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Progress in Oceanography 55 (2002) 287–333
Progress in Oceanography
www.elsevier.com/locate/pocean

Transparent exopolymer particles (TEP) in aquatic environments

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Abstract

Since the development of methods to quantify transparent exopolymer particles (TEP) 1993, it has been shown that these gel-particles are not only ubiquitous and abundant, but also play a significant role in the biogeochemical cycling of elements and the structuring of food webs. TEP may be quantified either microscopically or colorimetrically. Although data based on measurements using one or other of these methods are not directly comparable, the results are consistent. TEP abundances in fresh and marine waters are in the same range as those of phytoplankton, with peak values occurring during phytoplankton blooms. TEP are very sticky particles that exhibit the characteristics of gels, and consist predominantly of acidic polysaccharides. In marine systems the majority of TEP are formed abiotically from dissolved precursors, which are released by phytoplankton that are either actively growing or are senescent. TEP are also generated during the sloughing of cell surface mucus and the disintegration of colonial matrices. The impact of exopolymers in the creation of microhabitats and in the cycling of trace compounds varies with the state in which the polymers occur, either as particles or as solute slimes. As particles, TEP provide surfaces for the colonization by bacteria and transfer by adsorption, trace solute substances into the particulate pool. As dissolved polymers they are mixed with the water and can neither be filtered nor aggregated. Because of their high abundances, large size and high stickiness, TEP enhance or even facilitate the aggregation of solid, non-sticky particles. They have been found to form the matrices of all marine aggregates investigated to date. By aggregating solid particles, TEP promote the sedimentation of particles, and, because their carbon content is high, their direct contribution to fluxes of carbon into deep water is significant. The direct sedimentation of TEP may represent a mechanism for the selective sequestration of carbon in deep water, because the C:N ratios of TEP lie well above the *Redfield* ratio. The turnover time of TEP as a result of bacterial degradation appears to range from hours to months, depending on the chemical composition and age of TEP. TEP may also be utilized not only by filter feeders (some protozoans and appendicularian) but TEP-rich microaggregates, consisting of pico- and nano-plankton are also readily grazed by euphausiids, thus permitting the uptake of particles that would otherwise be too small to be grazed directly by euphausiids. This short-circuits food chains and links the microbial food-web to the classical food-web. It is suggested that this expansion of the concept of food webs, linking the microbial loop with an aggregation web will provide a more complete description of particle dynamics.

Keywords: transparent exopolymer particles; EPS; polysaccharides; exudation; aggregation; particle formation; carbon flux; food web

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0079-6611/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0079-6611(02)00138-6

Contents

1. Introduction

In marine ecosystems, polysaccharides are an important component of the labile fraction of DOC (Benner, Pakulski, McCarthy, Hedges, & Hatcher, 1992; Ogawa & Ogura, 1992; Kepkay, Niven, & Milligan, 1993; Kepkay, 2000). Because of their high molecular weight they predominantly belong to the colloidal fraction of DOC. Many aquatic organisms, including phytoplankton and bacteria generate large amounts of extracellular polysaccharides (e.g. Hoagland, Rosowski, Gretz, & Roemaer, 1993; Costerton, 1995; Myklestad, 1995). Diatoms are especially well known for excreting copious quantities of polysaccharides during all phases of their growth (Watt, 1969; Allan, Lewin, & Johnson, 1972; Hellebust, 1974; Hama & Handa, 1983; Sundh, 1989; Williams, 1990). Such exopolymeric substances, called EPS, range in structure from being loose slimes to tight capsules surrounding the cells. One type of EPS, the transparent exopolymer particles (Fig. 1), called TEP, has received increasing attention because the TEP exist as individual particles rather than as cell coatings or dissolved slimes (Alldredge, Passow, & Logan, 1993). The role of TEP in aquatic systems differs from other forms of EPS, because as individual particles not only can they aggregate but also they can be collected by filtration; whereas dissolved substances can only mix with the surrounding water. Although the role of EPS in marine environments has been outlined in

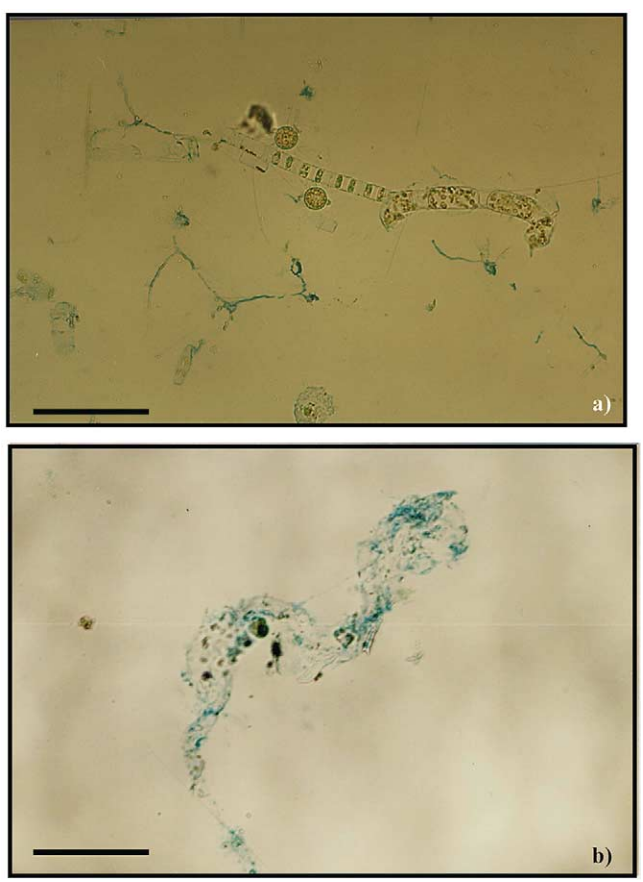

Fig. 1. (a) Transparent exopolymer particles (TEP) as commonly observed during growth of blooms dominated by *Chaetoceros* spp.. TEP are made visible by staining with alcian blue. (b) Sheet like TEP with attached nano-sized particles. Scale bar is 0.1 mm.

several reviews (Hellebust, 1974; Decho, 1990; Leppard, 1995; Myklestad, 1995), our knowledge of TEP has not yet been summarized, and generally these gel particles have been overlooked.

Operationally TEP are defined as transparent particles that are formed from acid polysaccharides and are stainable with alcian blue (Alldredge, Passow & Logan, 1993). Such transparent particles have been noted and described earlier (e.g. Gorden, 1970; Wiebe & Pomeroy, 1972; Emery, Johns, & Honjo, 1984) and there have been speculations about their potential importance in marine systems (Smetacek & Pollehne, 1986). However, because techniques for the visualization and quantification of these particles proved elusive, they were largely ignored, but once a method for their visualization was developed their high abundances in marine systems were revealed (Alldredge, Passow & Logan, 1993). How could these TEP have gone largely unnoticed for so long? Their transparency resulted in TEP escaping detection by microscopy, although many microscopists had suspected the presence of such non-visible particles. Other researchers who have spent long hours examining clogged filters have had experience of the effects of their presence. These and other clues, including coagulation theory, had long indicated that additional types of particle were present in seawater, so that the discovery of these elusive, sticky particles at high abundances has not come as a complete surprise.

