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Composition, assimilation and degradation of *Phaeocystis globosa*-derived fatty acids in the North Sea

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Abstract

The fate of a *Phaeocystis globosa* bloom in the southern North Sea off Belgium, the Netherlands and Germany in May 1995 was investigated during a cruise with RV 'Belgica'. We used fatty acids as biomarkers to follow the fate of *Phaeocystis*-derived biomass of a *Phaeocystis*-dominated spring bloom. The bloom, in which up to >99% of the biomass was contributed by *Phaeocystis*, showed a fatty acid composition with a characteristically high abundance of polyunsaturated C_{18}-fatty acids, which increased in concentration with number of double bonds up to 18:5 (n-3), and high concentrations of 20:5 (n-3) and 22:6 (n-3). In contrast to most previous studies, fatty acid analysis of the mesozooplankton community (mainly calanoid copepods) and meroplankton (*Carcinus maenas* megalope) indicated that *P. globosa* was a major component (ca. 70% and 50%, respectively) in the diet of these organisms. Massive accumulations of amorphous grey aggregates, in which *Phaeocystis* colonies were major components, were dominated by saturated fatty acids and contained only few of the polyunsaturated C_{18}-fatty acids. A hydrophobic surface slick that covered the water surface during the bloom showed very similar patterns. Foam patches contained few *Phaeocystis*-typical fatty acids, but increased amounts of diatom-typical compounds such as 16:1 (n-7) and 20:5 (n-3), and 38% fatty alcohols, indicating that wax esters dominated the lipid fraction in the foam with ca. 76% (w/w). The fatty acid compositions of surface sediment showed that no sedimentation of fresh *Phaeocystis* occurred during the study. The results indicate that *Phaeocystis*-derived organic matter degraded while floating or in suspension, and had not reached the sediment in substantial amounts.

Keywords: Phytoplankton; *Phaeocystis*; Trophic fate; Degradation; Fatty acids

1. Introduction

The genus *Phaeocystis* is known for its ability to form massive, almost monospecific blooms (Lancelot et al., 1998). Such blooms are dominated by a colonial form, which can become three orders of magnitude larger (up to >10 mm) than the single cells (ca. 6 μm). *Phaeocystis globosa*, which is abundant in temperate and tropical oceans (Baumann et al., 1994; Medlin et al., 1994), has shown a clear increase in biomass due to eutrophication during the last decades in the southern North Sea (Cadée, 1992). Recently, *P. globosa* has even become a more important primary producer in this area than the diatoms (Lancelot et al., 1998). However, in contrast to other phytoplankton, there is

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no comprehensive concept about the role of *P. globosa* in the marine food web, and the ultimate fate of *Phaeocystis*-derived organic matter in this area.

Grazing, lysis, bacterial degradation or sedimentation may decimate phytoplankton. While *Phaeocystis* colonies are grazed by a number of copepods (Weisse et al., 1994), there is also evidence that many copepods feed inefficiently on colonies of *P. globosa* (Daro, 1985; Hansen and Van Boekel, 1991). Most of these studies have been conducted in the laboratory (Weisse et al., 1994), so little is known about in situ feeding behaviour of mesozooplankton. Estimated copepod grazing rates represent only a small fraction of phytoplankton standing stock and production during *Phaeocystis* blooms (Daro, 1985; Davies et al., 1992). Information on the nutritional value of *Phaeocystis*, based on its fatty acid composition, is inconsistent. Al-Hasan et al. (1990), Claustre et al. (1990), Nichols et al. (1991), Cotonnec et al. (2001), and Tang et al. (2001) suggest that *Phaeocystis* has a low nutritional value, because they found low amounts of polyunsaturated fatty acids (PUFA) in *Phaeocystis* cultures and blooms. In contrast, large amounts of PUFA, indicating a high nutritional value, were found in *Phaeocystis* blooms in the Balsfjord (Sargent et al., 1985; Hamm et al., 2001), the Barents Sea and the Greenland Sea (Kattner, pers. comm., 2000).

Protozooplankton are even less efficient grazers of *Phaeocystis* colonies (Weisse et al., 1994). Termination of *Phaeocystis* blooms in the North Sea seems to be initiated by nutrient limitation, which is typically followed by a release of the cells from the colonies (Veldhuis et al., 1986; Verity et al., 1988), and massive cell lysis (Van Boekel et al., 1992; Brussaard et al., 1995). Based on these observations, organic matter from *Phaeocystis* cells is thought to degrade rapidly.

In contrast, part of the POC in the colony material of *Phaeocystis* which is classified as being refractory (Thingstad and Billen, 1994) is probably not subject to heavy grazing, and does not sink rapidly enough to escape resuspension in the shallow, tidally mixed North Sea (Riebesell, 1993). Thus, we would expect particulate material from *Phaeocystis* colonies to prevail in suspension until labile compounds such as polyunsaturated fatty acids (Kieber et al., 1997) are largely degraded. The massive events of cell lysis, on the other hand, are suited to release large amounts of 'dissolved' organic matter into the water column. While hydrophilic compounds of this fraction such as carbohydrates will tend to stay in the water column, the amphiphilic and lipophilic fraction (fatty acids, sterols) may not be truly dissolved and will tend to accumulate at the water surface or solid hydrophobic surfaces due to low specific weight and/or cohesive effects. Such surface films, caused by the lysis of cells during *Phaeocystis* blooms should have a clear effect on the physics of the water surface, such as roughness (Garrett and Bultmann, 1963) or surface tension (sensu Marangoni, 1871), and promote the formation of sea foam.

