

The carbohydrates of *Phaeocystis* and their degradation in the microbial food web

Anne-Carlijn Alderkamp · Anita G. J. Buma ·
Marion van Rijssel

Received: 18 November 2005 / Accepted: 23 March 2006 / Published online: 19 April 2007
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Abstract The ubiquity and high productivity associated with blooms of colonial *Phaeocystis* makes it an important contributor to the global carbon cycle. During blooms organic matter that is rich in carbohydrates is produced. We distinguish five different pools of carbohydrates produced by *Phaeocystis*. Like all plants and algal cells, both solitary and colonial cells produce (1) structural carbohydrates, (hetero) polysaccharides that are mainly part of the cell wall, (2) mono- and oligosaccharides, which are present as intermediates in the synthesis and catabolism of cell components, and (3) intracellular storage glucan. Colonial cells of *Phaeocystis* excrete (4) mucopolysaccharides, heteropolysaccharides that are the main constituent of the mucous colony matrix and (5) dissolved organic matter (DOM) rich in carbohydrates, which is mainly excreted by colonial cells. In this review the characteristics of these pools are discussed and quantitative data are summarized. During the exponential growth

phase, the ratio of carbohydrate-carbon (C) to particulate organic carbon (POC) is approximately 0.1. When nutrients are limited, *Phaeocystis* blooms reach a stationary growth phase, during which excess energy is stored as carbohydrates. This so-called overflow metabolism increases the ratio of carbohydrate-C to POC to 0.4–0.6 during the stationary phase, leading to an increase in the C/N and C/P ratios of *Phaeocystis* organic matter. Overflow metabolism can be channeled towards both glucan and mucopolysaccharides. Summarizing the available data reveals that during the stationary phase of a bloom glucan contributes 0–51% to POC, whereas mucopolysaccharides contribute 5–60%. At the end of a bloom, lysis of *Phaeocystis* cells and deterioration of colonies leads to a massive release of DOM rich in glucan and mucopolysaccharides. Laboratory studies have revealed that this organic matter is potentially readily degradable by heterotrophic bacteria. However, observations in the field of accumulation of DOM and foam indicate that microbial degradation is hampered. The high C/N and C/P ratios of *Phaeocystis* organic matter may lead to nutrient limitation of microbial degradation, thereby prolonging degradation times. Over time polysaccharides tend to self-assemble into hydrogels. This may have a profound effect on carbon cycling, since hydrogels provide a vehicle to move DOM up the size spectrum to sizes subject to sedimentation. In

A.-C. Alderkamp · A. G. J. Buma · M. van Rijssel
Department of Marine Biology, Centre for Ecological
and Evolutionary Studies, University of Groningen,
P.O. Box 14, 9750 AA Haren, The Netherlands

Present Address:

A.-C. Alderkamp (✉)
Department of Geophysics, Stanford University,
Stanford, CA 94305-2215, USA
e-mail: alderkam@stanford.edu

addition, it changes the physical nature and microscale structure of the organic matter encountered by bacteria which may affect the degradation potential of the *Phaeocystis* organic matter.

Keywords Carbohydrates · Glucan · Hydrogels · Mucilage · *Phaeocystis* · TEP

Introduction

Phaeocystis (Prymnesiophyceae) is a marine phytoplankton genus with a worldwide distribution. It is present from tropical to polar regions and can form blooms in areas with high nutrient concentrations, such as coastal or upwelling regions (Baumann et al. 1994; Lancelot et al. 1998; Schoemann et al. 2005). One of the characteristics of *Phaeocystis* species is the complex polymorphic life cycle. It consists of different stages of free-living cells 3–9 μm in diameter, alternating with colonial stages usually reaching several mm in diameter (Kornmann 1955; Rousseau et al. 1994; Peperzak et al. 2000), sometimes up to 3 cm (Chen et al. 2002). Although free-living *Phaeocystis* cells are ubiquitous in the world's oceans, it is the colonial form that has attracted most attention due to its massive blooms (Lancelot et al. 1987; Schoemann et al. 2005). At present six *Phaeocystis* species have been described (Zingone et al. 1999) of which only three are reported to form blooms; *P. globosa* in temperate regions (English Channel, coastal North Sea, China), *P. pouchetii* in temperate to polar waters of the Northern hemisphere, and *P. antarctica* in (sub)polar waters of the southern hemisphere (Schoemann et al. 2005). During blooms *Phaeocystis* may contribute over 90% to the total phytoplankton abundance and can be responsible for up to 65% of the local annual primary production (Joiris et al. 1982; Veldhuis et al. 1986b; Lancelot and Mathot 1987; Arrigo et al. 1999). The high productivity associated with blooms and its ubiquity make *Phaeocystis* an important contributor to the global carbon cycle (Smith et al. 1991; Arrigo et al. 1999; DiTullio et al. 2000; Schoemann et al. 2005). A significant part of the *Phaeocystis* carbon consists of

carbohydrates (Lancelot and Mathot 1987; Rousseau et al. 1990; Fernández et al. 1992; Mathot et al. 2000). This vast carbohydrate injection following *Phaeocystis* blooms has a significant impact on the carbon cycling in the ecosystem and the microbial food web. Carbohydrates are omnipresent in the marine ecosystem, as they are an important constituent of marine DOM (Benner et al. 1992) and particles and therefore play a key role in the marine carbon cycle. Carbohydrates display a remarkable structural diversity as a consequence of the wide variety in aldoses and the different glycosidic bonds between them. These differences in structure and size influence the behavior of polysaccharides in aqueous solution, i.e., solubility and aggregate formation, as well as microbial degradation potential. To understand the impact of the carbohydrate injection after a *Phaeocystis* bloom on the carbon cycling in the ecosystem, it is important to consider the different types of carbohydrates that are produced. In the following sections we will first discuss the current state of knowledge with respect to the characteristics and quantities of different pools of carbohydrates produced during the various life cycle stages. Secondly, mechanisms of DOM release during and following a bloom will be discussed, and finally, the fate of carbohydrates in the microbial food web.

Phaeocystis carbohydrates and their characteristics

Carbohydrates in algae and plants are often classified based on methodological discrimination. The structural carbohydrates are not water-soluble, whereas the other types of carbohydrates are water-soluble and typically extracted by hot water. In *Phaeocystis* five different pools of carbohydrates can be distinguished. Like all algal and plant cells, both solitary and colonial cells produce (1) structural carbohydrates, polysaccharides that are mainly part of the cell wall, (2) mono- and oligosaccharides, which are present as intermediates in the synthesis and catabolism of cell components, and (3) intracellular storage glucan. Colonial cells of *Phaeocystis* excrete (4) mucopolysaccharides, heteropolysaccharides that

are the main constituent of the mucous colony matrix and (5) dissolved organic matter (DOM) rich in carbohydrates, which is excreted mainly by colonial cells. A schematic on the procedure to extract the different types of particulate carbohydrates is depicted in Fig. 1.

Structural polysaccharides

In most algae and plants, structural carbohydrates are water-insoluble polysaccharides that are mainly present as cell wall constituents. Although *Phaeocystis* cells do not have a prominent cell wall, flagellate *Phaeocystis* cells are covered with body scales consisting of flat plates with a pattern of radiating ridges (Parke et al. 1971; Moestrup 1979; Hallegraeff 1983; Baumann et al. 1994). In two other haptophytes, *Pleurochrysis scherfelii* and *Chrysochromulina chiton*, the scales contain acidic, sulfated pectin-like polysaccharides,

cellulose and glycopeptides (reviewed by Leadbeater 1994). Likely, *Phaeocystis* scales contain similar polysaccharides.

In addition to cellular structural carbohydrates, flagellate cells of *Phaeocystis* excrete filaments composed of α -chitin, an *N*-acetyl-D-glucosamine polymer, forming star-like structures. In electron microscopic studies, five-rayed filamentous stars were observed around flagellate cells of *P. pouchetii*, *P. antarctica*, *P. globosa*, and *P. cordata*, whereas nine-rayed stars were observed around *P. scrobiculata* (Parke et al. 1971; Moestrup 1979; Baumann et al. 1994; Chretiennot-Dinet et al. 1997; Zingone et al. 1999). The biological function of the chitin filaments remains a mystery up to now (Chretiennot-Dinet et al. 1997).

The only quantitative data available on the contribution of structural carbohydrates to *Phaeocystis* biomass are from a culture of *Phaeocystis* sp. in the stationary phase, where structural

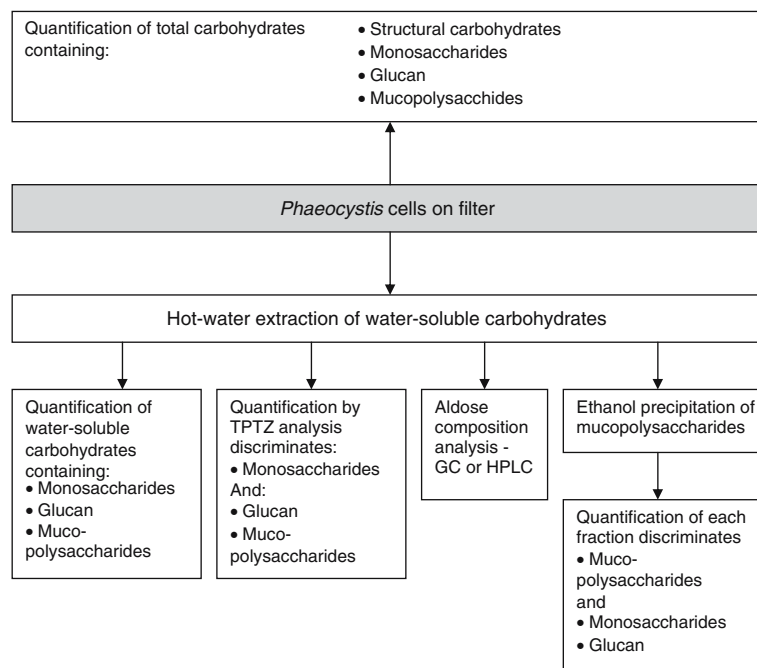


Fig. 1 Schematic representation of procedures to obtain different types of particulate carbohydrates from *Phaeocystis* cells concentrated on a filter. Total carbohydrates can directly be quantified colorimetrically. Water-soluble carbohydrates are typically extracted in hot water. They can be quantified colorimetrically. The 2,4,6-tripyridyl-s-triazine (TPTZ)-analysis (Myklestad et al. 1997) discriminates monosaccharides from larger carbohydrates. The

aldose composition of water-soluble carbohydrates can be analyzed by gas chromatography (GC) or anion-exchange high-pressure liquid chromatography (AE-HPLC). Mucopolysaccharides can be separated from glucan and monosaccharides by ethanol precipitation (Alderkamp et al. 2006a), followed by colorimetric quantification of each fraction

carbohydrates made up for 13% of the total organic carbon (TOC) (Biersmith and Benner 1998).

Mono- and oligosaccharides

Monosaccharides are the first products of photosynthesis and form the precursors for biosynthesis of all organic molecules, whereas oligosaccharides are intermediates in polysaccharide synthesis. During catabolism of storage glucan, monosaccharides are formed as intermediates (Granum and Mykkestad 1999). In addition to intermediates in metabolic processes, monosaccharides serve a role in osmoregulation (Craigie 1974; Dickson and Kirst 1987a, b). The monosaccharide concentration in phytoplankton cells is quite stable; for example in diatoms monosaccharide concentration was hardly influenced by light (Vårum et al. 1986; Van Oijen et al. 2003). During the growth phase of a bloom of *P. globosa* in the Marsdiep, The Netherlands, the monosaccharides made up for 28–60% of water-extractable particulate carbohydrates (Alderkamp, unpublished data). This ratio was similar to an Antarctic community dominated by diatoms (Van Oijen et al. 2003).

Storage glucan

The principle food reserve in plants and algae is an intracellular food reserve in the form of a glucan, whereas some energy can be stored in lipids. Storage glucans may be α -1,4-glucans like starch or glycogen, or β -1,3-glucans like laminarin. The actual type of glucan is an important taxonomic characteristic. The class of Prymnesiophyceae contains β -1,3-glucan (Van den Hoek et al. 1993). β -1,3-glucans have an essentially linear β -D-1,3-glucan backbone with some branching at position 6 or 2 (Percival 1970; Craigie 1974; Mykkestad 1978; Paulsen and Mykkestad 1978). They can be classified as laminarin (also spelled laminaran), paramylon, or chrysolaminaran, distinguished mainly on the basis of chain length and presence of mannitol end groups. Laminarin has a degree of polymerization (DP-number of aldoses in the molecule) of approximately 20, contains

mannitol-end groups, and is water-soluble. It is found in brown algae. Paramylon has a DP of more than 50, and does not contain mannitol end-groups or side chains. It is water-insoluble, and is found in euglenophytes (Manners et al. 1966). Chrysolaminaran (also called leucosin) has a DP of 16–38, contains no mannitol end-groups and is water-soluble. It is found in chrysophytes, haptophytes and diatoms (Mykkestad and Haug 1972; Craigie 1974; Paulsen et al. 1978; Mykkestad 1978, 1988). A different glucan structure has been found in the prymnesiophycean *Emiliania huxleyi*, that consists of a β -D-(1,6)-glucan backbone with branching at position 3 (Vårum et al. 1986). *Phaeocystis* cells contain chrysolaminaran as a storage glucan (Janse et al. 1996b). Chrysolaminaran is located in vacuoles, as was observed microscopically in *Phaeocystis* (Kornmann 1955; Parke et al. 1971; Chang 1984) and using immunolocalization of β -1,3-D-glucan in cell sections of the diatoms *Phaeodactylum tricorutum*, *Cylindrotheca fusiformis* and *Thalassiosira pseudonana* (Chiovitti et al. 2004). Due to its presence in ubiquitous bloom-forming phytoplankton chrysolaminaran it is considered to be one of the most abundant types of carbohydrate in the marine environment (Painter 1983).

