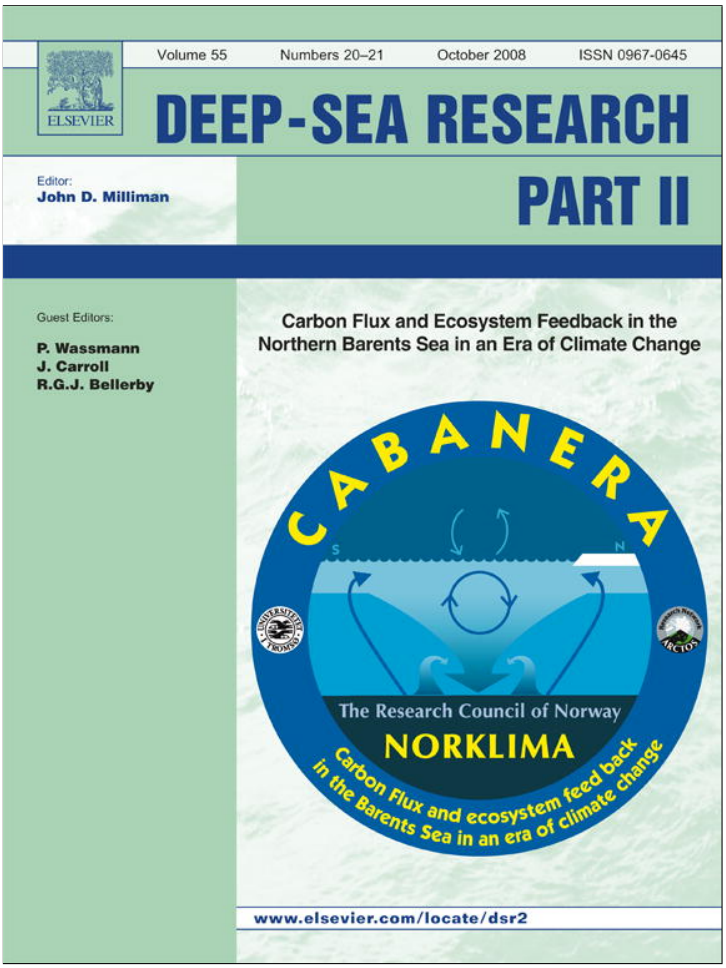

Deep-Sea Research II 55 (2008) 2381–2389

Contents lists available at ScienceDirect

Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Sedimentary pigments in the western Barents Sea: A reflection of pelagic–benthic coupling?

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ARTICLE INFO

Article history:
Accepted 8 April 2008
Available online 15 August 2008

Keywords:
Arctic
Marginal ice zone
Sedimentary pigments
Pelagic–benthic coupling
Carbon cycle
HPLC

ABSTRACT

Local pelagic and sympagic primary production are usually the base of the Arctic food webs, and can be the main inputs of organic matter to the benthos. In order to characterize the major sources of production and understand the fate of organic matter to the benthos, water-column, ice, and sedimentary pigments of the Barents Sea were studied by HPLC analysis at 12 stations during the summer 2003, summer 2004, and spring 2005, in the framework of the CABANERA project. Chlorophyll *a* (chl *a*) concentration in surface sediments correlated significantly with total chl *a* integrated throughout the water-column as well as the chl *a* fluxes measured at 1 and 90 m water depth. This suggests that local water-column and ice-associated algae production are the main sources of fresh organic matter to the benthos. In the sediment, water-column, and ice, the major accessory pigment found was fucoxanthin, the marker pigment of diatoms, particularly dominant in spring. In summer, chlorophyll *b*, a marker of green algae, was found in stations influenced by Arctic waters, while 19′-hex-fucoxanthin, a marker of prymnesiophytes, was found in stations influenced by Atlantic water. The source of organic matter inputs to the benthos is thus highly dependent of the water masses influences in the summer. The ratio of sedimentary chl *a* to total phaeopigments (chl *a*/phaeo) was higher in the spring, and the total of phaeopigments in the sediment was correlated with water-column phaeopigments and with sedimentary phaeophorbide *a*, a pigment typical of grazing by zooplankton. This suggests that in the summer, organic matter reaching the sediment already has been degraded through grazing, while in spring, more fresh material reaches the sediment. The chl *a*/phaeo ratio was correlated with benthic oxygen demand measured by other researcher in this project, suggesting the importance of the quality of the organic matter reaching the sediment for benthos activities. Our results confirm a close pelagic–benthic coupling in both spring and summer over the entire study area.

1. Introduction

The Arctic Ocean is characterized by broad continental shelves (51% of its surface area), many of which have high rates of primary productivity (Sakshaug, 2004). In some areas, much of this production falls to the bottom, supplying rich and active communities of benthic organisms (Piepenburg et al., 1997). In areas covered by ice, ice algae can be a major source of carbon for the food web (Gosselin et al., 1997; Nozais et al., 2001), and therefore can be an important source of nutrition for benthic communities (Klages et al., 2004). It is now generally accepted that global warming effects are expected to be enhanced in the Arctic (Mitchell et al., 1995; ACIA, 2004). Modification of ice distribution and seasonality due to global warming is expected to lead to a drastic shift of the productivity regime (phytoplankton vs. ice algae), and thus to an entire restructuring of the food web. It is therefore very important to characterize organic matter pathways to the sea floor across the Arctic.

The primary productivity in the Barents Sea is high for Arctic shelf systems, about 100 g C m^{-2} yr^{-1} (Sakshaug and Slagstad, 1992), and pelagic–benthic coupling may be particularly tight (Wassmann et al., 2006). The western Barents Sea is influenced by Atlantic waters in the south and west, while Arctic waters penetrate from the north and east (Wassmann et al., 2006). Different water masses are found to have different phytoplankton (Rat'kova and Wassmann, 2002; Reigstad et al., 2002) and zooplankton compositions (Colebrook, 1985). Moreover, variations in the inflow of warm and saline Atlantic Waters determines the sea-ice distribution (Wassmann et al., 2006). A marginal ice zone (MIZ) is defined as "that part of the ice cover which is close enough to the open-ocean boundary to be affected by its presence" (Wadhams, 1986). The Barents Sea MIZ plays an

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doi:10.1016/j.dsr2.2008.05.004

important role in timing, development, and magnitude of phytoplankton bloom (Wassmann et al., 1996). The match or mismatch of zooplankton with regard to phytoplankton blooms determines the fate of the produced carbon, which can be either retained in the water-column or exported to the bottom (Wassmann, 1991; Wassmann et al., 1996). In the Barents Sea, as much as 50% of the primary production is exported from the surface and may represent potential food for the benthic organisms (Wexels Riser et al., 2008).