Once the technique for their visualization of TEP was developed, awareness of the important role played by non-organismal particles in aquatic systems has increased rapidly (e.g. Schumann, Rentsch, Goers, & Schiewer, 2001). Other abundant mucoid particles, the Coomassie Stained Particles (CSP), which are protein-rich, have been discovered (Long & Azam, 1996). In three studies CSP have been found either to be more abundant than TEP (Long & Azam, 1996), or similar in abundance (Grossart, 1999) or less abundant (Prieto, Ruiz, Echevarría, García, Gálvez, Bartual et al., 2002). A careful comparison of both particle types in Lake Kinneret revealed that throughout the year there were, on average, fewer CSP than TEP, possibly because the former have faster turnover rates (Berman & Viner-Mozzini, 2001). The properties of mucoid particles differ in several important aspects from those of solid particles, which consist of organisms and detritus (dead organisms or parts thereof). As mucilage they have properties of gels, e.g. the volume to mass relationship is not constant. As excretion products, the mucoid particles are not subjected to the same constraints of organic C:N:P incorporation as occurs in the production of organic material.

Comparatively little is known about other non-TEP mucoid particles, and so this review will focus on TEP as case examples of mucoid particles, and will summarize the existing knowledge about TEP. Some of the insights gained from studies of TEP will be applicable to the other mucoid particles, but other results appertain more specifically to TEP. The main goal of this summary is to review the role of TEP in different pelagic processes, such as abiotic particle formation, aggregation, sedimentation, food web structure, and carbon cycling and to complement more specific reviews on these topics; e.g. reviews on the production of EPS by microorganisms (Decho, 1990; Myklestad, 1995), on the abiotic formation of particles (Kepkay, 1994), on aggregation (Alldredge & Jackson, 1995; Jackson & Burd, 1998; Thornton, 2002), on microbial ecology (Kirchmann, 2000) and on the role of colloids in carbon cycling (Kepkay, 2000).

The first section of this review describes TEP. After a comparison of methods used to quantify TEP, their global distribution patterns are summarized. Their physico-chemical characteristics will be introduced and their formation discussed. The second section explores their impact on particle dynamics and on the cycling of matter. The effect of the particulate nature of TEP on microorganisms and trace components is speculated upon and the role of TEP for aggregation, particle flux and food web structure is reviewed. The review concludes with a discussion of the role of TEP in the cycling of carbon and on future research goals.

2. Determination of TEP

TEP are operationally defined as particles retained on polycarbonate filters, which stain with the cationic dye alcian blue. At the pH and concentration used (aqueous solution of 0.02% alcian blue, 8 GX and

0.06% acetic acid, pH of 2.5), this dye stains both sulfated and carboxylated polysaccharides (Passow & Alldredge, 1995b). The particles have to be stained after filteration, as alcian blue precipitates in the presence of salt. Currently there are two methods of measuring TEP, both of which are based on staining with alcian blue. Firstly stained particles may be enumerated and sized microscopically. Alternatively the amount of stain bound to particles is acid-extracted from the filters and measured colorimetrically.

2.1. Microscopic enumeration

This method yields number abundance and sizes of TEP, from which their total surface area and/or their total volume can be estimated. Samples are prepared for microscopic enumeration by filtering the water samples through 0.4 or 0.2 μm polycarbonate filters. The TEP are stained directly on the damp filters. Semi-permanent slides can be prepared, using the Filter-Freeze-Transfer- technique (Hewes & Holm-Hansen, 1983), whereby the particles retained on the filters are transferred quantitatively to a glass slide and covered with a gel (Alldredge, Passow & Logan, 1993; Passow & Alldredge, 1994). Alternatively, particles can be directly viewed on the filters if they are transferred onto Cyto-clear® slides (Poretics, Corp) and covered with immersion oil and a cover slip (Logan, Grossart, & Simon, 1994a). The TEP can then be counted and sized on duplicate slides in size classes, either manually or semi-automatically using an image analysis system (Mari & Kiørboe, 1996). As their numerical concentrations depend heavily on the smallest size class counted, TEP are best quantified by calculating either their total surface area or their total encased volume. The encased volume (neglecting porosity) can be estimated, if it is assumed that stained particles on the filter surface represent the cross section of spherical particles. This assumption appears to work satisfactorily in some (Kiørboe & Hansen, 1993), but not all cases (Kiørboe, Lundsgaard, Olesen, & Hansen, 1994).

The size distributions of TEP follow a power law distribution:

$$dN/dl = al^{-b},$$

where N represents the number of TEP, and l the length of TEP (Passow & Alldredge, 1994; Mari & Kiørboe, 1996; Kiørboe, Tiselius, Mitchell-Innes, Hansen, Mari, & Mari, 1998; Mari & Burd, 1998; Worm & Søndergaard, 1998b), so estimates of their numerical abundance depend heavily on the smallest size classes included in counts (Fig. 2). Whereas, estimates of their total volume are dominated by the contributions of the few large particles, and those of the smaller TEP are virtually negligible (Fig. 2).

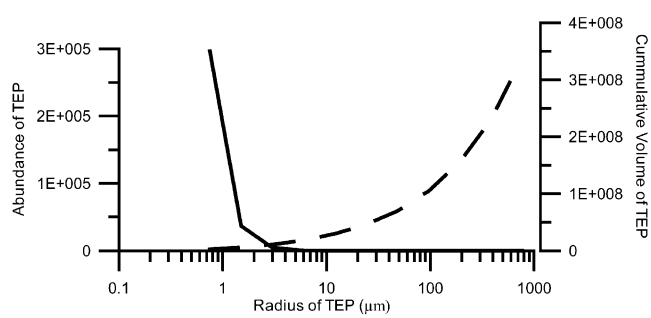

Fig. 2. Typical size frequency distribution with $b = 3$ (solid line) and the respective cumulative total volume distribution (dashed line; Volume = $4\pi/3\ R^{2.55}$, fractal dimension 2.55, Mari, 1999) of TEP. The figure clearly illustrates that numerical abundance data are extremely sensitive to the numbers of the small particles, whereas volume calculations are predominantly influenced by the large particles.

2.2. Colorimetric determination

In this method, TEP are initially stained as in the microscopic method, but then the dye bound to the particles is redissolved in 80% sulfuric acid and the amount eluted quantified colorimetrically (Passow & Alldredge, 1995b). At least 3–4 replicates are required for each sample, and blanks need to be used to correct for traces of dye taken up by the empty filters. This method is semi-quantitative, because the amount of adsorbed alcian blue is directly related to the weight of a specific polysaccharide (Ramus, 1977). Because of this specificity, the amount of dye bound to TEP is standardized using Gum Xanthan (Passow & Alldredge, 1995b). More precisely, a weight equivalent for the anion density of TEP, rather than the carbon content, is standardized with the exopolymer Gum Xanthan. TEP concentration is expressed in μg Gum Xanthan equivalent liter^{-1} (μg Xeq. l^{-1}).

The method needs to be adjusted if concentrations of non-TEP particles are extremely high, as commonly occurs in sediment trap samples (Passow, Shipe, Murray, Pak, Brzezinski, & Alldredge, 2001). Large amounts of detrital or non-organic matter interfere by covering TEP surfaces so inhibiting the complete staining of TEP. Moreover, high turbidity resulting from the presence of large amounts of suspended matter may interfere with the absorption measurement itself. To avoid such problems, the TEP in each sample is measured in a series of dilutions (using 0.2 μm filtered sea water for dilution), so that each sample is measured at 4–5 different concentrations, and the turbidity is determined by measuring light attenuation by unstained samples. The relationship between the corrected absorptions and concentrations is determined from the linear part of the graph, and TEP concentrations calibrated as described above (Passow et al., 2001).