Chrysolaminaran was characterized as principal storage glucan in a non-colony-forming strain of *P. globosa* that contained mainly non-flagellated cells (Janse et al. 1996b). In this strain, 95% of the water-extractable carbohydrates consisted of glucose and all glucose polymers were digested by the enzyme laminarinase (E.C. 3.2.1.6 from *Trichoderma* sp.). This enzyme preparation contained endo- β -1–3 glucanase activity and some chitinase, cellulase and α -amylase activity. Laminarin from the brown seaweed *Laminaria digitata* was digested to monosaccharides by this enzyme preparation. In colony-forming strains of *P. globosa*, however, no more than 40–70% of glucose polymers were digested (Van Rijssel et al. 2000; Alderkamp et al. 2006a). The reason for this partial digestion may be differences in the type of chrysolaminaran produced by single cells and colonial cells, e.g., with respect to polymer size or number of branches. Therefore, chrysolaminaran from colonial cells may not be fully degraded by the enzyme laminarinase. Alterna-

tively, there may be a different type of glucan produced by colonial *Phaeocystis* cells.

In all plants photosynthetic rates exceed metabolic demands when irradiance is optimal. The excess energy thus harvested is stored mainly as glucan. This glucan can be used as a respiratory substrate to maintain growth when irradiance is suboptimal, for example during the night. Chrysolaminaran is produced in the light and its production is dependent on light intensity. Nocturnal respiration of chrysolaminaran provides energy to maintain cell metabolism and its carbon skeletons can be used for protein synthesis (Cuhel et al. 1984; Lancelot and Mathot 1985; Janse et al. 1996b; Granum et al. 1999; Granum and Mykkestad 2001; Van Oijen et al. 2004b; Alderkamp et al. 2006a). Diel rhythms in storage carbohydrate concentrations have been well documented in laboratory cultures of diatoms (Hitchcock 1980; Vårum et al. 1986; Van Oijen et al. 2004b), field populations of pelagic marine phytoplankton dominated by diatoms (Barlow 1982; Hama and Handa 1992, Van Oijen et al. 2004b) and mesocosms dominated by *P. pouchetii* (Alderkamp et al. 2006a). Notably the diel variations in carbohydrate concentrations are a direct result of the variations in light intensity, but diel carbohydrate dynamics may also be the result of an intrinsic circadian clock (Post et al. 1985; Falkowski and Raven 1997). This was shown by Loogman (1982), who found that the diel dynamics in carbohydrate concentrations introduced by a diel light cycle, continued for several days after the light was switched to a continuous regime.

Under normal bloom conditions, *Phaeocystis* will experience varying light conditions during the day. On top of the diel light cycle, vertical mixing in the water column may mix colonies down to suboptimal light conditions, or even below the euphotic zone (Joint and Pomroy 1993; Arrigo et al. 1999; Wassmann et al. 2000). A capability to utilize stored energy is therefore likely to be important during the day as well as during the night. This may be relevant for *Phaeocystis*, since *P. antarctica* blooms occur in regions with deep wind-mixing (Arrigo et al. 1999), and *P. globosa* blooms often occur in turbid waters with high mixing rates, such as the coastal North Sea and estuaries. During sudden transitions from high to

low light levels, carbohydrates can provide energy until cells are acclimatized to the new situation, as was shown in the diatom *Thalassiosira weissflogii* (Post et al. 1985). This was, however, not confirmed during a mesocosm study of *P. pouchetii*. Carbohydrate concentrations were unaffected by placing cells at low irradiances or in the dark during the day (Alderkamp et al. 2006a).

Upon nutrient limitation excess energy and carbon tend to accumulate as storage glucan, because the Calvin cycle and the tricarboxylic acid (TCA) cycle are uncoupled. Carbohydrate accumulation has been observed during the stationary growth phase of a single cell culture (Janse et al. 1996b), colonial cultures (Van Rijssel et al. 2000), and a bloom of *P. globosa* (Veldhuis et al. 1986a), and at the end of *P. pouchetii* blooms in mesocosms (Alderkamp et al. 2006a). This so-called overflow metabolism under nutrient limitation is common in phytoplankton (Mykkestad 1974, 1988). It leads to an increased contribution of carbohydrates to the organic matter produced during bloom and an increased C/N ratio. Whereas the C/N ratio of exponentially growing free-living *Phaeocystis* cells and colonies is 4–7 (reviewed by Schoemann et al. 2005), C/N ratios as high as 20.5 were reported in nutrient limited mesocosms of *P. pouchetii* (Verity et al. 1988), 17.5 during blooms of *P. pouchetii*, and 30 during blooms of *P. globosa* at low ambient inorganic nitrogen concentrations (Baumann et al. 1994). Energy and carbon produced during overflow metabolism in *Phaeocystis* can be channeled towards both glucan and mucopolysaccharides. During the stationary phase of a *P. pouchetii* bloom in mesocosms the ratio glucan/mucopolysaccharides increased (Alderkamp et al. 2006a), whereas it decreased during the stationary phase of cultures of colonial *P. globosa* (Van Rijssel et al. 2000).

Blooms of *P. antarctica* occur in regions where trace metals, notably iron, are limiting phytoplankton growth (Martin et al. 1990; Coale et al. 2003, Schoemann et al. 2005). The effect of iron limitation on the overflow production by *P. antarctica* is largely unknown. Since iron limitation directly affects the photosynthetic process (Geider and La Roche 1994) the production of carbohydrates is likely to be hampered,

thereby decreasing the overflow metabolism. Indeed, the diurnal production of water-extractable carbohydrates was reduced under iron limitation in the Antarctic diatom *Chaetoceros brevis* (Van Oijen et al. 2004a) and in an iron-limited phytoplankton community in the Southern Ocean, dominated by diatoms (Van Oijen et al. 2005). In accordance with these findings, only a minor increase in C/N ratio of *P. antarctica* was reported upon nutrient limitation in enclosures in the Ross Sea, where iron limitation is likely to occur (Smith et al. 1998). Therefore, it is unlikely that the overflow production under iron limitation will be as dramatic as under nitrogen or phosphorus limitation.

From the above it is clear that the concentration of storage glucan in phytoplankton is highly variable; it is dependent on the time of the day, light intensity and nutrient status of the cell. To evaluate the contribution of glucan to *Phaeocystis* carbon, quantitative data were compiled on the contribution of glucose to the aldose composition of particulate water-extractable carbohydrates (Fig. 1; Table 1a). Assuming that mucopolysaccharides consist of 10% glucose (Janse et al. 1999), the remaining glucose can be attributed to glucan. This leads to a highly variable contribution of glucan to the particulate water-extractable carbohydrate fraction of *Phaeocystis* colonies. During the exponential growth phase glucan contributes 14–85% and during the stationary phase 0–85%, both in culture and field samples. Alternatively, glucan and mucopolysaccharides were separated based on polymer size differences by ethanol precipitation (Fig. 1). During the growth phase of a *P. pouchetii* bloom in a mesocosm, glucan contributed 46–78% to particulate water-extractable carbohydrates, depending on the time of the day. This increased to 82% during the stationary phase of the bloom (Alderkamp et al. 2006a). To compute the contribution of glucan to colonial *Phaeocystis* POC, the carbohydrate-C/POC ratio of Alderkamp et al. (2006a) was used (Table 2). This leads to a contribution of glucan-C to POC of 2–11% during exponential growth, dependent on the time of the day. During the stationary phase the contribution ranges between 0% and 51%. The results are summarized in Table 3. In a non-colony-forming,

non-flagellate strain of *P. globosa*, chrysolaminaran contributed 40% to TOC during the stationary phase (Janse et al. 1996b).

Mucopolysaccharides

The mucus matrix of *Phaeocystis* colonies consists predominantly of hetero-polysaccharides (Guillard and Hellebust 1971; Painter 1983; Lancelot and Mathot 1985; Eberlein et al. 1985; Van Boekel 1992). The mucopolysaccharides consist of at least nine different aldoses, are water-soluble, and polymers are larger than 1,000 kDa (Janse et al. 1999). Qualitative staining of the colony matrix indicated the absence of lipophilic compounds and chitin, but the presence of amino groups (Hamm et al. 1999). Matrix-assisted laser desorption/ionization (MALDI) analysis showed that N was not proteineous, but probably present in aminosugars (Solomon et al. 2003). The presence of the aminosugar sialic acid was confirmed by aminolabeling (Orellana et al. 2003). The presence of aminosugars may affect the C/N ratio of mucopolysaccharides, leading to a small difference between C/N ratios of single cells and colonial cells (Verity et al. 1988). Verity et al. (1991) concluded that the C/N ratio of the mucus constituents is lower than 9, whereas Biersmith and Benner (1998) measured a C/N ratio of 15.6 in the fraction containing mucopolysaccharides.

The aldose composition of *P. globosa* and *P. pouchetii* carbohydrates has been studied in bloom samples and in strains from different origins (Table 1a). The main non-glucose aldoses are arabinose, galactose, mannose and xylose. In addition, a minor contribution of rhamnose was detected in all samples, whereas fucose, ribose, *O*-methylated hexoses, *O*-methylated pentoses and glucuronic acid were detected in some samples only. The glucosamine detected by two groups may have been derived from copepod chitin contamination in the samples. The aldoses detected in *Phaeocystis* material are the same as those detected in other phytoplankton extracellular carbohydrates (Hoagland et al. 1993; Biersmith and Benner 1998), however, the ratio of constituents seems specific for *Phaeocystis*. There were no major differences in the presence or ratio of non-glucose aldoses between a bloom sample

Table 1a Sugar composition of *Phaeocystis* carbohydrates

Species	% non-glucose sugars														Reference
	glc	ara	fuc	gal	glcA	lyx	man	rib	rha	xyl	Omh	Omp	heA	glcN	
<i>P. pouchetii</i>	26–40	1–8	9–30	13–30		10–31		6–10	15–38				2–6	Metaxatos et al. (2003)	
dominated mesocosm															
<i>P. globosa</i> colonial	7–85	25–32	12–25	0–3		12–24		7–12	11–12	0–2	0–3		NP	Van Rijssel et al. (2000)	
cultures, four strains															
from the North Sea															
<i>P. pouchetii</i> bloom,	45	35	10	5		15		2	8	17	2			Janse et al. (1999)	
Balsfjord															
<i>Phaeocystis</i> sp. culture	27	13	6	35		2		2.5	11	20				Biersmith and Benner (1998)	
<i>P. globosa</i> bloom,	20–75	32–43	17–25	2–8		12–20		3–8	11–20	2–4	0.5–2		NP	Janse et al. (1996a)	
North Sea															
<i>Phaeocystis</i> sp. bloom,		P	P	P				P	P				P	Painter (1983)	
English Channel															

ara: arabinose, fuc, fucose, gal: galactose, glc: glucose, lyx, lyxose, man: mannose, rha: rhamnose, rib: ribose, xyl: xylose, gla: glucuronic acid, glcN: glucosamine, Omp: O-methylated pentoses, Omh: O-methylated hexoses, Hea: hexuronic acid, gln: glucosamine, P: present, NP: not present and included in analysis

Table 1b Sugar composition of *Phaeocystis* extracolonyal DOM^a

Species	% total carbohydrates														Reference
	glc	ara	fuc	gal	glcA	lyx	man	rib	rha	xyl	Omh	Omp	heA	glcN	
<i>Phaeocystis</i> sp. culture	4	17	2	16		30	5	21	6					Aluwihare and Repeta (1999)	
<i>Phaeocystis</i> sp. culture	17	13	4	28		3	15	1	6	13				Biersmith and Benner (1998)	
<i>P. pouchetii</i> cultures,	4.5–30	0–5.2	2–5.6			27–64	3–8	16–20	1.5–3				4–5.5	Guillard and Hellebust (1971)	
two strains															

Note: Abbreviations as in Table 1a

^a Although classified as DOM, these studies include carbohydrates derived from mucopolysaccharides as DOM fractions were obtained by filtration with the application of pressure

Table 2 Contribution of carbohydrates to POC of *Phaeocystis*

Species	Growth stage	Carbohydrate to POC	Reference
<i>P. pouchetii</i> mesocosm	Exponential	13%	Alderkamp et al. (2006a)
<i>P. pouchetii</i> mesocosm	Stationary	60%	Alderkamp et al. (2006a)
<i>P. globosa</i> culture	Exponential	10%	Van Rijssel et al. (2000)
<i>P. globosa</i> bloom	No info	19–35%	Van Rijssel et al. (1997)
<i>Phaeocystis</i> sp. culture	Stationary	38%	Biersmith and Benner (1998)
<i>Phaeocystis</i> sp. culture	All	20–30%	Biddanda and Benner (1997)
<i>P. globosa</i> single cell culture	Stationary	40%	Janse et al. (1996b)

Table 3 Contribution of glucan-C to POC of *Phaeocystis* colonies

Method	<i>Phaeocystis</i> species	Growth phase	Glucan-C to POC	Reference
Aldose composition	<i>P. pouchetii</i> and <i>P. globosa</i>	Exponential Stationary	2–11% 0–51%	Compiled in this study
Ethanol precipitation	<i>P. pouchetii</i>	Exponential Stationary	6–10% 49–60%	Alderkamp et al. (2006a)

from Balsfjord, Norway, dominated by *P. pouchetii* and a sample from the North Sea dominated by *P. globosa* (Janse et al. 1999). No data are available for other species of *Phaeocystis*, including *P. antarctica*. In five different strains of *P. globosa* differences in the ratio of non-glucose constituents were small (Van Rijssel et al. 2000). Nutrient status of the cells does not seem to influence the ratio, as was shown in a batch culture of *P. globosa* (Van Rijssel et al. 2000) or in bloom samples taken at different stages of a bloom (Janse et al. 1996a). The change in colony shape and appearance at the end of *Phaeocystis* blooms (e.g., Verity et al. 1988; Rousseau et al. 1994) is therefore not reflected in the aldose composition of the mucopolysaccharides. This is different from the situation reported in diatoms, where upon nutrient limitation, the benthic diatom *Cylindrotheca closterium* excretes a separate extracellular polysaccharide with a different monosaccharide composition compared to optimal growth conditions (De Brouwer et al. 2002; Underwood et al. 2004).