In fact, the formation of foam benches on beaches of the North Sea is a well-known phenomenon usually associated with the termination of *Phaeocystis* blooms (Rogers and Lockwood, 1990). It is generally assumed that the foam is derived from breakdown products of the presumably polysaccharide-composed colony material of *Phaeocystis* (Lancelot et al., 1987; Rogers and Lockwood, 1990). However, it is not known whether the foam is formed due to the presence of proteins, carbohydrates, lipids, or a combination of these compounds.

The aim of this study was to follow potential pathways of *Phaeocystis* cells and colony material in the North Sea by identifying *Phaeocystis*-derived fatty acids in different fractions of organic matter during and after the culmination of a *Phaeocystis* bloom in the North Sea. Thereby, fatty acid patterns were used to identify the diet of zooplankton, and to indicate the origin and degradative state of amorphous organic matter in aggregates, foam, surface slick and on the sediment surface. Since fatty acids occur exclusively in the cells, but not in extracellular material of *Phaeocystis* colonies (Hamm et al., 1999), amount and degradative state of *Phaeocystis* specific fatty acids were related to the presence and degradative state of *Phaeocystis* cells.

2. Material and methods

2.1. Study area and study period

This study was conducted during a cruise with RV 'Belgica' along the Belgian and Dutch North Sea coast in May 1995 (Fig. 1), thus, in an area and a season of recurrent massive blooms of *Phaeocystis globosa*.

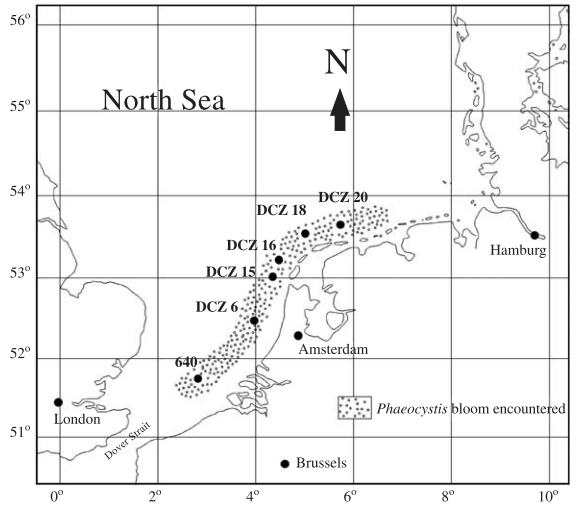

Fig. 1. Map of the southern North Sea showing sampling sites and the area where a *Phaeocystis* bloom was observed.

2.2. Sampling

Suspended material was sampled at a depth of 10 m with 10-L Niskin bottles; mesozooplankton was taken with a WP-2 net. Aggregates (Fig. 2) were taken with a bucket from the water surface, where they occurred in abundance. A hydrophobic surface film, whose presence was inferred from the observations described in Fig. 3 (sensu Marangoni, 1871), was concentrated by repeatedly pouring surface water (representing approximately 0.7 m^2 of water surface) into a glass beaker, and removing the underlying water with a silicon tube. When only 10 ml were left in the beaker, it was transferred to a 10 ml glass culture vial. The upper ml of this material was immersed with a glass pipette in the extraction solvent. Material from a foam patch (foam containing green aggregates, Fig. 4), and megalope larvae of *Carcinus maenas*, which were abundant

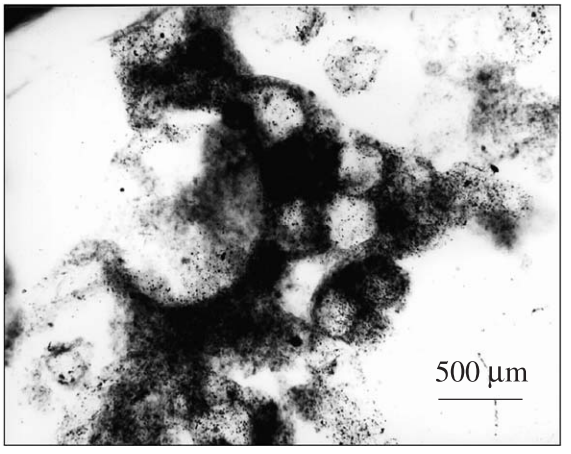

Fig. 2. Aggregate from st. DCZ 20, containing amorphous material, and no diatoms. A contribution of *Phaeocystis*-derived organic matter is indicated by the circular spaces within the aggregate.

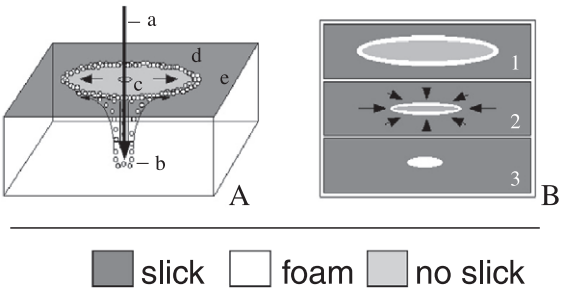

Fig. 3. Schematic surface slick at st. DCZ 20, (A) formation of a foam ring encircling a hydrophilic surface, (a) water poured from 3 m height, (b) air bubbles rising to the water surface and causing local upwelling, (c) area were the surface slick was driven back by the upwelled water, (d) area of surrounding surface slick, (e) foam accumulated at the boundary between hydrophilic and hydrophobic surfaces; (B) successive compression of the hydrophilic surface (black) and foam (white) by the lipophilic surface slick (grey) as described in the text.

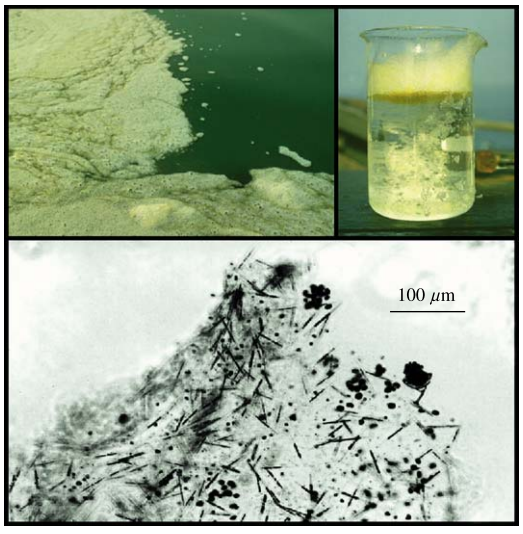

Fig. 4. Above left: foam patch at st. DCZ 16; right: foam in a beaker, showing an accumulation of algae under the foam. Below: degraded colony from the foam, colonised by *Nitzschia* and a rotifer.

under the foam, were sampled from a zodiac with a bucket. Small sediment cores of 1 cm^3 were taken with open plastic syringes from a box corer (ca. 50 cm diameter) at all stations as described by Boetius and Lochte (1994).

2.3. Plankton composition

Phytoplankton and zooplankton was fixed with hexamethylenetetramine buffered formaldehyde. The quantitative assessment phytoplankton and protozooplankton composition was determined by the method of Utermöhl (1958), cell counts were converted into phytoplankton biomass according to Edler (1987) and Rousseau et al. (1990). Zooplankton composition was qualitatively assessed under a stereomicroscope.

2.4. Lipid extraction

For fatty acid extraction, the POC from the water column, zooplankton and aggregates were filtered on glass fiber filters (GF/C), immersed in 6 ml dichloromethane:methanol (2:1; v/v) in glass culture vials with teflon-sealed screw caps and stored at −30 °C. Filters and culture vials were precombusted at 550 °C for 4 h. The screw caps were rinsed with a detergent (Decon), deionised water and dichloromethane: methanol (2:1; v/v) to avoid contamination. Concentrated surface slick and sediment samples were directly immersed in dichloromethane:methanol (2:1; v/v) (Folch et al., 1957). Aggregates and zooplankton were homogenised for efficient extraction. Polar compounds were separated by mixing with 0.88% KCl and discarded after phase separation (Bligh and Dyer, 1959).

2.5. Fatty acid analysis

Methyl esters of fatty acids (FAME) were prepared from phospholipids, triacylglycerols and wax esters, additionally, free fatty alcohols were prepared from wax esters. Transesterification was performed for 4 h at 80 °C in methanol containing 3% sulfuric acid under N_2-atmosphere. After extraction with hexane, FAME and free fatty alcohols were analysed with a CP-900 gas–liquid chromatograph on a 30 m × 0.25-mm-i.d.wall-coated open tubular column (liquid phase: DB-FFAP; film thickness: 0.25 μm), using temperature programming, and flame ionisation detection. A known standard was used for identification. For further details see Kattner and Fricke (1986). The fatty acid 18:5 (n-3) was identified by relative retention time (Okuyama et al., 1992). Platinum-catalysed hydration of double bonds showed a quantitative increase of the 18:0 peak compared to an untreated control with suspected high amounts of 18:5 (n-3). We considered only fatty acids comprising more than 0.5% of the respective fatty acid patterns.

2.6. Fatty acid interpretation

To assess the degradative state of the fatty acids, we listed the proportions of saturated, monounsaturated and polyunsaturated fatty acids (PUFA). Degradation causes a relative increase of the saturated fatty acids and a decrease of PUFA (De Baar et al., 1983). The relative abundance of *Phaeocystis*-derived fatty acids was assessed by the percentage of C_{18}-PUFA and 22:6 (n-3) (sensu Hamm et al., 2001), the abundance of diatoms by the percentage of 16:1 (n-7) and 20:5 (n-3) (sensu Kates and Volcani 1966). The ratio between these *Phaeocystis*- and diatom-specific fatty acids was used as an indication of the relative proportions of *Phaeocystis*- and diatom-derived organic matter. The sum of fatty alcohols indicated the presence of wax esters, which are clearly related to zooplankton-derived biomass.

3. Results

3.1. Physical conditions

During the cruise, a high pressure system caused unusually calm, warm and sunny weather. In spite of the virtual absence of wind-induced mixing, there was no significant density stratification in the water column. Temperatures in the water column ranged between 9 and 15 °C.

3.2. Plankton community

The phytoplankton composition at the stations discussed here was clearly dominated by *Phaeocystis globosa* colonies, with 89.6% (Station DCZ 16), 94.2% (DCZ 18), 94.5% (DCZ 6) and 98.9% (640)

of the combined phytoplankton and protozooplankton carbon. Mostly centric diatoms represented another substantial fraction (0.01–8.4%). Protozooplankton (mainly dinoflagellates) were present, but their biomass was low (1.07–5.42%) of the phytoplankton biomass (Becquefort, unpubl. results). Mesozooplankton could be only assessed qualitatively, since the *Phaeocystis* colonies clogged the net, which most likely resulted in undersampling, and hampered quantification. *Temora longicornis*, *Calanus finmarchicus*, *Calanus helgolandicus*, *Metridia lucens*, *Centrophages* sp., *Pseudocalanus* sp. and *Oithona similis* were abundant in the copepod communities at stations DCZ 6, 15 and 16. At station DCZ 16 megalope larvae of *Carcinus maenas* occurred in high concentrations below a patch of sea foam. Within the phytoplankton bloom, we found fatty acid patterns typical of *Phaeocystis* blooms (Fig. 2), with low amounts of 16:1 (n-7), representing the contribution of diatoms, and high amounts of 18:1 (n-9) 18:2 (n-6), 18:3 (n-3), 18:4 (n-3), and 18:5 (n-3) (Table 1), which are typical of many *Prymnesiophycea* (Conte et al., 1994). This pattern was found at stations 640, DCZ 6, DCZ 16 and DCZ 18, confirming the dominance of *Phaeocystis* in the different parts of the bloom (Fig. 5). The fatty acid 18:5 (n-3), which occurred in higher concentrations than the other C_{18}-PUFA, has not yet been observed in blooms of *P. globosa*. Significant amounts of 20:5 (n-3) and 22:6 (n-3) were also detected, but their concentrations varied more than the C_{18}-PUFA. Likewise,

Table 1
Fatty acid and fatty alcohol compositions of the *Phaeocystis* bloom, zooplankton and amorphous matter

Fatty acid	*Phaeocystis* bloom	SD	bottom	copepods	SD	*Carcinus* megalopes	foam	aggregates	slick
14:O	13.89	+/- 3.53	20.10	6.52	+/- 1.71	2.07	5.59	11.92	7.99
14:0 A				1.04	+/- 1.58		3.65	4.23	
16:O	20.93	+/- 1.23	20.03	13.48	+/- 2.41	15.44	10.22	28.75	38.11
16:1 (n-7)	2.48	+/- 0.29	9.01	13.14	+/- 1.28	3.66	9.05	1.43	
16:0 A				2.07	+/- 3.06		12.45	22.02	13.49
16:1A							4.10		
18:O	3.86	+/- 0.75	7.13	4.37	+/- 1.55	7.28	2.61	8.59	18.26
18:1 (n-9)	25.24	+/- 3.95	13.78	10.88	+/- 4.60	7.63	4.73	7.42	10.14
18:1 (n-7)	1.93	+/- 0.49		1.89	+/- 0.26	5.53	1.05	1.00	
18:2 (n-6)	2.19	+/- 0.53	6.51	2.27	+/- 0.62	1.07	0.82	5.24	5.27
18:3 (n-3)	4.74	+/- 0.47	3.47	3.22	+/- 0.80	1.71	0.65	3.49	6.74
18:4 (n-3)	6.40	+/- 0.80	4.31	7.55	+/- 0.88	2.86	3.09	0.86	
18:5 (n-3)	9.12	+/- 1.27	4.48	1.93	+/- 0.28	0.62			
20:1 (n-9)				0.93	+/- 0.43	1.42	2.59		
20:4 (n-3)				5.76	+/- 7.77		0.51	1.45	
20:1A						9.68			
20:5 (n-3)	3.09	+/- 0.89	5.38	14.28	+/- 1.32	25.43	12.76	1.94	
22:1 (n-11)						2.75			
22:1 A						8.30			
22:5 (n-3)						1.12	0.65		
22:6 (n-3)	6.13	+/- 1.07	5.79	20.67	+/- 2.61	24.15	2.96	1.65	
saturated	38.69	+/- 4.14	47.27	24.37	+/- 5.67	24.80	18.43	49.26	64.37
MUFA	29.64	+/- 3.88	22.79	16.84	+/- 7.47	16.82	14.83	9.85	10.14
PUFA	31.67	+/- 3.62	29.94	55.69	+/- 2.67	55.84	20.29	13.19	12.01
C_{18}-PUFA +22:6	28.58	+/- 3.08	24.56	35.65	+/- 3.86	30.41	7.53	11.24	12.01
16:1 + 20:5	5.57	+/- 1.16	14.39	17.42	+/- 0.88	29.09	21.82	3.38	0.00
ratio	5.14	+/- 1.11	1.71	2.05		1.05	0.35	3.33	-
fatty alcohols	0.00		0.00	3.11	+/- 4.64	0.00	38.18	26.25	13.49
20:5 + 22:6	9.22	+/- 1.77	11.17	34.95	+/- 3.92	49.58	15.72	3.59	0.00

high values indicate a high concentration of *Phaeocystis*-derived material.

high values indicate a high concentration of diatom-derived material.

high values indicate a high concentration of material derived from Crustacean Zooplankton.

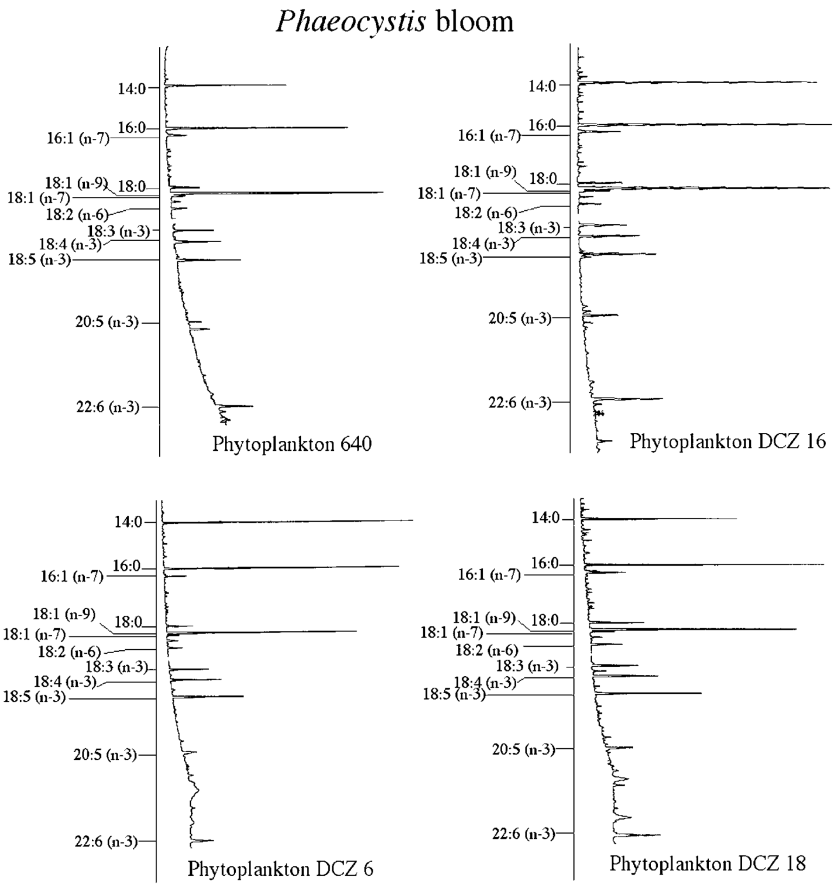

Fig. 5. Fatty acid compositions (chromatogramms) of the *Phaeocystis* bloom from st. 640, DCZ 6, DCZ 16 and DCZ 18. Please note the low amount of contaminating compounds in all samples.

the unspecific, stable saturated fatty acids 14:0, 16:0 and 18:0, though present in high concentrations, varied considerably.

3.3. Amorphous

A foam patch, which belonged to a long foam streak probably accumulated at a front, was observed at st. DCZ 16 (Fig. 2). It contained many aggregates, and large numbers of copepods and megalope larvae were found directly under the foam. The foam itself contained large amounts (38%) of fatty alcohols, indicating a dominance of wax esters (ca. 76%, Table 1) An elevated concentration of 16:1 (n-7) and 20:5 (n-3) compared to the bloom indicated a high abundance of diatoms; in contrast, the typical pattern of fresh *Phaeocystis*-specific fatty acids, as shown for the bloom, was not discernible. Microscopic examination of the foam showed a high abundance of *Phaeocystis* colonies and diatoms (*Nitzschia* sp., Fig. 2) colonising the *Phaeocystis* colonies, but except for some copepod eggs no zooplankton.

At station DCZ 20, we observed an unusual smoothness of the water surface, indicating an efficient damping of capillary waves ($n < 1.7$ cm), which could not be fully explained by the calm weather conditions. Likewise, we noted that foam rings of about two metres diameter, caused by the pouring of water from board, were rapidly (i.e. within several seconds) compressed to a small patch, while the foam persisted (Fig. 3). From these details we inferred the presence of a hydrophobic layer on top of the water

surface (sensu Marangoni, 1871; Garrett and Bultmann, 1963). This surface slick contained mainly saturated and monounsaturated fatty acids, indicating that it consisted of largely degraded material (Table 1; Fig. 7). As shown by the dominance of *Phaeocystis*-specific fatty acids, and the lack of diatom-specific fatty acids and zooplankton-specific fatty alcohols, the surface slick most likely originated from *Phaeocystis*-derived organic matter.

At the same station, high concentrations of several cm large, tough grey aggregates, resembling cotton waste, were observed, and first taken for an unidentified case of pollution. Microscopic analysis revealed that these aggregates consisted of round objects enclosed in an unidentified amorphous matrix, but contained no diatoms (Fig. 4). A potential pollution was ruled out as aliphatic hydrocarbons and highly esterified oils, which dominate anthropogenic surface slicks (Baier et al., 1974), were not detected. Its fatty acid composition was similar to that of the surface slick (Table 1, Fig. 7), but it contained additional fatty alcohols.

3.4. Zooplankton

In copepods sampled at stations DCZ 6, 15 and 16, the biomarker fatty acids from *Phaeocystis* (C_{18}-PUFA and 22:6) and diatoms (16:1 (n-7) and 20:5) were clearly present (Table 1), which indicated that *Phaeocystis* had been a main food source during accumulation of the present lipids. A rough estimate, based on the percentages of *Phaeocystis*-specific

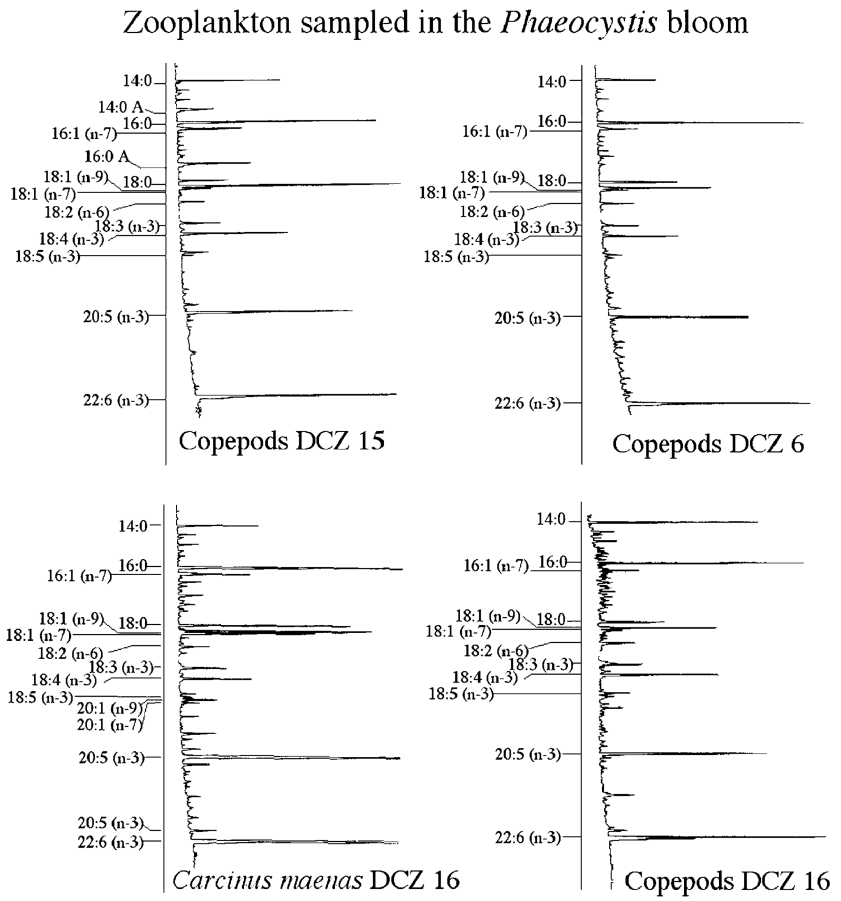

Fig. 6. Fatty acid compositions (chromatogramms) of the sampled copepods at st. DCZ 6, DCZ 15 and DCZ 16, and megalope larvae of *Carcinus maenas* from st. DCZ 16.

versus diatom-specific fatty acids, would indicate that ca. 70% of the copepod fatty acids were derived from *Phaeocystis* and 30% from diatoms. Likewise, megalope larvae from *Carcinus* sp. contained both C_{18}-PUFA and 16:1 (n-7), and thus probably fed on *Phaeocystis* as well as on diatoms at an estimated ratio of 50:50. In copepods and decapods encountered during this study, the long chained and highly unsaturated fatty acids 20:5 and 22:6 were greatly enriched compared to the *Phaeocystis* bloom. Fatty alcohols in the zooplankton were only found at station DCZ 15, where 16:0 A was clearly present (Fig. 6).

3.5. Sediment

Fatty acid patterns of the surface sediment taken during the cruise were highly variable in content and composition. The fatty acid composition typical of the *Phaeocystis* bloom at the surface was encountered at none of the stations, indicating that undegraded organic matter derived from *Phaeocystis* cells did not reach the sediment surface.

4. Discussion

4.1. Phaeocystis fatty acids have a high nutritional value

The very simple and clearly *Phaeocystis*-related fatty acid pattern of the *Phaeocystis* bloom (Fig. 5) indicates simplicity of the plankton community, i.e. low abundance of bacteria, protozooplankton, other algae and mesozooplankton. This is consistent with our data on phytoplankton, and protozooplankton. Stations with up to 99% *Phaeocystis* biomass confirm the connection between the observed fatty acid pattern and *P. globosa*. This is also consistent with the view that *Phaeocystis* blooms can be almost monospecific (Lancelot et al., 1998) and inhibit heterotrophic growth (Van Boekel et al., 1992). A low nutritional value of *Phaeocystis* due to low PUFA content, as suggested by Al-Hasan et al. (1990), Claustre et al. (1990), Nichols et al. (1991), Cotonnec et al. (2001) and Tang et al. (2001), was not found. This agrees with several studies that suggest that the *Phaeocystis* colonies are mechanically protected (e.g. Hamm et al., 1999; Jakobsen and Tang, 2002).

The low PUFA contents of *Phaeocystis* cells reported earlier most likely reflect the extreme susceptibility of *Phaeocystis* cells and PUFA to degradative processes (Van Boekel et al., 1992, this study), especially since a high concentration of PUFA is essential for maintaining membrane fluidity and the functioning of biochemical pathways at temperatures below 20 °C. The bulk of the cell membranes in phytoplankton is typically situated in chloroplasts (Cohen et al., 1988), where electron transport is maintained by the mobility of plastoquinone. This is mediated by the fluidity of the thylakoid membrane, which in turn requires high concentrations of PUFA. A recent study of the gene knockout of fatty acid desaturases has demonstrated the direct involvement of the unsaturation of membrane lipids in the functioning of the photosynthetic mechanism (Tasaka et al., 1996): *Synechocystis* sp. PCC 6803 contains four desaturases, which can be inactivated by gradual insertional mutation. After deletion of polyunsaturated fatty acids in membrane glycerolipids, this organism does not grow at 20 °C, at which the wild-type strain grows very well. Thus, in growing phytoplankton cells, high amounts of PUFAs are a necessity, and species-specific variations in fatty acid composition may concern their chain length, but much less so the cumulative amount of double bonds. In degrading cells, however, a rapid loss of PUFA is very likely. Degradation may be due to nutrient limitation, effects of pedators and pathogens, or mechanical and thermal stress such as occurs during the difficult and extended filtration procedure of *Phaeocystis* colonies.

High amounts of C_{18}-PUFA in the *Phaeocystis globosa* bloom of the North Sea in 1995 can thus be considered to be typical of *Phaeocystis* blooms in general: They were also detected in a *Phaeocystis pouchetii* bloom in Balsfjorden of northern Norway (Hamm et al., 2001). The North Sea bloom had higher amounts of 18:1 (n-9) and 18:3 (n-3) than the Balsfjorden bloom, and a lower concentration of 20:5 (n-3) and 22:6 (n-3). These moderate differences between the two blooms may reflect adaptations to differing abiotic conditions such as light (Thompson et al., 1990), nutrients, or temperature (Baash et al., 1984), or represent species-specific fatty acid patterns for *P. pouchetii* and *P. globosa*, respectively. As *P. globosa* and *P. pouchetii*, a third colony-forming *Phaeocystis* species, *Phaeocystis antarctica*, has been found to

contain a very high percentage of 18:5 (n-3) (Kattner, pers. comm., 2000).

4.2. Zooplankton accumulates Phaeocystis-specific fatty acids

The copepods as well as the decapod larvae (*Carcinus maenas*) clearly contained the *Phaeocystis*-typical fatty acid pattern (including the polyunsaturated C_{18}-fatty acids), and, to a lesser extent, the fatty acids typical of diatoms (especially 16:1 (n-7)), indicating that *Phaeocystis* served as the major (ca. 70 and 50%, respectively) food source for these organisms (sensu Kattner and Krause, 1989; Graeve et al., 1994). This finding is consistent with previous reports, which showed that major copepods in the North Sea (e.g. *Calanus finmarchicus*, *Acartia clausi*, and *Temora longicornis*) are able to ingest *Phaeocystis* colonies (Weisse et al., 1994). We cannot completely exclude the possibility that some fatty acids, which we assigned to *P. globosa* biomass, originated from dinoflagellates, which have a fatty acid composition similar to the pattern we considered to be typical of *P. globosa* (Mansour et al., 1999). However, we suggest that this had little effect on our results, since the abundance of protozooplankton was very low (<4%, Becquefort, unpubl. results), and dinoflagellates typically contain little 18:1 (n-9) fatty acid (Mansour et al., 1999), which was very abundant in the bloom and in the zooplankton sampled. While *Carcinus* Zoea larvae have problems to feed on single cells of *Phaeocystis* (Hansen, 1992), the colonies appear to be readily utilised by *Carcinus* megalopes. An estimation of zooplankton abundance was hampered by the *Phaeocystis* colonies, which clogged the zooplankton net. This situation has been reported earlier (Atkinson et al., 1978). Hence, it seems to be generally difficult to assess the abundance, and consequently the grazing impact, of zooplankton in the presence of *Phaeocystis* colonies. Low in situ grazing rate estimates (Hansen and Van Boekel, 1991; Bautista et al., 1992) should also be seen as the potential consequence of undersampling of zooplankton during *Phaeocystis* blooms. Surprisingly, the fatty acid 18:5 (n-3), which was very prominent in the *Phaeocystis* bloom, was not accumulated accordingly in the zooplankters. To our knowledge, this fatty acid is never as important in zooplankton as fatty acids such as 18:4 (n-3), 20:5 (n-3) or 22:6 (n-3). During gut passage of *Phaeocystis*-dominated material in krill, 18:5 (n-3) increased in concentration relative to the other fatty acids (Hamm, unpubl. results). This indicates that assimilation of 18:5 (n-3) may be less efficient than assimilation of other fatty acids.

4.3. Aggregates represent the refractory fraction of Phaeocystis colonies

The aggregates contained little identifiable material. As also previously described by Riebesell (1993) for *Phaeocystis* aggregates, they seemed to be more or less neutrally buoyant, and were thus abundant in the upper layer of the water column. Microscopic examinations (Fig. 3), and the lack of alternative sources indicated that *Phaeocystis* colonies were main components of these aggregates. However, absence of discernible cells (Fig. 3) and the depletion of polyunsaturated fatty acids (Table 1, Fig. 7) indicated that degradation of the *Phaeocystis* cells was already in an advanced state. Thus, the aggregates contained mostly material from the colony matrix (Thingstad and Billen, 1994), although Janse et al. (1999) have shown that the mucopolysaccharides of the colony matrix are principally highly degradable. In this respect, *Phaeocystis*-derived aggregates differed fundamentally from diatom aggregates, which can contain large amounts of physically intact cells (Riebesell, 1991), and a higher percentage of PUFA (Najdek, 1996). The similarity between the fatty acid patterns of these aggregates and the surface slick (Table 1, Fig. 7) indicated a comparable origin and degradative state of this material. Since the water surface is a highly oxidative environment (e.g. due to direct contact with atmospheric O_2 and solar radiation), the polyunsaturated fatty acids were mostly degraded (sensu Kieber et al., 1997). This phenomenon has been observed earlier (Garrett, 1967; Marty and Saliot, 1974; Kattner and Brockmann, 1978; Marty et al., 1979).

4.4. Fatty acid composition in the foam was influenced by diatoms and zooplankton

The foam, which consisted of particulate identifiable, particulate amorphous, and dissolved matter (Fig. 4), did not contain the typical pattern of *Phaeocystis*-derived fatty acids, as shown in Table 1 and Fig.

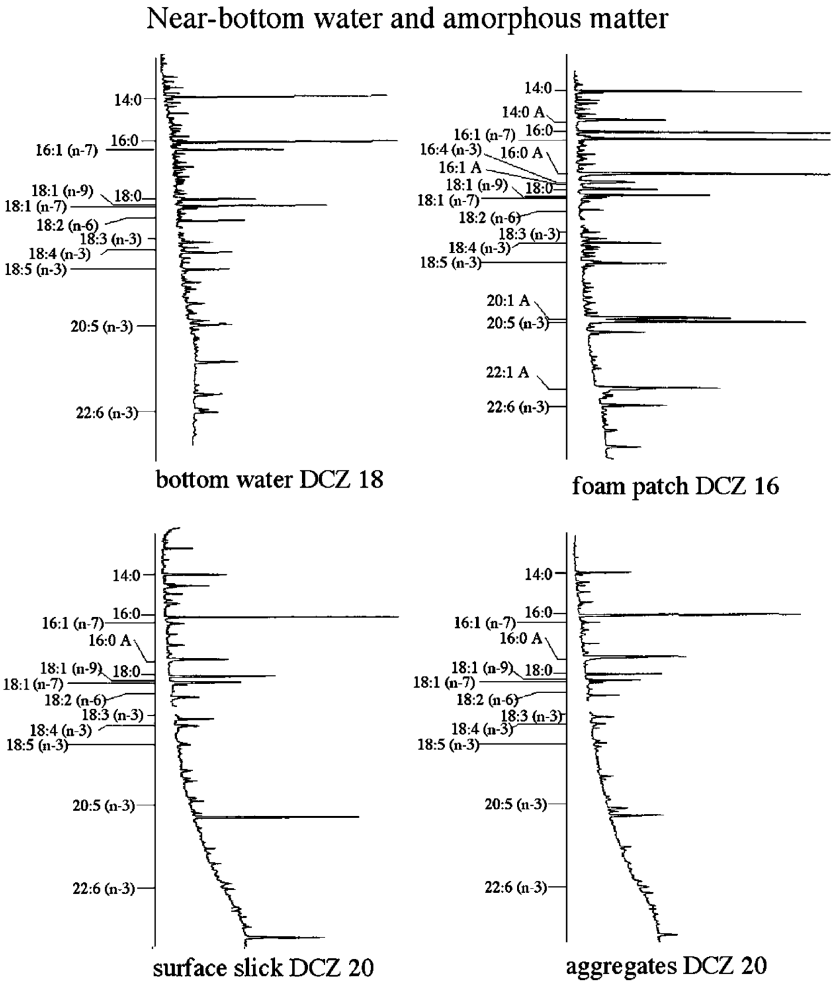

Fig. 7. Fatty acid compositions (chromatogramms) of bottom water (DCZ 18), foam (DCZ 16), surface slick (DCZ 20), and aggregates (DCZ 20).

5. As indicated by the increased amount of diatom-specific fatty acids, such as 16:1 (n-7) and 20:5 (n-3) compared to 22:6 (n-3), diatoms dominated the fresh phytoplanktonic material (Fig. 5). The high abundance of fatty alcohols, which are indicators of wax esters and thus zooplankton (Volkman et al., 1981), in the foam was surprising, since apart from a few copepod eggs, no zooplankton was found in the foam.

In contrast, senescent *Phaeocystis* colonies, often colonised by diatoms of the genus *Nitzschia*, but still containing many cells, dominated the particulate fraction (Fig. 4). We suggest that the fatty alcohols may have originated from dissolved zooplanktonic wax esters, a phenomenon which has been observerd earlier by Volkman et al. (1981) within a 'milky water' event in the North Sea. Classically, wax esters are thought to occur in high concentrations in overwintering, but less so in vernal zooplankton (Sargent and Falk-Petersen, 1988). On the other hand, Kattner and Krause (1989) demonstrated that high percentages (20-92%) of wax esters are found in the lipids of *Calanus finmarchicus* in all stages of its development. In our study, a causal connection between the *Phaeocystis* bloom and a potential mortality of the prevalent copepods or *Carcinus* larvae (sensu Volkman et al., 1981) is unlikely, since the zooplankton sampled in

this study contained only few wax esters, as indicated by the low concentration of fatty alcohols (Table 1, Fig. 6). We therefore speculate that the occurrence of the dissolved fatty alcohols indicates the mortality of a copepod population (e.g. in relation with reproduction, Ohman et al., 1996) distinct from the copepods we sampled during the bloom.

4.5. *Phaeocystis* cells are degraded while in suspension

Previous studies have shown that sea surface slicks are never, as it might be intuitively assumed, dominated by fatty acids, but mainly composed of other surface-active compounds such as proteins, polysaccharides, humic-type materials and waxes (Kattner et al., 1983; Van Vleet and Williams, 1983), glycoproteins and proteoglycans (Baier et al., 1974). The same composition was found in stable foams on the ocean, which are thought to originate from surface slicks. As fatty acids are main components of phytoplankton (Thompson et al., 1990), low fatty acid concentrations in foam and surface slick indicate extensive degradation of this material, which is also consistent with the shift of fatty acid composition to the more stable, saturated compounds (Table 1). Though indications of a bloom termination (i.e. aggregates, foam, surface slick) were present, and *Phaeocystis* colonies were entangled in the crown of a bottom dwelling polychaete (*Lanice concilega*) sampled with a box corer, indicating the presence of *Phaeocystis* at the bottom, no accumulation of *Phaeocystis*-derived or other phytoplankton material on the sediment surface was observed, and *Phaeocystis*-derived fatty acids were never an important fraction in the upper cm of the sediment. In contrast, sediment taken from a tidal flat near the North Sea barrier island of Norderney clearly showed the fatty acid signature of the diatoms (high amounts of 16:1 (n-7) and 20:5 (n-3); Hamm, unpublished results), which reflected the typical dominance of diatoms in this ecosystem. Hence, freshly sedimented *Phaeocystis* cells should have created a recognisable signal.

5. Conclusion

In contrast to previous studies, results from this study indicate that colonies of *Phaeocystis globosa* have a fatty acid pattern of a high nutritional value. Accordingly, they were the major food source of copepods and decapod larvae during the *Phaeocystis* bloom. In contrast, organic matter derived from *Phaeocystis* cells seems to be rapidly degraded once the colonies disintegrate. As only *Phaeocystis* cells, but not the colony material contain fatty acids, our results indicate that the cells of *Phaeocystis* and the organic matter therein are highly susceptible to degradation. Accumulations of dissolved and particulate organic matter with a largely degraded fatty acid pattern suggest that part of the organic matter, supposedly originating from the extracellular colony, is more refractory.

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