Sedimentary pigments have demonstrated their usefulness in short- and long-term studies of ecosystem changes, such as changes in organic matter production (Harris et al., 1996), eutrophication (Chmura et al., 2004; Kowalewska et al., 2004), and cyanobacterial blooms (Bianchi et al., 2000; Poutanen and Nikkilä, 2001), as well as larger scale sea-level (Squier et al., 2002) and hydrodynamic changes (Kowalewska, 2001; Zhao et al., 2000). HPLC (high pressure liquid chromatography) analysis allows the identification of various chloropigments and carotenoids (Bianchi et al., 1997; Kowalewska, 1995; Kowalewska et al., 1998, 2004; Sun et al., 1991, 1994). The advantage of HPLC analyses over fluorometric methods is that it allows identification of these accessory pigments and of degradation pigments. Many of the accessory pigments are specific for certain algal groups and can be used as taxonomic markers (Gieskes and Kraay, 1984; Jeffrey and Vesk, 1997). Chlorophyll *a* (chl *a*) is a pigment present in all photosynthetic organisms. Thus, sedimentary chl *a* is a marker of the "freshness" of the algal matter inputs to the sediment (Boon and Duineveld, 1996), while its degradation products are markers indicating physiological status and the processes they went through (Mantoura and Llewellyn, 1983; Villanueva and Hastings, 2000). Very few studies have investigated the sedimentary chl *a* and its derivatives (phaeo) in the Barents Sea (Pfannkuche and Thiel, 1987; Thomsen et al., 1995) and, to our knowledge, there are no other published studies of using HPLC to investigate sedimentary pigments anywhere in the Arctic.

By studying sedimentary pigments during the CABANERA (carbon flux and ecosystem feedback in the northern Barents Sea in an era of climate change) program, we addressed the following questions: How do sedimentary pigment composition and concentration vary seasonally and spatially? Do the sedimentary pigments reflect the local production and processes in the water-column and the ice? What are the main processes responsible for degradation of pigments in the sediment?

2. Methods

2.1. Study area and sampling techniques

The Barents Sea is permanently ice-free in the south, seasonally ice-covered in the center and the east and has a more or less permanent ice cover above 80°N. The North Atlantic Current coming from the southwest separates into two branches while the Arctic waters come from the northern Barents Sea (Fig. 1). The northwestern Barents Sea region was investigated in summer 2003 (benthic stations 1, 2, 3, and 4) and 2004 (benthic stations 8, 10, 11, and 12), and spring 2005 (benthic stations 15, 16, 17, and 18), during the CABANERA project, onboard the R/V *Jan Mayen* (Fig. 1 and Table 1). For each station where sediment was collected, 2–6 l of water from the water-column chlorophyll maximum determined by a CTD (Sea-bird Electronics) were collected and filtered through GF/F filters. Hodal and Kristiansen (2008) determined that all stations were in bloom phase. When ice was present, samples of ice algae and detritus were collected by SCUBA diving below the ice, using a 20 μm mesh net mounted

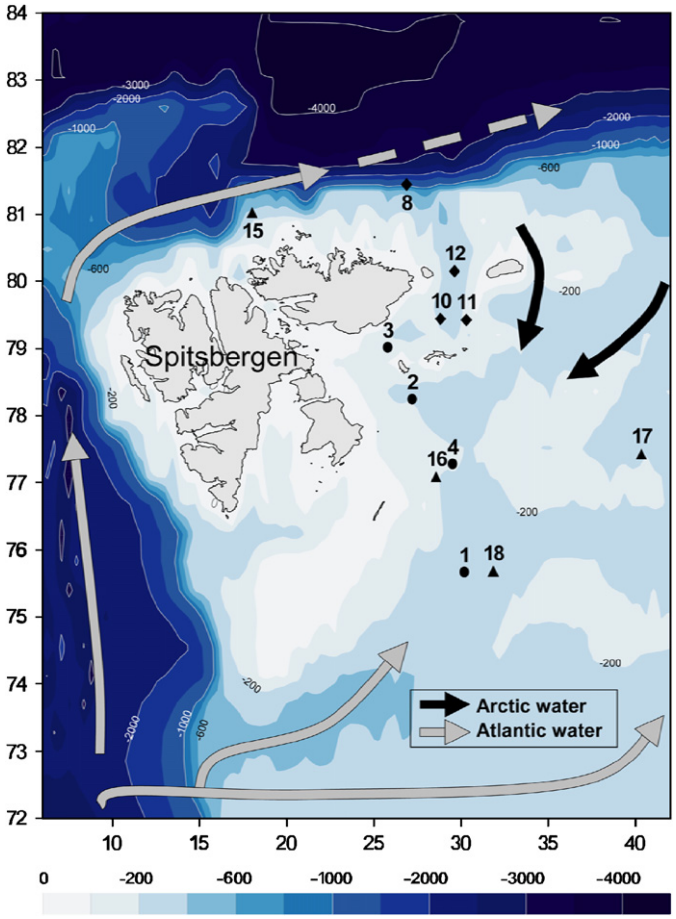

Fig. 1. Map of the CABANERA study area. The stations where sedimentary pigments were sampled are represented by dots (CABANERA I, July 2003, stations 1, 2, 3, and 4), diamonds (CABANERA II, July–August 2004, stations 8, 10, 11, and 12), and triangles (CABANERA III, April 2005, stations 15, 16, 17, 18). Arctic and Atlantic waters are represented by a black and a gray line, respectively. The gray dash line represents Atlantic waters sinking underneath Arctic water.

in electrical suction pump. Samples were then filtered through GF/F filters (0.7 μm). POM and ice-algae filters were stored at −20 °C prior HPLC analysis.

At stations 3 and 10, fecal material was collected from pelagic and sympagic crustaceans to investigate pigments characteristic of degradation due to grazing. About 50 pelagic copepods (*Calanus* spp.) and sympagic amphipods (*Gammarus wilkitzkii*) were placed in separated chambers with filtered seawater. Animals in the overlying water were separated from the bottom by a mesh, so the fecal pellets were isolated from the animals. After 24–48 h, animals were retired and the water was filtered on GF/F filters. Filters were frozen for HPLC analysis.

Sediment was sampled by replicate deployments of a box corer (45 cm × 45 cm) or multicorer. Multiple sub-samples (5 cm diameter × 10 cm deep) for sedimentary pigments were taken from each station. Each sub-core was extruded and the first 2 cm were sliced. Each slice was divided in two, half for pigment analysis by fluorometer, half for pigment analysis by HPLC. Both sub-samples were wrapped in foil and frozen directly after slicing in order to avoid pigment degradation.

2.2. Pigment analysis

2.2.1. HPLC analysis

POM and ice-algae filters were extracted in 2 ml of 100% HPLC-grade acetone for 12–24 h. Extracts were filtered through 0.2-μm

Table 1
Location, date, depth, ice coverage, and water column chlorophyll *a*

Station	Date	Location	Latitude (°N)	Longitude (°E)	Depth (m)	Ice cover (%)	Tchl *a* ($mg\,m^{-2}$)	Flux 1 m ($m^{-2}\,d^{-1}$)	Flux 90 m ($m^{-2}\,d^{-1}$)
1	11 July 2003	Hopen Trench	75°40.0′	30°10.0′	345–352	40–70	40.38	0.06	0.11
2	14 July 2003	S. Kong Karlslandet	78°14.7′	27°09.7′	320	40–70	239.48	0.15	2.94
3	16 July 2003	Erik Eriksenstretet	79°01.2′	25°46.3′	198	50–70	158.14	0.30	1.63
4	19 July 2003	Hopen Bank	77°01.1′	29°29.2′	222	40–70	62.99	1.60	0.68
8	28 July 2004	N. Kvitøya Trench	81°16.6′	26°51.2′	503				
10	29 July 2004	N. Kongkarlsland	79°26.5′	28°48.4′	303	40	68.78		1.84
11	1 August 2004	NE. Kongkarlsland	79°56.6′	30°17.0′	195	30	207.57		2.48
12	2 August 2004	Kvitøya Trench	80°09.0′	29°36.0′	286				
15	21 May 2005	Questrenna Shelf	81°01.5′	18°01.1′	311	30	471.86*	20.97*	6.22*
16	26 May 2005	N. Hopen Trench	77°05.2′	28°33.0′	206	80–90	548.32		3.48
17	29 May 2005	E. Storbanken	77°25.6′	40°18.3′	208	60–70	131.24	2.04	0.98
18	30 May 2005	Hopen Trench	75°40.8′	31°48.7′	340	Open water	213.48		13.58

Tchl *a* represent the total of chlorophyll *a* integrated over the entire water column (data from Hodal and Kristiansen, 2008). Flux 1 m is the surface flux of chlorophyll *a* determined in traps at 1 m while flux 90 m is the flux of chlorophyll *a* determined by traps placed at 90 m. Flux data are from Reigstad et al. (2008).

* Fluxes at station 15 were not studied, but station 14 was close and in similar condition so fluxes data are from station 14.

nylon syringe filters. Freeze-dried sediment (1–5 g) was transferred to a 50 ml polypropylene centrifuge tube where 15 ml of 100% HPLC-grade methanol was added. The mixture was sonicated for 5 min in an ice bath and extracted in the freezer overnight. Extracts were separated from the sediment by centrifugation (10 min, 2000 rpm) and 10 ml of the supernatant were filtered through a 0.2 μm syringe filter. Extracts were blown to dryness under nitrogen, and then redissolved in 1 ml of 90% acetone.

Quantitative analysis of all pigments was conducted with a Waters HPLC equipped with an online photodiode array (Waters 996 PDA) and fluorescence detector (Waters 616) with excitation set a 440 nm and emission at 660 nm. Two hundred to 500 μl of the samples were injected through a guard column to a reverse phase Alltech Absorbsphere C18 column (5 μm particle size; 250 × 4.6 nm i.d.) using ammonium acetate as buffer. The three-step gradient program was a modification of Wright et al. (1991) as described by Chen et al. (2001) for enhancing the separation of phaeopigments.

Identification of pigments was performed by comparing retention time and PDA spectra with standards (DHI Water and Environment, Denmark). Carotenoids were quantified on the PDA at 438 nm, while chlorophylls and phaeopigments were quantified on the fluorescence detector. The response factor (RF) was determined for each pigment by single run of each pigment standard. When no standard was available, RF from similar pigments was used. For chlorophylls breakdown products, RF of chl *a* and *b* were adjusted by the difference in molar mass (Reuss et al., 2005).

2.2.2. Fluorometer analysis

Within a month, each sub-sample of sediment was analyzed by fluorometer. The samples were placed on a 60 ml centrifuge tube, and 20 ml of 100% acetone were added. Tubes were stored at −20 °C in the dark for 48 h, and shaken periodically. Prior to fluorometer analysis, the sediment was centrifuged (4000 rpm for 10 min at 0 °C). The supernatant was analyzed in a Turner Model 10-AU fluorometer before and after acidification with 20% HCl, in order to determine the ratio of chl *a* to total phaeopigments (chl *a*/phaeo).

2.3. CHEMTAX and statistical treatment

The contribution of the three major algal groups (diatoms, haptophytes and green algae) was estimated using the CHEMTAX program (Mackey et al., 1996). The ratios used were determined by Not et al. (2005) for the Barents Sea. The use of CHEMTAX as an estimation of the algal groups from pigments is controversial. It is often very hard to have accurate pigment ratios, which can vary highly depending on environmental conditions. The use of CHEMTAX in the present study is not intended to determine the exact proportion of the different algal groups, but to confirm the dominant species as suggested by pigment results.

Differences between summer and spring were analyzed by *t*-test. Correlation of pigments between each other and between pigments and other data were analyzed by correlation table. The study of similarity and differences of the various sedimentary pigments found were studied by principal components analysis (PCA). Significances of the *t*-tests and correlations were tested by Pearson's product-moment correlation. Correlation analyses, *t*-tests, and PCA were performed using R (R Development Core Team, 2005).

3. Results

3.1. Water-column and ice pigments

Relative percentages of the major accessory pigments found at the chlorophyll maximum are represented in Fig. 2A. Chl *a* and phaeopigments over the entire water-column and in the sediment traps were studied by Hodal and Kristiansen (2008) and Reigstad et al. (2008) and are presented in Table 1. The present study intended only to determine the proportion of the major accessory pigments, not the absolute concentration. The pigments studied are fucoxanthin (marker of diatoms and haptophytes), 19′-butanoyloxyfocoxanthin and 19′-hexanoyloxyfocoxanthin (markers of haptophytes), peridinin (marker of dinoflagellates), alloxanthin (marker of cryptophytes), zeaxanthin (marker of cyanobacteria) and chl *b* (marker of green algae and higher plants). Fucoxanthin was by far the most abundant pigment. The ratio of diatoms, haptophytes and green algae determined by the CHEMTAX program, confirmed that diatoms were the dominant species at most of the stations. For all but three stations, diatoms represented more than 80% of the species composition (Fig. 2B). The three stations where diatoms were the less dominant were the same suggested by the pigment composition before the CHEMTAX transformation: stations 1, 8, and 17. Fucoxanthin was also the main accessory pigment found the detritus collected at the water–ice interface at stations 7, 10, 17, confirming diatoms as dominant taxonomic component of ice algae.

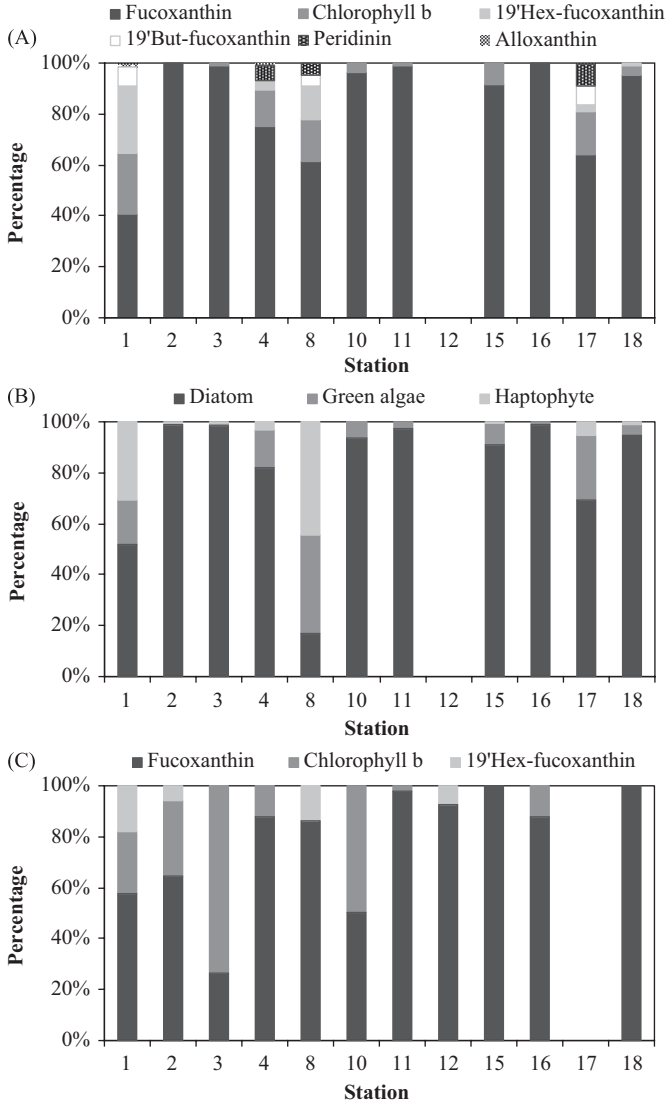

Fig. 2. (A) Relative proportion of water-column accessory pigments for each station. (B) Percentage of the three main algae groups (diatoms, green algae, and haptophytes) determined by the CHEMTAX program from the previous pigments ratios. (C) Ratios of the major accessory pigments found in the sediment. Note that no water-column samples were collected for station 12, and no accessory pigments were found in the sediment in station 17.

During the grazing process, chl *a* in phytoplankton can be degraded to phaeophorbide *a* and phaeophytin *a*. These degraded pigments were found in the fecal material collected from zooplankton. However, another peak was observed at 12.897 min, in the PDA and the fluorometer (Fig. 3). This peak is a combination of phaeophorbide *a* and fucoxanthin, and was recently identified as a carotenol chlorin ester (CCE), a specific marker of diatom grazing (Goericke et al., 1999; Chen et al., 2003).

3.2. Sediment pigments

Chl *a* and other sedimentary chlorophylls and carotenoids were determined by HPLC in the first 2 cm of sediments (Table 1). Sedimentary chl *a* and total phaeopigments in the same interval were determined by fluorometer in order to compare the HPLC and the fluorometer results, and to know the ratio of chl *a* over total phaeopigments (Table 2). Fluorometer and HPLC results for chl *a* strongly correlated significantly ($r = 0.93$, $p < 0.05$). Chl *a* was determined by fluorometry at all stations, but was below the limit

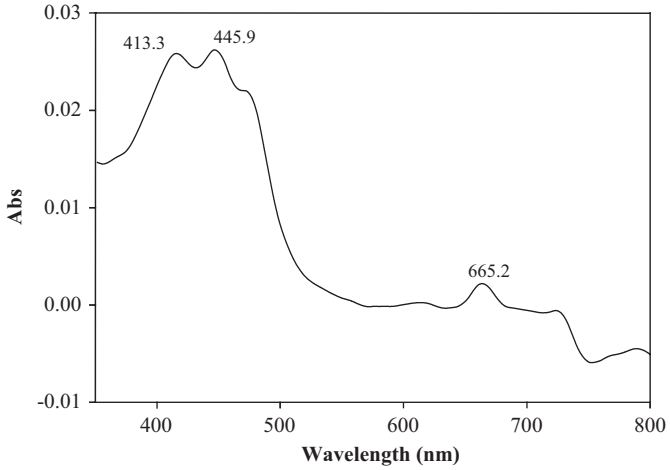

Fig. 3. PDA spectrum (438 nm) at 12.897 min of the chromatogram of fecal material. This spectrum show a peak at 413.3 and 665.2, as phaeophorbide *a*, but also a peak at 445.9 nm, like fucoxanthin. This combination of phaeophorbide *a* and fucoxanthin appears to be a carotenol chlorine ester (see text).

of HPLC detection at one station. 19′-hex-fucoxanthin occurred at only four stations (1, 2, 8, and 12), while chlorophyll *b* was detected at seven stations (mainly in summer). All but two stations had fucoxanthin. All stations had phaeophytin *a* and all but three summer stations had phaeophorbide *a*.

Chl *a*, phaeophorbide *a*, CCE, and fucoxanthin determined by HPLC were strongly correlated with each other, as well as with the chl *a* determined with fluorometer (Table 3) Pyrophaeophorbide *a*, pyrophaeophytin *a* and 19′-hex-fucoxanthin were not correlated to any other pigment.

Chl *a* concentrations varied from being undetectable (by HPLC method) at station 17, to comprising 2.8 μg of pigment per gram of dry sediment ($\mu g\,g^{-1}$ dw) at station 15. As at station 15, station 11 had more than 1 $\mu g\,g^{-1}$ dw, while all other stations had less. There was no significant difference (t-test > 0.05) between the chl *a* concentrations at the spring stations (15, 16, 17, and 18) and the summer stations (1, 2, 3, 4, 8, 10, 11, and 12).

Phaeophorbide *a* and phaeophytin *a* were the main degradation products of chl *a*. Phaeophorbide *a* is usually considered as a degradation product of chl *a* issued from grazing while phaephytin *a* can also be due to senescence. The pyro-derivatives, pyrophaeophorbide *a* and pyrophaeophytin *a* were less abundant and were not correlated with any other pigment. Phaeophorbide *a* was significantly correlated with chl *a* ($r = 0.65$, $p < 0.05$) and CCE ($r = 0.91$, $p < 0.05$). The total of phaeopigments determined by fluorometer was significantly correlated with the grazing pigments phaeophorbide ($r = 0.83$, $p < 0.05$) and CCE ($r = 0.92$, $p < 0.05$), while was not correlated with the other degradation products of chl *a* determined by HPLC. The ratio of chl *a* to total phaeopigments, was significantly higher (t-test: $p < 0.05$) in the spring than in the summer.

The main accessory pigment found in the sediment was fucoxanthin (Fig. 2C). Only three stations, stations 1, 3, and 8, had less than 60% of fucoxanthin as a main accessory pigment. Fucoxanthin was found in each station but station 17, where almost no pigments were found. The station with the highest concentration of fucoxanthin was station 15, while stations 3, 10, and 17 had the lowest amounts.

3.3. Principal components analysis

The 1st and 2nd axis of the PCA explained 72% of the variance in sediment pigments among stations. Axis 1 (41% of variance)

Table 2
Sedimentary pigments concentration by HPLC (in μg of pigment g^{-1} dw) in the first 2 cm

Station	Chl *a*	Phorbid *a*	Pphorbid *a*	Phytin *a*	Pphytin *a*	CCE	Fuco	Hex	Chl *b*	Chl *a*/Tpheo
1	0.464	0.296	0.006	1.090	0.142	0.075	0.133	0.041	0.056	
2	0.784	0.470	0.022	3.491	0.537		0.203	0.018	0.093	
3	0.064	1.202	0.015	0.962	0.218	0.037	0.004		0.010	
4	0.309	0.260	0.024	0.501	0.030	0.213	0.152		0.021	
8	0.166	0.081	0.006	0.152	0.026	0.240	0.081	0.013		0.197
10	0.163	0.795	0.039	1.451	0.189		0.024		0.024	0.046
11	1.069	0.633	0.025	1.142	0.159	0.337	0.404		0.010	0.420
12	0.656	0.113	0.016	0.666	0.527	0.036	0.288	0.023		0.073
15	2.801	1.810	0.024	0.245	0.251	1.649	1.541			0.507
16	0.676		0.011	0.134	0.032		0.127		0.017	0.595
17			0.065	0.040						0.140
18	0.421	0.010	0.454	0.171	0.013		0.163			0.591

Chl *a*: chlorophyll *a*, Phorbid *a*: phaeophorbide *a*, Pphorbid *a*: pyrophaeophorbide *a*, Phytin *a*: phaeophytin *a*, Pphytin *a*: pyrophaeophytin *a*, CCE: carotenol chlorine ester, Fuco: fucoxanthin, Hex: 19′-hex-fucoxanthin, Chl *b*: chlorophyll *b*, Chl *a*/Tphaeo is the ratio chlorophyll *a*/total phaeopigments both determined by fluorometer.

Table 3
Correlations between sedimentary chlorophyll *a*, degradation products and accessory pigments (0–2 cm)

	Chl *a*	Phorbid *a*	Phytin *a*	CCE	Fuco	Chl *b*	Chl *a*Fluo	PhaeoFluo
Chl*a*	1							
Phorbid *a*	0.65*	1						
Phytin *a*	−0.08	0.01	1					
CCE	0.95*	0.76	−0.49	1				
Fuco	0.98*	0.68	−0.19	0.97*	1			
Chl *b*	0.24	−0.48	0.82*	−0.4	0.07	1		
Chl *a*Fluo	0.92*	0.80*	−0.26	0.98*	0.88*	−0.65	1	
PhaeoFluo	0.99*	0.86*	−0.1	0.97*	0.97*	−0.86*	0.96*	1

Chl *a*: chlorophyll *a*, Phorbid *a*: phaeophorbide *a*, Pphorbid *a*: pyrophaeophorbide *a*, Phytin *a*: phaeophytin *a*, Pphytin *a*: pyrophaeophytin *a*, CCE: carotenol chlorine ester, Fuco: fucoxanthin, Hex: 19′-hex-fucoxanthin, Chl *b*: chlorophyll *b*, Chl *a*Fluo: chlorophyll a determined by fluorometry, PhaeoFluo: phaeopigments determined by fluorometry.
Significant correlation ($p<0.05$) are indicated by an asterisk "*" after the correlation coefficient.

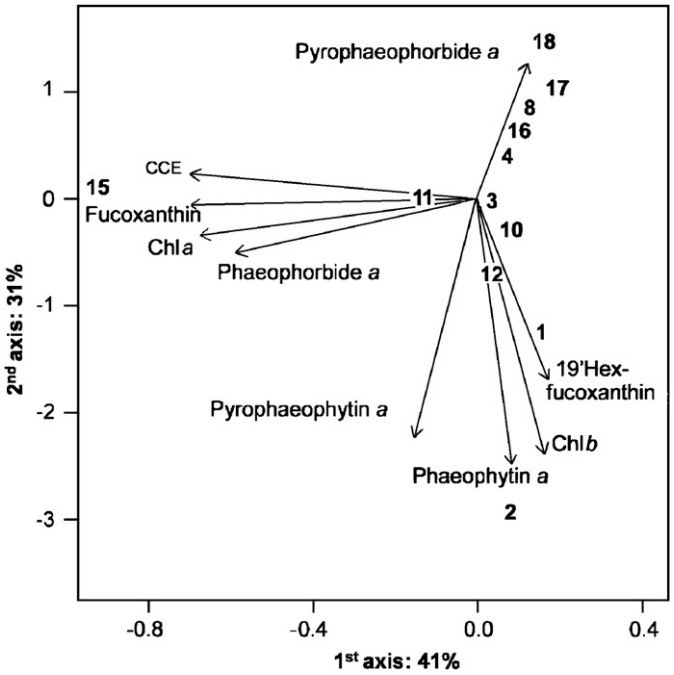

Fig. 4. Principal components analysis of sedimentary pigments compositions from the 12 stations. The plot displays 72% of the total variability of the dataset.

was largely defined by chl *a*, fucoxanthin, CCE, and phaeophorbide *a*, and served to separate stations 15 and 11 (high concentrations of these pigments) from the other stations (Fig. 4). The second axis (31%) separates the remaining stations on the basis of high concentrations of the accessory pigments 19′-hex-fucoxanthin and chlorophyll *b*, and the degradation pigments phaeophytin *a* and pyrophaeophytin *a* (stations 10, 12, 1, and 2), or high levels of pyrophaeophorbide *a* (stations 4, 16, 8, 17, and 18).

4. Discussion

The study of sedimentary pigments by HPLC method allowed us to study sedimentary chl *a* and make a comparison with fluorometer values, but also to separate various chl *a* degradation products and some accessory pigments, especially fucoxanthin, 19′-hex-fucoxanthin and chl *b*. This is, to our knowledge, the first time such a study has been realized in the Arctic Ocean. Sedimentary pigments have been studied by HPLC in various other ecosystems, especially in lacustrine, coastal, marine eutrophic and anoxic ecosystems, where inputs of organic matter are usually high (see review in Beaulieu, 2002). Sedimentary chl *a* in marine shallow or eutrophic environments show extremely high values, typically tens of μg g^{-1} dw. Kowalewska (2005) defined three zones in the Baltic Sea: in the permanently eutrophic area, sedimentary chl *a* in 0–1 cm is higher than 35 μg g^{-1}, in the coastal area, chl *a* ranges from 8 to 35 μg g^{-1}, while in the mesotrophic open sea, chl *a* is lower than 8 μg g^{-1}. Deep-sea oligotrophic ecosystems showed values <0.06 μg g^{-1} in the central equatorial Pacific (Smith et al., 1996) and an average of 0.04 μg g^{-1} in the Indian sector of the Southern Ocean, with a maximum of 0.15 μg g^{-1} at the permanently open-ocean zone (Riaux-Gobin et al., 1997). Our data ranged from 0.06 to 2.80 μg g^{-1}, which is lower than previous studies in marine eutrophic systems, but higher than in deep-sea sediments. Despite the modest values, we are able to relate sedimentary chl *a* to water-column inputs, use accessory pigments as markers of phytoplankton taxonomy, and relate degraded pigments to the source of degraded material and processes they went through.

4.1. Local chlorophyll a inputs

Local water-column chl *a* is clearly the most determinant factor of sedimentary chl *a* concentration. Sedimentary chl *a* is significantly correlated with the total of chl *a* (Tchl *a*) integrated over the entire water-column ($r=0.69$, $p<0.05$) and the chlorophyll concentration at the chl *a* max ($r=0.57$, $p<0.05$),

measured by fluorometry by Hodal and Kristiansen (2008). Sedimentary chl *a* is even better correlated to fluxes of chl *a* in the water-column determined by fluorometry by Reigstad et al. (2008). It is highly correlated to the surface (1 m) chl *a* fluxes ($r=0.96$, $p<0.05$) and deep fluxes (90 m) ($r=0.86$, $p<0.05$, excluding the station 18). These correlations between sediment and water-column pigments are similar to those found by Renaud et al. (2008) in the same region. All but one station (station 18) had ice presence on the surface. Even though no significant correlation were found between percent ice cover and sedimentary chl *a*, the strong correlation between sedimentary chl *a* and surface (1 m traps) chl *a* fluxes suggests that ice-associated production plays a key role in the input of fresh organic matter to the benthos.

The relationship between sedimentary chl *a* and Tchl *a* is not significantly different in the spring than in the summer, suggesting that sedimentary chl *a* depends on short-term local production and vertical flux. Phytoplankton blooms tend to be highly localized in space and time and occur as episodic events from early spring to late autumn in the Barents Sea (Codispoti et al., 1986; Wassmann et al., 1996) when sufficient light and nutrients are available (Hegseth, 1997, 1998). However, Engelsen et al. (2002) found that a large bloom is most likely to occur two weeks after the ice edge has receded from a given area. Thus, we could have expected to find in the spring more chl *a* in the water-column, and thus in the sediment than in the summer. In the spring, very high water-column chl *a* values were observed at two of the four studied stations by Hodal and Kristiansen (2008). Sedimentary chl *a* does not show higher concentration in the spring than in summer; however, the ratio of chl *a*/phaeo is higher in the spring, suggesting an input of "fresher" material.

Previous studies (Grahl et al., 1995) pointed out the correlation between the sedimentary chl *a* and water depth. These two parameters are not correlated in the present study. This is probably a result of our small water depth range, 198–503 m. Sedimentary pigments are also not significant related to the percentage of ice cover. Wassmann et al. (1996) explained that sea-ice cover does not directly control the pelagic–benthic coupling in the Barents Sea, but is a factor in the episodic character of vertical fluxes.

4.2. Phytoplankton and ice-algae species

In this study, we used fucoxanthin as a marker of diatoms, 19′-hex-fucoxanthin as a marker of prymnesiophycae (which include *Phaeocystis pouchetii*) and chl *b* as a marker of green algae. Typically, diatoms and prymnesiophytes are dominant producers in the spring, while flagellates are more important in the summer (Luchetta et al., 2000; Rat'kova and Wassmann, 2002). Moreover, different water masses in this area are found to have different phytoplankton compositions (Rat'kova and Wassmann, 2002; Reigstad et al., 2002). Atlantic waters contain more prymnesiophytes (Wassmann et al., 2005) while Arctic waters contain more green algae, especially *Micromonas pusilla* (Not et al., 2005). Our pigment composition and taxonomic results from the water-column support this. The spring stations (15, 16, 17, and 18) show a high percentage of diatoms, while the stations 1 and 8, with Atlantic water inflow, show high percentage of haptophytes, and station 17, under Arctic water inflow, show high amount of green algae.

Sakshaug (2004) pointed out the dominance of diatoms in waters mixed to <40 m. Due to the relatively low silicate concentrations in the Barents Sea, the proliferations of diatoms is reduced when compared to Chukchi Sea or North Atlantic (Wassmann et al., 2006). However, in our study in the western Barents Sea, fucoxanthin is by far the most dominant pigment in the sediment as well as in the water-column and ice. Diatoms are especially abundant in spring stations and summer stations in bloom stage (2, 3, 10, and 11). Hancke, pers. comm. found similar dominance of diatoms in the water-column when studying the effects of light on pigments compositions. Diatoms are an important producer in the water-column, and are usually the most common algal group in ice algae (Lizotte, 2003; Riaux-Gobin et al., 2000; Von Quillfeldt et al., 2003). The high levels of fucoxanthin found in our ice–detritus samples confirm the importance of diatoms in ice algae, and thus ice-associated diatoms are likely to be an important part of trap material from 1 m. It is impossible to differentiate ice-algae diatoms from phytoplankton diatoms by HPLC, ice-algae diatoms have previously been observed in Arctic sediment (Sancetta, 1981; Ambrose et al., 2005). Moreover, ice algae can play an important part of vertical fluxes of organic matter in some stations in the Barents Sea (Tamelander et al., 2008). The important proportion of diatoms in surface (under-ice) fluxes and the high correlation between sedimentary fucoxanthin and chl *a* fluxes at these stations ($r=0.99$, $p<0.05$) suggest the important role of ice-associate production as a source of fresh organic matter inputs to the benthos.

Interestingly, summer stations determined in peak-bloom phase (stations 2, 3, 10, and 11) showed the highest percentage of diatoms in the water-column. However, even if they also showed important percentage of fucoxanthin in the sediment, they also revealed the presence of chl *b*. Chl *b* is a marker of green algae, which are common in Arctic waters (Not et al., 2005). The half-life of chlorophyll pigments is approximately three weeks in polar sediments (Graf et al., 1995). Thus, sedimentary chlorophylls integrate inputs of fresh organic matter from the water-column over several weeks to a few months. While sedimentary chl *a* was clearly related to the water-column chl *a* measured during the cruise time, other, less abundant pigments might integrate events that occurred at a longer time scale. The presence of sedimentary chl *b* in the summer in stations influenced by Arctic waters shows that green algae can be also a source of fresh organic matter input to the benthos.

In the summer, the northernmost and southernmost stations (stations 1 and 8) show an important contribution of prymnesiophytes, reflected by the presence of 19′-hex-fucoxanthin, in both the water-column and the sediment. These stations are influenced by Atlantic water (Fig. 1; Sundfjord et al., 2007), where *P. pouchetii* is often abundant (Wassmann et al., 2005). Prymnesiophytes are an important source of organic matter inputs to the benthos at these stations.

In the summer, the type of water (Atlantic vs. Arctic) influences the water-column production and thus the type and degradation stage of organic matter reaching the sediment. Alternately, the spring stations showed a high percentage of fucoxanthin in the water-column as well as in the sediment, regardless of their influence by Atlantic or Arctic waters.

The PCA indicated diatom-dominated inputs at stations 15 and 11, while the presence of accessory pigments is important at stations 1, 2, 10, and 12, suggesting significant inputs of other algal groups at these stations (Fig. 4). The differences in primary producer taxonomy were reflected in sedimentary pigments and may represent a difference in quality of algal detritus reaching the benthos.

4.3. Input of grazed material

Total sedimentary phaeopigments correlate significantly to the phaeopigments fluxes at 90 m ($r=0.70$, $p<0.05$, excluding station

18) but this relationship is weaker than the correlation between sedimentary chl *a* and chl *a* fluxes at 90 m ($r=0.87$, $p<0.05$, excluding station 18). This suggests that even though degraded pigments in the sediment can come from the overlying waters the relationship may also depend on processes occurring within the sediment.

The highly significant relationship between both phaeophorbide *a* and CCE and the total phaeopigments in the sediment ($r=0.86$ and 0.97, respectively, $p<0.05$), as well as their significant relationship with the total phaeopigments in the water-column ($r=0.85$ and 0.94, respectively, $p<0.05$), clearly suggest that the main input of degraded pigments from the water-column in grazed material. The summer stations showed the highest amount of grazed pigments in the sediment. Moreover, in the summer, the stations with the highest amount of phaeophorbide *a* with respect to the chl *a* in the sediment (stations 3 and 10) are the same stations determined by Wexels Riser et al. (2008) as having the highest proportion of carbon flux as fecal pellets flux.

Faecal material has been found to be an important part of the sinking organic matter in the Barents Sea (Wassmann et al., 1996), especially in the summer (Wexels Riser et al., 2002). However, in the spring, the mismatch between primary producers and consumers (Rat'kova and Wassmann, 2002) can lead to fluxes of ungrazed material. Moreover, zooplankton tends to graze on large cells such as diatoms. In our study, the higher ratio of chl *a*/phaeo in the spring and the presence of CCE suggest the input of "fresher" organic matter to the benthos in the spring, while in the summer, organic matter reaching the sediment is more degraded, especially by grazing.

Because of the few-week-long half-life of chlorophyll pigments in polar sediments and the rapid consumption by benthic organisms (Graf et al., 1995; Renaud et al., 2008), sedimentary chl *a* relates relatively short-term water-column inputs, while degraded pigments represent a longer time scale of accumulation and additional processing. PCA confirmed that highly degraded pigments, such as pyrophaeophorbide, can be important at stations where inputs are low (as stations 17) or inputs are highly processed (as station 16). Inputs of fresh organic matter can be quickly processed (Ritzrau and Thomsen, 1997; Renaud et al., 2006, 2008). The ratio of chl *a*/phaeo is significantly ($r=0.90$, $p<0.05$) correlated to the sediment oxygen demand determined by Renaud et al. (2008) suggesting an increase of benthic activities during inputs of fresher material. Moreover, the sediment oxygen demands are significantly higher (*t*-test: $p<0.05$) in the spring than in the summer. Thus, benthic community activities are particularly enhanced by inputs of fresher, not degraded, material, and probably play an important role in the benthic degradation of organic matter and pigments.

4.4. Comparison with other Arctic shelves

Sedimentary pigments are useful indicators of organic matter inputs to the sediment (Sun et al., 1991) and have been used previously to characterize food deposition to Arctic benthos (Table 4). However, previous studies used fluorometry methods, which only detect chl *a* and total phaeopigments. It is impossible to directly compare our HPLC chl *a* results with previous studies in the Arctic, but chl *a* values determined by fluorometer were highly correlated to chl *a* determined by HPLC in our study, and ranged from 0.6 to 40 mg m^{-2} with total chloropigments ranging from 5 to 120 mg m^{-2} in the first 2 cm. The chl *a* values are slightly higher

Table 4
Chlorophyll *a* (chl *a*), total of chlorophyll *a*+phaeopigments also called chloropigment equivalent (CPE), and ratio chlorophyll *a*/total phaeopigments (chl *a*/phaeo) in offshore Arctic sediment

Location	Date	Water depth (m)	Chl *a* (mg m^{-2})	CPE (mg m^{-2})	Chl *a*/phaeo	Sediment depth (cm)	Study
Western Barents Sea	May	206–340	0.3–30 0.7–40	2–90 5–120	0.18–0.42 0.14–0.59	1 2	This study
	July–August	195–503	0.2–1 0.6–13	5–13 14–44	0.03–0.16 0.05–0.42	1 2	
Northern Barents Sea (Svalbard Shelf)	July–August	226–405 854–3920	1–4 <1 to 1	7–23 1–7	0.16–0.2 0.16	5 5	Pfannkuche and Thiel (1987)
Barents Sea slope	July	1400		66–102	0.07–0.1	10	Thomsen et al. (1995)
Bering Sea	May–June	202–523	2–15			1	Cooper et al. (2005)
	July–August	189–478	2–37			1	
Ellesmere Island–W Greenland (N Water)	April–May	247–680	0–2	4–30	0–0.07	1	Grant et al. (2002)
	July		<1 to 5	11–42	0.01–0.1	1	
NE Greenland (NE Water)	July–August	150–515		9–46		1	Ambrose and Renaud (1995)
NE Greenland (NE Water)	May–August	290–340	<1 to 3	12–44	0.07–0.1	1	Ambrose and Renaud (1997)
NE Greenland	September	183–774		6–33		1	Brandt and Schnack (1999)
		1098–1965		3–7		1	
Laptev Sea (Eurasian Arctic)	August–September	50	45	100	0.82	1	Boetius and Damm (1998)
		1000–3500	<2	10–40	0.05–0.11	1	
Arctic Ocean section	July–August	68	<1	7	<0.16	2	Clough et al. (1997)
		540–4190	0	<1		2	
Central Arctic Ocean	August–September	1055–4180		1–12		1	Soltwedel and Schewe (1998)

The depths of surface sediment of the integrated pigments are variable and are presented in the sediment depth column. Most studies' values are for the upper 1 cm. Our data are presented for the upper 1 and 2 cm integration depths.

than in studies at similar water depth in the North Water (Grant et al., 2002) and the Northeast Water (Ambrose and Renaud, 1995, 1997) polynyas, and much higher than in the central Arctic Ocean determined by Soltwedel and Schewe (1998), where primary production is particularly low. The Barents Sea and the Bering Sea have the highest rates of primary production among the Arctic shelves (see review in Sakshaug, 2004), the Bering Sea having higher rates (Wang et al., 2005). Interestingly, despite the higher production in the Bering Sea respect to the Barents Sea, sedimentary chl *a* contents have similar ranges and are the highest of the Arctic shelves for similar depths. Moran et al. (2005) proposed that 20% of the production in the Bering Sea, at some times of the year, is directly exported out of the production area to the deep Arctic basin. The ratios chl *a*/phaeo are the highest in the Barents Sea suggesting fresher material than in other Arctic shelves reaching the benthos. This might suggest that a higher percentage of local production reached the bottom of the Barents Sea. Pelagic–benthic coupling in Arctic MIZs is particularly tight (Carmack and Wassmann, 2006), and seems as tight in the Barents Sea as than anywhere else in the Arctic.

5. Conclusion

Because of the episodic character of water-column events, it is hard to study temporal or spatial variations in the Barents Sea. However, our first attempt to use sedimentary pigments to characterize pelagic–benthic coupling variation allowed us to observe spatial and seasonal variations. Local primary production by phytoplankton and ice algae is clearly the main source of organic matter to the benthos. In the spring, fresher (ungrazed) material, mainly composed of diatoms, reaches the benthos, while in the summer, inputs are more degraded (especially by grazing), and other phytoplanktonic groups are important.

Pelagic–benthic coupling is tight in both spring and summer. The correlation between benthic activities and chl *a*, and also with the ratio chl *a*/phaeopigments shows that not only the quantity of organic matter reaching the sediment is important for the benthos, but also its stage of degradation. Any climate-induced change in productivity or water mass position will likely be immediately reflected in quality and quantity of carbon input to the benthic ecosystem, potentially leading to changes in the benthic carbon cycling.

Acknowledgments

We would like to thank M. Carroll, K. Hancke H. Hodal, H. Hop, M. Reigstad, and T. Tamelander for sharing data. Thanks are also due to R/V *Jan Mayen* officers and crew, CABANERA scientists, especially Chief Scientist Paul Wassmann. We are extremely grateful to Jason Perl (San Diego State University Research Foundation) for providing pigment standards. This investigation is part of the project CABANERA financed by the Norwegian Research Council and has received funding from NSF (OPP-0326371 to PER), the University of Connecticut, and Akvaplan-niva. This manuscript benefited from comments by three anonymous reviewers.

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