Phaeocystis acts as a secretory cell; mucopolysaccharides are excreted in a way similar to animal cells and vascular plants in which the regulated export of cellular products takes place via exocytosis. While stored in secretory vesicles inside the cells, the mucopolysaccharides remain in condensed phase. Upon exocytosis, they undergo a characteristic phase transition accompanied by extensive swelling, resulting in the formation

of hydrated gels (Chang 1984; Chin et al. 2004). The negatively charged mucopolysaccharides become entangled and form ionic links, such as calcium bridges (Van Boekel 1992). They then form a thin, yet strong, semipermeable colony matrix, with a pore size between 1 and 4.4 nm diameter, with plastic and to a limited extent also elastic properties (Kornmann 1955; Hamm et al. 1999). Electron microscope studies of a *Phaeocystis* sp. from Tasman Bay, New Zealand, show that the matrix has a multilayered gelatinous structure, with an average thickness of 5 μm (Chang 1984). Van Rijssel et al. (1997) calculated a thickness of 7 μm based on carbohydrate measurements and the assumption of a mucous layer with a fixed thickness for various colony sizes, whereas a thickness of 10 μm was determined based on confocal laser scanning imagery. As colonial cells of *Phaeocystis* have similar (Baumann et al. 1994), or even higher growth rates (Veldhuis et al. 2005) compared to single cells, the allocation of the material needed to build the colonial matrix obviously does not hamper cell metabolism.

In addition to a structural function in the mucous matrix, mucopolysaccharides were also suggested to serve as storage polysaccharides as nocturnal consumption of extracellular polysaccharides was reported in *P. globosa* (Lancelot and Mathot 1985; Veldhuis and Admiraal 1985). In both studies cells were separated from mucous matrix by filtration under pressure. Since this

treatment may cause cells to break, thus releasing intracellular substances (see above), nocturnal consumption of intracellular chrysolaminaran may have been misreported as consumption of extracellular substances. Using the same method to separate extracellular material from cells, Matrai et al. (1995) observed no nocturnal utilization of extracellular polymers in an Antarctic strain of *Phaeocystis*. Also, when mucopolysaccharides and glucan were separated based on polymer size differences, no utilization of mucopolysaccharides was found when a culture of *P. globosa* was placed in the dark for prolonged times (Alderkamp et al. 2006a). Given the size and structure of mucopolysaccharides it seems unlikely that they serve as storage carbohydrate. Degradation and uptake of these complex polysaccharides would require multiple extracellular enzymes as well as transport systems to take up the different monosaccharides and oligomers. Moreover, since the gel matrix is such a definite structure stabilized by ionic bridges, it will be hard to disentangle polymers from the gel.

Contribution of mucopolysaccharides-C to POC

The contribution of mucus carbon to *Phaeocystis* organic carbon can be assessed in three different ways. In the first, cells are mechanically separated from the mucus matrix by filtration through GF/C filters. Fractionation by filtration yields contributions of 5–80% of mucus carbon to POC (reviewed by Riegman and Van Boekel 1996). As many have pointed out, however, *Phaeocystis* cells are fragile and may be disrupted by filtration under pressure (Veldhuis and Admiraal 1985; Van Rijssel et al. 1997; Mathot et al. 2000). By releasing their water soluble carbon the fraction of mucus-carbon may be overestimated. On the other hand, mucopolysaccharides may form gels on the filter (Chin et al. 1998) as a result of which their contribution may be underestimated. Therefore, all studies in which colonies were fractionated by filtration or centrifugation have to be interpreted with care.

When assuming that carbohydrates are the only significant source of carbon in the mucus matrix, the second method consists of determination of the contribution of mucopolysaccharides

to the water-extractable carbohydrates. Mucopolysaccharides are estimated as the combined sum of all non-glucose aldoses and 10% of the glucose. Based on the aldose composition of water extractable carbohydrates (Fig. 1), the contribution of mucopolysaccharides to the water extractable particulate carbohydrates is 15–86% during the exponential growth phase, and 15–100% during the stationary phase (Table 1a and references therein). Alternatively, glucan and mucopolysaccharides were separated based on polymer size (Fig. 1; Alderkamp et al. 2006a). During the exponential growth phase, mucopolysaccharides contributed 38% to the water extractable carbohydrates, decreasing to 9% during the stationary phase. Based on the carbohydrate-C to carbon ratios of Alderkamp et al. (2006a; Table 2) the contribution of mucopolysaccharides to POC is estimated as 2–11% during exponential growth and 5–60% during the stationary phase.

The third method to estimate the carbon of colony matrices is based on conventional conversion factors for determining the carbon content of the average cell biovolume of *Phaeocystis* cells and an additional carbon content of the mucus matrix. In *P. antarctica*, Mathot et al. (2000) found on average 14% of POC devoted to matrix formation, increasing to a maximum of 33%. In *P. globosa* Rousseau et al. (1990) using a colony-volume-based model, calculated up to 90% of POC devoted to matrix formation in large colonies. Van Rijssel et al. (2000), assuming a hollow colony surrounded by a thin mucus layer and using a colony-surface-based model, calculated a contribution up to 35%. Comparisons of estimates obtained by these authors, however, show similar POC contributions for colony sizes predominantly observed in the field (reviewed by Schoemann et al. 2005). The estimates for the contribution of mucous matrix-C to POC are summarized in Table 4.

Extra-colonial DOM

Extra-colonial DOM rich in carbohydrates was reported in cultures of *Phaeocystis* (Table 5 and references therein). Carbohydrates similar in aldose composition to that of mucopolysaccharides form a major contribution to this DOM

Table 4 Contribution of mucous matrix-C to POC of *Phaeocystis* colonies

Method	<i>Phaeocystis</i> species	Growth phase	Matrix-C to POC	Reference
Mechanical filtration	<i>P. pouchetii</i> and <i>P. globosa</i>	All	5–80%	Riegman and Van Boekel (1996)
Aldose composition	<i>P. pouchetii</i> and <i>P. globosa</i>	Exponential	2–11%	Compiled in this study
		Stationary	10–60%	
Ethanol precipitation	<i>P. pouchetii</i>	Exponential	3–5%	Alderkamp et al. (2006a)
		Stationary	5–13%	
Model	<i>P. antarctica</i>	Exponential	14 ± 4%	Mathot et al. (2000)
		Stationary	Up to 33%	
Model	<i>P. globosa</i>	Exponential (lab.)	Up to 10%	Van Rijssel et al. (1997)
		All (field) ^a	Up to 35%	
Model	<i>P. globosa</i>	All ^b	Up to 90%	Rousseau et al. (1990)

^a Highest values at low ambient nitrate concentrations

^b Size dependent

Table 5 Characteristics of *Phaeocystis* DOM

Species	Growth stage	carbohydrates to DOC	C/N ratio	DOC to TOC	Reference
<i>Phaeocystis</i> sp. (culture)	Exponential through stationary	25–50%	19.3 (HMW) 6.3 (LMW)	27%	Biddanda and Benner (1997)
<i>Phaeocystis</i> sp. (culture)	Stationary	56%	19.3 (HMW)	14%	Biersmith and Benner (1998)
<i>Phaeocystis</i> sp. (culture)	Late exponential	>67% (HMW)	12 (HMW)		Aluwihare and Repeta (1999)
<i>P. globosa</i> (culture)	Late exponential		8.3 (axenic) 7.4 (xenic)		Solomon et al. (2003)
<i>P. antarctica</i> (culture)	Late exponential		6.9 (axenic) 6.2 (xenic)		Solomon et al. (2003)

(Table 1b). There seem to be two different pools of DOM; (1) a high-molecular-weight (HMW)-DOM pool with a high C/N ratio of over 12 and a carbohydrate content of over 67% and (2) a low-molecular-weight (LMW)-DOM pool with a low C/N ratio of 6.3. Since all studies used filtration techniques applying pressure, it is most likely that the DOM also contained mucopolysaccharides. The overall C/N ratio of the DOM is low, around 7 (Biddanda and Benner 1997; Solomon et al. 2003). Similar to mucopolysaccharides, extra-colonial polymers self assemble in hydrated polymer gels on a time scale of approximately two days (Solomon et al. 2003).

High DOM concentrations have been reported in natural assemblages dominated by *Phaeocystis* (Eberlein et al. 1985), and high DOM excretion rates in cultures (Guillard and Hellebust 1971). Upon careful filtration, however, true extra-colonial DOM excretion was only 14% of primary

production in the late exponential phase of a *P. globosa* culture (Veldhuis and Admiraal 1985; Veldhuis et al. 1986a; Biersmith and Benner 1998), and 2–14% of primary production in natural assemblages dominated by *P. globosa* (Laanbroek et al. 1985; Veldhuis et al. 1986a; Lancelot and Mathot 1987). Similar values were observed for *P. pouchetii* (1–19%; Verity et al. 1991), and during a bloom of *P. antarctica* (11%; Carlson et al. 1998).

Mechanisms of DOM release during a *Phaeocystis* bloom

In general 10–25% of phytoplankton primary production is released as DOC (Sharp 1977; Larsson and Hagström 1979; Lignell 1990; Teira et al. 2003; Marañón et al. 2004). The three main mechanisms of DOM production are: (1) release

after cell lysis, e.g., as a result of viral infection, zooplankton sloppy feeding and egestion, (2) bacterial cleavage of exopolysaccharides (Smith et al. 1995), or (3) direct release as a physiological process of intact cells (reviewed by Nagata 2000). Two physiological mechanisms of DOM production have been advocated: a passive diffusion of small metabolites through the cell membrane (Bjørnsen 1988) and an overflow mechanism whereby excess photosynthetic products are actively released when the C fixation rate exceeds the rate of macromolecular production (Fogg 1983).

During the exponential growth phase of a *Phaeocystis* bloom DOM release as a result of non-physiological processes will be low. In a *P. globosa* bloom rates of cell lysis were low in the growth phase (Van Boekel et al. 1992; Brussaard et al. 1995, 1996, 2005a), therefore DOM release as a result of cell lysis will be insignificant. Since *Phaeocystis* colonies largely escape grazing control (Breteler and Koski 2003; Nejstgaard et al. 2007), sloppy feeding will not be a cause of significant DOM release either. In a diatom bloom it was shown that bacteria colonized healthy, actively growing *Chaetoceros* and *Thalassiosira* cells with high ectoenzyme activity. When the hydrolysis rate of phytoplankton surface material by bacteria exceeds the uptake rate, DOM will be released into the environment (Smith et al. 1995). Although the growth phase of *P. globosa* blooms are typically accompanied by an increase in bacterial numbers, bacterial production, and enzyme activity (Billen and Fontigny 1987; Van Boekel et al. 1992; Putt et al. 1994; Becquevort et al. 1998; Arrieta and Herndl 2002; Brussaard et al. 1996, 2005b), young healthy colonies are generally free of bacteria (Thingstad and Billen 1994; Lancelot and Rousseau 1994). Therefore, it is unlikely that hydrolysis of the mucous matrix by bacteria will lead to significant DOM production during the growth phase of the bloom. The only significant mechanisms for DOM production is probably direct release of DOM from healthy cells. During all growth stages DOM excretion from healthy cells was observed in cultures of *Phaeocystis* sp. (Biddanda and Benner 1997). Since DOM excretion rates are low (see above) on the whole DOM release during the growth phase of the bloom will be low.

During the stationary phase of a bloom, however, DOM release increases. During the stationary phase colonies become disrupted, and flagellate cells develop within the colonies (Peperzak et al. 2000). Due to the overflow production of mucopolysaccharides and glucan, the ratio of carbohydrates-C to POC increases. During this phase of a bloom DOM production through non-physiological processes will be high. Cell lysis rates of up to 33% day⁻¹ were observed at the peak of *P. globosa* blooms (Van Boekel et al. 1992; Brussaard et al. 1995, 1996, 2005a). In this way the carbohydrate rich cell content is released as DOM. When the flagellate cells that develop inside colonies detach from the colony matrix, they are readily grazed upon by microzooplankton (Weisse and Scheffel-Möser 1990; Tang et al. 2001). This leads to DOM release by egestion of the microzooplankton. During the stationary phase of a bloom, bacterial communities attach to *Phaeocystis* colonies and to ghost colonies. Bacteria with high glucosidase activity are present in both free-living and particle-attached communities (Billen and Fontigny 1987; Becquevort et al. 1998). If hydrolysis rates of mucopolysaccharides from the colony matrix exceeds uptake of the sugars, the sugars and oligomers derived from mucopolysaccharides may be released as DOM.

The excess release of DOM under nutrient limitation has not been observed in *Phaeocystis*. In *Phaeocystis* sp. cultures DOC production was coupled to POC production at different growth stages (Biddanda and Benner 1997). Also in enclosures of *P. antarctica*, ratios of recently produced DOC increased only slightly after nutrient depletion (Smith et al. 1998; Carlson et al. 1998). This indicates that nutrient limitation does not lead to increased excretion of DOM resulting from an overflow mechanism.

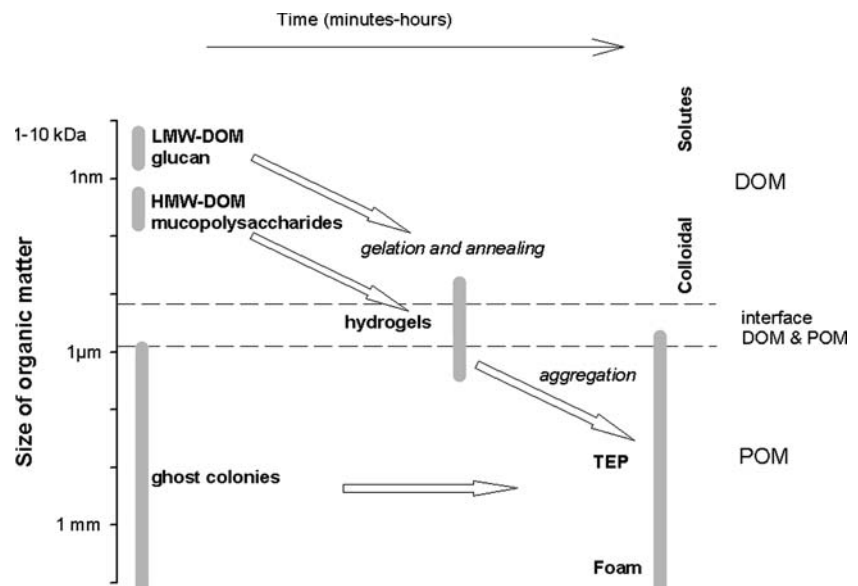
Formation of hydrogels by *Phaeocystis* carbohydrates

Polysaccharides in aqueous environments may spontaneously assemble into hydrogels. These polymer gels can then penetrate neighboring gels, and anneal them together, increasing the size spectrum. Recent discoveries have highlighted

the importance of polymer gels for biogeochemical cycling of organic carbon (see the review by Verdugo et al. 2004). As was discussed above, mucopolysaccharides spontaneously form polyanionic gels in aqueous solution. In addition to gel formation by mucopolysaccharides, β -1,3-glucans are also known to form non-ionic gels in aqueous solutions (Renn 1997; Kim et al. 2000). In general, gelling properties of β -glucans are dependent on the concentration of the molecules, their size, primary and secondary structure and temperature (Bohm and Kulicke 1999; Lazaridou et al. 2003). Therefore, gel-forming properties of laminarin in the marine environment are hard to predict. Preliminary results from our laboratory show that dissolving laminarin in seawater leads to an increase in viscosity, but to our knowledge no further investigations have been conducted to this end. Seuront et al. (2007) showed that *Phaeocystis* derived polymeric matter could increase seawater viscosity up to two orders of magnitude. Because of the high aggregation potential of both glucan and mucopolysaccharides, the carbohydrates released during senescence of the *Phaeocystis* bloom will likely contribute to the increase in seawater viscosity (Fig. 2), thereby changing the physical nature and microscale structure of the organic matter encountered by bacteria.

Gels provide an abiotic vehicle to move organic molecules up the size spectrum to sizes capable of sedimentation, and may also constitute an intermediate in the formation of the foam often observed after *Phaeocystis* blooms (Fig. 2). Large gel particles, also known as transparent exopolymeric particles (TEP) can contribute significantly to sedimentation processes. This may be by direct sedimentation (Wassmann et al. 1990; Riebesell et al. 1995; Hong et al. 1997), or by acting as glue, adhering together organic matter present during a bloom and thus enhancing their contribution to a vertical flux (Passow and Wassmann 1994). Mari et al. (2005) showed that the properties of TEP produced under N or P limitation are different, as a result of which the export versus retention balance of the organic matter may be affected. It is tempting to speculate that the different N/P ratios may determine whether overflow metabolism is directed towards either glucan or mucopolysaccharide production. This would resemble the situation described for the diatom *Cylindrotheca fusiformis*, where P depletion leads to an increase in the ratio of heteropolysaccharides to glucan, compared to N-limitation (Magaletti et al. 2004). In this way the glucan/mucopolysaccharides ratio may influence properties of the hydrogels and TEP that is

Fig. 2 Conceptual representation of the formation of marine gels from different pools of *Phaeocystis* organic matter (after Verdugo et al. 2004). (abbreviations: LMW-DOM: low-molecular-weight DOM, HMW-DOM: high-molecular-weight DOM, POM: particulate organic matter, TEP: transparent exopolymeric particles)



formed, and thereby the degradation potential of *Phaeocystis* organic matter.

Microbial degradation

Generally, most of the biomass produced in *Phaeocystis* blooms is remineralized in the water column (Wassmann 1994, Rousseau et al. 2000) by heterotrophic bacteria. Occasionally, however, accumulation of DOM and foam have been reported (e.g. Eberlein et al. 1985; Lancelot et al. 1987; Seuront et al., 2007). This seems to indicate that bacterial degradation of organic matter produced by in *Phaeocystis* blooms varies between blooms, and sometimes is hampered. There may be various reasons for slow degradation and they may be different in different stages of a bloom.

Microbial degradation of *Phaeocystis* carbohydrates

During the growth phase of a bloom of *P. antarctica* all DOM produced was found to be rapidly degraded by bacteria (Smith et al. 1998). With time, however, the composition and contribution of organic matter that can be utilized by bacteria will change from readily degradable freshly excreted DOM during the growth phase, to the DOM dominated by mucopolysaccharides and glucan during the senescent stage. In laboratory experiments it was shown that carbohydrates derived from *P. globosa* and *P. pouchetii* colonies were readily degraded by bacterial communities under both oxic and anoxic conditions (Osinga et al. 1997; Janse et al. 1999). The degradation rate of glucan was higher than that of mucopolysaccharides (Osinga et al. 1997), but during degradation of the mucopolysaccharides the sugar composition of the mucopolysaccharides remained unchanged. Therefore, there is no indication of refractory parts within the mucopolysaccharide fraction (Janse et al. 1999).

Identification of bacteria involved in mucopolysaccharide degradation in cultures and a mesocosm revealed the presence of bacteria from different phylogenetic groups, such as α - and

γ -Proteobacteria, *Cytophaga-Flavobacter* (CF) cluster of the Bacteroidetes and the *Planctomycetes* and *Verrucomicrobiales* clade (Janse et al. 2000; Brussaard et al. 2005b; Alderkamp et al. 2006b). During a *P. globosa* bloom in a mesocosm the bacterial community showed distinct changes with time (Brussaard et al. 2005b). The nature of the phytoplankton growth controlling substrate (i.e., N or P) did not influence the microbial community. In addition, since the species composition of the bacterial community remained unchanged during mucopolysaccharide degradation, degradation of mucopolysaccharides in itself does not require a succession of species (Janse et al. 2000). Therefore, the changes in the microbial community were likely induced by the growth stage of the *P. globosa* bloom and enhanced cell lysis and concomitant release of DOM during the senescent stage (Brussaard et al. 2005b). Degradation of polymers requires specialized extracellular enzyme systems to hydrolyze polymers prior to uptake by bacteria. These enzymes can be attached to the bacterial cell (ectoenzymes), or free extracellular enzymes (Chróst 1991). Arrieta and Herndl (2002) revealed a succession of different types of bacterial β -glucosidases during a *P. globosa* bloom, which was related to a change in the bacterial community. Therefore, the copious amounts of glucan and mucopolysaccharides produced during a *Phaeocystis* bloom may shape the composition of bacterial communities specialized in degradation of complex carbohydrates. Bacteria appearing during the senescent stage of the *P. globosa* bloom in the mesocosm mainly belonged to the α -Proteobacteria and CF cluster of the Bacteroidetes (Brussaard et al. 2005b). In the coastal North Sea, bacteria from CF clusters of the Bacteroidetes were dominant during and following a bloom of *P. globosa* (A. C. Alderkamp et al. 2006b). Members of the CF cluster are chemo-organotrophic, and known for their capacity to degrade complex carbohydrates such as pectin, cellulose and chitin (Reichenbach and Dworkin 1991; Cottrell and Kirchman 2000; Kirchman 2002). Therefore, it may be that certain taxa of this cluster have adapted specifically to degradation of complex mucopolysaccharides produced by *Phaeocystis*.

Mineral nutrient limitation of microbial degradation has been put forward as an explanation for accumulation of carbon-rich DOM after a *Phaeocystis* bloom (Thingstad and Billen 1994). The increase in carbohydrate/POC due to overflow metabolism will give rise to a substrate with a C/P and C/N ratio that is unfavorable to bacteria. Since the C/P ratio of bacteria may be considerably lower than that of phytoplankton (Vadstein et al. 1988), especially phosphate limitation may hamper microbial degradation (Thingstad et al. 1997). In addition, since *P. antarctica* was found to remove more CO₂ per mole of phosphate than do diatoms (Arrigo et al. 1999), phosphate limitation during bacterial degradation of *Phaeocystis* material may be more severe than during degradation of diatom material. Indeed, while bacterial growth was carbon limited during the growth phase of a bloom of *P. globosa*, bacterial growth was colimited by carbon and phosphate during the massive release of the glucan and mucopolysaccharides at the end of the bloom (Kuipers and Van Noort, in preparation). This may impede degradation of carbohydrates that are otherwise easily degradable, and prolong the degradation times.

Microbial degradation of hydrogels

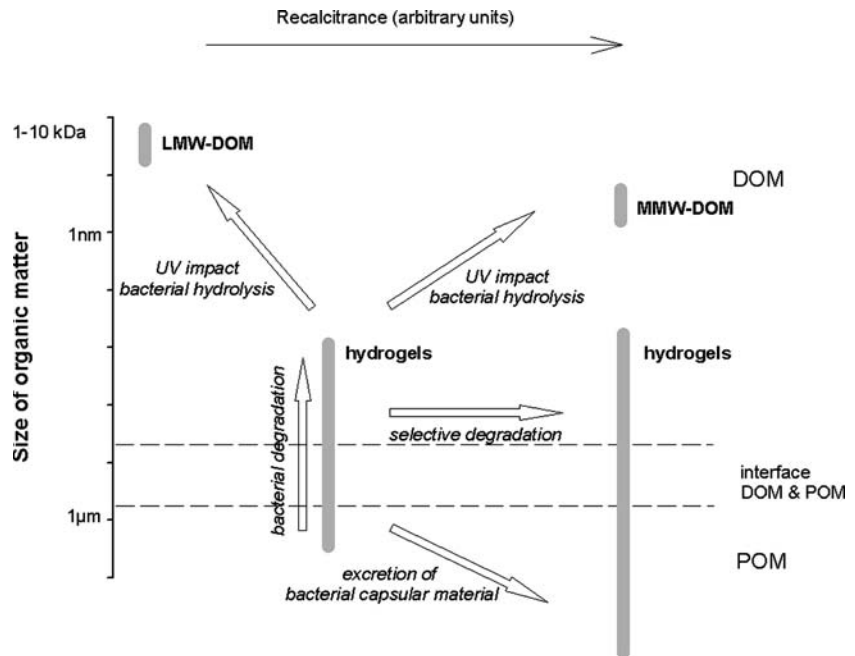
Marine gels likely have an effect on microbial degradation of organic matter, yet few studies have examined this effect directly. Based on the current knowledge, gel formation may either enhance or slow down degradation of organic matter. In general HMW-DOC and gels have a higher rate of biodegradation and turnover than LMW-DOC (Amon and Benner 1996). Gels may serve as nutrient and/or attachment surfaces and offer hot-spots of high substrate concentrations for bacteria. They form enclosed microenvironments of substrate for bacteria to colonize, release their extracellular enzymes and efficiently take up the degradation products at high local concentrations (Azam 1998; Azam and Long 2001). Indeed, following a *P. globosa* bloom bacteria attached to particles were more active than the free-living community (Becquevort et al. 1998). On the other hand, assembly of free polymers into gels may complicate degradation.

Enzymatic degradation of carbohydrates that form insoluble gels was approximately 50 times slower than degradation of polymers composed of the same monomer linkages, but not forming gels (Alderikamp et al. 2007). If this difference is exemplary of the difference in degradation potential of 'free' polymers and polymers embedded in a gel, turnover times may slow down from days to years.

Microbial degradation dissolves the hydrogels when hydrolysis rates exceed the carbon demand of the bacteria, thereby releasing LMW products from the hydrogels (Smith et al. 1992; Fig. 3). Moreover, the kinetic properties of bacterial enzyme systems may result in the release of oligomers at a higher rate than the release of monomers that can be directly incorporated by the bacteria, resulting in release of LMW and medium molecular-weight (MMW) products (Alderikamp et al. 2007). In addition, polymer photocleavage by ultraviolet radiation can shorten polymer chains making tangled networks unstable (Edwards 1986) and can readily disperse marine polymer gel matrices (Orellana and Verdugo 2003). These three processes produce a random fragmentation, yielding LMW products that may be readily incorporated and metabolized by bacteria (Mopper et al. 1991; Moran and Zepp 1997; Mopper and Kieber 2001), adding to a rapid degradation of the organic matter in hydrogels. On the other hand, polymers may be released that are too large to be transported by bacterial permeases, yet too small to assemble into stable networks that bacteria can colonize and efficiently degrade with their extracellular enzymes. These polymers, indicated as DOM (MMW-DOM) in Fig. 3, may contribute to the formation of refractory DOM.

Bacterial activity may also increase aggregation of gels (Fig. 3). Studies on bacterial exopolymer production suggest that a significant portion of assimilated carbon is incorporated into exopolymer capsular envelopes (Stoderegger and Herndl 1998). These capsular exopolymers increase aggregation probabilities of phytoplankton and other particles and act as stabilizers of already existing aggregates (Allison and Sutherland 1987; Decho 1990; Heissenberger and Herndl 1994). In addition, bacterial exopolymers are

Fig. 3 Conceptual representation of biotic and abiotic processes altering the size and recalcitrance of organic matter. (Abbreviations as in Fig. 1, MMW-DOM: medium-molecular-weight DOM)



resistant against bacterial enzymatic degradation, since a considerable fraction of bacterial extracellular enzymes are embedded in the exopolymer capsule. Therefore, release of bacterial derived exopolymers decreases the degradation potential of hydrogels. Finally, selective degradation of readily degradable compounds may alter the composition of the gels, and decrease the degradation potential of the remaining gel (Sannigrahi et al. 2005). At present it is not known to what extent the mechanisms discussed above influence microbial degradation of hydrogels. Therefore, microbial degradation of *Phaeocystis* derived DOM may either be enhanced or hampered by formation of hydrogels.

Conclusions

Phaeocystis produces at least five different pools of carbohydrates, each with their own characteristics. Since the overflow metabolism during the stationary phase of a bloom can be channeled towards glucan and mucopolysaccharides, these two pools are quantitatively the most important when the impact on the ecosystem is considered. The contribution of the pools is strongly dependent on environmental conditions. High light

conditions and nutrient limitation lead to excess carbohydrate production, but thus far the effect of either N or P limitation on the ratio of glucan to mucopolysaccharide production is unclear, as is the effect of Fe limitation on carbohydrate production in *P. antarctica*.

Phaeocystis-derived organic matter appears to be readily degradable, however, the high C/N and C/P ratios may give rise to mineral nutrient limitation of bacteria and therefore hamper degradation. Subsequent assembly into gels could have a dramatic effect on bacterial degradation of *Phaeocystis* derived organic matter, however, the nature of this effect is unclear. Gels may provide a convenient microhabitat to colonize and degrade with extracellular enzymes, thereby enhancing degradation rates of organic matter. Conversely, degradation of polymers embedded in gels may be slowed down by sterical hindrance. Furthermore, bacterial activity may reduce the degradation potential of gels by selective degradation of labile organic matter in the gels, and by production of carbon into bacterial capsular material.

Acknowledgements We thank M.J.E.C. van der Maarel and H. Helmers for the analysis of the viscosity of laminarin. L. Seuront is acknowledged for stimulating comments on an earlier version of the manuscript.

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