2.3. Determination of carbon content

The carbon content of TEP (TEP-C) may be estimated either from the size-frequency distribution of TEP, or from the colorimetric measurements calibrated with gum xanthan. The carbon content of TEP sized microscopically is calculated assuming a fractal scaling of size to mass. Assuming a fractal structure implies that the neither the mass nor the encased volume of a particle increase with the length cubed (Jiang & Logan, 1991). Based on an empirical relationship derived from TEP generated by *Thalassiosira weissflogii,* TEP-C was estimated using the following relationship:

$$\mathrm{TEP} - \mathrm{C} = 0.25 * 10^{-6} R^{2.55}$$

where TEP-C is expressed as μg C and R is the volume equivalent spherical radius of TEP in μm and the fractal dimension is assumed to be 2.55 (Mari, 1999). In addition to the assumption of the fractal dimension, this empirically determined relationship between TEP and carbon content also assumes that the quantities of any inclusions of non-TEP material are negligible and that the chemical composition of TEP derived from *T. weissflogii* is representative for the TEP being measured.

The carbon content of TEP can also be estimated from colorimetric determinations:

$$\mathrm{TEP} - \mathrm{C} = 0.75 * \mathrm{TEP}_{\mathrm{colour}}.$$

where the carbon content of TEP (TEP-C) is given in μg and $\mathrm{TEP}_{\mathrm{color}}$ in μg Xeq. (Engel & Passow, 2001). This empirical relationship assumes that the polysaccharide composition of TEP is similar to that released by the mixture of diatoms used to derive this relationship, as species-specific differences were statistically significant (Engel & Passow, 2001). The ratio between TEP-C (μg) and TEP (μg Xeq.) varied between 0.51 and 0.88 between 3 diatom species tested (Engel & Passow, 2001).

2.4. Comparison of methods

Three studies from the Pacific coast, the Baltic Sea and a fresh water lake, respectively, have confirmed that the total amount of TEP determined colorimetrically correlates significantly and linearly with the total area of TEP determined microscopically (Passow & Alldredge, 1995b; Engel, 1998; Berman & Viner-Mozzini, 2001). Measurements of 13 samples collected between January and June 1994 at a station in the Santa Barbara Channel (34°15′ 04″N, 119°54′ 66″ W), ranged from 30 to 300 μg Xeq. l^{-1} and from 2 to 200 mm^2 l^{-1} and revealed a linear relationship where the total area of TEP (TEP_{area}, in mm^2 l^{-1}) can be calculated from colorimetric determinations of TEP_{color} (μg Xeq. l^{-1}) according to:

$$TEP_{area} = 0.65 * TEP_{color} - 4.4; (r^2 = 0.61)$$

(Passow & Alldredge, 1995b). In the Spring of 1997, a second comparison of the two methods was undertaken on samples collected on nine sampling dates during a time series study of a senescent diatom bloom grown in a microcosm, in water from the Baltic Sea. During this experiment TEP concentrations ranged between 877 and 5586 μg Xeq. l^{-1} and between 15 to 200 mm^2 l^{-1}. The linear relationship between both sets of measurements was best described by

$$TEP_{area} = 0.04 * TEP_{color} - 16.5; (r^2 = 0.99)$$

(Engel, 1998).

The total area of TEP was very similar in samples of both data sets. The colorimetric measurements, however, indicate that the amount of dye bound was an order of magnitude higher in the TEP generated by the bloom from the Baltic Sea. This may reflect differences in the characteristics of TEP generated in the two areas, possibly because of differences in salinity, but the differences may also have been the result of methodological differences between the two sets of observation.

In these two studies the species generating TEP were different, so presumably the chemical composition of TEP also differed. As the relationship between the extent of staining and mass is specific for each polysaccharide, differences in chemical composition would have lead to variations in the quantities of stain being bound. The microscopic method assesses the total area of the particles rather than the integrated amounts of stain binding to the particles, so any differences in chemical composition would not be expected to affect the microscopic determinations. Differences in the relationships between the two methods may also result form differences in the structure of TEP. The divalent cations available during formation of algal gels determine, among other properties, the rigidity and size of gels (Kloareg & Quatrano, 1988). Cation concentrations are lower in Baltic Sea water than in surface Pacific water, hence the properties of TEP formed in the two areas may differ, even if their chemical composition does not. A larger volume to mass ratio of TEP would lead to higher values for the microscopic determination, but would have little effect on the colorimetric measurements.

Methodological differences between both studies may, however, explain the discrepancy in the comparisons of the two methods without assuming actual differences in the properties of TEP. Only TEP $>$ 8 μm were counted in the Baltic Sea study, whereas in the study from the Santa Barbara Channel (SBC) TEP $>$ 5 μm were counted. Thus the area of TEP, calculated from microscopic counts, in the Baltic Sea study will be an underestimate compared to that in the SBC study. However, in both studies the colorimetric method included all particles retained on a 0.4 μm filter. Microscopic counts, which can not include particles $<$ 1–5 μm, can always be expected to be lower than the colorimetric determinations. Although the contributions of the smaller particles to the total area is small, this methodological difference may explain the discrepancy, if small TEP, which have a high relative mass, also have a high relative anion density. Other methodological differences presumably had a minor impact. For example, fresh seawater samples were used for the colorimetric determination of TEP in the study from the SBC, but formalin-fixed samples were used in the Baltic Sea study. However, earlier comparisons between fresh and formalin-fixed samples

showed no differences except if mucus-colony forming species like *Phaeocystis* spp. were present (Passow & Alldredge, 1995b), but such species were absent from the Baltic Sea and Pacific samples. In the Baltic Sea study TEP were counted and sized with the help of an image analysis system, but were sized and counted manually in the SBC study. The sizing of odd-shaped particles is potentially more accurate using the image analysis system; however, the system tends to ignore lightly-stained particles because of their lack in contrast.

In a third study the colorimetric and microscopic technique were compared indirectly. The carbon content of TEP was estimated both from counts and from colorimetric determinations conducted on aliquots from samples collected in spring 1999 in the Baltic Sea (Engel & Passow, 2001). The carbon content of TEP derived from both methods was not significantly different, if the conversion factors derived from *Thalassiosira weissflogii* were used for both conversions, although variability was high and values calculated from the microscopic enumeration tended to be lower. Based on theoretical considerations, it is argued that the microscopic technique would systematically underestimate TEP-carbon concentration, whereas the colorimetric method would overestimate carbon content, especially in an area where colony forming cyanobacteria are common, such as the Baltic Sea in summer. Overall, both estimates of the carbon content of TEP in natural systems were consistent both with each other and with auxiliary data (Engel & Passow, 2001).

Both, the colorimetric and the microscopic methods for determining TEP have advantages and disadvantages, so the choice of the optimum method depends on the information being sought. Microscopic enumeration is the better technique when information on the size distribution of TEP is important. However, such enumerations and calculations of the total area and total volume of stained particles are slow compared to the colorimetric method, and the sizing of odd-shaped particles and assumptions necessary for making the volume and/or area calculations are prone to error. Conversely, although the colorimetric method is faster, easier and a better measure of the mass, it yields no information on size distributions. TEP may be overestimated by the colorimetric method if organisms with stainable coatings are abundant, as TEP per definition should not include cell coatings. Usually this is not a problem but it can locally be important, so it is recommended that control slides are prepared when the colorimetric method is being used in areas where the species composition is unknown.

3. Abundance and distribution of TEP

The availability of two simple methods to measure TEP has enabled their measurement to be routine, and so providing us with a growing understanding of the role of TEP in aquatic systems. They have been found to be abundant in all waters whether fresh or marine, with concentrations of TEP > 5 μm varying between 1 and 8000 ml^{-1} and concentrations of TEP > 2 μm varying between 3000 and 40000 ml^{-1} (Table 1). Generally, peak concentrations of TEP were associated with phytoplankton blooms (Passow & Alldredge, 1994; Kozlowski & Vernet, 1995; Passow, Kozlowski & Vernet, 1995; Riebesell, Reigstad, Wassmann, Noji & Passow, 1995; Mari & Kiørboe, 1996; Grossart & Simon, 1997; Hong, Smith & White, 1997; Alldredge, Passow & Haddock, 1998; Grossart, Berman, Simon & Pohlmann, 1998; Mari & Burd, 1998; Passow et al., 2001; Reigstad, Wassmann, Ratkova & Riser, pers. com.), but high concentrations have also been found to be associated with macroalgae (Ramaiah, Yoshikawa, & Furuya, 2001). Higher TEP concentrations have been found in the euphotic zone than below it, and in coastal areas compared to the open ocean (Passow & Alldredge, 1994; Engel & Passow, 2001). The temporal and spatial distribution patterns of TEP suggest there is a coupling with phytoplankton.

The maximum observed TEP concentrations, 11000 μg Xeq. l^{-1} were determined colorimetrically in samples from the Adriatic Sea (Table 1), an area known for its large mucus production. In most other areas, peak concentrations are commonly around 1000 μg Xeq. l^{-1} during bloom periods (Table 1). Very

Table 1
Global distribution of TEP: Concentrations of TEP are given either as abundance (third column), as total area (fourth column), volume fraction or $mm^3\ l^{-1}$ (fifth column) or as a weight equivalent calibrated with Gum Xanthan. Either ranges or average values are presented. Where size frequency distributions were calculated ($dN/dl = al^{-b}$) the value of the slope b is also shown (third column). See text for detail[a]

Sample area	Sampling time/depths	TEP counts[g] $10^3\ l^{-1}$	TEP-area $mm^2\ l^{-1}$	TEP-volume fraction ppm	TEP μg Xeq. l^{-1}	Reference
Pacific						
SBM station 1, CA, USA	94/95, (1-year), ≤ 20 m	NV	NV	(4)[e]	89, max: 461, $n = 124$	unpubl. Passow
SBM station 2 , CA, USA	95/97, (2-years), ≤ 20 m	NV	NV	(8; max 39)[e]	213, max: 1042, $n = 188$	Passow et al., 2001
SBC, CA, USA	Summer 92, 5–20 m	25–625, $b = 1.7–2.8$	1–2200	2–423	NV	Passow et al., 1994
SBC, CA, USA	Summer 93, ≤20 m	NV	NV	(3–12)[e]	80–310, $n = 8$	Passow and Alldredge, 1995b
SBC , CA, USA	Spring 97, ≤75 m	NV	NV	(7)	183	Dunne et al., 2003 (pers. com.)
East Sound, WA, USA	Spring 94; ≤20 m	NV	NV	(3)[e]	83, max: 159, $n = 50$	Kiørboe et al., 1996
SBC , CA, USA	6/95, 10 m	193–625	NV	(3)[e]	72, max.: 74, $n = 3$	Passow, 2000
Monterey Bay, CA, USA	7/93, ≤10m	NV	NV	(2–12)[e]	50–310, $n = 18$	Passow and Alldredge, 1995b
Monterey Bay, CA, USA	8/92; 0–400m	877–5168, $b = 2.7–3.6$	0.2–650	4–5	NV	Passow and Alldredge, 1994
Subarctic ria, Japan[h]	1/98–4/98	100–3400	NV	(36–93))[e]	901–1442, max.: 2321	Ramaiah et al., 2001
Great Barrier Reef, Austr.	12/99–2/00; 5m	NV	NV	(1–32)[e]	23–791, $n = 41$	Wild, 2000
ALOHA (off Hawai)	12/1999	NV	NV	(2.5–19)[e]	253, max.: 477	Prieto, pers. com.

(*continued on next page*)

Table 1 (*continued*)

Sample area	Sampling time/depths	TEP counts[g] 10^3 l^{-1}	TEP-area mm^2 l^{-1}	TEP-volume fraction ppm	TEP µg Xeq. l^{-1}	Reference
Atlantic						
BATS, off Bermuda	3/93, 300–1500m	2-7, b = 2.2–3.7	0.2–4.6	0.002–0.08	NV	Passow and Alldredge, 1994
NE Atlantic, 47°N,	Summer 96, surface	NV	NV	−2	53, 27–294	Engel et al., 1997
NE Atlantic, 47°N,	Fall 96, surface	NV	NV	(2)	36 ± 13	Engel and Passow, 2001
Benguela upwelling current	2/95, ≤30m	NV, b = 3.2 ± 0.09	NV	5–16	NV	Kiørboe et al., 1998
Indian Ocean						
Arabian Sea	0–1000 m	130–350	(114–860)[d]	(2–53)[d]	NV[b]	Kumar et al., 1998
Bay of Bengal	0–1000 m	4400–7790	(185–1350)[d]	(1–14)[d]	NV[b]	Kumar et al., 1998
Polar Oceans						
Norwegian Fjords	Spring 92, ≤ 36 m	NV	NV	(8)[e]	193, max: 258, n = 16	Riebesell et al., 1995
Norwegian subarctic fjord	96, (1-year), ≤ 175 m	NV	NV	(max: 57)[e]	max: 1415	Reigstad et al., subm.
Chukchi Sea, Alaska, *in ice*	Spring 99	NV	NV	(40–308)[e]	1003–7667	Krembs et al., 2000
Laptev Sea, *in ice*	Summer 95	NV; b = 1.9	1600	0–48	NV	Krembs and Engel, 2001
Laptev Sea, under ice	Summer 95	NV; b = 1.2–3.7	100	0-0.8	NV	Krembs and Engel, 2001
off Anvers Is. 64°S; 64°W	Spring 94/95, ≤ 6 m	NV	NV	(8)[e]	207, max: 407, n = 24	Passow et al., 1995
Ross Sea	Spring 94	NV	NV	(12)[e]	308, max: 2800	Hong et al., 1997
Kita-no-seto Strait,	Summer 93/94, ≤ 15 m	26–41,	39–1178[d]		NV	Marchant et al., 1996
Mediterranean Sea						
Gulf of Cadiz	Summer 97	NV	NV	-4	100, max: 600	Garcia et al., 2002
N. Adriatic Sea	4/96, 1m	NV, b = 2.7–2.9		(64–442)[e]	1600–11000	Engel, pers. com.
N. Adriatic Sea	Fall 93, ≤ 20m	0–2400	400–1750	(4–35)	NV	Schuster and Herndl, 1995
Strait of Gibraltar	2/99	NV	NV	(1–4)[e]	41, max.: 93	Prieto, pers. com.

Table 1 (*continued*)

Sample area	Sampling time/depths	TEP counts[g] 10^3 l^{-1}	TEP-area mm^2 l^{-1}	TEP-volume fraction ppm	TEP µg Xeq. l^{-1}	Reference
Brackish Water						
Kattegat	Spring 94, ≤ 30m	3000–60000 b = 1.7–5.4	NV	0.3–9	NV	Mari and Kiørboe, 1996
Kattegat	95/96, (1-year), ≤ 30m	50000–380000 b = 2.6–3.4	NV	3–310	NV	Mari and Burd, 1998
Delaware Bay	Spring	NV	NV	(26–42)[e]	653–1034[f]	B. Logan & D. Kirchmann, pers. com.
Baltic Sea	Spring 97	NV		(52)[e]	1300	Engel, 2000
Baltic Sea	Summer 99	NV		(10)	241 ± 66	Engel and Passow, 2001
Central Baltic Sea	Summer 99	60000–130000	NV	2–7; (6–13)	145–322	Engel et al., 2002b
Kieler Bucht	Spring 96	NV	NV	(14–32)[e]	50–200	Kraus, 1997
Fresh water						
Lake Constanz (Germany)	93 (1-year)	≤ 2500	NV	NV	NV	Grossart and Simon, 1997
Lake Kinneret (Israel)	Fall 95	700–7000	NV	NV	NV	Grossart et al., 1998
Lake Kinneret (Israel)	12/97–1/00	440–2500	897–15073	80–5503	NV	Berman and Viner-Mozzini, 2001
Lake Frederiksborg, Denmark	Summer 95	84000–870000[c] b = 2.2 ± 0.2	NV	NV	NV	Worm and Søndergaard, 1998b
River Danube	Summer/fall 93	Present (NV)	NV	NV	NV	Berger et al., 1996
Mono Lake, CA, (USA)	Spring 93	Present (NV)	NV	NV	NV	Passow, unpub.

Max: maximum values; n: number of samples; NV: no value; (): estimates from reported data; SBM: Santa Barbara Mooring Station; SBC: Santa Barbara Channel off the Californian coast; BATS: Bermuda times series station.

[a] $dN/dl = a\ l^{-b}$ where l is the length, a and b constants.

[b] Algenic Acid used as a standard: 25–100 mg AAeq. l^{-1} in Arabian Sea and 7–13 mg AAeq. l^{-1} in the Bay of Bengal.

[c] pH of staining solution differs (not acidified).

[d] Calculated from average length and average abundance assuming circular and spherical particles, respectively.

[e] Estimated from colorimetric determination by first calculating TEP-carbon assuming a carbon conversion factor of TEP − carbon = 0.7 TEP_{color}.; The volume fraction is then estimated from TEP-carbon assuming a carbon density of 17.4 g carbon dm^{-3} TEP (Engel & Passow, 2001).

[f] Sampled along a salinity gradient

[g] Because TEP numbers decrease exponentially with size, the total number concentration depends heavily on the smallest size class counted: TEP < 3 µm were included by (Mari & Kiørboe, 1996; Kiørboe et al., 1998; Mari & Burd, 1998), TEP > 3 or 5 µm were counted (Passow & Alldredge, 1994; Marchant, Kentaro & Masanobu, 1996; Grossart & Simon, 1997; Kumar, Sarma, Ramaiah, Gauns & De Sousa, 1998; Passow, 2000; Ramaiah, Yoshikawa & Furuya, 2001).

[h] Macroalgae dominated TEP production at times.

high concentrations of TEP have also been found in sea ice with values ranging from 1000 to 7700 μg Xeq. TEP per liter melted ice (Krembs, Eiken, Junge, & Deming, 2002).

Expressed as total area, concentrations of TEP varied between 0.2 and >2000 $mm^2\ l^{-1}$, with peak values of >500 $mm^2\ l^{-1}$ found in coastal California, the coastal Indian Ocean, the Kattegat and the Adriatic Sea (Table 1). In the open, more oligotrophic Atlantic Ocean values were two orders of magnitude lower.

Assuming TEP exist as spherical particles with an equivalent spherical diameter (ESD) equal to the cross section of TEP in two dimensions, the volume fraction of TEP (total volume of TEP per volume of water) can be estimated from microscopic determination of TEP. Reported values of TEP range from 0.1 to >300 ppm (parts per million; Table 1). In Table 1 the volume fractions of TEP were also estimated from colorimetric determinations as suggested in Engel and Passow (2001) to allow a comparison to be made between TEP concentrations determined either microscopically or colorimetrically. Since the assumptions made regarding the conversion between length and volume of TEP used for this calculation (e.g. fractal scaling of TEP = 2.55) may not be valid in all systems, these values must be considered to be approximate, and calculated to allow rough comparisons to be made between studies, which have used different methods. The total volume fraction of TEP varied over 4 orders of magnitude, with the extreme low values (<< 1 ppm) being reported from samples taken below 300 m in the open Atlantic (Table 1). Average values in most coastal systems normally ranged between 1 and 60 ppm, but the peak concentrations of between 100 and 500 ppm were observed during intense blooms in different coastal systems and in sea ice (Fig. 3). Differences between data collected in different regions, appear to reflect predominately the prevailing status of the ecosystem, rather than any systematic regional differences. A large range between minimum and maximum values was not only observed in areas where intense blooms were encountered, but also where TEP were quantified during more oligotrophic conditions (e.g. coastal Pacific, see Fig. 3). It may, for example, be expected that the maximum TEP concentrations in the coastal Atlantic waters will prove to be very high during a diatom bloom, but no such measurements exist currently. The high minimum value for estuaries on the other hand may reflect a consistent pattern, because the presence of a salinity gradient may enhance the formation of TEP.

In general TEP are found to be in the same size and abundance range as phytoplankton, i.e. the volume fraction of TEP lies in the same range or higher than that of phytoplankton (Mari & Burd, 1998), emphasizing that TEP contribute significantly to the total particle pool. A major impact on particle dynamics may therefore be expected from their abundance alone. But specific properties of these gel particles, such as their flexibility, their stickiness, their high carbon content and their high C:N ratio, also contribute to their large impact on pelagic processes.

4. Properties of TEP

TEP are a chemically diverse and heterogeneous group of particles. They are exopolymers, but not all exopolymeric substances (EPS) occur as TEP or can form TEP. The precise chemical composition of TEP is unknown, but is known to be highly variable, because the chemical composition of TEP (and their precursors) depend on the species releasing them and the prevailing growth conditions (see below). The physical properties of TEP, such as volume and stability also depend on environmental conditions. Even so considering these particles as a single category can be justified. Chemically, TEP are distinct from the bulk particulate or dissolved organic carbohydrate pools (Mopper et al., 1995; Zhou, Mopper, & Passow, 1998). In contrast to solid particles, they exhibit the properties of gels, such as high flexibility and their volume to mass ratios depend on environmental factors. They are highly sticky, which is another important characteristic.

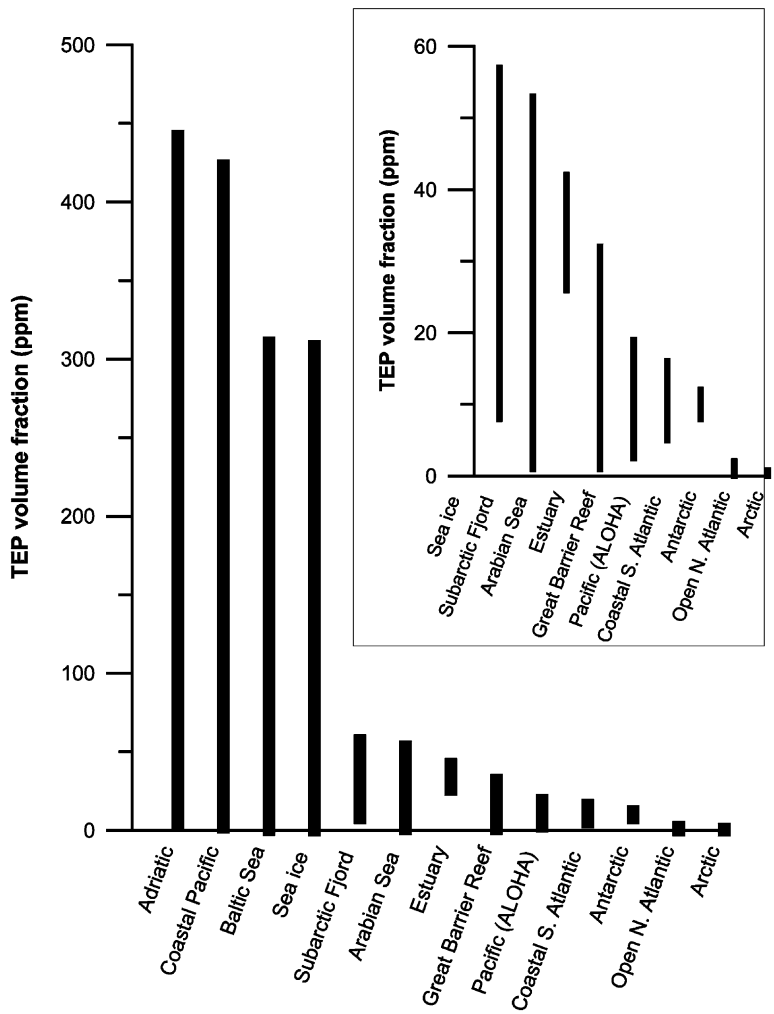

Fig. 3. The range of the amount of TEP (measured as volume fraction in ppm) in different regions of the oceans. High maximal values were observed in areas where large phytoplankton blooms were observed. The relatively high minimum value observed in an estuary may be the result of salinity effects, which enhance the formation of TEP (see text for detail).

4.1. Chemical composition

TEP are particles stained by alcian blue, and so by definition, consist largely of acidic polysaccharides. They disappear with the addition of glucosidase (Smith, Steward, Long, & Azam, 1995), confirming that they consist predominantly of sugars. TEP-rich material extracted from water collected at four different oceanic sites consisted of highly surface-active material, which was enriched in fucose, rahmnose and to a lesser degree arabinose, but was relatively depleted in glucose and galactose (Mopper et al., 1995; Zhou, Mopper & Passow, 1998). Only traces of uronic acids ($R\text{-}COO^-$) were found in the material sampled (Mopper et al., 1995). The acidity of TEP from all sites predominantly resulted from the presence of sulfate half ester ($R\text{-}OSO_{3-}$) groups (Zhou, Mopper & Passow, 1998). Sulfated polysaccharide mucilage has been reported to occur in the excretion products of many marine organisms, especially diatoms, but are rare in

the excretion products of fresh water organisms (Kloareg & Quatrano, 1988). This suggests that in fresh water the chemical composition and thus the properties and formation mechanisms of TEP may differ.

The chemical composition of TEP suggests that they are formed from phytoplankton excretion products, which are released into the water as dissolved organic matter (DOM). The chemical composition of phytoplankton excretion products is known to vary between species and with physiological status (for reviews, see Arnosti, 1993; Myklestad, 1995; Aluwihare & Repeta, 1999), but the predominant sugars (fucose, rhamnose and arabinose) are the same as in TEP (Myklestad, Haug, & Larsen, 1972). In addition, the polysaccharide composition of both phytoplankton exudates and TEP closely resemble the polysaccharides that are identified as major constituents of naturally occurring high molecular weight DOM from seawater (Aluwihare, Repeta, & Chen, 1997; Aluwihare & Repeta, 1999). Moreover, the seasonal patterns of DOM released by phytoplankton and TEP are similar, providing evidence for TEP being formed from DOM (Kepkay, Niven, & Jellett, 1997; Mari & Burd, 1998).

All measurements of the carbon content of TEP indicate that, although they seem likely to consist predominantly of water, their carbon content in natural systems can be very high. Estimates of TEP-C calculated from microscopic or colorimetric determinations suggest that the carbon content of TEP lies in the same range as that of phytoplankton, suggesting that TEP make a large and significant contribution to the carbon pool that can not be ignored (Mari, 1999; Engel & Passow, 2001). However, the amount of TEP that gets included in standard measurements of POC will vary, depending on their size distribution and characteristics (Engel & Passow, 2001). Because of their flexibility, TEP may pass through pores of filters smaller than their apparent size, so the GF/F-filters commonly used to measure POC fail to retain a large fraction of TEP (Passow & Alldredge, 1995b).

Other types of material may be enclosed in or adsorbed on to TEP. At times, proteinaceous particles appear to be associated with TEP (Long & Azam, 1996) and inclusions, that may be lipid droplets, have also been observed (pers. com. Rossella Amodio). The C:N ratio of TEP is generally appreciably higher than the normal Redfield ratio of organisms (Redfield, Ketchum, Richards & Hill, 1963). The mean molar C:N ratios of TEP derived both from cultures grown under different conditions and natural diatom populations was 26. These C:N ratios are often lower than would be expected if they were purely polysaccharides, suggesting that nitrogen rich substances like amino acids become adsorbed on to TEP (Engel & Passow, 2001). Because TEP have large surface areas and high binding affinities (see below), other solutes, including trace elements and heavy metals, become associated with them.

4.2. Physical characteristics

TEP are gels, which exist at the interface between particulate and dissolved material. Their physical characteristics can be described in terms of polymer gel theory (Chin, Orellana, & Verdugo, 1998). The polymer network entraps seawater (the solvent), which is in thermodynamic equilibrium with the surrounding seawater. Gels can undergo reversible phase transitions between condensed and hydrated phases (Tanaka, 1981). Consequently the size and volume of TEP may change without significant changes in mass. These phase transitions depend on environmental factors like pH, temperature, pressure and ion density. So like other mucilage gels, TEP undergo continuous chemical reactions involving dehydration, aging and other phenomena, which are in part reversible and in part irreversible. The physico-chemical properties of TEP thus depend on their history and specific formation conditions (Kloareg & Quatrano, 1988).

4.3. Size distribution

The size range of TEP and precursors ranges from colloidal (1 kDa) to 100s of micrometers. On average the exponent b of the size frequency distribution of TEP $dN/dl = a\, l^{-b}$ (see above) is close to 3 (Mari &

Kiørboe, 1996; Mari & Burd, 1998), and ranges from 1.7 to 3.7 (Table 1). During the aggregation phase of diatom blooms, *b* is around 2 or lower (0.7–2.2), indicating a reduction in the fraction of small particles, as aggregation dominates TEP size distribution (Passow & Alldredge, 1994; Engel, 1998). The exponent *b* of the size distribution can therefore be used as an indicator for the degree of aggregation. In sea ice, observed TEP size distributions have an average *b* of 1.9, with larger values occurring in the water directly below the ice (Krembs & Engel, 2001), suggesting a differing formation mechanism (see below). As well as aggregation, other processes such as bacterial utilization or zooplankton activity will affect the size distributions of TEP (Passow & Alldredge, 1994); activities of copepods, for example, result in the formation of larger TEP, and shift the size distribution upward (Prieto, Sommer, Stibor, & Koeve, 2001).

Size frequency distributions, the size specific carbon content and bacterial colonization patterns, all suggest that the nature of TEP is fractal (Mari & Kiørboe, 1996; Mari & Burd, 1998; Mari, 1999). Fractal dimensions of 2.55 (Mari & Burd, 1998; Mari, 1999) and 1.5 (Mari & Kiørboe, 1996) have been reported in naturally occurring TEP. Although many processes potentially appear to be capable of altering the size distributions of TEP, it is the production of TEP by coagulation of colloidal precursors and the losses of TEP by aggregation with solid particles that significantly shape the size distributions of TEP found in situ.

As gels, TEP are extremely flexible. This high flexibility, which allows them to pass through pores many times smaller than their apparent size, poses a technical challenge, as plankton research relies heavily on the separation between dissolved and particulate matter. Because TEP are not retained quantitatively on GF/F filters, some fraction of TEP is often considered dissolved, although in most respects they behave as particles (e.g. removal by aggregation or filtration is possible).

4.4. Stickiness

The interactions between TEP and other particles are primarily determined by the high stickiness (probability that two particles remain attached after collision) of TEP. The high fraction of sulfate half-ester groups explains the strong tendency of TEP to form metal ion bridges and hydrogen bonds and makes these polysaccharides highly surface-active (Mopper et al., 1995). It is extremely difficult to measure stickiness of TEP directly, because it is difficult to isolate them. Because the overall stickiness of natural particles of different stickiness is determined by the few sticky particles (Hansen & Kiørboe, 1997), the stickiness of TEP may be estimated from measurements of a combined stickiness coefficient (α) by evaluating the relative contribution of TEP to overall stickiness (Kiørboe & Hansen, 1993; Dam & Drapeau, 1995).

The combined stickiness coefficient of a sample containing different particles, such as phytoplankton, bacteria, detritus and TEP, is determined by measuring the aggregation rate and the size frequency distribution of all particles in an environment of constant and known laminar shear, e.g. in a Couette flocculator. Such determinations of combined α indicate that during diatom blooms the overall stickiness of particles is largely determined by the high stickiness of TEP, which exhibit an alpha larger than 0.1 (Dam & Drapeau, 1995; Engel, 2000). The same type of relationship between normalized TEP concentration and overall stickiness was also observed in a batch culture of *Chaetoceros affinis* (Kiørboe & Hansen, 1993). The stickiness coefficient of old, bacteria-covered mucus particles, which were generated by a batch culture of *Coscinodiscus sp.* were also very high ($\alpha = 0.7$) (Kiørboe & Hansen, 1993). Stickiness of most solid particles, including detritus, sediment and phytoplankton, has generally been estimated to be low with attachment probabilities $<1\%$ ($\alpha = 10^{-2}$–10^{-4}) (Gibbs, 1983; Kiørboe, Andersen, & Dam, 1990; Alldredge & Mcgillivary, 1991).

The stickiness of TEP compared to phytoplankton can also be estimated from changes in particle size frequency distributions during the aggregation of blooms. During two diatom blooms, a stickiness of TEP > 0.1 was suggested from the rate of decrease of TEP, whereas estimates for the stickiness of cells were three orders of magnitude lower (Passow, Alldredge, & Logan, 1994; Logan, Passow, Alldredge, Grossart, & Simon, 1995).

Studies estimating stickiness of TEP thus suggest that generally the stickiness coefficient of TEP is >0.1, which is 2–4 orders of magnitude higher than that of most other particles. However, there are exceptions; for example, TEP from non-diatom origin may not be as sticky (Kiørboe & Hansen, 1993; Passow & Alldredge, 1994), and cells of some diatom species can be sticky (Kiørboe & Hansen, 1993; Passow, Alldredge & Logan, 1994; Logan, Passow, Alldredge, Grossart & Simon, 1995).

5. Formation of TEP

Dissolved organic matter (DOM), which includes colloids (Koike, Hara, Terauchi, & Kogure, 1990; Wells & Goldberg, 1991; Longhurst, Koike, Li, Rodriguez, Dickie, Kepay et al., 1992; Wells & Goldberg, 1992) constitutes the largest pool of organic carbon in the ocean and knowledge of the rates and mechanisms by which dissolved organic substances are produced, destroyed, or converted to particulate form is essential if we are to gain a predictive understanding of marine biogeochemical cycling. The pathways by which DOM is converted to particulate organic matter (POM) are particularly important because these different forms of organic matter have different dynamics and are subject to different fates and have differing roles in the chemistry and biology of the ocean. In aquatic ecosystems bacterial uptake has been assumed to be the major pathway whereby DOM is transformed into particles. The abiotic formation of particles from dissolved substances by bubbling was first discovered about 35 years ago (Riley, 1963; Sutcliffe, Baylor, & Menzel, 1963) and despite being confirmed (Johnson & Cooke, 1980; Johnson, Zhou, & Wangersky, 1986) has not been considered significant enough to be included in models and concepts on carbon cycling. But the discovery of the occurrence and importance of TEP suggests otherwise, implying that TEP formation is a major pathway whereby DOM is converted to POM.

5.1. Formation mechanisms

The production of TEP from dissolved material involves two separate steps, one abiotic and one biotic. TEP are formed spontaneously from dissolved precursor substances (Passow, 2000), which contribute appreciably to the colloidal DOM pool in aquatic systems (Leppard, 1997; Santschi et al., 1998). This abiotic formation of TEP depends on environmental parameters (turbulence, ion density, concentration of inorganic colloids) as well as on the types and concentrations of the precursors present. These precursors are, however, released by aquatic organisms, and thus their abundances and properties depend not only on the composition of the pelagic community, but also on the physiological status of the individual organisms, which is a complex function of their growth conditions. In a separate pathway, TEP are formed via the release of particulate material by the organisms.

Colloidal TEP-precursors consist of fibrils 1–3 nanometers in diameter, and 100s of nanometers long (Leppard, Massalski, & Lean, 1977). Their fibrillar nature, enables TEP-precursors to pass through 8 KDa pore size membranes (Passow, 2000), although polysaccharides have high molecular weights (100–300 KDa) (Decho, 1990). During exponential growth phytoplankton cells release fibrillar TEP-precursors from their cell surfaces into the water (Leppard, Massalski & Lean, 1977; Leppard, Burnison, & Buffle, 1990; Leppard, 1995; Leppard, Heissenberger, & Herndl, 1996; Leppard, West, Flannigan, Carson, & Lott, 1997). Polysaccharide fibrils are also released from capsular material of metabolically active bacteria (Stoderegger & Herndl, 1998). Intracellular substances released into the water during lysis or breakage of cells as a result of bacterial or viral infections or during sloppy feeding also contribute to the pool of TEP precursors (Baldi, Minacci, Saliot, Mejanelle, Mozetic, Turk et al., 1997; Shibata, Kogure, Koike, & Ohwada, 1997).

Such fibrillar polymers coagulate to form submicron-aggregates (Wells & Goldberg, 1993; Kepkay, 1994), and also form submicron gels by gelation (assembly of free polymers) and annealing (Chin, Orel-

lana & Verdugo, 1998). These submicron particles coagulate further to form larger aggregates and eventually TEP (Fig. 4) (Kepkay, 2000). Heteroaggregation between polymer fibrils and compact colloids may explain the formation of submicron aggregates (Buffle, Wilkinson, Stoll, Filella, & Zhang, 1998). Nano- and micro-gels are formed from free fibrillar polymers, which self-assemble spontaneously to form 3-dimensional tangled polymer networks (Chin, Orellana & Verdugo, 1998). The formation of such gels is promoted or stabilized by cations, especially Ca^{2+} as macromolecules bond by cationic bridge formation (Kloareg & Quatrano, 1988) and hydrogen bonding (Chin, Orellana & Verdugo, 1998). TEP disintegrate rapidly in the presence of EDTA (0.1–1 M), a chelating agent of Ca^{2+} and Mg^{2+} (Alldredge, Passow & Logan, 1993), confirming the importance of Ca^{2+} in maintaining the structural integrity of TEP. The concentration of Ca^{2+} can be low in some fresh water systems, suggesting that this formation mode may be rarer in some lakes. Functionally, both the submicron aggregates and the submicron gels appear to be similar (Kepkay, 2000).

The formation of TEP from fibrillar precursors links the dissolved and particulate pools, not through microbial activity, but by the spontaneous abiotic formation of gel particles or by aggregation. While precursors and their submicrometer aggregates behave like colloids (Leppard, 1995), they act as particles when they swell to form TEP.

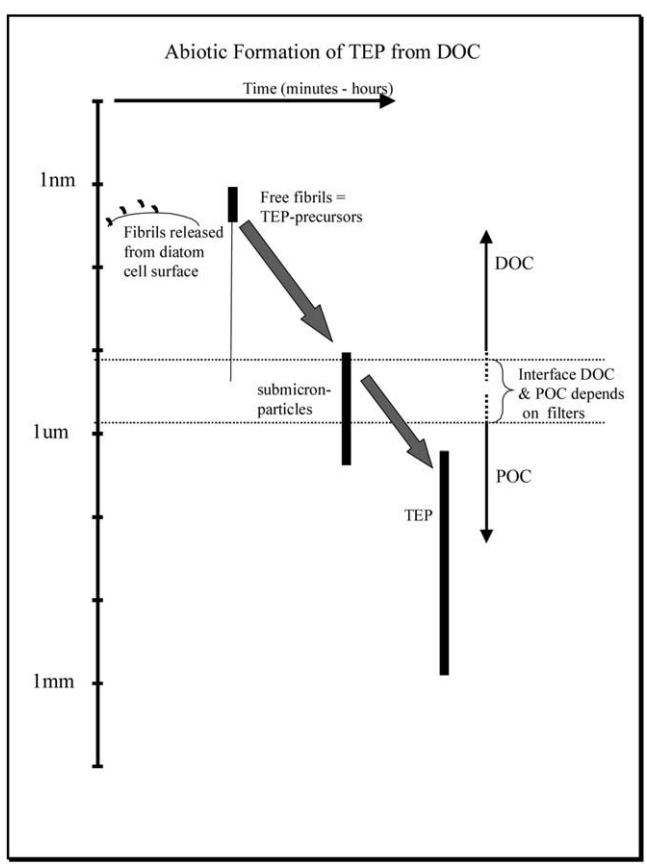

Fig. 4. Concept of the abiotic formation of new TEP from precursors after all TEP is removed from the water. TEP and their precursors exist on a continuum of size ranges from colloidal to particulate matter. Fibrillar precursors, which are only a few nanometer wide, but can be several 100 nm long, first form submicron particles by gelation, annealing and aggregation, and eventually TEP. The formation of TEP links colloidal DOM with the pool of POM.

The abiotic formation of new TEP from precursors in the size fraction between 0.4 and 1.0 μm is promoted by surface coagulation onto bubbles (Mopper et al., 1995; Zhou, Mopper & Passow, 1998; Mari, 1999). No TEP were formed by bubbling 0.45 μm-filtered seawater and the TEP-poor material extracted by bubbling material $\leq$0.45 μm differed chemically from the TEP-rich material extracted by bubbling 1.0 μm-prefiltered water (Mopper et al., 1995; Zhou, Mopper & Passow, 1998).

Abiotic TEP formation from precursors $<$0.2 μm proved to be enhanced by both laminar (Passow, 2000) and turbulent shear (Engel & Passow, 2001). The formation of TEP by shear is very efficient (Passow, 2000), suggesting that the mechanism of TEP formation by shear differs from that by bubbling (Kepkay, 1994). Presumably, shear detangles and stretches individual polymer fibrils, enhancing their alignment and the formation of larger particles.

TEP formation was also enhanced by adsorption onto particles already present in the water (Kepkay, 1994; Passow & Wassmann, 1994). The formation of particulate matter from colloids by scavenging depends on the fractal dimension, size, concentration and sinking velocity of the scavenging particles or aggregates as well as on the concentration of colloids (Li & Logan, 1997a; Li & Logan, 1997b). Particulate matter, which is formed by scavenging, enlarges existing particles, but does not increase particle numbers.

The amount of TEP formed from 0.2 μm filtered seawater depends on the concentration of TEP-precursors, which varies depending on the history of the seawater used (Passow, 2000). After TEP has been removed by filtration, almost the same amount of TEP can again be formed from precursors, which suggests that only a very small fraction of precursors exist as TEP (Passow, 2002). An estimated 10% of all polysaccharide material exists as nanogels (Chin, Orellana & Verdugo, 1998), and the fraction, which exists as TEP is presumably lower. Removed TEP are replenished rapidly.

The size frequency distributions of TEP observed in situ as well as the observed relationships between TEP size and attached bacteria are consistent with the hypothesis that TEP in marine systems are predominantly formed by coagulation of colloidal precursors (Mari & Kiørboe, 1996; Mari & Burd, 1998). The different size distribution of TEP observed in sea ice indicates that in the ice the TEP is not originating from the aggregation of colloidal particles. This is supported further by the observation that in the ice the size distribution was very constant, whereas in the underlying water the variability was very high (*b* varied between 1 and 4). TEP from within the ice may have been formed when film-like TEP covering the ice surface is fragmented during melting.

TEP may, however, also form when pieces of mucus detach from phytoplankton cell surfaces (Kiørboe & Hansen, 1993). Some diatoms and cyanobacteria excrete an alcian blue-stainable cell surface coating, which forms free TEP when pieces slough off, often during the decline of a bloom (Schuster & Herndl, 1995; Grossart & Simon, 1997; Grossart, Berman, Simon & Pohlmann, 1998). Bacterial hydrolysis of mucus from the surface of diatom cells may enhance the formation of free TEP (Smith, Steward, Long & Azam, 1995). TEP are also formed during the sloughing or disintegration of large colonies of *Phaeocystis spp.* both during their growth and their senescence (Passow & Wassmann, 1994; Hong, Smith & White, 1997; Passow, 2000). Formation of TEP by direct release of particulate material or from detritus may temporally or locally dominate TEP production and may be especially important in some lakes (Grossart & Simon, 1997; Grossart, Berman, Simon & Pohlmann, 1998; Berman & Viner-Mozzini, 2001).

5.2. Release of TEP or TEP-precursors

A wide variety of plants, animals and microbes release mucus-like substances, which fulfill varying ecological functions in marine environments. Excretions of extracellular products and their ecological significance have been extensively studied (see reviews by Decho, 1990; Hoagland, Rosowski, Gretz & Roemaer, 1993; Myklestad, 1995; Costerton, 1999). EPS occur especially copiously, whenever microbes are associated with surfaces and particles, e.g. at the sediment surface or in aggregates, and during stationary

phase. TEP-precursors appear to be secreted by unattached phytoplankton during exponential or stationary growth phase.

In situ peak concentrations of TEP were usually associated with phytoplankton blooms, especially in blooms dominated by diatoms (Passow & Alldredge, 1994; Passow et al., 1995; Mari & Kiørboe, 1996; Grossart & Simon, 1997; Mari & Burd, 1998; Passow et al., 2001; Reigstad et al. pers.comm.) or *Phaeocystis* spp. (Riebesell et al., 1995; Hong et al., 1997; Reigstad et al. pers.comm.), although not every diatom bloom was associated with high concentrations of TEP (Kiørboe, Hansen, Alldredge, Jackson, Passow, Dam et al., 1996; Reigstad et al. pers.comm.). High concentrations of TEP have also been monitored during blooms dominated by dinoflagellates (Passow & Alldredge, 1994; Alldredge, Passow & Haddock, 1998; Berman & Viner-Mozzini, 2001), cyanobacteria (Grossart & Simon, 1997; Grossart, Berman, