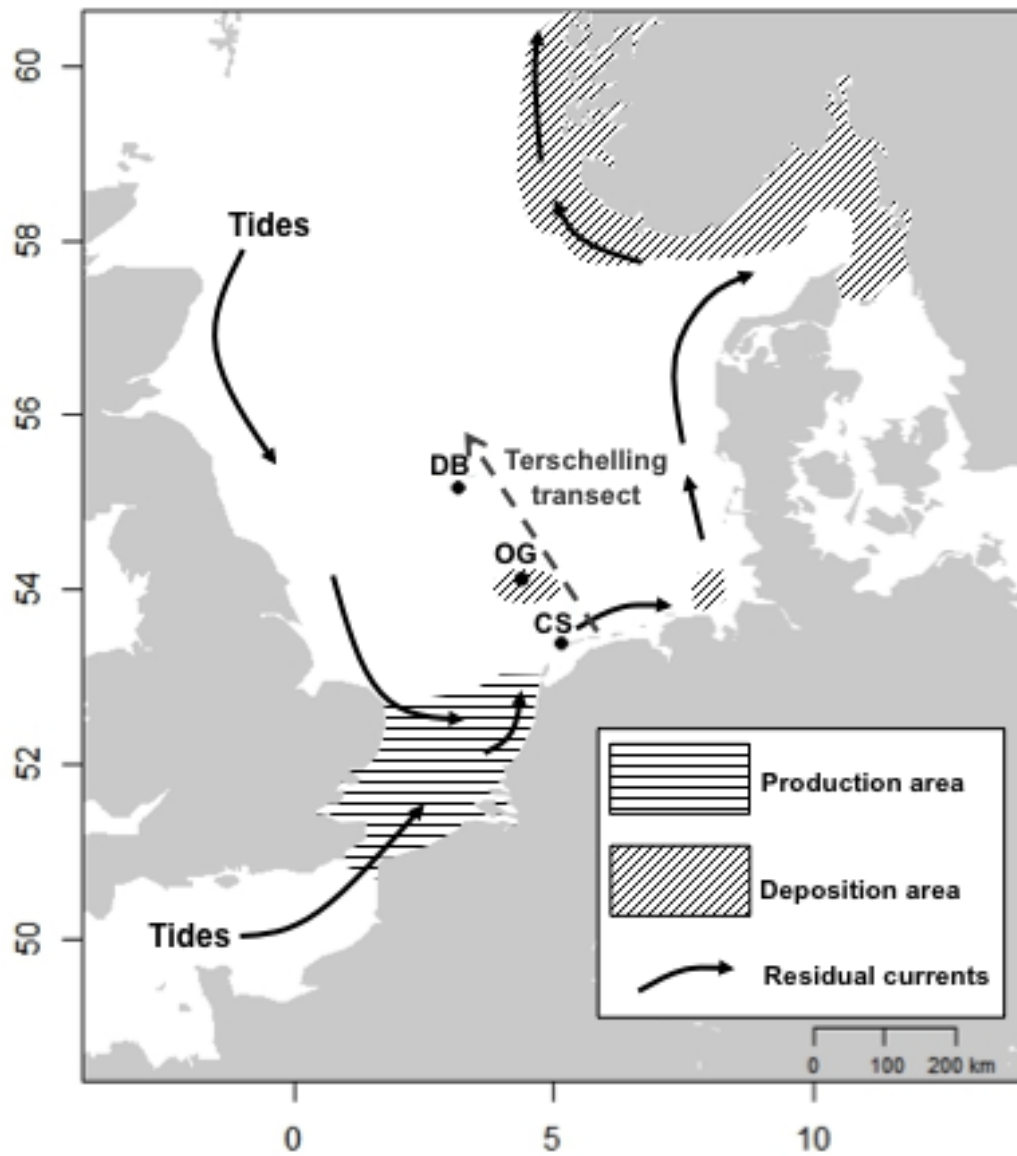


Fig. 1. Map of the North Sea with sampling stations adapted from Dauwe and Middelburg (1998) with DB = Dogger Bank, OG = Oyster Grounds, CS = Coastal Station.

2.3. POM quality derived parameters.

The POM quality was explored in terms of OM degradation and microbial reworking based on the timescales of molecule degradation rates (Cowie and Hedges, 1994, Veuger and van Oevelen, 2011; Veuger *et al.*, 2012). We considered three time scales:

- i. *Short time scales* - Pigments have higher degradation rates compared to lipids (Cowie and Hedges, 1994), thus we used pigments-derived parameters to assess the freshness of POM (Le Guitton *et al.*, 2015): the chlorophyll a to phaeopigment ratio (CHLA/PHAEOs), and the intact to total pigments ratio (ITPIG) (Woulds and Cowie, 2009). Here the phaeopigments are defined as the sum of pheophytin and phaeophorbide, and intact pigments are the sum of chlorophyll a, alloxanthin, diatoxanthin, zeaxanthin and β carotene. High ratios indicate fresh OM.
- ii. *Intermediate time scales* – Lipids have a lower degradation rate compared to pigments, but a higher one compared to bulk OM and amino acids (Hoefs *et al.*, 2002; Sinninghe Damsté *et al.*, 2002; Veuger *et al.*, 2012). Thus, the composition of the PLFA pool in terms of saturated fatty acid (SFA), monounsaturated fatty acid (MUFA), polyunsaturated fatty acid (PUFA) and branched fatty acid (Br-FA) was used to investigate POM quality. Low percentage of PUFA and high percentage of SFA indicate more extensive OM degradation and high percentages of MUFA and Br-FA indicate higher bacterial contribution (Bechtel and Schubert, 2009; Christodoulou *et al.*, 2009).
- iii. *Long time scales* – The CN-ratio was used to represent POM quality on the long time scale. The CN-ratio increases from Redfield (6.6) up to values as high as 10 with on-going marine OM decomposition (Henrichs, 2005).

3. Results

3.1. Main characteristics

Table 1 presents the main characteristics of the stations. The lowest temperatures were observed in February and the highest in May at all stations; temperature ranged from 4.9°C to 14°C. Thermal stratification was only observed at Oyster Grounds in May (1.9°C difference between surface and bottom temperature). The salinity was relatively constant (34-35) at Dogger Bank and Oyster Grounds, whereas at Coastal Station, the salinity was more variable and lower (32 in November and May, 30 in February). In the water column, the organic carbon (OC) content of SPM samples was constant over the studied period at Dogger Bank and Oyster Grounds (0.1-0.2 mg-C.l⁻¹). At Coastal Station, the OC content of SPM was similar though a bit higher than the one at Dogger Bank and Oyster Grounds (0.3 vs. 0.1-0.2 mg-C.l⁻¹) in November and was in the same range in May (0.5 mg-C.l⁻¹), while in February it reached 2.6 mg-C.l⁻¹. The TOC content of surface sediment and the porosity were higher at Oyster Grounds (0.28 to 0.50 %wt and 0.4 for porosity) compared to Dogger Bank and Coastal Station (0.03-0.08 %wt and 0.3 for porosity). The former varied over the studied period, while the later was constant. The grain size composition of Dogger Bank and Coastal Station showed a dominance of medium and fine sand, whereas the Oyster Grounds sediment was composed of very fine sand and silt.

3.2. OM composition

3.2.1. Surface waters

The highest values of total pigments and total PLFAs in SPM were observed in May at Oyster Grounds and Coastal Station (Tab. 2). At Dogger Bank, the total pigment value was the highest in November and the total PLFAs showed high values in November and May (Tab. 2).

Figure 2 and figure 3 present some specific pigments and PLFAs biomarkers that were used to investigate the OM composition (Tab. 3). At all stations, the most abundant pigment biomarkers were chlorophyll *a* (38-56 %-total pigments) and fucoxanthin (12-30 %-total pigments); chlorophyll *c* also had a relatively high contribution (5-7 %-total pigments) (Fig. 2). However, their contributions varied over the studied period. At Dogger Bank chlorophyll *a* percentage was the highest in November (51%-total pigments), whereas it was highest in February at Oyster Grounds (56 %-total pigments) and in May at Coastal Station (46 %-total pigments). The fucoxanthin contribution was highest in November at all stations, while the highest contribution of chlorophyll *c* was recorded in February at Dogger Bank and in May at Oyster Grounds and Coastal Station. At Oyster Grounds, other chlorophylls (*b* and *c*₃), alloxanthin, 19'-hexanoyloxyfucoxanthin and peridinin were observed over the studied period, while at Dogger Bank and Coastal Station, some pigments, such as chlorophyll *b* and alloxanthin at Dogger Bank in November, were not observed. None of the pigment biomarkers cited above was found at Coastal Station in February. The pigment biomarker lutein was only recorded at Coastal Station in February, contributing for about 1% to total pigments.

The PLFAs C20:5 ω 3, C22:6 ω 3 and to a lesser extent C16:1 ω 7c contributed significantly to the total PLFAs pool at all stations over the studied period (12-24%, 7-25% and 4-16%-total PLFAs, respectively) (Fig. 3), whereas the PLFA C18:1 ω 7c and the iso- and anteiso-PLFAs, *i.e.* i-C14:0, i-C15:0, ai-C15:0, i-C17:0 and ai-C17:0, were less important (2-9% and 1-2%-total PLFAs, respectively). Among the PLFA biomarkers presented in figure 3, C20:5 ω 3 was the most abundant at Dogger Bank in November (23%) and February (20%), at Oyster Grounds in February (15%) and at Coastal Station over the studied period (18-24%-total PLFAs). The PLFA second in abundance was C22:6 ω 3, its highest contribution was recorded

in May at Dogger Bank (21%), in November and May at Oyster Grounds (19% and 25%, respectively) and in May at Coastal Station (18%-total PLFAs).

3.2.2. Surface sediments

At all stations, the pigment biomarker composition in SS was less diverse than in SPM (Fig. 2). Similar as for SPM, chlorophyll *a* and fucoxanthin were the most abundant pigment biomarkers at all stations over the studied period (Fig. 2). The abundance of chlorophyll *a* comprised up to 3% at Dogger Bank and Oyster Grounds and up to 6%-total pigments at Coastal Station over the studied period. The fucoxanthin pigment biomarker values showed a larger variability with depth in the sediment, constituting up to 8% at Dogger Bank, 9% at Oyster Grounds and 6%-total pigments at Coastal Station during the studied period. The chlorophyll *c* pigment biomarker was also recorded at all stations over the studied period and down to 10 cm depth in the sediment, except at Oyster Grounds in November. Other pigment biomarkers such as 19'-hexanoyloxyfucoxanthin, lutein, alloxanthin, chlorophyll *b* or zeaxanthin were also present in the sediments, with concentrations generally higher in November than in February. In May, only alloxanthin, chlorophyll *a*, fucoxanthin and chlorophyll *c* were found at all depths at Oyster Grounds.

Contrary to the pigment biomarkers, the abundance of PLFA biomarkers was in a similar range in SS as in SPM, contributing on average 40-60% to the total PLFA pool (Fig. 3). A higher variability with depth in the sediment was observed at Oyster Grounds and Coastal Station, especially in February (Fig. 3). The PLFAs C16:1 ω 7c and C18:1 ω 7c were the most abundant PLFA biomarkers at all stations over the studied period (Fig 3). The PLFAs C20:5 ω 3 and C22:6 ω 3 contributed less than 10% to the total PLFA pool over the studied period, while the iso- and anteiso-PLFA biomarkers, *i.e.* i-C14:0, i-C15:0, ai-C15:0, i-C17:0

and ai-C17:0, contributed 13-30% in November, 6-39% in February and 11-20%-total PLFAs in May.

Tab. 2. Total pigments and total PLFAs in SPM and SS samples, presented as mean \pm standard deviation or as single value (mainly the May data) at Dogger Bank (DB), Oyster Grounds (OG) and Coastal Station (CS) in November (N) 2010, February (F) and May (M) 2011.

		DB-N	DB-F	DB-M	OG-N	OG-F	OG-M	CS-N	CS-F	CS-M
SPM										
	Total pigments ($\mu\text{g/L}$)	7.94 \pm 1.51	2.25 \pm 0.15	1.06 \pm 0.08	1.63 \pm 0.09	1.56 \pm 0.02	4.15 \pm 0.33	1.74 \pm 0.02	2.07 \pm 0.21	8.40 \pm 1.15
	Total PLFAs ($\mu\text{g/L}$)	4.43 \pm 1.84	2.40 \pm 0.83	5.28 \pm 0.23	1.10 \pm 0.14	0.88 \pm 0.21	9.61 \pm 0.77	5.09 \pm 0.47	4.91 \pm 0.75	16.65 \pm 1.84
SS										
Total pigments ($\mu\text{g/gdw}$)	0-1 cm	2.60 \pm 0.08	2.34 \pm 0.06	4.62	3.65 \pm 0.17	2.47 \pm 0.80	14.27	0.89 \pm 0.11	0.33 \pm 0.07	2.30
	1-2 cm	2.46	2.00 \pm 0.08	2.31	3.10 \pm 1.29	2.39 \pm 1.17	8.12	0.72 \pm 0.10	0.23 \pm 0.02	2.40
	2-3 cm	2.29	1.90 \pm 0.12	1.88	3.64 \pm 1.68	1.56 \pm 0.17	2.53	0.37 \pm 0.01	0.30 \pm 0.06	2.85
	3-4 cm	2.21 \pm 0.19	1.96 \pm 0.12	1.27	3.78 \pm 0.49	1.91 \pm 0.57	1.72	0.27 \pm 0.05	0.22 \pm 0.04	4.07
	4-5 cm	2.24 \pm 0.02	2.02 \pm 0.16	1.26	2.93 \pm 0.42	2.72 \pm 1.22	2.05	0.35 \pm 0.06	0.26 \pm 0.02	2.89
	5-6 cm	2.01 \pm 0.54	2.18 \pm 0.09	1.10	1.79 \pm 1.03	2.17 \pm 0.03	1.34	0.44 \pm 0.02	0.31 \pm 0.16	1.66
	6-7 cm	2.20	2.32 \pm 0.16	1.21	1.26 \pm 0.04	1.85 \pm 0.67	1.38	0.44 \pm 0.10	0.30 \pm 0.01	1.58
	7-8 cm	2.07	1.86 \pm 0.15	1.14	1.18 \pm 0.15	1.89 \pm 0.70	1.47	0.32 \pm 0.02	0.42 \pm 0.15	2.25
	8-9 cm	1.66	1.35	0.99	0.92 \pm 0.09	1.54 \pm 0.27	1.07	0.34 \pm 0.04	0.21 \pm 0.01	1.20
	9-10 cm		1.23	0.76	0.99 \pm 0.00	1.48 \pm 0.08	0.86	0.41	0.13 \pm 0.04	1.03
Total PLFAs ($\mu\text{g/gdw}$)	0-1 cm	1.34 \pm 0.32	0.62 \pm 0.13	2.59	1.98 \pm 0.79	0.63 \pm 0.03	3.27	1.17 \pm 0.75	0.31 \pm 0.07	1.99
	1-2 cm	1.00 \pm 0.18	0.54 \pm 0.03		3.06 \pm 2.19	0.51 \pm 0.11		1.23 \pm 0.63	0.20 \pm 0.10	
	2-3 cm	1.48 \pm 0.44	1.76 \pm 0.91	2.49	2.63 \pm 0.94	0.64 \pm 0.01	1.57	1.04 \pm 0.23	0.49 \pm 0.35	1.10
	3-4 cm	1.16 \pm 0.27	1.56 \pm 1.33		2.66 \pm 0.37	0.55 \pm 0.39		0.91 \pm 0.26	0.66 \pm 0.59	
	4-5 cm	1.22 \pm 0.53	0.64 \pm 0.17		1.25 \pm 0.41	0.69 \pm 0.09		0.98 \pm 0.40	0.41 \pm 0.22	
	5-6 cm	1.08 \pm 0.19	0.53 \pm 0.12		1.23 \pm 0.62	0.79 \pm 0.60		0.99 \pm 0.60	0.42 \pm 0.37	
	6-7 cm	0.95 \pm 0.32	0.77 \pm 0.25		1.27 \pm 0.89	5.54 \pm 3.76		1.65 \pm 0.72	0.21 \pm 0.05	
	7-8 cm	1.67 \pm 0.72	0.39 \pm 0.12		0.87 \pm 0.20	0.61 \pm 0.29		2.03 \pm 1.19	0.35 \pm 0.14	
	8-9 cm	0.91 \pm 0.25	1.30		0.94 \pm 0.35	0.73 \pm 0.18		1.20 \pm 0.12	0.44 \pm 0.26	
	9-10 cm		1.17		0.66 \pm 0.12	1.23 \pm 0.92		1.11 \pm 0.01	0.22 \pm 0.13	

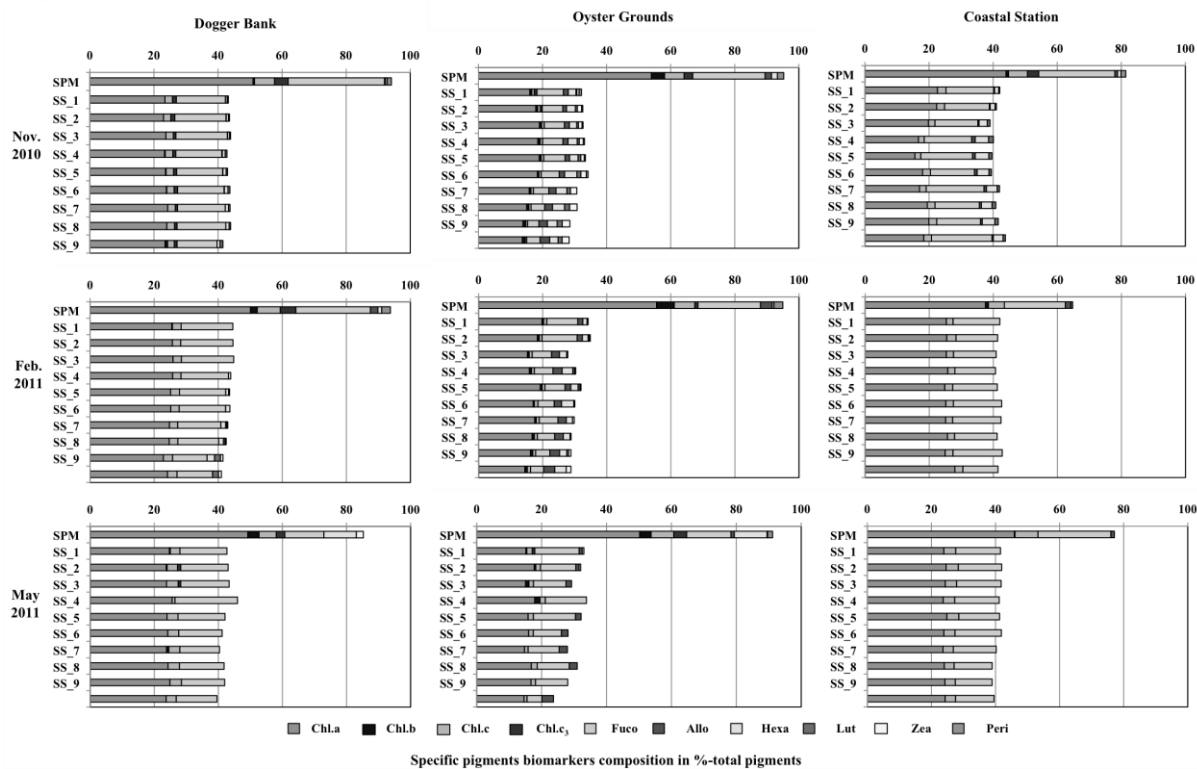


Fig. 2. Specific pigment biomarkers composition (in %-total pigments) of SPM and SS samples (from 0 to 10 cm deep) at Dogger Bank, Oyster Grounds and Coastal Station in November (Nov.) 2010, February (Feb.) and May 2011.

Chl.a = chlorophyll *a*, Chl.b = chlorophyll *b*, Chl.c = chlorophyll *c*, Chl.c₃ = chlorophyll *c*₃, Fuco = fucoxanthin, Allo = alloxanthin, Hexa = 19'-hexanoyloxyfucoxanthin, Lut = lutein, Zea = zeaxanthin, Peri = peridinin.

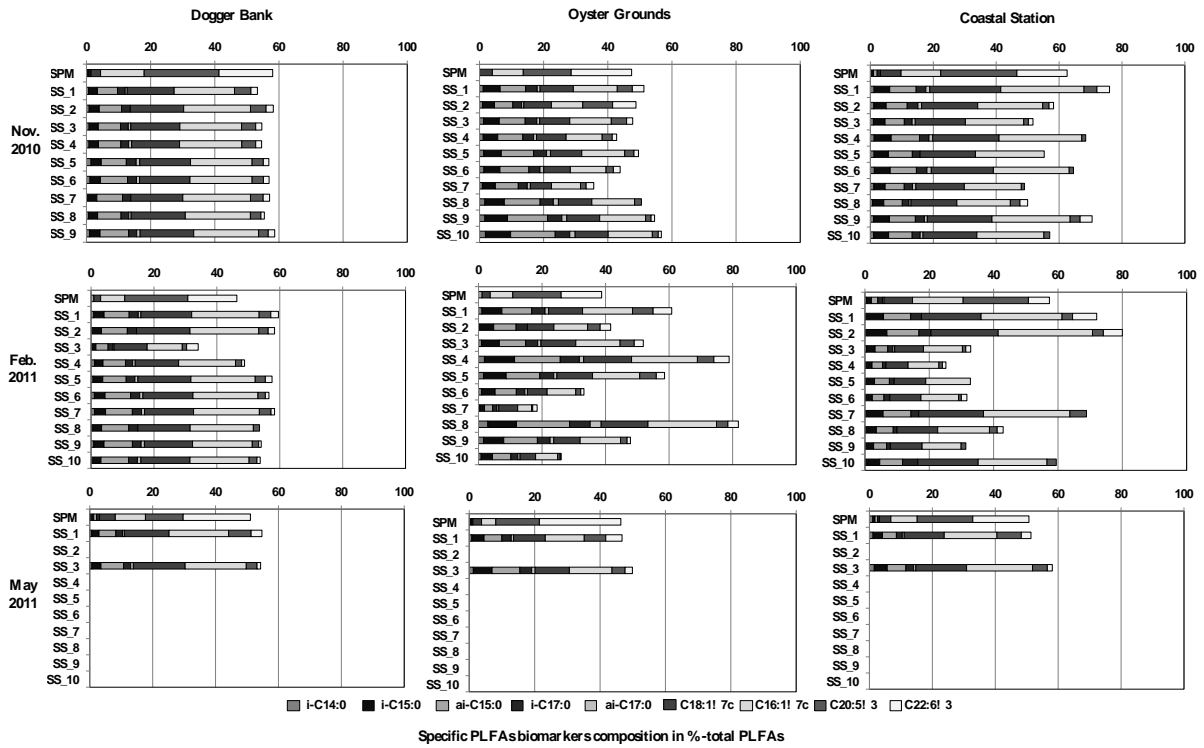


Fig. 3. Specific PLFA biomarkers composition (in %-total pigments) of SPM and SS samples (from 0 to 10 cm deep) at Dogger Bank, Oyster Grounds and Coastal Station in November (Nov.) 2010, February (Feb.) and May 2011.

Tab. 3. Specific pigment and PLFA biomarkers in phytoplankton used to investigate OM composition.

Biomarkers	Group	Reference
Pigments		
Chlorophyll a	All photosynthetic microalgae, except prochlorophytes	1
Chlorophyll b	Chlorophytes, prasinophytes, euglenophytes, prochlorophytes	1, 2
Chlorophyll c	Chromophyte algae	3
Chlorophyll c ₃	Some prymnesiophytes, chrysophytes, diatoms	3, 4, 5
Fucoxanthin	Diatoms, prymnesiophytes, chrysophytes, raphidophytes, a few dinoflagellates	1, 6
Alloxanthin	Cryptomonads	7
19'-hexanoyloxyfucoxanthin	Some chrysophytes, prymnesiophytes, 1 diatom, a few dinoflagellates	5, 6, 8, 9
Lutein	Green algae (chlorophytes and some prasinophytes)	1
Zeaxanthin	Cyanobacteria (blue-green algae), prochlorophytes, green-algae	10, 11
Peridinin	Most photosynthetic dinoflagellates	12, 13
PLFAs		
i-C14:0, i-C15:0, ai-C15:0, i-C17:0, ai-C17:0	Bacterial: Cytophaga–Flavobacteria and Gram-positive bacteria	14
C18:1! 7c	Bacterial: mainly Gram-negative, and Proteobacteria	15
C16:1! 7c	Diatoms, bacteria	14
C20:5! 3	Diatoms (Bacillariophyceae)	16, 17, 18
C22:6! 3	Dinoflagellates, <i>Phaeocystis</i>	14

References:

1. Jeffrey, 1974; 2. Chishlom *et al.*, 1988; 3. Jeffrey, 1989; 4. Jeffrey and Wright, 1987; 5. Vesik and Jeffrey, 1987; 6. Bjørnland and Liaaen-Jensen, 1989; 7. Pennington *et al.*, 1985; 8. Wright and Jeffrey, 1987; 9. Bjørnland *et al.*, 1989; 10. Guillard *et al.*, 1985; 11. Gieskes *et al.*, 1988; 12. Jeffrey *et al.*, 1975; 13. Johansen *et al.*, 1974; 14. Dalsgaard *et al.*, 2003; 15. Braeckman *et al.*, 2012; 16. Ahlgren *et al.*, 1992; 17. Dunstan *et al.*, 1993; 18. Volkman *et al.*, 1989.

3.3. POM quality

The POM quality parameters are presented in figure 4 (pigment derived parameters), figure 5 (PLFA composition) and figure 6 (CN-ratio).

3.3.1. Pigment-derived parameters

In the water column, both pigment-derived parameters, *i.e.* the chlorophyll *a* to phaeopigments (CHLA/PHAEOs) ratio and the intact to total pigments (ITPIG) ratio, were highest at Oyster Grounds (Fig. 4). No data of CHLA/PHAEOs can be presented at OG in February because phaeopigment data are missing. The SPM CHLA/PHAEOs ratio was highly variable over the studied period at Dogger Bank ranging from 5 ± 0.3 in May to 20 ± 0.2 in February while at Coastal Station, this ratio ranged from 2 in February to 7 in May. The seasonal variability of SPM ITPIG ratio was very limited with a difference of only 0.1 at Oyster Grounds (0.5 in May, 0.6 in November and February) and Coastal Station (0.4 in February, 0.5 in November and May), and no variation at Dogger Bank (0.5).

In the sediment, the CHLA/PHAEOs ratio was rather constant and very low (<1) at Oyster Grounds. At Dogger Bank and Coastal Station, the sediment CHLA/PHAEOs ratios varied with depth and between the samplings (Fig. 4). The ITPIG ratio also varied substantially, with Oyster Ground values lower than Dogger Bank over the studied period and Coastal Station values lower in November (≥ 0.1 differences). In February and May, ITPIG ratios at Dogger Bank and Coastal Station were relatively similar (< 0.1 differences) over the full depth profile, except for a rather high value at 10 cm deep in February at Coastal Station.

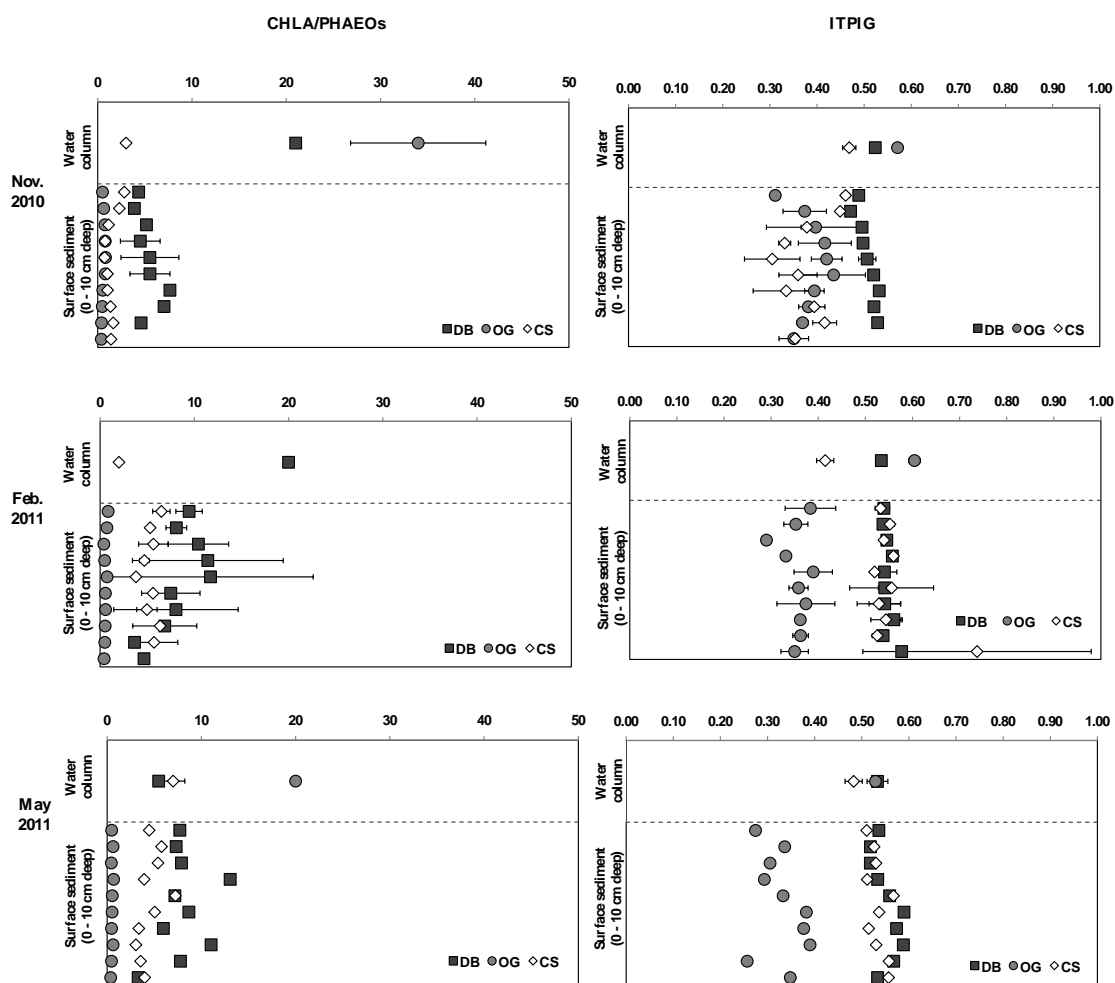


Fig. 4. Chlorophyll a to phaeopigments (CHLA/PHAEOs) on the left and intact to total pigments (ITPIG) ratios on the right for SPM (water column) and SS (from 0 to 10 cm deep) at Dogger Bank (DB – dark grey square), Oyster Grounds (OG – grey circle) and Coastal Station (CS – white diamond) in November (Nov.) 2010, February (Feb.) and May 2011.

3.3.2. Phospholipid derived fatty acid composition

Phospholipid derived fatty acids were characterized by high contributions of PUFA in SPM (Fig. 5). They ranged from 50 ± 3 to $59 \pm 7\%$ -total PLFA at Dogger Bank, from 46 ± 6 to $62 \pm 0\%$ -total PLFA at Oyster Grounds, but contributing less at Coastal

Station (41 ± 2 to $48 \pm 4\%$ -total PLFA). Branched fatty acids (Br-FA) were low (less than 10%) at all stations and especially at Dogger Bank ($\leq 3\%$) and at Oyster Grounds ($\leq 2\%$). At Coastal Station, the Br-FA contribution was higher, ranging from 6 ± 1 to $9 \pm 3\%$ -total PLFAs. At Dogger Bank, the highest contribution of SFA and Br-FA was found in May, whereas the highest contribution of MUFA was found in November. The PUFA contribution was the highest in February. At Oyster Grounds, the highest contribution of SFA was found in November, while Br-FA and MUFA were the highest in February and PUFA in May. At Coastal Station, Br-FA and MUFA contributions were also the highest in February, but the highest contribution of SFA was found in May and the highest contribution of PUFA in November.

In sediments, the PLFA composition was dominated by MUFA at all stations over the studied period, especially at Dogger Bank and Coastal Station (Fig. 5). The PUFA contributions were much lower in sediments than in SPM ($\leq 26 \pm 19\%$ vs. $\geq 41 \pm 2\%$) and tended to decrease with depth. The Br-FA contributions were higher in sediments than in SPM ($\geq 12 \pm 6\%$ vs. $\leq 9 \pm 3\%$) and tended to increase with depth at Oyster Grounds. Each station showed a relatively similar PLFA composition depth profiles in November and February, but with a higher variability in February. In May, the data recorded in the sections 0-1 cm and 2-3 cm fitted in the same range of the data recorded in November and February at all stations.

3.3.3. Carbon to nitrogen ratio

In the water column, the molar organic carbon to total nitrogen ratio (CN-r) was higher at Coastal Station than at Dogger Bank and Oyster Grounds (8 vs. 6-7 on average) in November and February (Fig. 6). The CN-r was lowest in February at Dogger Bank and Oyster Grounds and in May at Coastal Station. In sediment depth profiles, the CN-r was variable, especially at Coastal Station in February, where it varied from 4 ± 3 in the 2-3

cm section to 12 ± 6 in the 4-5 cm section. At Oyster Grounds, the CN-r SS depth profile ranged around $9-10 \pm 1$ over the studied period, whereas at Dogger Bank, it ranged from 4 ± 1 to 7 ± 2 in November and February. In May, a CN-r of 9 was found in the 0-1 cm section at Dogger Bank and a CN-r of 6 was found in the same section at Coastal Station.

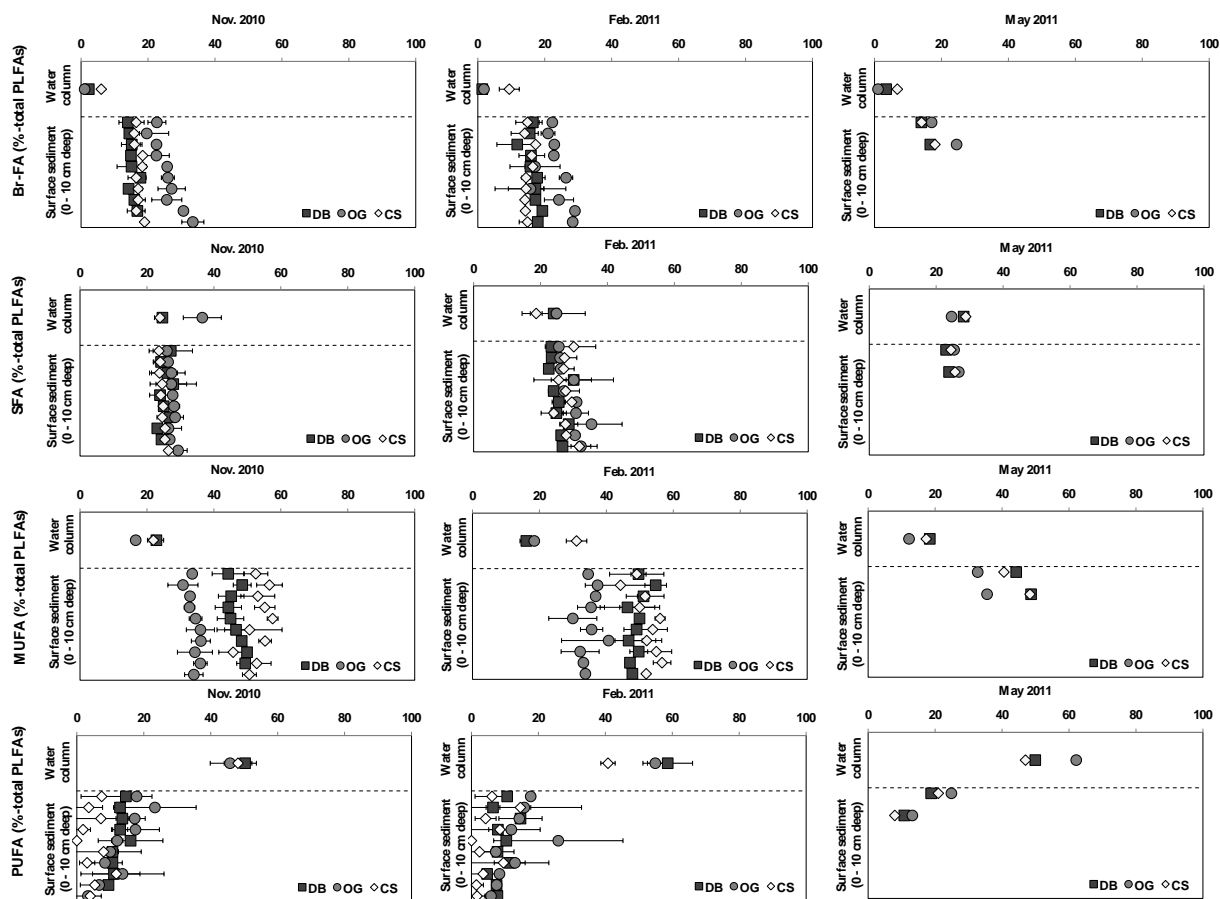


Fig. 5. Composition of the phospholipid derived fatty acids (PLFAs) pool in terms of Br-FA, SFA, MUFA and PUFAs (see significance of abbreviation in section 2.3.ii) (in %-total PLFAs \pm standard deviation) for SPM (Water column) and SS (from 0 to 10 cm deep) at Dogger Bank (DB – dark grey square), Oyster Grounds (OG – grey circle) and Coastal Station (CS – white diamond) in November (Nov.) 2010, February (Feb.) and May 2011.

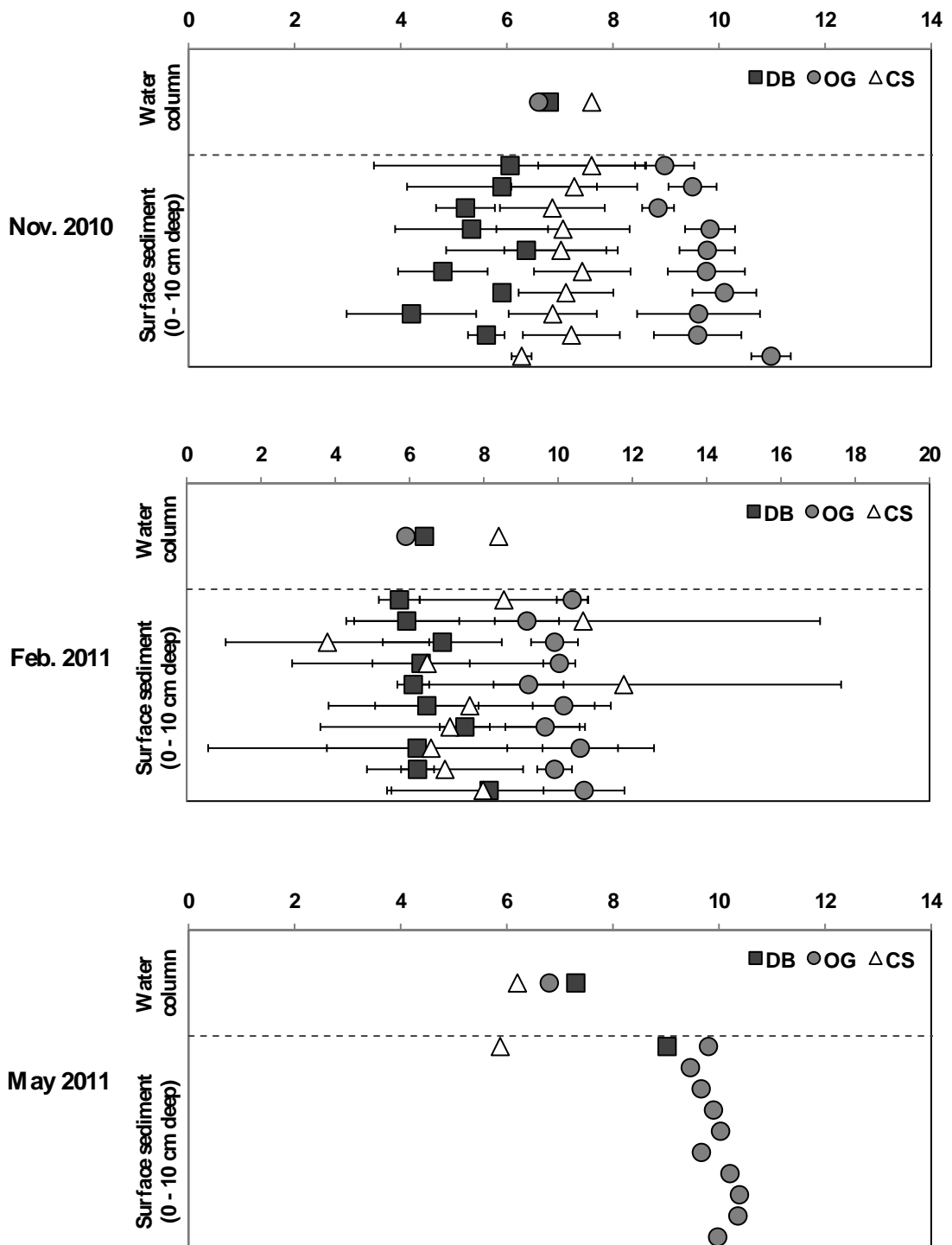


Fig. 6. Carbon to nitrogen ratio (CN-r) for SPM (Water column) and SS (from 0 to 10 cm deep) at Dogger Bank (DB – dark grey square), Oyster Grounds (OG – grey circle) and Coastal Station (CS – white diamond) in November (Nov.) 2010, February (Feb.) and May 2011. Mind the different scale in February.

4. Discussion

4.1. Seasonal variation of the OM composition

Short branched fatty acids and the PLFA C18:1 ω 7c are often used to trace Bacteria (Boschker and Middelburg, 2002, Braeckman et al., 2012), while the PLFAs C20:5 ω 3 and C22:6 ω 3 are commonly used to trace diatoms and dinoflagellates (Dalsgaard *et al.*, 2003). Specific pigments allow better resolution of major groups of phytoplankton (van den Hoek *et al.*, 1994), although this method also has limitations such as the presence of the same pigment in more than one taxon (Martin and Kowallig, 1999; McFadden, 2001) and the underestimation of non-pigmented, heterotrophic microplankton species such as some Dinophyceae (Sherr and Sherr, 2007). In this study, we used both specific PLFAs and pigments biomarkers in phytoplankton (Tab. 3) to investigate the OM composition and its seasonal variation.

4.1.1. Surface waters

PLFAs and pigment biomarkers indicated that Bacillariophyceae (*e.g.* Diatoms), Chrysophyceae, Raphidophyceae, Prymnesiophyceae (*e.g.* Phaeocystis) and Dinoflagellates dominated the OM composition at all stations over the studied period (Fig. 2, Fig. 3, Tab. 3). It was somehow less clear at Coastal Station, because some pigments concentrations such as chlorophyll *c*₃, 19'-hexanoyloxyfucoxanthin and peridinin were below the detection limits defined as three times the standard deviation of a very low sample (*e.g.* 0.01 $\mu\text{g.l}^{-1}$ for chlorophyll *c*₃ and 0.02 $\mu\text{g.l}^{-1}$ for 19'-hexanoyloxyfucoxanthin and peridinin). At this station, our results indicate that Raphidophyceae contribute much to the OM composition (Fig.2, Tab. 3), which is consistent with literature. Raphidophyceae are nowadays regularly found in the Dutch coastal waters (Vrieling *et al.*, 1985; Elbrächter, 1999). Evidence of the presence of Euglenophyceae, Cryptomonads, Cyanobacteria, Prochlorophyceae, Chlorophyceae and

Prasinophyceae were also found, but they were less abundant, and not at all stations nor at each sampling time (Fig. 2, Tab. 3). Results of i-C14:0, i-C15:0, ai-C15:0, i-C17:0 and ai-C17:0, as well as C18:1 ω 7c suggested the presence of heterotrophic bacteria at Dogger Bank and Coastal Station (Fig. 3, Tab. 3).

The seasonality in the OM composition differed between stations. At Dogger Bank, maximum abundance of specific PLFAs and pigments biomarkers of Bacillariophyceae (*e.g.* Diatoms), Chrysophyceae, Raphidophyceae and Prymnesiophyceae associated with high value of total pigments and total PLFAs indicated that a late fall bloom might have occurred at this station in November 2010. Our results for this station were consistent with previous studies indicating that high primary production occurs through the year in this region (Brockmann and Wegener, 1985; Richardson and Olsen, 1987; Brockmann *et al.*, 1990). Maximum primary production occurred in winter and spring in the Dogger Bank area (Kröncke and Knust, 1995). As our samples were collected in May, *i.e.* after the spring bloom, this can explain the highest presence of Bacteria in May at this station (Fig. 3, Tab. 3). At Oyster Grounds, no clear seasonal variation was observed in the OM composition of SPM. However the total pigments, total PLFAs (Tab. 2) and the OC content in SPM (Tab. 1) varied in a similar way, being higher in May than in November and February, suggesting a bloom of primary production then, consistent with results of Joint and Pomroy (1993) for this area. At Coastal Station, the highest abundance of bacterial biomarkers was measured in February (Fig. 3, Tab. 3) as well as the highest OC content in SPM (2.6 mg C.l⁻¹) and the lowest salinity (30.1). These high values may reflect the shallow depth of Coastal Station (Tab. 1) and its location close to the Wadden Sea (Fig. 1); it may also be due to it being located along the major OM transport route (De Haas *et al.*, 1997; Dauwe and Middelburg, 1998; Le Guitton *et al.*, 2015) (Fig. 1).

4.1.2. The sediments

Pigments in the sediment were far less recognizable than in the water due to diagenesis. However our results of specific pigments and PLFA biomarkers suggest the presence of the same phytoplankton groups as in SPM, *i.e.* Bacillariophyceae (*e.g.* Diatoms), Chrysophyceae, Raphidophyceae, Prymnesiophyceae (*e.g.* Phaeocystis) and Dinoflagellates, at all stations over the studied period and down to 10 cm deep (Fig. 2, Fig. 3, Tab. 3). Evidence of the presence of Chlorophyceae, Prasinophyceae, Prochlorophyceae and Cyanobacteria were also observed at Oyster Grounds, especially in the deeper section of the sediment (Fig. 2, Tab. 3). In addition, PLFA biomarkers specific for heterotrophic bacteria were found in higher abundance in the sediment than in SPM (Fig. 3, Tab. 3), especially at Oyster Grounds, confirming the temporary deposition character of this station (De Haas, 1997).

The depth profiles of specific pigments and PLFA biomarkers are often uniform, indicating that sediments were well mixed down to 10 cm at the three stations (Fig. 2, Fig. 3), consistent with Dauwe and Middelburg (1998). No clear seasonality was observed in the sediment depth profile compared to SPM, except in the first layers (0-1 cm, down to 1-2 cm). At all stations, the highest abundance of total pigments and total PLFAs were measured in May (Tab. 2). At Dogger Bank, this reflects the deposition of the spring bloom as only a small part of the spring bloom degrades within the water column, the major part of this primary produced material settles to the sediment surface (Nielsen and Richardson, 1989). At Oyster Grounds, these results suggested that either the OM produced in the stratified water column (Tab. 1) deposited on the seafloor and/or the OM originating in the southern area, where primary production also mainly occurs during spring (Fig. 1) (Dauwe and Middelburg, 1998; Le Guitton *et al.*, 2015), was deposited on the surface sediment of Oyster Grounds.

4.2. Seasonal variation of the POM quality

To investigate the seasonal variation of the POM quality three time scales were defined in terms of OM degradation and microbial reworking, based on molecule degradation sensitivities (Cowie and Hedges, 1994, Veuger and van Oevelen, 2011; Veuger *et al.*, 2012).

4.2.1. Surface waters

At Dogger Bank, the ‘late November bloom’ deduced from the pigment and PLFA composition (Fig. 2, Fig. 3) was not clear from the SPM quality parameters. If primary produced OM would dominate then, one would have expected to observe the highest CHLA/PHAEOS, ITPIG and PUFA and the lowest MUFA, Br-FA and CN-r values in November in SPM. However, the CHLA/PHAEOS and the ITPIG in November were relatively similar as those in February, and May for the later (Fig. 4). The highest PUFA value was observed in February in SPM (Fig. 5) and PUFA are known to be relatively good indicators of the presence of fresh algal sources (Shaw and Johns, 1985; Canuel and Martens, 1993; Bianchi and Bauer, 2011). Only the high MUFA value (Fig. 5) and the CN-r of 6.8 in November (Fig. 6) combined with the highest values of pigment and PLFA biomarkers for algae are consistent with the presumed late November bloom, as most of MUFA are considered to be indicative of algal species (Volkman *et al.*, 1989; Dunstan *et al.*, 1993).

At Oyster Grounds, the POM quality parameters were also not in accordance with the POM composition. On the one hand, highest values of ITPIG (Fig. 4) as well as Br-FA and MUFA (Fig. 5), and the lowest CN-r (Fig. 6) were observed in February in SPM, indicating fresh POM in the water column at this period and a higher bacterial biomass (Bechtel and Schubert, 2009). On the other hand, the highest value of pigments and

PLFA biomarkers for algae observed in May (Tab. 2), suggested that the phytoplankton production occurs in this region mainly when the water column is stratified. The PUFA abundance was highest in May (Fig. 5) but this was not so for the other POM quality parameters, suggesting that the fresh POM produced at Oyster Grounds in May is quickly consumed and degraded in the water column. Another surprising result is the high value of CHLA/PHAEOs in SPM in November, suggesting freshly produced POM, whereas results of the POM composition in this area showed that the bloom occurs in spring. It is possible that this fresh POM comes from the Dogger Bank area located close by: the Oyster Ground area receives Atlantic waters coming from the north, which meets residual currents to the south of the Dogger Bank (Böhnecke, 1922) and joins the anti-clockwise current system of the North Sea.

At Coastal Station, the POM quality parameters were rather consistent with the results deduced from the pigments and PLFAs composition (Fig. 2, Fig. 3. See section 4.1.2.). The highest values of MUFA and Br-FAs and the highest CN-r were also found in February (Fig. 5, Fig. 6), emphasizing the presence of a higher bacterial biomass (Bechtel and Schubert, 2009) then. Similar values of ITPIG and PUFA were observed in November and May, indicating the presence of relatively fresh algal OM (Shaw and Johns, 1985; Canuel and Martens, 1993; Bianchi and Bauer, 2011) (Fig. 4, Fig. 5). Indicators of fresh OM were more expected in May at this station, rather than in November as primary production usually occurs in spring like at Oyster Grounds. A recent study of Le Guitton *et al.* (2015) showed that the OM in SPM along the principal OM route from the southwestern North Sea to the Skagerrak was of relatively high quality in September. Flushing time (in days), calculated from three numerical models and from measurements ranged from 28 to 73 days for this area (ICES, 1983; Backhaus, 1984; Lenhart and Pohlmann, 1997; Skogen *et al.*, 1995). Therefore one

could hypothesize that this fresh OM comes from the main primary production area (Fig. 1), as the time scale for degradation of POM was relatively short (Le Guitton *et al.*, 2015).

4.2.2. The sediments

Similarly to OM composition, no clear seasonal variation was observed in the sedimentary quality parameters. Moreover, the slight variation with depth confirm that the sediment was well mixed down to 10 cm deep at all stations and indicate that OM was of relatively ‘fresh’ quality especially at Dogger Bank (Fig. 4, Fig. 5, Fig. 6). The three stations investigated are inhabited by benthic macrofaunal species known to facilitate ecological processing of organic matter and burial. Several specimen of *Echinocardium cordatum* at Dogger Bank, *Upogebia deltaura* at Oyster Grounds and *Ensis directus* at Coastal Station were observed over the studied period. The high abundance of *Ensis directus* at Coastal Station could explain the highest variability of the OM quality parameters.

Results of OM quality parameters sets apart the nature of the Oyster Ground sediments from the other two stations and confirms its semi-depositional status (De Haas, 1997). Short-time scales proxies, i.e. the pigment-derived parameters, were the lowest at this station compared to the other stations, denoting higher OM degradation. At intermediate time scales, the PUFA sediment profiles clearly showed that the diagenetic alteration was more advanced at Oyster Grounds compared to Dogger Bank and Coastal Station (Fig. 5). In addition, the abundance of Br-FA and MUFA were the highest compared to the other stations, tending to increase with depth, indicating increasing bacterial biomass (Bechtel and Schubert, 2009). Finally on the long time scales, the CN-r was the highest in the Oyster Grounds also indicating OM has been degraded more.

5. Conclusion

The seasonal variation of POM composition and quality was investigated at three stations located on the Terschelling transect in the southern North Sea. Despite the close distance between stations, the POM composition and quality in SPM and SS were quite distinct. Pigments and PLFAs results showed evidence of a late fall bloom at Dogger Bank and a spring bloom at Oyster Grounds and Coastal Station. POM was of 'better' quality in SPM compared to SS at all stations over the studied period, except at Coastal Station in February, where POM was of higher quality in SS than in SPM. We could not find evidence of intensification of the erosion-deposition cycle due to bad weather conditions, but perhaps the sampling frequency was too low for that.

Our study also highlights strong differences in composition and quality of organic matter in both SPM and the sediments. Nevertheless in Dogger Bank and Oyster Grounds, the OM composition and quality was relatively constant down to 10 cm deep in the sediment, while at Coastal Station, more variability was observed, most likely due to the processing by benthic macrofauna and microbes. The semi-depositional status of Oyster Grounds was clearly highlighted as well by specific pigments and PLFAs biomarkers, and by all OM quality parameters that indicated higher diagenetic alteration of the OM in this station.

The southern North Sea is a complex and heterogeneous system with large spatial and temporal variation in lateral and vertical transport and in the extent of the processing of organic matter. Whereas the use of biomarkers does not allow full reconstruction of OM origin, it does elucidate spatial and temporal signals in OM quality, therefore aiding in interpreting the biogeochemical carbon cycle. These degradation sensitive

biomarkers clearly revealed the extensive pre-depositional degradation of OM before eventual burial in coastal sediments.

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7. Terms and acronyms

Br-FA – Branched fatty acid
CHLA/PHAEOs – Chlorophyll a to phaeopigments ratio
CN-r – Carbon to nitrogen ratio
ITPIG – Intact to total pigments ratio
MUFA - Monounsaturated fatty acid
OM – Organic matter
PLFA – Phospholipid derived fatty acids
POC – Particulate organic carbon
POM – Particulate organic matter
PUFA – Polyunsaturated fatty acid
SFA – Saturated fatty acids
SPM – Suspended particulate matter
SS – Surface sediment

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