

APPROVAL PAGE

Doctor of Philosophy Dissertation

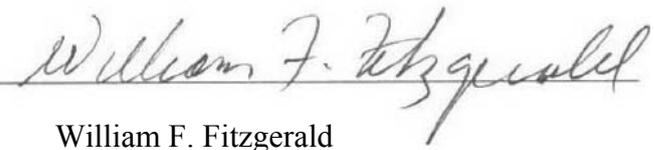
Sedimentary Pigments as Biomarkers of Spatial and Seasonal Variations
in Arctic Pelagic-Benthic Coupling

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To the memory of Mimi and Andr   Labarr  re, Maire de Pau.

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List of papers

This thesis is based on the following papers, which are referred to by their Roman numerals I-VI and are presented as appendices.

- I. **Morata N**, Renaud PE (in press) Sedimentary pigments in the western Barents Sea: a reflection of the pelagic-benthic coupling? Deep-Sea Research II
- II. **Morata N**, Renaud PE, Brugel S, Hobson KA, Johnson BJ (submitted to Marine Ecology-Progress Series) Spatial and seasonal variations in the pelagic-benthic coupling of the southeastern Beaufort Sea revealed by sedimentary biomarkers
- III. Renaud PE, **Morata N**, Carroll ML, Denisenko SG, Reigstad M (in press) Pelagic-benthic coupling in the western Barents Sea: processes and time scales. Deep-Sea Research II
- IV. Renaud PE, **Morata N**, Ambrose WG, Bowie JJ, Chiuchiolo A (2007) Carbon cycling by seafloor communities on the eastern Beaufort Sea shelf. Journal of Experimental Marine Biology and Ecology 349:248-260
- V. Renaud PE, Riedel A, Michel C, **Morata N**, Gosselin M, Juul-Pedersen T, Chiuchiolo A (2007) Seasonal variation in benthic community oxygen demand: A response to an ice-algal bloom in the Beaufort Sea, Canadian Arctic? Journal of Marine Systems 67:1-12
- VI. **Morata N**, Poulin M, Renaud PE (in preparation for Polar Biology) Does an input of ice-algal phytodetritus to the sea floor automatically lead to an increase in sedimentary pigments?

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1. Introduction and background

1.1 Climate change and carbon cycling in the Arctic Ocean

Effects of global warming are expected to be enhanced in the polar regions, especially the Arctic. Mitchell et al. (1995) predicted temperature increase of 3-4°C in the Arctic during the next 50 years, which would lead to a substantial retreat of Arctic ice cover. From a permanently ice-covered region with multiyear ice, the Arctic Ocean would become ice-free during the summer (ACIA 2005, IPCC 2007). The sea ice cover is an important component of both the global and the Arctic climate system, modulating the exchange of heat and moisture between ocean and atmosphere, as well as stratification and winter deepwater formation (Johannessen & Miles 2000). Changes in ice cover will restructure some of carbon cycling pathways in the Arctic Ocean by affecting primary production.

Recent studies (Wheeler et al. 1996, Chen et al. 2002, Klein et al. 2002, Tremblay et al. 2002, Vidussi et al. 2004) have shown that primary production is much higher in the Arctic than previously believed. Total primary production in the Arctic Ocean contributes >329 Tg C y⁻¹ and most of it, 279 Tg C y⁻¹, occurs in the shelf areas (Sakshaug 2004). Ice algae contribute a large fraction of primary production in some areas on the Arctic (Gosselin et al. 1997, Arrigo 2003). A reduction in ice cover as a result of global warming will increase the relative importance of phytoplankton production.

Because of the ice-dependent character of Arctic primary production (see section 1.2 for more details), climate change is expected to affect both primary production and vertical fluxes by favouring phytoplankton production over ice algae (Carroll and Carroll 2003).

In addition to primary production, terrestrial organic matter is an important source of organic matter for the Arctic Ocean. The Arctic Ocean, on a volume basis, has the highest terrestrial input of freshwater and organic matter (10% of the global river discharge and 8% of the total global organic carbon flux, Maybeck 1993, Dittmar & Kattner 2003). Climate models suggest that global warming will affect riverine fluxes by intensifying the hydrological cycle (Peterson et al. 2002, Wu et al. 2005). The increased riverine organic matter fluxes will affect the entire Arctic carbon cycle.

In addition to the role of the continental margin as a source of terrestrial organic matter, the continental shelf is an important site for organic matter sedimentation and burial. Thirty percent of the world's continental shelves are found within the Arctic region (Macdonald et al. 1998), while the Arctic Ocean comprises only 1% of the global ocean area (Dittmar & Kattner 2003). These huge continental shelves represent an important sink of

carbon, since 70% of the total sediment input is accumulating there, and 7 to 11% of the world ocean organic carbon burial occurs in the Arctic Ocean (Stein & Macdonald 2004). The amount and composition of particulate organic matter preserved in the sedimentary records of the continental shelves are controlled by factors such as terrigenous input, primary production, transformation processes in the water column and at the seafloor as well as bulk sedimentation (Stein and Macdonald, 2004). Each of these factors can be affected by global warming, leading to changes in organic carbon burial.

1.2 Primary production and fluxes

Marine primary production in the Arctic is based principally on phytoplankton in the water column and microalgae associated with ice (Sakshaug 2004). Sea-ice microalgae generally occur at the bottom of the ice sheet, in contact with the underlying sea water (Michel et al. 1996, Nozais et al. 2001, Arrigo 2003, Lizotte 2003). Although the primary production rate by sea-ice algae is generally low compared to pelagic phytoplankton, it can be a main source of carbon for the food web in ice-covered regions (Gosselin et al. 1997, Nozais et al. 2001, Arrigo 2003).

Ice can also regulate primary production in the water column in other ways. Phytoplankton blooms are commonly associated with ice retreat in marginal ice zones (Froneman et al. 1997, Murphy et al. 1998, Goffart et al. 2000, Olli et al. 2002, Wassmann et al. 2005). When ice melts, the high input of fresh water increases stratification. These stable conditions, and the abundance of nutrients brought to the surface during winter mixing create optimal conditions for phytoplankton growth. Production at ice edges can be very high (Engelsen et al. 2002). Thus, ice margins and polynyas are highly productive ecosystems (Stirling 1981, Savidge et al. 1996, Rat'kova & Wassmann 2002, Reigstad et al. 2002, Leventer 2003, Ferreyra et al. 2004).

Although primary production determines the maximum concentration of organic carbon potentially available for the system, the flux of this energy toward higher pelagic trophic levels and toward the seafloor can be highly controlled by zooplankton grazing. Match and mismatch of zooplankton biomass with primary production rates can be responsible for variations in vertical flux of organic carbon, which might not always be proportional to primary production rates. When phytoplankton blooms and large zooplankton stocks coincide in space and time (i.e. match scenario), the grazing efficiency is high and sedimentation of intact phytoplankton cells is low. Conversely, when phytoplankton blooms

and large zooplankton stocks are separated in time and space (i.e. mismatch scenario), grazing efficiency is lower and sedimentation large.

It has been suggested that ice abundance may influence whether there is a “match” or “mismatch” relation between primary production rate and grazing. The early ice-algal production and the episodic character of production in the Arctic (Wassmann et al. 1996), lead Carroll & Carroll (2003) to suggest a matching scenario in the case of limited ice, where carbon is mainly used and recycled in the water column. In the second scenario of abundant ice, primary production is dominated by ice algae, and herbivorous grazers and ice fauna are scarce. Ice fauna grazing has been suggested to inefficiently control ice-algal biomass (Werner 2000, Michel et al. 2002) resulting in higher vertical fluxes of organic matter, representing a potential food source for the benthos.

1.3 Pelagic-benthic coupling

The continental shelves of the various Arctic seas (Figure 1) can be sites of high production (Sakhaug 2004), and in some areas, much of this production falls to the bottom. In areas where conditions (light, nutrients) do not support local benthic primary production, benthic organisms depend primarily on organic matter derived from the euphotic zone. Some of the incoming organic matter is stored in benthic biomass and utilized for growth and maintenance of benthic populations, while some part is respired and remineralized by the benthos into CO₂, dissolved organic carbon (DOC), and nutrients. In addition, a residual part of the carbon reaching the sea floor may be buried in the sediment and sequestered for millions of years (Figure 4).

The quality and abundance of particulate organic matter (POM) available for Arctic benthic communities is highly variable in space and time. Due to the importance of Arctic rivers (Figure 1), most of the POM reaching the sea floor on Arctic continental shelves is terrestrially derived and considered to be refractory, poor in nutritional quality (Dittmar & Kattner, 2003). However, in some areas where lateral transport and riverine input are negligible, the metabolism of the benthic community depends on local primary production (Klages et al. 2004). Surprisingly, the benthic carbon remineralization rates found on Arctic continental shelves are similar to those of lower latitudes (Glud et al. 1998, Rysgaard et al. 1998; Glud et al. 2000; Grant et al. 2002, Clough et al. 2005), suggesting that benthic remineralization is regulated primarily by the availability of organic matter and not by temperature. Moreover, in some regions, high benthic abundance, biomass and production reflect the production patterns of the overlying water column (Grebmeier et al. 1988,

Ambrose & Renaud 1995, Piepenburg et al. 1997b). This significant transfer of organic matter and the efficient assimilation by the benthic community (Grebmeier et al. 1988, Grebmeier & Barry 1991, Ambrose & Renaud 1995, Klages et al. 2004) suggest a tight pelagic-benthic coupling in Arctic ecosystems.

In summary, the amount and composition of organic matter preserved in the sedimentary record are controlled by factors such as terrigenous input, primary production, sedimentation rate, and transformation processes in the water column and in the sediment (e.g. anoxia, abundance of fauna). All these factors are highly variable and depend on the region, and are responsible for spatial and seasonal variations in pelagic-benthic coupling.



Figure 1. Map of the seas, major rivers and major polynyas in the Arctic Ocean. NEW: Northeast Water Polynya, NOW: North Water Polynya, CBP: Cape Bathurst Polynya. Adapted from AMAP (1998) and University of Texas Perry-Castaneda Library map collection.

2. Aim of this study

Global warming is expected to affect organic carbon production and cycling and, thus, the entire Arctic ecosystem. Characterizing and understanding factors responsible for variations in pelagic-benthic coupling is a key to better understanding the effects of global warming on Arctic ecosystems.

The overall goal of this dissertation was to use biomarkers of the origin and nutritional quality of POM to study its transfer from the water column to the benthos as a function of environmental and biological factors, such as ice conditions (presence/absence of ice), riverine input, and productivity regime. The main biomarkers were pigments, which are expected to reflect POM sources and degradation pathways. In addition, other biomarkers were also studied (stable carbon and nitrogen, percentages of carbon and nitrogen, diatom frustules), and sediment oxygen demand was used as indicator of benthic carbon cycling. This is the first time such a study was performed in the Arctic, and these different techniques helped addressing the following hypotheses:

H₁: Qualitative and quantitative differences in sedimentary pigments reflect changes in algal source and variation in organic matter flux to the seafloor.

This hypothesis was addressed for the Barents Sea in Papers I, for the Beaufort Sea in Paper II and for the winter/spring season in Paper VI.

H₂: Benthic carbon cycling depends on inputs of phytodetritus from overlying water.

This hypothesis was addressed for the Barents Sea in Papers III, for the Beaufort Sea in Paper IV, for the winter/spring season in Paper V.

H₃: Environmental factors (ice, current and river) and biological parameters (primary and secondary production) shape pelagic-benthic coupling differently in the Barents and Beaufort Seas

This hypothesis was addressed in all papers, in order to identify these factors. They are summarized in the present synthesis.

3. Study sites

This study included two study areas (Figure 2a). The southeast Beaufort Sea was studied four times (October/November 2003, January/February 2004, April/May 2004 and July/August 2004) during the Canadian Arctic Shelf Exchange Study (CASES) project funded primarily by Canada (Figure 2b). The Barents Sea was studied three times (summer 2003 and 2004, and spring 2005) during the Norwegian/EU funded “CARbon flux and ecosystem feedback in the northern BAREnts sea in an ERA of climate change (CABANERA)” project (Figure 2c).

3.1 Southeastern Beaufort Sea

The Beaufort shelf receives the outflow of the Mackenzie River, the fourth largest Arctic river in terms of freshwater discharge, and the largest in the world in terms of sediment supply (Macdonald et al. 1998). Much of this material is either buried or recycled on the wide continental shelf (Macdonald et al. 1998). Primary production rates are usually low and the area is mainly considered to be oligotrophic (Arrigo & Van Dijken 2004, Carmack et al. 2004). Although the area is generally ice-free from May to early October, the spring Cape Bathurst polynya and ice-associated algae could be a source of early-season primary production. In summary, carbon input to the southeast Beaufort Sea seafloor derives primarily from three sources: marine biological production, the Mackenzie plume, and coastal and seabed erosion (O'Brien et al. 2006).

The CASES project had 2 major components. The first included studies of the Mackenzie shelf, slope, Amundsen Gulf and Franklin Bay during fall 2003 and late spring/summer 2004. The second component followed the evolution of the system through an entire year. This was achieved by freezing an icebreaker into the annual shore-fast ice in western Franklin Bay (station 200, Figure 2b) over the winter at a water depth of 231 m, when this area is usually not accessible for regular scientific cruises. To allow sampling while frozen into the ice, the icebreaker was equipped with a “moon pool”, an opening in the ship's hull. The project was international and covered physical, biological, chemical and geological oceanography.

3.2 Western Barents Sea

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 have different phytoplankton (Rat'kova & Wassmann 2002, Reigstad et al. 2002) and

zooplankton (Colebrook 1985) compositions. Primary production in the Barents Sea is one of the highest among the Arctic shelf systems (Sakshaug & Slagstad 1992), and pelagic-benthic coupling may be particularly tight (Wassmann et al. 2006). As much as 50% of the primary production is exported from the surface and represents potential food for benthic organisms (Wexels Riser et al. in press). Much of the Barents Sea is a marginal ice zone (MIZ), which 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). Therefore, inputs of organic matter to the benthos will vary spatially and temporally as a function of physical processes influencing patterns of ice melt in the region (Reigstad et al. 2002).

The CABANERA project focused on the Barents Sea continental shelf (200-500 m). The goal was to investigate how primary production, the biological pump, and pelagic-benthic coupling are regulated in spring and summer.

3.3 Comparison of the two sites

The Barents Sea represents a strong contrast to the Beaufort Sea. Primary production is expected to be higher in the Barents Sea than in the Beaufort Sea and to be strongly influenced by surrounding currents. In contrast, the Beaufort Sea is expected to be more oligotrophic than the Barents Sea and to be influenced by the Mackenzie River (Macdonald et al. 1998). However, both systems should show strong seasonal and spatial variations of POM inputs to the benthos. An important element of seasonal variation is expected to be due to productivity regime (phytoplankton vs. ice algae), while the riverine influence, currents and water depth might be responsible for spatial variations.

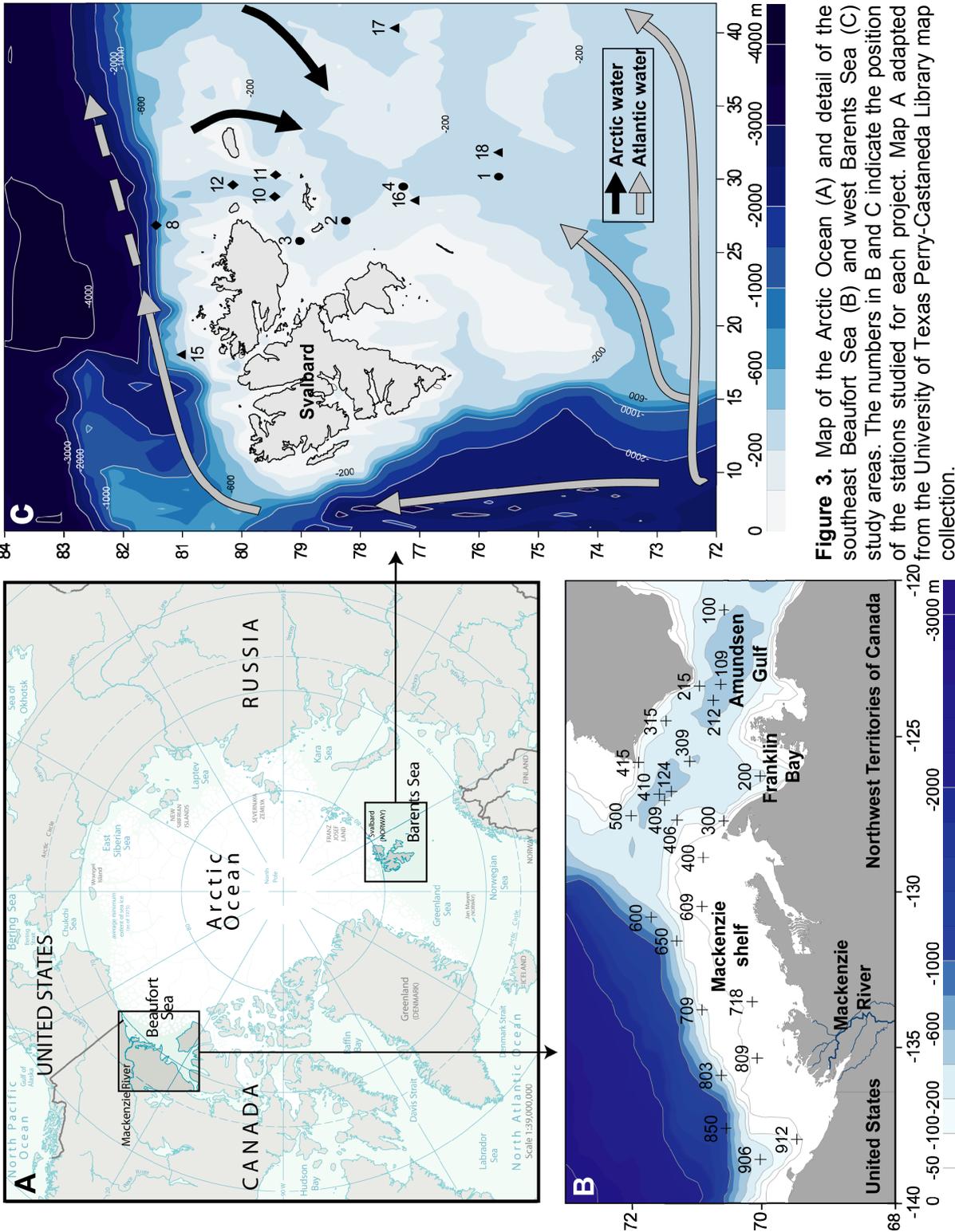


Figure 3. Map of the Arctic Ocean (A) and detail of the southeast Beaufort Sea (B) and west Barents Sea (C) study areas. The numbers in B and C indicate the position of the stations studied for each project. Map A adapted from the University of Texas Perry-Castaneda Library map collection.

4. Methods

For both study sites, samples for biomarker analysis (pigments and isotopes) were collected in the water column and ice when present (Table 2). At each station, when possible, sediment was sampled for biomarker analysis (pigments and isotopes), for benthic community composition, and for sediment oxygen demand (SOD).

Table 2: Type of samples and method used in each study.

Method	Sample	Paper						Reference
		I	II	III	IV	V	VI	
Pigment	Ice	√	√				√	Wright et al. (1991)
	Water column	√	√				√	Wright et al. (1991)
	Sediment (HPLC)	√	√				√	Chen et al. (2001)
	Sediment (Fluo)	√	√	√	√	√	√	Holm-Hansen et al. (1965)
Stable isotope	Water column		√					Hobson et al. (1995)
	Sediment		√				√	Hobson et al. (1995)
Sediment O ₂	Total			√	√	√		e.g. Clough et al. (2005)
Demand	Macrofauna free				√	√		Grant et al. (2002)
Diatom frustule	Sediment						√	Adapted from Hamilton et al. (2005)

4.1 Ice, water column and sediment sampling for biomarker analysis

Suspended particulate organic matter was determined in the following manner: water from the water column chlorophyll maximum determined by an *in vivo* fluorescence probe was filtered onto precombusted (5 h at 500°C) Whatmann GF/F filters. Filters were stored at -20°C prior to pigment and isotope analysis. During the CASES program, ice cores were collected with a manual corer (Mark II coring system, 9 cm internal diameter; Kovacs Enterprises). The bottom 4-10 cm of the cores were cut and melted in 1-5 L of 0.2 µm filtered surface sea water to minimize osmotic stress (Garrison & Buck 1986). The melted cores were then filtered onto GF/F filters as for POM. During the CABANERA program, ice algae and ice detritus (IPOM) were collected from the underside of the ice by SCUBA divers using an electric suction pump as described by Tamelander et al. (2007). IPOM was filtered onto GF/F filters as described previously for POM.

Samples for organic carbon and nitrogen percentages (%C and %N), and stable isotope ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) analysis were collected with a truncated syringe from the top 2 cm of the sediment column. Samples were immediately frozen. Sediment cores (5 cm diameter×10 cm deep) were collected for determination of of sedimentary pigment concentration and composition profiles. Immediately after sampling, the sediment cores were extruded and sliced at 1 cm intervals under low light conditions. Each interval was divided in two, half to

be used for an estimate of chlorophyll *a* and total chloropigment concentration by fluorescence and half for determination of individual pigment concentration by high pressure liquid chromatography (HPLC). See section 4.4 for detail pigment analysis methodology. Both pigment sub-samples were wrapped in foil and frozen immediately after slicing in order to avoid pigment degradation. The overall slicing procedure did not exceed 1-2 hours.

4.2 Sediment oxygen demand and benthic community composition

SOD was used as an indicator of benthic activity. Sediment cores (10 cm diameter×20–25 cm deep with as much overlying water preserved as possible, 3–12 replicates per station) for SOD were collected with a multicorer during the CABANERA program, and sub-sampled from a spade corer (45 cm×45 cm) during the CASES program. Sediment cores were topped off with oxygenated bottom water and incubated in a cold room (<4°C). The measurement of SOD after addition of O₂ to reach 100% can be seen as measurement of the “potential sediment oxygen demand”. However near-bottom oxygen concentrations were never below 2 ppm (i.e. hypoxia) and so differentiating potential from in situ sediment oxygen demand is probably not relevant in this study. Oxygen was monitored every 2-8 hours using a microelectrode (Unisense, A/S; Aarhus, Denmark) until 15-30% had been consumed (usually 24-48 h). The slope of the linear relationship between time and oxygen concentration was used as estimation of the SOD. In some cores, common large epifauna species were added in order to evaluate the oxygen consumption of individual organisms. Control cores with only bottom water were also incubated under the same conditions. After the end of incubations, sediment cores were sieved (1 mm) and macrofauna fixed in buffered 5% formalin in seawater and later preserved in 70% ethanol. Faunal composition of CABANERA samples was determined by taxonomic experts at the Russian Academy of Sciences Zoological Institute, St. Petersburg.

In order to estimate how much of the whole-core respiration was due to micro- and meio- fauna, additional incubations (minivials) were performed following procedures of Grant et al. (2002). Approximately 24 sub-cores (1.4 cm diameter×2 cm deep) were collected at each station with a truncated syringe. Visible macrofauna were removed as the sediment was transferred into pre-cleaned 24 mL glass scintillation vials. Vials were checked again afterward and replicates with macrofauna were rejected. Vials were filled with filtered (0.45 µm) near-bottom water and the oxygen concentration in half the vials was determined using a microelectrode. The remaining vials were incubated in a cold room for 48–56 h (drop in O₂: 2-28%), after which the oxygen concentrations were determined. The difference between

readings at the beginning and end of the incubation was attributed to oxygen consumption by meiofauna, protozoa and bacteria. It is however important to keep in mind that these minivial incubations have been found to overestimate bacterial activity since exposure of the sediment to oxygenated waters can lead to break up of nutrient microgradients and redox conditions, and possibly enhance bacterial oxygen demand (Aller & Aller 1998, Dauwe et al. 2001, Grant et al. 2002). Once the minivial incubations were complete, samples were fixed for diatom-frustule analysis by withdrawing 2 mL of water and adding 2 mL of 37% buffered formaldehyde. Sedimentary diatom analyses were performed at the Canadian Museum of Nature, under the supervision of Dr. Michel Poulin, using an adaptation of the method of Hamilton et al. (2002).

Because estimates of epifaunal density are difficult to obtain from classical methods (i.e. sediment sieving), pictures of the surface sediment were taken during CASES. The underwater digital camera (Benthos, 1.2 megapixel resolution) and two strobes were mounted on a 1×1 m frame, equipped with a bottom-triggered shutter release. Organisms were identified and counted, and densities were scaled to values per square meter.

4.3 Stable isotopes and CHN analysis

Stable isotope analysis of the suspended particulate organic matter (i.e. POM filters) were performed after acidification for removing inorganic carbon, by the National Hydrology Research Institute in Saskatoon, Saskatchewan, Canada, using the method of Hobson et al. (1995). Frozen sediment samples for stable isotope analysis were dried at 60°C overnight. In order to decalcify sub-samples for carbon analysis, about 2 g of dry, homogenised sediment were placed in a crucible, 2 mL of 1 N HCl was added, and the sample was dried overnight. The operation was repeated 3 times, or until no bubbling occurred after acid addition. In order to avoid the carbon isotopic signature of carbonate, the decalcified sediment was used for %C and $\delta^{13}\text{C}$ determination. However, since acidification can alter the nitrogen isotope composition, undecalcified samples were used for %N and $\delta^{15}\text{N}$ analysis. Stable isotope analysis of sediments was performed by the Environmental Geochemistry Laboratory, Department of Geology, Bates College, U.S. Some of the decalcified sub-samples were also used for CHN analysis on a Fisons model 1108 CHN Analyzer with acetanilide as a standard.

4.4 Pigment analysis

Concentrations of individual pigments in POM and ice samples were determined by HPLC (Wright et al. 1991). Concentrations of sedimentary pigments were determined using

both HPLC (Chen et al. 2001) and fluorometry (Holm-Hansen et al. 1965). Ice samples and POM filters were extracted in 2 mL of 100% HPLC-grade acetone for 12-24 h. Extracts were filtered through 0.2- μ m-pore-size nylon syringe filters. Freeze-dried sediment (1-3 g) was transferred to a 50 mL polypropylene centrifuge tube where 8 mL of 80:20 (v:v) HPLC grade acetone:methanol was added. The mixture was sonicated for 5 minutes in an ice bath and extracted in the freezer overnight. Extracts were separated from the sediment by centrifugation (10 min, 2000 rpm) and 5 mL of the supernatant was filtered through a 0.2- μ m-pore-size syringe filter. Extracts were blown to dryness under nitrogen, and then redissolved in 250 μ l of 90% acetone in water.

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 at 440 nm and emission at 660 nm. Two hundred μ l of each sample were injected through a guard column to a reversed-phase Alltech Absorbosphere C18 column (5 μ m particle size; 250 \times 4.6 mm i.d.). The 3-step gradient program was a modification of Wright et al. (1991) as described by Chen et al. (2001) for enhancing the separation of chlorophyll degradation products, also called phaeopigments.

Identification of pigments was performed by comparing retention time and spectra from photodiode array (PDA) detector of samples (See Appendix 7 for an example) with standards (DHI Water and Environment, Denmark, Appendices 8 and 9). Carotenoids were quantified using absorbance at 438 nm using the PDA detector, while chlorophylls and phaeopigments were quantified on the fluorescence detector (excitation 440 nm, emission 660 nm). The response factor (RF) was determined for each pigment from single run of each pigment standard.

Within two weeks of sample collection, total pigment concentrations were determined in sub-samples of sediment by fluorometry. The samples were placed in 60 mL centrifuge tubes, and 20 mL of 100% acetone was added. Tubes were stored at -20°C in the dark for 48h, and shaken periodically. Prior to fluorescence determination, the sediment was centrifuged (4000 rpm for 10 minutes at 0°C). The fluorescence of the supernatant was determined using a Turner Designs Model 10-AU fluorometer (excitation 440 nm, emission 660 nm) before and after acidification with 5% HCl (Holm-Hansen et al. 1965), in order to determine chlorophyll *a* (chl *a*) and phaeopigments (phaeo).

5. Pigments as biomarkers

5.1 Photosynthetic pigments

Pigments are bound in pigment-protein complexes. Chlorophylls are a combination of cyclic complexes with a magnesium ion in the center (also called Mg-phorbin ring) and a long-chain isoprenoid alcohol ester group (also referred to as phytol chain, Figure 3a). Carotenoids are hydrocarbons consisting of eight isoprenoid units (carotenes) and their oxygenated derivatives (xanthophylls) (Figure 3b).

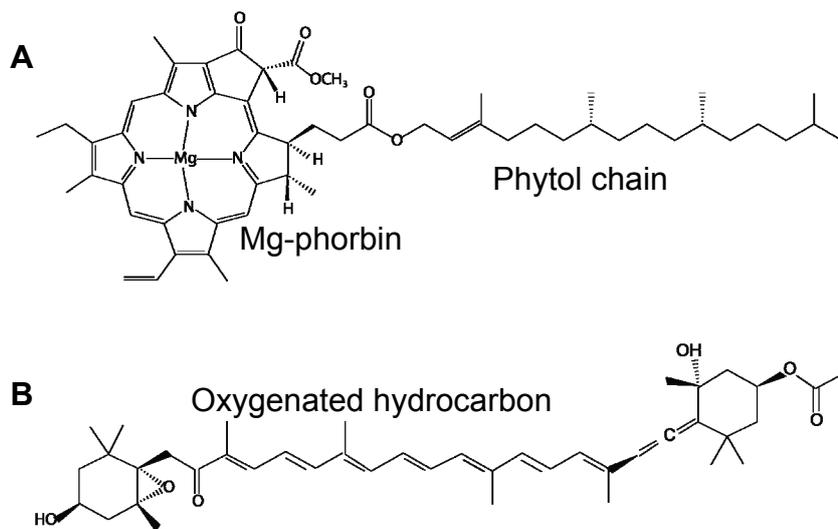


Figure 3. Chemical structure of (A) chlorophyll *a* and (B) fucoxanthin (carotenoid).

Pigments are present in all photosynthetic organisms and function primarily as light-harvesting agents for photosynthesis and for photo-protection (Porra et al. 1997). Chl *a* is the most common pigment, but other kinds of closely related chlorophylls and carotenoids also exist. While chl *a* is common to all algal species, many other accessory pigments are present in the different organisms and often have a restricted taxonomic distribution (Table 1). Thus pigments are useful as biomarkers of the algal groups responsible for primary production due to their taxonomic specificity (Jeffrey et al. 1997).

Preservation of pigments in sediment is generally favored by high plankton production, high sedimentation rates, and anoxia, the three main features of eutrophic basins (Schulte et al. 1999, Kowalewska et al. 2004). Thus, sedimentary pigments have been used in short-term and long-term studies of marine 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 & Nikkilä 2001), as well as

in larger-scale studies of sea level (Squier et al. 2003) and hydrodynamic changes (Zhao et al. 2000, Kowalewska 2001). In the Arctic, production can be very high, major phytoplanktonic groups can change spatially and seasonally, and downward fluxes can also be high. This makes pigments good candidates for studying pelagic-benthic coupling dynamics in Arctic systems. HPLC techniques represent the best way to study sedimentary pigments, since they allow separation of various chlorophylls, carotenoids and their degradation products (Sun et al. 1991, Sun et al. 1994, Kowalewska 1995, Bianchi et al. 1997, Kowalewska et al. 1998, Kowalewska et al. 2004). Few studies have investigated sedimentary chl *a* and phaeopigments by fluorometry in the Arctic (see summary in **Paper I**). The study of other pigments by HPLC has, to my knowledge, never been performed in Arctic marine sediments.

Table 1. Summary of pigments recovered in the water column and in sediment and their provenance. Compiled from Jeffrey et al. (1997) and Leavitt & Hodgson (2001). The relative degree of chemical stability and preservation is ranked from most (1) to least (4) stable. Pigments with the least stability are rarely found in the sediment. The predominant source is identified as planktonic (P), littoral (L), terrestrial (T) or sedimentary (S, post-depositional derivatives); upper case letter indicates the quantitatively more important sources, while lower case a less important source. - = not determined.

Pigment	Major groups or process	Stability	Source
Chlorophylls			
Chlorophyll <i>a</i>	All photosynthetic algae, higher plants	3	P L
Chlorophyll <i>b</i>	Green algae, euglenophytes, higher plants	2	P L
Chlorophyll <i>c</i> family	Dinoflagellates, diatoms, chrysophytes	1	P I
Carotenoids			
β-Carotene	Most algae and plants	1	P L t
Fucoxanthin	Diatoms, prymnesiophytes, chrysophytes, raphidophytes, several dinoflagellates	2	P L
Peridinin	Dinoflagellates	4	P
Alloxanthin	Cryptophytes	1	P
19'But-fucoxanthin	Prymnesiophytes, chrysophytes	-	P L
19'Hex-fucoxanthin	Prymnesiophytes	-	P
Zeaxanthin	Cyanobacteria, prochlorophytes, rhodophytes, chlorophytes	1	P I
Chlorophyll degradation products			
Phaeophytin <i>a</i>	Chlorophyll <i>a</i> derivative (general)	1	P L t s
Phaeophytin <i>b</i>	Chlorophyll <i>b</i> derivative (general)	2	P L t s
Phaeophorbide <i>a</i>	Grazing, senescent diatoms	3	P I s
Pyro-phaeo(pigment)	Derivatives of <i>a</i> and <i>b</i> -phaeopigments	2	L S

5.2 Flux and degradation of pigments

Pigments are degraded in the aquatic environment by biological processes (Figure 4), as well as chemical and photochemical processes, and in the water column (Cuddington & Leavitt 1999) and following deposition in the sediment (Hodgson et al. 1998). Chlorophylls

contain nitrogen and are therefore more prone to degradation than carotenoids. Within the water column, pigment degradation is usually very rapid and extensive (hours to weeks, Figure 4). In the sediment, chl *a* has a half life of several weeks (Graf et al. 1995).

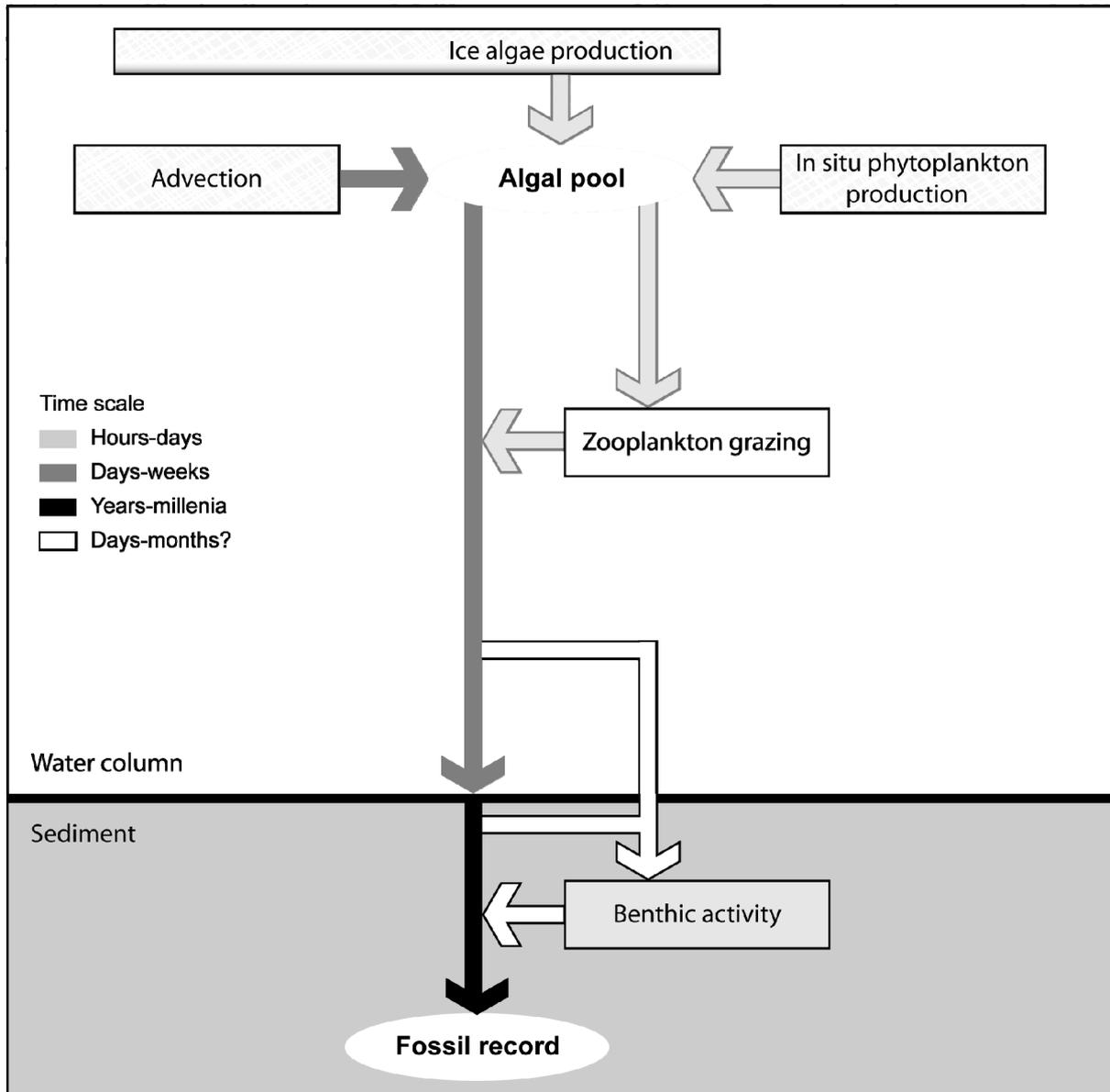


Figure 4. Main biological pathways of pigment production in the “algal pool”, transformation and degradation in the Arctic marine ecosystem. Most degradation of pigments occurs during deposition through the water column and in the surface sediments. Note that the scale of the effect of benthic activity is not well defined, and is addressed in this study.

The fate of pigments in Arctic sediments is not fully understood. Smith et al. (in press) suggested the existence of a "foodbank" for Antarctica. This foodbank consists of organic matter maintained in the sediment throughout the year, and thus available to the benthos during low depositional periods. Another explanation consists of fast response to POM inputs, especially to spring ice-algae inputs, as discussed in **Paper V**. The benthic

activity increases as soon as fresh POM reaches the sea floor. A third option would be a combination of the two previous hypotheses, where the benthos responds quickly to inputs, but a part of the carbon arrival is stocked in the sediment and can be use through the entire year, as suggested in **Papers II and VI**.

Different pathways of pigment degradation affect the integrity of the Mg-phorbin ring, the phytol chain, or both, and result in different degradation products (Figure 5). Formation of phaeophorbide is mainly due to herbivore activity, chlorophyll is degraded to chlorophyllide by chlorophyllase during cell senescence, and phaeophytin is formed during herbivory, cell senescence, and microbial degradation.

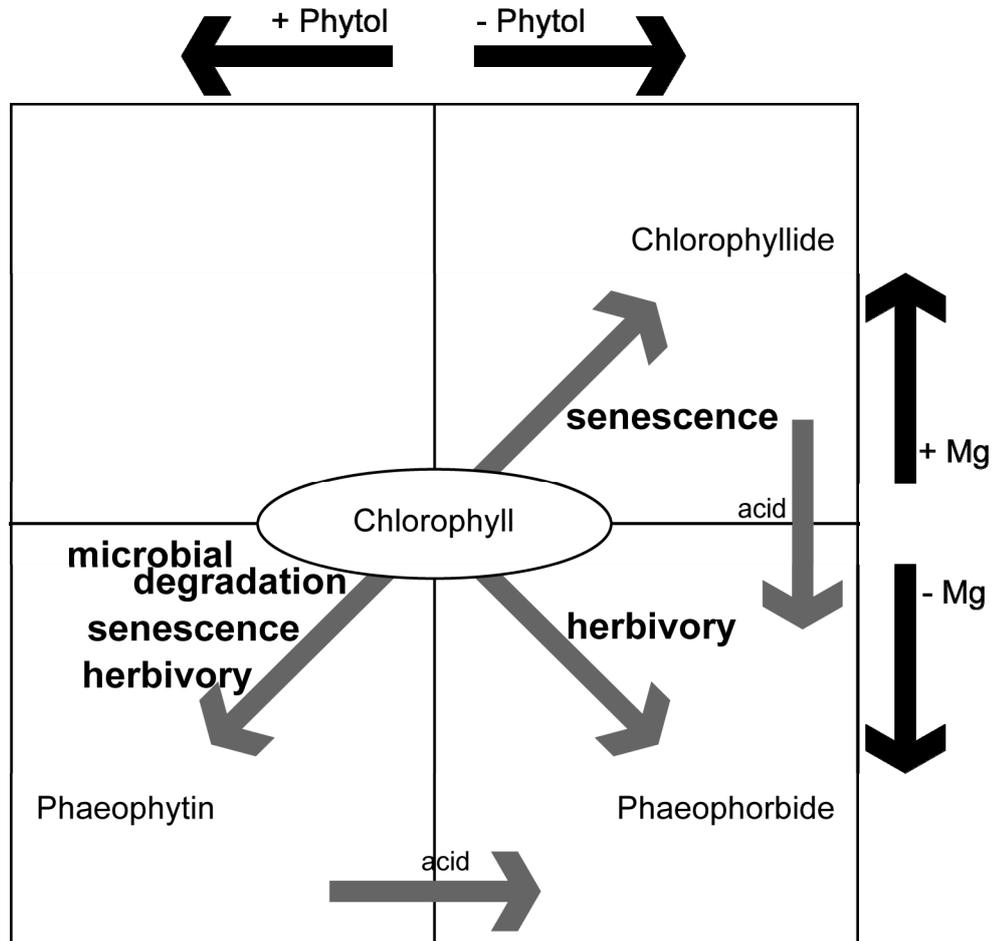


Figure 5. Production of the 3 main colored chlorophyll derivatives under oxic conditions: chlorophyllide, phaeophytin and phaeophorbide. Adapted from Leavitt (1993).

To summarize, relative abundance of sedimentary chl *a* is a marker of the freshness of algal matter inputs to the sediment (Boon & Duineveld 1996), sedimentary accessory pigments specific for different algal groups can be used as taxonomic markers (Gieskes & Kraay 1984, Jeffrey & Vesik 1997), and degradation products indicate physiological status

and nature of chlorophyll processing organic matter has undergone (Mantoura & Llewellyn 1983, Villanueva & Hastings 2000).

5.3 Results obtained in this study

As expected, the study of sedimentary pigments by HPLC allowed the separation of various chlorophylls, carotenoids, and pigment degradation products. The chl *a* results from the HPLC method correlated strongly with the results from the fluorometric method (Figure 6, **Papers I, II and VI**).

The main sedimentary accessory pigments found in all studies were chlorophyll *b* (chl *b*), a marker of green algae, and fucoxanthin, a marker of diatoms

(**Papers I, II and VI**). Other accessory pigments were also found in the sediment, and an even larger number of pigments were identified in water column and ice (**Papers I and II**). The large number of pigments found in water and ice samples is likely due to the fact that in the water column and ice, degraded pigments were usually not very abundant, while in the sediment, degradation products were sometimes extremely abundant, and could have masked other pigment signals. This is illustrated in the Figure 7, where, for the same station, the chromatogram of the water column POM presents distinct peaks, and easily identifiable spectra, while the chromatogram in the two first cm of sediment presents many more peaks of unidentified degradation products.

Sedimentary chl *a* abundance showed strong correlations with local primary production and fluxes (**Papers I, II, III and IV**), and was inversely correlated with depth (**Papers II, III and IV**). Moreover chl *a* abundance was also correlated with benthic activities (**Papers III and IV**). The ratio of chl *a* to total phaeopigment concentrations (chl *a*/phaeo) was also used as an indicator of the freshness of sedimentary organic matter.

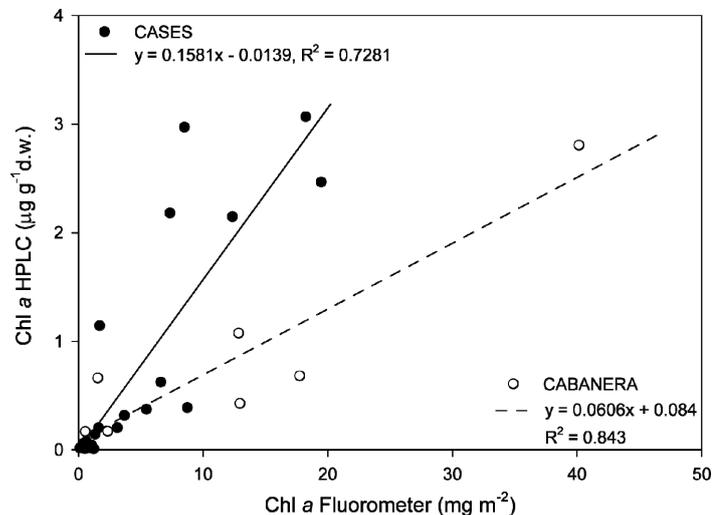


Figure 6: Comparison of the results of sedimentary chlorophyll *a* content (0-2 cm) by Fluorometer and HPLC analysis for the Beaufort (CASES) and Barents (CABANERA) seas.

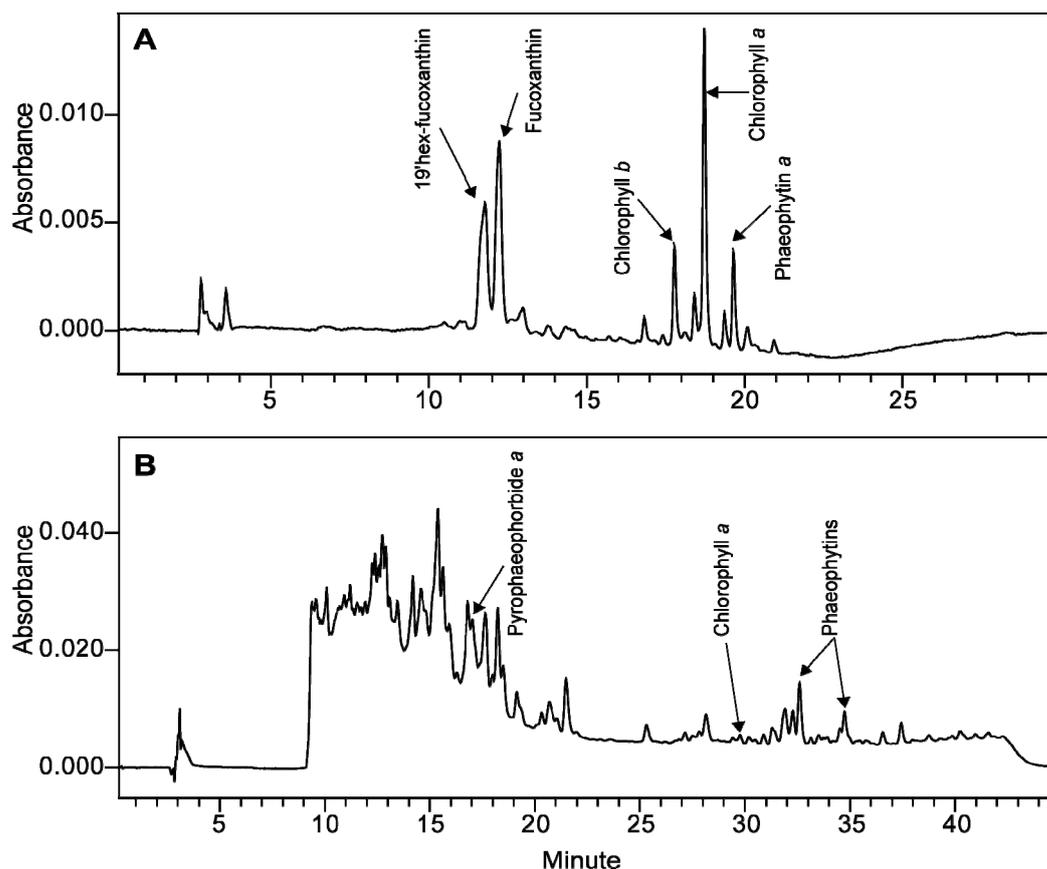


Figure 7. Characteristic pigment chromatogram from (A) a POM sample and (B) a 0-1 cm sediment slice from station 100, CASES, fall 2003. In the POM sample, main peaks are easily identifiable. In contrast, in sediment, peaks overlap and the chromatogram includes many unidentified degradation products. Absorbance signals were detected at 438 nm using a PDA detector. Note that the retention time for the same compounds differ between the chromatograms, because different gradients were used.

Fucoxanthin, a marker of diatoms, was by far the most abundant accessory pigment found in ice, water column, and sediment. Although it is impossible to differentiate ice-derived diatoms from phytoplankton diatoms from their similar pigment signature, it was hypothesized in **Papers I** and **II** that a part of sedimentary fucoxanthin derived from ice. **Paper VI** suggested that this hypothesis was valid as fresh intact ice-algal cells were found in the surface sediment of the Beaufort Sea when ice-algal biomass increased in the spring.

Other accessory pigments were used as taxonomic markers of various phytoplankton groups. Moreover the use of the CHEMTAX program (Mackey et al. 1996) allowed us to relate the water column pigment composition to phytoplankton taxonomic composition. In the Beaufort Sea for example, the three major phytoplanktonic groups (>90% total groups) determined by CHEMTAX were diatoms, green algae (prasinophytes + chlorophytes classes) and haptophytes (prymnesiophytes). In the cell counts, the major classes found were diatoms, prasinophytes, prymnesiophytes and flagellates (Poulin et al. pers. comm.). Lovejoy et al. (2007) found that *Micromonas*-like picoprasinophytes were very abundant in the Western

Arctic, which suggests that an important part of the flagellates found in the Beaufort Sea could be prasinophytes. Paired t-tests between the CHEMTAX and cell-count results showed no significant difference ($p > 0.05$) of the total percentages of diatoms and green algae in summer and fall, and no difference for the haptophytes in the summer. Haptophyte percentages were however significantly different in the fall. A part of the cell count might have ignored some haptophytes counted as “flagellates”. The comparison of CHEMTAX with cell counts is hard to perform because of the difference of the different limitations of identification for each group and class for both techniques. However, although the use of CHEMTAX is somewhat controversial, the results obtained in both the Barents and Beaufort Seas (**Papers I and II**) gave similar results as microscope cell counts for the major groups.

Both pigment signature and CHEMTAX results showed that small flagellated cells such as prasinophytes and prymnesiophytes were important during the fall in the Beaufort Sea (**Paper II**). In the Barents Sea, green algae (which includes prasinophytes) and prymnesiophytes were influenced by the predominant water-mass (Arctic or Atlantic water were the predominant water mass) (**Paper I**). Degradation products of chl *b* were used to track riverine influence (**Paper II**).

Finally, phaeophorbide and carotenol chlorine esters (CCE) were used as markers of macrozooplankton and macrobenthos grazing (**Papers I, II and VI**). CCE are created during grazing processes by a combination of carotenoid and phaeophorbide (Goericke et al. 1999, Soma et al. 2001, Chen et al. 2005), and were only recently identified. It was thus extremely interesting to find them in the sediment of the Barents Sea as a marker of diatom grazing (**Paper I**). It is important to note that although phaeophorbides have been used to trace grazing processes in both the water column (Jeffrey 1974, Carpenter et al. 1986, Spooner 1994) and the sediment (Brotas and Plante-Cuny 1998, Riaux-Gobin 2000) it has recently been argued that it might not always be a relevant indicator of herbivorous activities (Villanueva and Hastings 1999, Ford and Honeywill 2002). However the correlation of phaeophorbide with CCE in the Barents Sea (**Paper I**) and with macrozooplankton fecal pellets in the Beaufort Sea (**Paper II**) confirmed the reliability of this pigment as marker of grazing.

This work found sedimentary pigments to reflect changes in environmental factors, in sources of organic matter, in food web structure, and in benthic activity. Although useful information is gained from the pigment patterns alone, the addition of other biomarkers, such as stable isotopes and diatoms frustules, allowed further elucidation of factors influencing spatial and seasonal changes in pelagic-benthic coupling.

6. Effects of environmental factors

The present study in the Beaufort and Barents Seas highlighted three major abiotic factors affecting pelagic-benthic coupling: water depth, water masses, and riverine input. Not surprisingly, these factors had very different impacts in the two ecosystems. Depth and riverine inputs were important in the Beaufort Sea (**Papers II, IV and VI**) while in the Barents Sea, oceanic source waters seemed more important in determining organic matter inputs to the benthos (**Papers I and III**).

6.1 Water depth

Previous studies pointed out the importance of depth for determining the quality and quantity of organic matter reaching the benthos in marine systems, both polar (e.g., Grebmeier 1993) and temperate (e.g., Suess 1980). In the Arctic, increasing depths have been correlated with decreasing sedimentary chl *a* (Ambrose & Renaud 1995, Grahl et al. 1995, **Paper II**), decreasing SOD (Pfannkuche & Thiel 1987, Ambrose & Renaud 1995, Piepenburg et al. 1995, Glud et al. 2000, Clough et al. 2005, **Paper IV**), and changes in benthic community composition (Grebmeier et al. 1988, Clough et al. 1997, Piepenburg 2005, Conlan et al. in press). Shallower depths seemed to be associated with shorter pelagic food chain (Grebmeier et al. 2006), probably allowing greater inputs of organic matter of better quality. Indeed, sedimentary chl *a*, chl *a*/phaeo ratio, and SOD were higher in the shallower Mackenzie shelf than in the surrounding deeper environment (Tables 2, 3, **Papers II and IV**). For a given water depth, sediment type and water column nutrient regime, benthic macrofaunal biomass in the Arctic appears to be greater than at lower latitudes (Petersen & Curtis 1980, Rowe 1983), suggesting a stronger pelagic-benthic coupling in the Arctic.

Pronounced depth zonation has been found in the composition and distribution of benthic assemblages, leading Piepenburg (2005) to separate 3 distinct zones: shelf, slope, and basin. This concept was used in **Paper II**. However, even though the study areas are defined by water depths, differences are not the result of just one single factor, but several direct and indirect depth-dependent ecological processes (Carney et al. 1983). Indeed, water depth can have an influence on factors such as mixed layer depth, current speed, ice cover, primary production, bacterial degradation, and sea floor sediment properties, which are often interrelated (Piepenburg et al. 2001). This means that although pressure, directly related to water depth, can impact benthic organisms (Somero et al. 1983), it is most likely the inverse

relationship between water depth and sedimentation rates that explains the fundamental influence of water depth on the quality and quantity of organic matter reaching the sea floor (Graf 1992). Surprisingly, in the Barents Sea, depth did not seem to be an important factor for determining benthic activity and sediment properties (**Papers I and III**), depth range was too narrow to make correlations (200-350 m, station 8 was at 500 m).

6.2 Water masses and currents

In addition to depth zonation, current regime has been found to be the most prominent feature in the distribution of some Arctic assemblages (Piepenburg 2000). Currents can directly influence carbon source and fate by bringing allochthonous organic matter to the system in water (Feder et al. 1994) or ice (Reimnitz et al. 1993). Alternatively, currents can export organic material, making it unavailable for the local benthos. Allochthonous terrestrial inputs have been found to balance the overall carbon demand in the Laptev Sea (Schmid et al. 2006), and off-shelf export has been suggested to feed communities of the deep Arctic basin during some seasons (Moran et al. 2005). Thus, the prevailing water masses and currents in the area are important in determining the potential characteristics of food deposition to the benthos and can have significant impacts on local and regional carbon cycling pathways.

As noted, the Barents Sea is influenced by warm Atlantic Water in the south and by Arctic Water in the north (Figure 2c). These water masses have different phytoplankton compositions (Rat'kova & Wassmann 2002, Reigstad et al. 2002), which were reflected in the sedimentary pigment composition (**Paper I**). The effect of dominant water mass on phytoplankton composition has also been observed in the Chukchi Sea where changes in phytoplankton species and water-column pigment composition due to water mass variations (Hill et al. 2005) were apparent in the sedimentary pigment composition (Pirtle-Levy et al. in press).

In the Beaufort Sea, an upwelling off Cape Bathurst is suspected to be responsible for areas of elevated benthic biomass (Conlan et al. in press). Sedimentary chl *a* concentrations and the chl *a*/phaeo ratio were higher in this area (see Figure 2 a,c, station 300 of **Paper II**). This increase of benthic biomass in upwelling areas is similar to sites in the Chukchi Sea, where upwelling of nutrient-rich waters causes high primary production and sustained high benthic biomass (Grebmeier et al. 1988, Grebmeier & Barry 1991).

6.3 Riverine inputs

As mentioned previously, about 10% of the global river discharge enters the Arctic Ocean, which is only 1% of the world ocean water (Dittmar & Kattner 2003). Despite pronounced seasonal patterns, organic matter concentrations in Arctic rivers are generally among the highest in the world, while nutrient concentrations are among the lowest (Dittmar & Kattner 2003). Terrigenous organic carbon inputs into the Arctic Ocean are mainly due to the particulate organic carbon discharged by river (80% of total organic carbon flux). Coastal erosion contributes about 15% of the terrigenous organic carbon, with the rest due to underground water discharge, sea-ice input, and eolian deposition (Rachold et al. 2004). The Barents Sea did not show markers of riverine inputs (**Papers I and III**), probably because river inputs and sediment load are substantially lower in the Barents Sea than on other Arctic shelves (Rachold et al. 2004). Isotopic signatures typical of terrestrial organic matter and freshwater algae have been found in the sediment of the Kara Sea (Fernandes & Sicre 2000, Fahl et al. 2003, Polyakova 2003, Stein et al. 2004), Laptev Sea (Cremer 1999, Matthiessen et al. 2000), and Beaufort Sea (**Paper II** and references within), influenced by the Yeniseya and Ob', the Lena, and the Mackenzie Rivers, respectively (Figure 1). Moreover, the sedimentary pigment composition (chl *b* degradation products) corroborated the terrestrial isotope signature in the Beaufort Sea (**Paper II**). However, most of the imported fluvial organic matter is usually fairly degraded (Stein 1996, Fahl et al. 2001, **Paper II**), and likely represents low-quality food for the benthos. Thus, although riverine inputs are important for the pelagic-benthic coupling and impact bulk organic inputs to the sediments, they do not seem to be an important food resource for benthic communities in the Arctic (Klages et al. 2004).

7. Effects of biotic factors

Environmental factors often control variations in biological factors. In the Barents Sea, for example, water masses seemed to play an indirect role in pelagic-benthic coupling by influencing phytoplankton composition in the summer. However, biological parameters including primary production, phytoplankton taxonomy, and zooplankton grazing seemed to predominate in shaping pelagic-benthic coupling over time.

7.1 Local water-column production

Previous studies on Arctic ecosystems have suggested local autochthonous primary production as the major factor determining sedimentary chl *a* and SOD (Pfannkuche & Thiel 1987, Ambrose & Renaud 1995, Piepenburg et al. 1997a, Grant et al. 2002, Bessière et al. 2007). In the deep Arctic Ocean, sedimentary chl *a* and SOD were lower than on the Arctic shelves (Clough et al. 2005). They are also lower than on the NE-Atlantic abyssal plain (Pfannkuche 1992), reflecting limited primary production under the permanent ice cover (Boetius & Damm 1998, Soltwedel & Schewe 1998).

Although sedimentary chl *a* and SOD were not correlated with depth in the Barents Sea, they were correlated with overlying biomass of primary producers and vertical fluxes in both the Barents and Beaufort Seas (**Papers I, II and III**). For similar depths (>200 m), sedimentary pigments and SOD were usually higher in the Barents Sea (**Papers I and III**) than in the Beaufort Sea (**Papers II and IV**). Primary production rates in the Barents Sea and the Bering/Chukchi Sea are among the highest in the Arctic (see review by Sakshaug 2004), and sedimentary pigments reflect this by exhibiting high contents of chl *a* and high chl *a*/phaeo ratios (Table 3). Although sedimentary chl *a* and SOD at depths >200 m in the southeastern Beaufort Sea were lower than in more productive ecosystems, values in the shallower areas of the Mackenzie shelf were comparable with other Arctic shelves (Table 3).

An important feature of primary production in the Arctic Ocean is its strong episodic character (Wassmann et al. 1996), leading to important temporal/seasonal variations in addition to the spatial variations addressed previously. Seasonal variations in abundance and composition of sedimentary pigments were observed in both the Barents and Beaufort Seas (**Papers I, II and VI**). In the Beaufort Sea, the chl *a*/phaeo ratios were higher in the summer compared to the fall, representing a material less degraded and thus “fresher”. In the spring study (**Paper V**), SOD increased through time, while chl *a* did not. Other sedimentary pigments, markers of phytoplankton taxonomy (section 7.2) and pigment degradation

(Section 7.3), provided insights regarding the benthic response to the spring pulse of organic matter (**Paper VI**). In the Barents Sea, chl *a* and SOD did not show significant differences between spring and summer, although accessory-pigment composition reflected seasonal changes in productivity regime (section 7.2).

Seasonal variations are often due to changes in ice-associated production and this will be discussed below. Chl *a* and SOD can reveal spatial variations in pelagic-benthic coupling due to changes in total algal biomass. However in order to track changes in primary producers, the only study of chl *a* and SOD is not sufficient and other pigments have to be identified by HPLC.

7.2 Productivity regime (phytoplankton vs. ice algae)

Variation in ice cover indirectly impacts organic matter inputs by its influence on ice-algal production. Sea-ice algae have been found to contribute considerably to total primary production in polar seas (Legendre et al. 1992, Gosselin et al. 1997) and to be dominated by diatoms (von Quillfeldt et al. 2003, Hill et al. 2005). Sea-ice algal production is particularly favoured in the spring, when sea ice has not melted yet and light is sufficient. It can also indirectly impact the overall water column production. The release of ice algae into the water column by ice melt is commonly associated with phytoplankton blooms (Leventer 2003) suggesting that sea-ice algae may serve as the seeding population for bloom onset (Syvertsen 1991, Gradinger 1999). In the present study, primary producers occurring directly within the ice and in the underlying water due to ice-algae inoculums are referred to as “ice-associated algae”.

Ice-associated algae can sink, representing a potential source of food for the benthos. Frustules of ice-associated algae have been found in the sediment of Arctic shelves (Sancetta 1981, Cremer 1999, Djinoridze et al. 1999, Polyakova 2003, Ambrose et al. 2005, **Paper VI**, Figure 8) or their presence has been indicated by high concentrations of chl *a* and/or fucoxanthin (Schewe & Soltwedel 2003, Pirtle-Levy et al. in press, Papers I, II, VI). Moreover, indications that benthic organisms can derive energy directly from ice algae have been observed (Hobson et al. 1995, McMahon et al. 2006, Papers V, VI). However, while SOD correlated with increased ice-algal production (**Paper V**), it was unclear how sedimentary pigments were reflecting this episodic input of ice algae to the sediment of the Beaufort Sea, and this will be discussed in section 7.4.

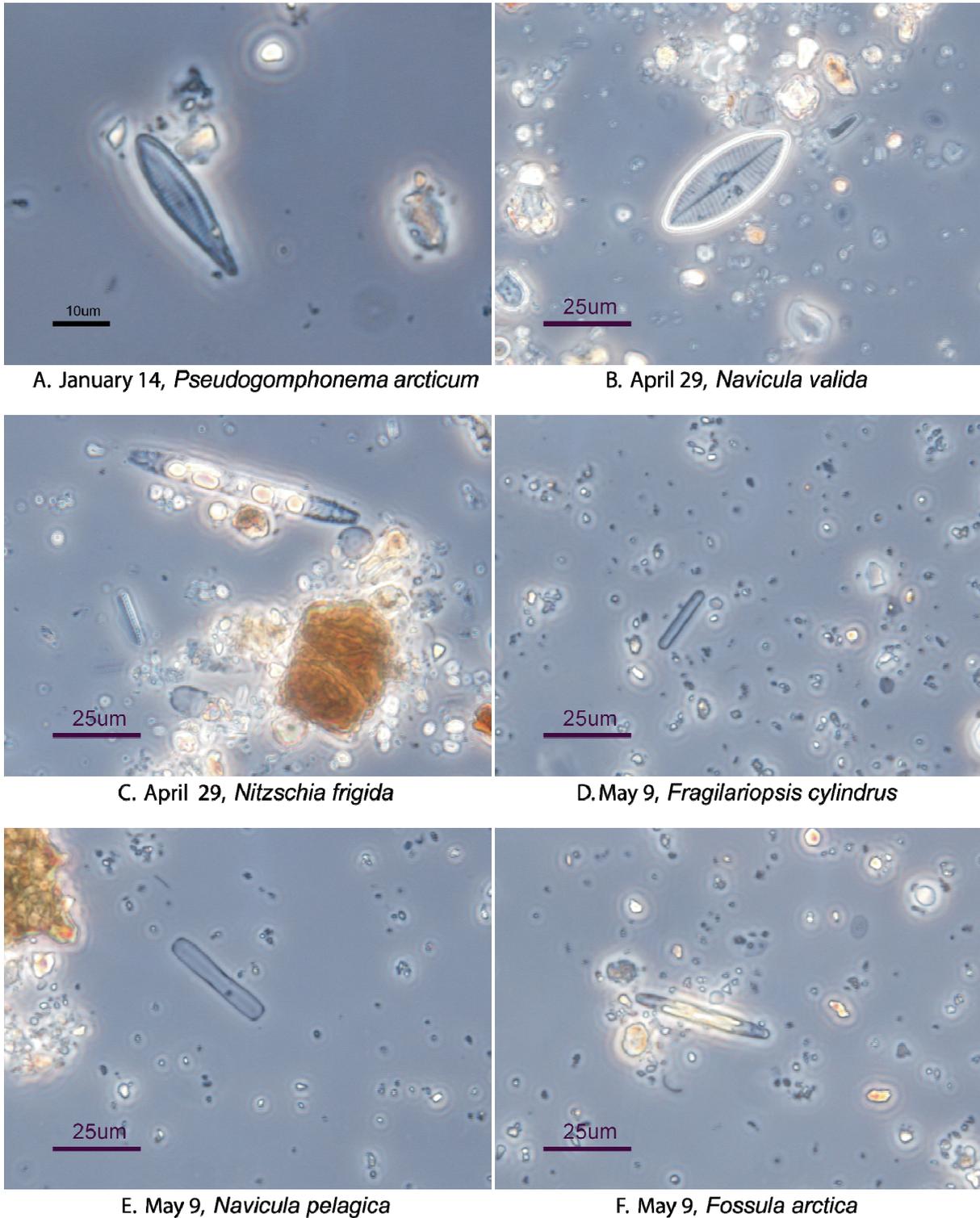


Figure 8. Photography of ice-algae frustules found in the sediment of Franklin Bay during CASES overwintering.

The importance of diatoms in the ice-associated algal community was noted earlier. They are also major producers throughout the Arctic (Hill 2005), and were found to dominate in the summer on the Mackenzie shelf (**Paper II**), and associated with sea ice in the Barents Sea (**Paper I**). The significance of diatoms during the summer was indicated by the high

levels of fucoxanthin in the Beaufort Sea (**Paper II**), Barents Sea (**Paper I**), and in the Bering/Chukchi Sea (Pirtle-Levy et al. in press). It was interesting, however, to find that in the summer, other phytoplankton species were important in the Amundsen Gulf area and the Beaufort Sea (**Paper II**). As discussed earlier, the different phytoplankton taxonomy in the Barents Sea can be largely attributed to the influence of variations in the dominant water-mass. Atlantic waters contain more prymnesiophytes (Wassmann et al. 2005), whereas Arctic waters contain more green algae (Not et al. 2005). In the Cape Bathurst polynya (Figure 2b), early melting of ice probably leads to an earlier growing season as in other polynyas (Smith et al. 1997). Thus, in the summer, although the surrounding areas are at their peak of production with diatoms as dominant group, the Cape Bathurst polynya is already in post-bloom condition, with smaller cells.

In the fall, small algal cells seem to predominate algal population in Arctic waters. Traditionally, Arctic marine production has been thought to be dominated by large phytoplankton (von Quillfeldt 1997). However, recent studies have shown that picophytoplankton can be abundant in late summer/fall (Not et al. 2005, Lovejoy et al. 2006). Indeed, haptophytes and prasinophytes were dominant in the water column of the Beaufort Sea (**Paper II**). This was also found in the accessory pigment composition in the sediment. Interestingly, and contrary to previous thoughts, small cells seem to sink relatively fast (Richardson & Jackson 2007, **Paper II**), and might be a significant late-season source of food for the benthos.

7.3 Grazing and bacterial degradation

The match or mismatch of high zooplankton biomass with phytoplankton blooms determines the fate of the produced organic carbon, which can be either retained in the water column or exported to the bottom (Wassmann 1991, Wassmann et al. 1996). Thus grazing by zooplankton can have a strong impact on pelagic-benthic coupling by shaping the magnitude and composition of the vertical particle flux (Olli et al. 2002, Wexels Riser et al. in press). Large copepods of the genus *Calanus* are important grazers on phytoplankton in all Arctic seas. Grazing by macro- and meso- zooplankton has been found to degrade chl *a* to phaeophorbide *a*, so sedimentary phaeophorbide *a* was used in the present study to estimate abundance of zooplankton-degraded organic matter. In the Barents Sea sediment, phaeophorbide *a* was the most abundant phaeopigment (**Paper I**), and input of grazed material was the highest in the summer. The stations where fecal pellets represented the highest proportion of carbon flux (Wexels Riser et al. in press) also had the highest

sedimentary phaeophorbide *a* content. Moreover, the presence of CCE, a combination of phaeophorbide and fucoxanthin, suggested the importance of grazing on diatoms, and perhaps on ice-associated diatoms. In the spring, material reaching the benthos had higher chl *a*/phaeo ratio, and thus a higher nutritional quality (**Paper I**). SOD was also higher (**Paper III**), suggesting that the mismatch of zooplankton and phytoplankton in the spring allows inputs of higher quality organic matter to the sea floor, where the benthos responds by increasing activity.

In the Beaufort Sea, higher macrozooplankton grazing in the summer (Forest et al. 2007) also resulted in higher sedimentary phaeophorbide *a* (**Paper II**). In the fall, however, grazing activity by macro- and meso- zooplankton was lower and fecal pellets were mainly from microzooplankton (Forest et al. 2006). Indeed, the sedimentary phaeopigment composition switched from a clear phaeophorbide *a* signal to a less clear phaeopigment composition. In the spring, phaeophorbide *a* increased from January to April. However, grazing in the water column did not seem to be responsible for this increase, instead, the increase in phaeophorbide *a* was attributed to increased of benthic macrofaunal activity (**Paper VI**).

Although inputs of grazing-degraded organic matter to the sea floor can be estimated by the identification of phaeophorbide *a*, microbial degradation is much harder to estimate using pigment composition. No specific marker of microbial degradation was identified in the present study. Phaeophytin is created during herbivory (grazing), microbial degradation and cell senescence (see section 5.2), and thus microbial degradation was mainly implied when no proof of grazing was found. In the Amundsen Gulf, the importance of sedimentary phaeophytin *a* relative to other phaeopigments was observed (**Paper II**), suggesting that less grazing by macro- and meso- zooplankton occurred and therefore relatively more microbial degradation.

7.4 Benthic communities

SOD has been used as an estimate of carbon going through the whole benthic community (Table 4), while minivial incubations and bottom photography allowed partitioning of carbon degradation between epifauna, macrofauna, and microfauna/bacteria to be assessed (Table 5). The relationship between the whole benthic community activity and the environmental and biological factors has been discussed in the previous sections. Depth and downward carbon fluxes seemed to be the most important factors in determining SOD. Moreover, sedimentary chl *a* concentrations correlated strongly with SOD (**Papers I, II, III**

and IV), and availability of high quality food (i.e., higher chl *a* content and chl *a*/phaeo ratio) has been found to correlate with SOD also on other Arctic shelves (Grant et al. 2002, Clough et al. 2005, Dunton et al. 2005). As a further indicator of the robustness of the positive correlation between chl *a* and SOD, sedimentary chl *a* has been accepted for use in models as a predictor of SOD in steady state systems (Sun et al. 1991).

However, as episodic organic matter inputs to the benthos occur, SOD and chl *a* may not be sufficient to explain the benthic response, necessitating additional parameters. Although SOD increased, the higher inputs of ice algae in the spring did not lead to higher sedimentary chl *a* (**Paper V**). This led us to carry out a further detailed study of sedimentary pigments and diatom frustules (**Paper VI**). From January to May, the phaeophorbide *a* to chl *a* ratio increased at the Franklin Bay overwintering site, as did sediment bioturbation. This suggests that macrobenthos activity was enhanced by fresh detrital inputs, increasing bioturbation. The rapid use of phytodetritus led to a quick degradation of the chl *a* to its grazing degradation products. Compared to temperate areas, Arctic macrobenthos have been found to have an enhanced role in benthic carbon cycling relative to meio- and micro- fauna (Piepenburg et al. 1995, Rowe et al. 1997, Clough et al. 2005, Grebmeier et al. 2006). In the Beaufort Sea, microbial oxygen demand varied from 25-90% (average 60%). In the Barents Sea, when comparing total SOD (from **Paper III**) with microbial oxygen demand determined by Vandieken et al. (2006), it appeared that 38-62% (average 52%) of the total SOD was due to microbial activity. Although the minivial incubation technique is thought to overestimate oxygen consumption, in both studies, macro- and micro- fauna seemed to have similar contributions to oxygen demand. However, as suggested in other Arctic studies, these macrofauna oxygen-demands appear to remain higher than in studies of non-polar ecosystems (Boucher & Clavier 1990, Mahaut et al. 1995, Heip et al. 2001).

In some Arctic areas, epifauna can reach very high abundances and ophiuroids are among the most abundant megafauna on Arctic continental shelves (Piepenburg 2000). The results in the Beaufort Sea confirmed this tendency, where ophiuroids were abundant in the shallow shelf area and contributed an important part, up to 41%, of the SOD (**Paper IV**). The importance of ophiuroids in the Arctic Ocean is due to flexibility of their feeding mode (Piepenburg 2000) and considerable mobility, allowing a rapid response to episodic food pulses (Smith 1986), which are common in the Arctic.

Different groups of the sediment community respond in different ways and on different time scales to the deposition of phytodetritus (Pfannkuche et al. 2000). Some previous studies have found a time lag between the pulse of organic matter to the seafloor and

the benthic response. In contrast, the present study shows that the benthos can quickly respond to these inputs. Benthic macrofauna seems to be particularly efficient in degrading carbon. This has also been previously suggested by Witte et al. (2003). Consequently, the benthic faunal composition (epi-, macro-, or micro- fauna) can determine the fate of organic matter reaching the sea floor.

Table 3. Summary of sedimentary pigments in the Arctic. Chl *a*: Chlorophyll *a*; CPE: ChloroPlastic Equivalent (Chlorophyll *a* + Phaeopigments); Chl *a*/Phaeo: ratio chlorophyll *a* to total phaeopigments. Note that the units used and the sediment depth differs in the various studies, and are indicated in the columns “Units” and “Sediment depth (cm)” respectively.

Location	Date	Water depth (m)	Chl <i>a</i>	CPE	Units	Chl <i>a</i> Phaeo	Sediment Depth (cm)	Study
Western Barents Sea	May	206-340	0.3-30	2-90	mg m ⁻²	0.2-0.4	1	Paper I
	Jul-Aug	195-503	0.2-1	5-13	mg m ⁻²	0.03-0.2	1	
	Jul-Aug	226-405	1-4	7-23	mg m ⁻²	0.16-0.2	5	
Northern Barents Sea (Svalbard Shelf)	Jul-Aug	854-3920	<1-1	1-7	mg m ⁻²	0.16	5	Pfannkuche & Thiel (1987)
	Jul	1400		66-102	mg m ⁻²	0.07-0.1	10	
Mackenzie shelf	Jul-Aug	32-82	1-14	13-37	mg m ⁻²	0.09-0.7	1	Paper II
	Oct-Nov	45-86	0.8-3.5	15-27	mg m ⁻²	0.06-0.3	1	
Southeastern Beaufort Sea	Jul-Aug	180-440	0.2-3.7	5-22	mg m ⁻²	0.03-0.2	1	Paper II
	Oct-Nov	395-420	0.06-0.7	5-11	mg m ⁻²	0.06-0.07	1	
Laptev Sea (Eurasian Arctic)	Aug-Sep	50	45	100	mg m ⁻²	0.8	1	Boetius & Damm (1998)
	Sep-Oct	37-107	<2	10-40	mg m ⁻²	0.05-0.1	1	
	Jul-Aug	213-3427		2-13	µg cm ⁻³		1	Grahl et al. (1995)
	Jul-Aug	39-140		0.6-3	µg cm ⁻³		1	
Bering/Chukchi Sea	May-Jun	34-170	1-19		µg cm ⁻³		1	Cooper et al. (2005)
	July Aug	202-523	2-15		mg m ⁻²		1	
	Jul-Aug	46-185	9-31		mg m ⁻²		1	
Chukchi Sea	Jul-Aug	189-478	2-37		mg m ⁻²		1	Clough et al. (2005)
	Jul	40-600	0.07-2.8	1-26	µg cm ⁻³	0.03-0.3	1	
Western Arctic	Jul-Aug	540-3648	0-0.01	0.03-0.3	µg cm ⁻³	0-0.07	1	Clough et al. (2005)*

Fram Strait	Jul-Aug	750-3020	0.03-0.9	2-6	$\mu\text{g cm}^{-3}$	0.01-0.2	1	Schewe & Soltwedel (2003)
Ellesmere Island- W Greenland (NOW)	Apr-May	247-680	0-2	4-30	mg m^{-2}	0-0.07	1	Grant et al. (2002)
	Jul		<1-5	11-42	mg m^{-2}	0.01-0.1	1	
NE Greenland (NEW)	Jul-Aug	150-515		9-46	mg m^{-2}		1	Ambrose & Renaud (1995)
	May-Aug	290-340	<1-3	12-44	mg m^{-2}	0.07-0.1	1	Ambrose & Renaud (1997)
	Sept	183-774		6-33	mg m^{-2}		1	Brandt & Schnack (1999)
		1098-1965		3-7	mg m^{-2}		1	
Central Arctic Ocean	Jul-Aug	68	<1	7	mg m^{-2}	<0.16	2	Clough et al. (1997)
		540-4190	0	<1	mg m^{-2}		2	
	Aug-Sep	1055-4180		1-12	mg m^{-2}		1	Soltwedel & Schewe (1998)

* Barrow Canyon station not included due to its extremely high pigment content

Table 4. Summary of SOD values determined in the Arctic (modified from Clough et al. 2005).

Location	Water depth (m)	SOD mmol O ₂ m ⁻² day ⁻¹	Study
Barents Sea	195-503	2.3-10.4	Paper III Piepenburg et al. (1995)
	80-1000	1.6-2.8	
Eastern Svalbard	226-320	3.2-11.9	Pfannkuche & Thiel (1987) Hulth et al. (1994)
	170-240	3.9-11.2	
Mackenzie shelf	42-82	3.2-9.4	Paper IV
Southeastern Beaufort Sea	167-420	2-6.5	Paper IV Paper V (over winter-spring)
	234	4.9-20.2	
Laptev Sea continental slope	200-1000	0.5-7.8	Boetius & Damm (1998)
Eastern Chukchi Sea	40-600	0.7-13.2	Clough et al. (2005)
Bering Shelf-Anadyr Water	49-68	10.3-20.7	Clough et al. (2005)
Northern Bering-Chukchi Seas			
Alaskan Coastal Water	20-55	0.6-19.4 (mean 8.7)	Grebmeier & McRoy (1989)
Bering Shelf-Anadyr Water	20-55	1.8-45.6 (mean 19.2)	Grebmeier & McRoy (1989)
Northern Bering-Chukchi Seas	11-48	7.4-18	Devol et al. (1997)
Western Arctic Ocean	540-3648	0.3-1.4	Clough et al. (2005)
Young Sound, Greenland	36	5-13 (over year)	Rygsgaard et al. (1998) Glud et al. (2000)
	20-163	4-20	
Northeast Greenland Shelf	250-350	1.4-2.6	Rowe et al. (1997)
Resolute Bay, Canadian Arctic	16	2-18 (over year)	Welch et al. (1997)
Baffin Bay	300-680	1.7-4.1	Grant et al. (2002)

Table 5. Summary of oxygen-demand partitioning between macro- and epi- fauna in the Arctic (modified from **Paper IV**).

Location	Depth (m)	Macrofauna (%)	Epifauna (%)	Study
Barents Sea	198-503	38-62 (avg 47)*		Paper III , Vandieken (2006) Piepenburg et al. (1995)
	<200	14-75 (avg 17)	20-94 (avg 21)	
	>200	5-75 (avg 21)	2-4 (avg 3)	
Beaufort Sea	38-440	33-50	0.1-41	Paper IV
Chukchi Sea	30-280	Up to 61		Grebmeier & McRoy (1989) Ambrose et al. (2001)
	29-213		0-26	
Young Sound	<40		17.5	Rysgaard & Nielsen (2006)
	>40		26	
NOW	250-570	0-70 (spring) 70-80 (summer)		Grant et al. (2002)

8. Concluding remarks

The study of sedimentary pigments by HPLC confirmed Hypothesis 1 showing quantitative and qualitative changes in algal sources of organic matter and in organic matter fluxes, and thus allowed the identification of different variables affecting the pelagic-benthic coupling in the Arctic. Changes in primary production were accompanied by changes in abundance of chl *a* and accessory pigments; changes in food web structure were indicated by changes in abundance of phaeopigments (i.e. phaeophorbide due to grazing); changes in environmental factors (depth and riverine influence) were reflected in changes in the chl *a*/phaeo ratio and abundance of chl *b* degradation products.

Pigment analysis also helped confirm Hypothesis 2, indicating that SOD was strongly dependent on inputs of organic matter from overlying waters. Moreover the combination of sedimentary pigments with SOD and other biomarkers, such as stable isotopes and diatom frustules, allowed a better assessment of the pelagic-benthic coupling.

As suggested by Hypothesis 3, the present study highlighted some spatial and seasonal changes in the pelagic-benthic coupling of the Barents and Beaufort Seas (Table 6), emphasizing the important contrast between the two ecosystems (primary production, secondary production, and hydrography). In the Barents Sea, spatial changes were highly influenced by currents (**Paper I**) while in the Beaufort Sea, spatial changes were due to water depth and river influence (**Papers II and IV**). Physical factors seemed to be responsible for spatial variability.

From a seasonal point of view, productivity regime, especially ice-algal production and match/mismatch of grazing with primary production, seemed to impact the organic matter inputs to the benthos. In the spring, ice-algal production largely influenced organic matter inputs to the benthos in both the Barents and Beaufort Seas (**Papers I, V and VI**). In the summer, grazing was responsible for inputs of degraded material in both ecosystems (**Papers I and II**). In addition to biological factors, environmental factors were also important in summer and/or fall. In the Barents Sea, during the summer, the different currents lead to phytoplankton taxonomy variations (**Paper I**), and in the Beaufort Sea, during the fall, riverine inputs were found to be responsible for the presence of allochthonous material in the sediment.

Table 6. Summary of the environmental and biological factors shaping the pelagic-benthic coupling in the Beaufort and Barents Seas.

	Beaufort Sea	Barents Sea
Ice algae	spring and summer	spring and summer
Phytoplankton	seasonal variation	spatial variation in summer
Grazing	summer	summer
River input	√	
Current		√
Water depth	√	
	marine (gulf)	
Benthic activities	terrestrial (shelf)	overlying productivity

Both environmental and biological factors were found to affect seasonal and spatial variations in pelagic-benthic coupling. Physical variables such as water depth, riverine inputs and dominant water mass, seemed to impact spatial variations, while biological factors such as primary production, grazing, and composition of benthic communities, seemed to mainly impact seasonal variations.

Global warming is expected to directly or indirectly affect each factor shaping the Arctic pelagic-benthic coupling, and thus will most likely lead to large changes in organic matter cycling on Arctic shelves.

9. Overall significance and perspectives

This is the first time sedimentary pigments have been studied by HPLC technique in the Arctic, allowing identification and quantification of various pigments and degradation products in the Barents and Beaufort Seas. This provided the opportunity to assess multiple factors (spatial, temporal, biotic, abiotic) simultaneously affecting POM inputs to the sea floor. Biotic and abiotic factors shaping pelagic-benthic coupling have usually been addressed individually (i.e. study of macrozooplankton grazing, study of primary production, study of currents). The new approach used in this work is unique in the sense that it increased the knowledge of pelagic-benthic coupling the Barents and Beaufort Seas by including many components of the ecosystem, environmental factors and biological parameters.

However, although this method allowed the relative comparison of factors such as input from the river or grazing, it was not possible to quantify the effects of each factor on the quality and quantity of POM inputs to the sediment. As outlined below, some improvements in this approach could allow creating POM-fluxes models using only concentration and composition of sedimentary pigments.

Firstly, in order to use pigments as markers of particulate organic carbon (POC) flux to sediment, it is important to know the ratio between photosynthetic pigments and POC. Measuring this ratio under different conditions would allow determination of quantitative relationships between pigment and POC fluxes.

Secondly, a better understanding of pigment degradation in both the water column and the sediment would make it possible to estimate the relative contribution of the different secondary producers to pigment degradation. Compounds derived from a specific degradation process could be studied in laboratory experiments where one single process occurs (i.e. zooplankton grazing, benthos grazing, bacterial degradation in the water column and in the sediment, photooxidation). However the evaluation of the results from such an experiment is complicated since some pigments are degraded to colorless compounds and some pigments have multiple degradation products. The degradation products could be identified by nuclear magnetic resonance spectroscopy (NMR), which identifies functional groups, or by HPLC coupled with a mass spectrometer (HPLC-MS), which gives the composition of the compound by measuring the mass-to-charge ratio of ions.

Third, in order to differentiate phytoplankton diatoms from ice-associated diatoms, it would be necessary to use another marker, such as lipid composition. Although the pigment composition itself (i.e. fucoxanthin) is not different between phytoplankton diatoms and ice-

associated diatoms, the degradation products may be different. For example, ice-algal diatoms are closer to the water surface and thus their pigments may be more photodegraded. The degradation products of fucoxanthin could differ between ice algal and phytoplankton diatoms and could be identified, as mentioned previously, either by NMR or HPLC-MS.

Finally, in order to assess the quality of POM derived from ice algae reaching the seafloor and understand if the quality of ice algae is higher than phytoplankton, the degradation products of fucoxanthin could be used. This could actually explain the tighter coupling of the benthic response in the ice covered scenario of Carroll and Carroll (2003).

10. References

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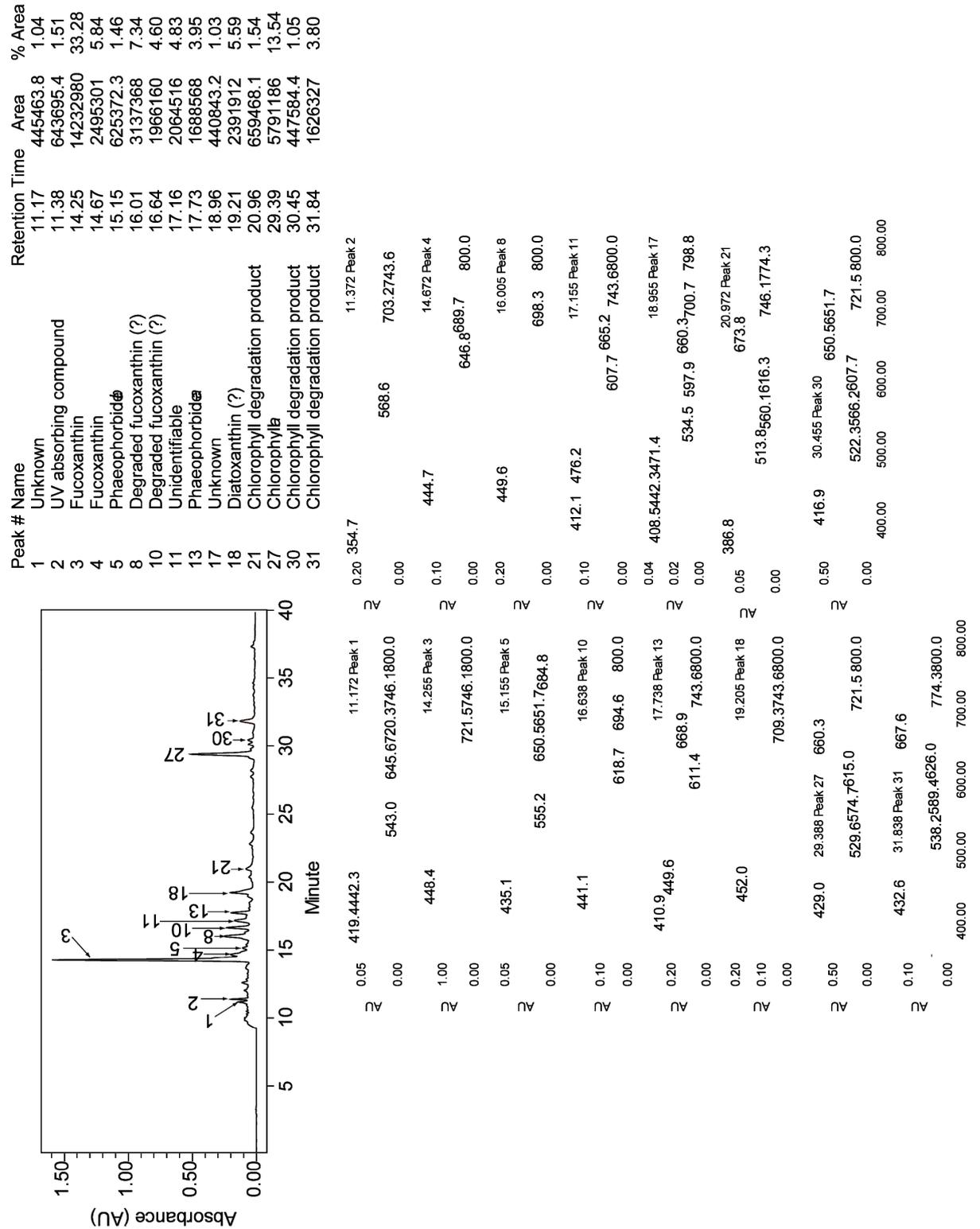
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Appendices 7-9

Appendix 7a: Chromatogram and PDA absorbance: CASES summer 2004, station 718, sediment depth 1-2 cm.

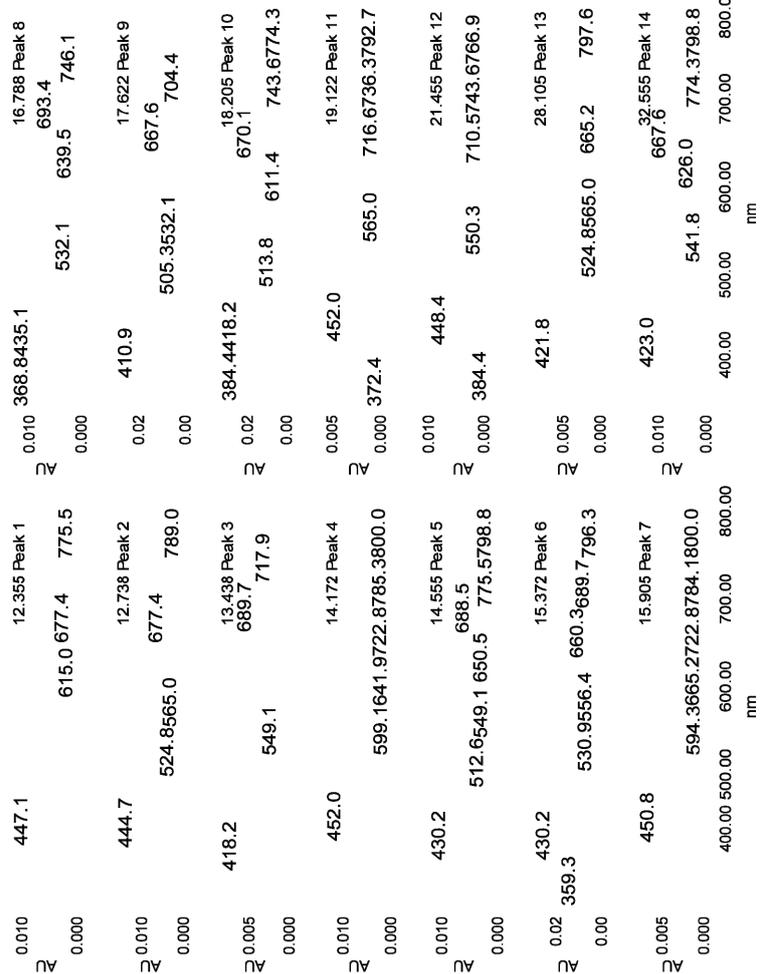
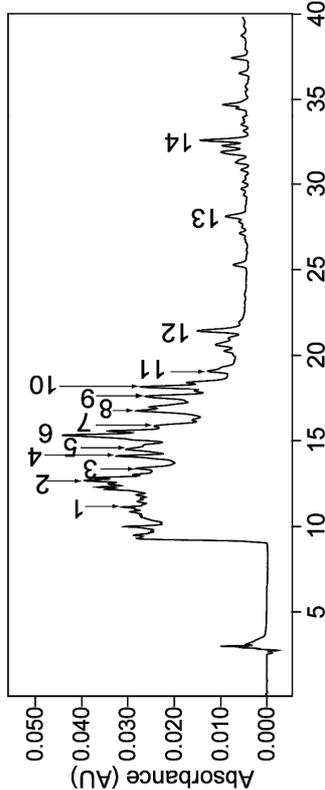
Note that peaks of area >1% are identified in the PDA chromatogram by numbers. Their PDA spectrums at 438 nm are presented below the chromatogram, and their identification and area is presented in the table on the right of the chromatogram.



Appendix 7b: Chromatogram and PDA absorbance: CASES fall 2003, station 100, sediment depth 0-1 cm.

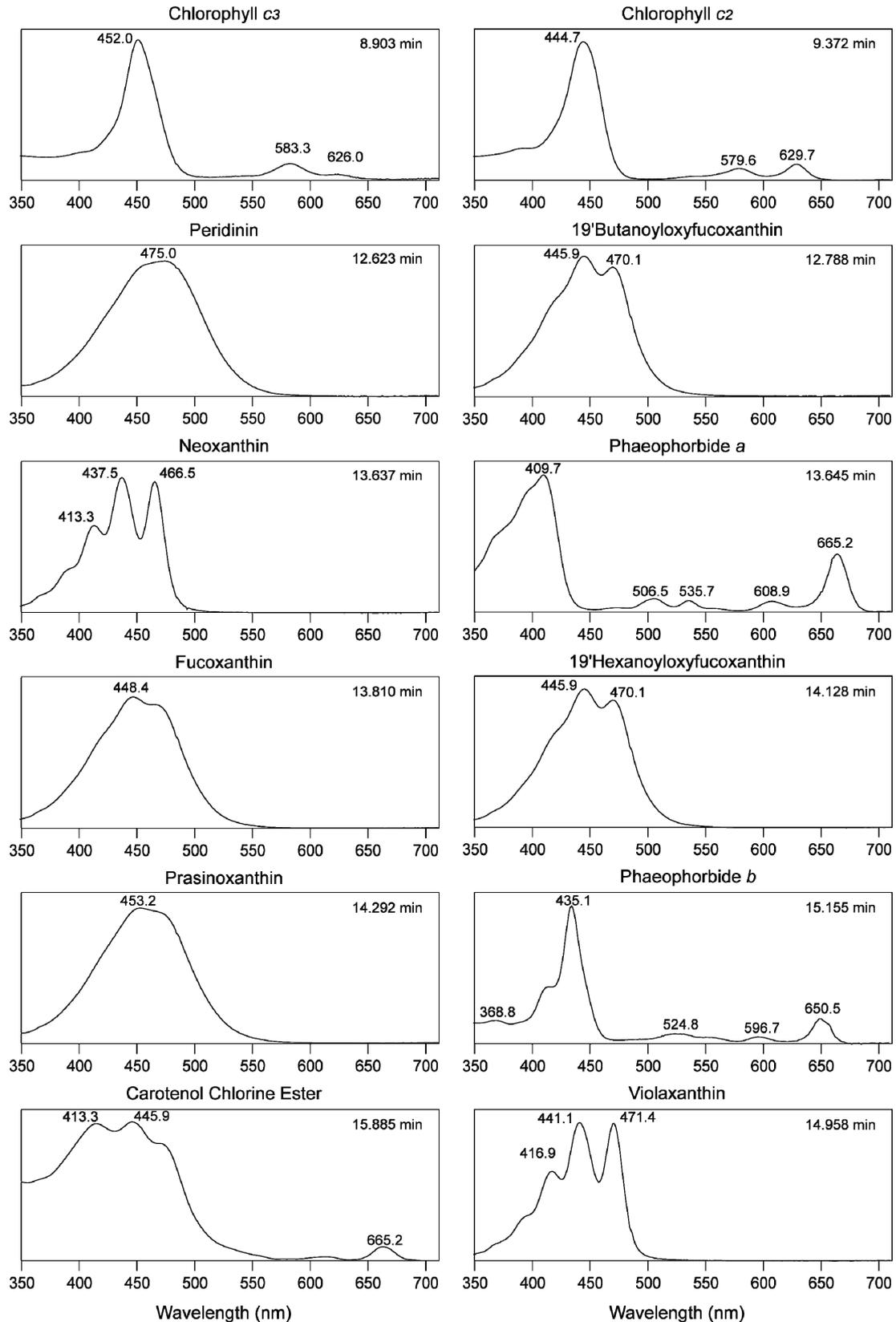
Peaks are identified in the PDA chromatogram by numbers. Their PDA spectrums at 438 nm are presented below the chromatogram, and their identification and area is presented in the table on the right of the chromatogram.

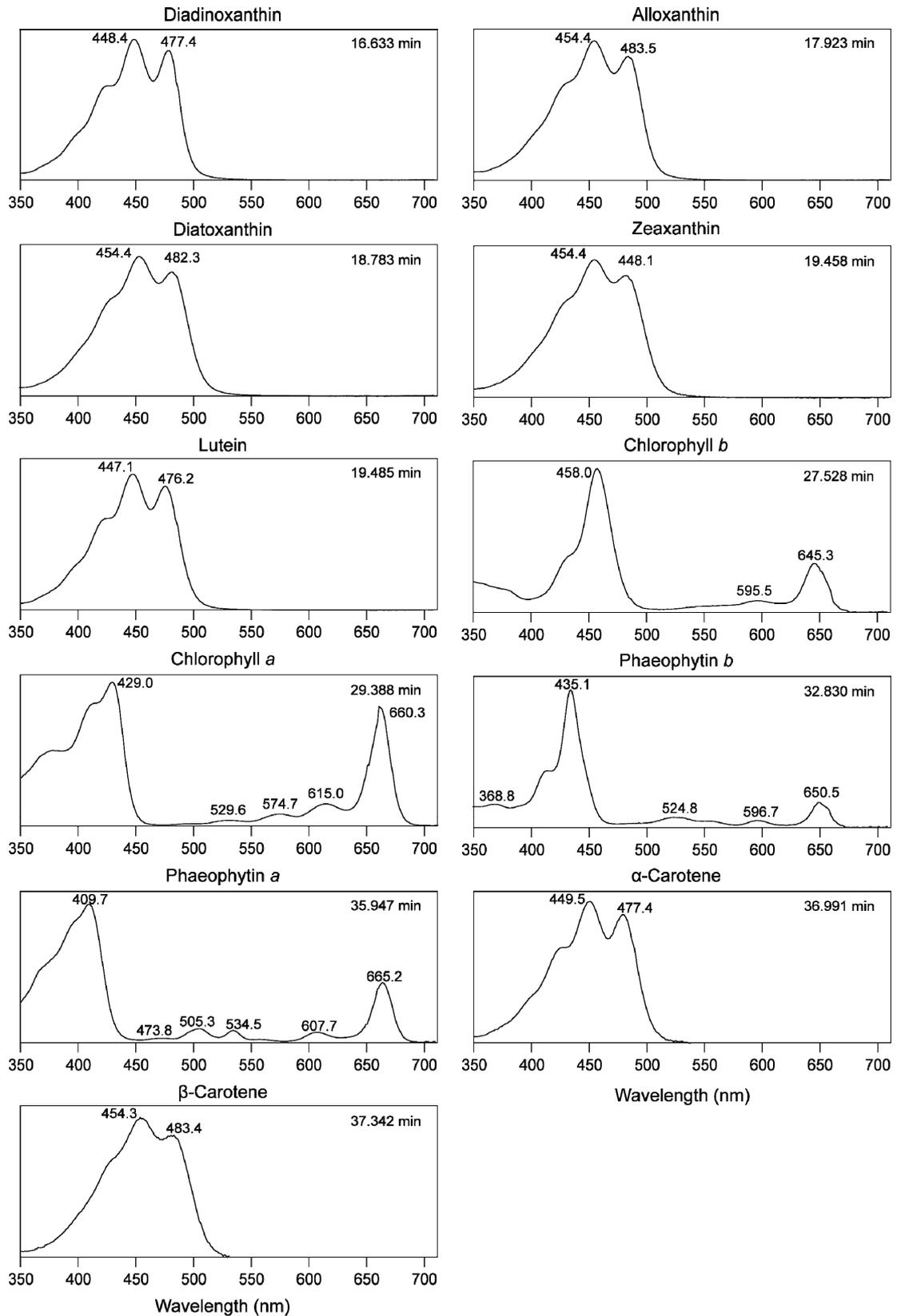
Peak #	Name	Retention Time	Area	% Area
1	Unknown	12.36	140358.1	4.50
2	Unknown (c2?)	12.73	323384.9	10.36
3	Unknown	13.44	114872.6	3.68
4	Prasinocanthin	14.16	138417.7	4.44
5	Chlorophyll degradation product	14.55	280173.5	8.98
6	Chlorophyll degradation product	15.36	637110.3	20.42
7	Unk. (Prasinocanthin allomere?)	15.90	90965.91	2.92
8	Chlorophyll degradation product	16.79	354977.8	11.38
9	Phaseophorbide a	17.62	227539.5	7.29
10	Unknown	18.20	329047.7	10.54
11	Unk. carotenoid (Diatocanthin?)	19.12	72104.43	2.31
12	Unk. carotenoid	21.46	115001.8	3.69
13	Chlorophyll degradation product	28.11	41763.67	1.34
14	Chlorophyll degradation product	32.55	254716.5	8.16



Appendix 8: Absorption spectrum of pigments studied.

Spectrums identified on the PDA (438 nm) from single runs of standards (DHI, Denmark), with the exception of phaeophytin *b* (standard prepared in the lab by acidification of chlorophyll *b*) and phaeophorbide *b* and CCE (only identified in samples, and quantified with RF of similar pigment).





Appendix 9: Comparison of absorption spectrum between standard and sample for selected pigments

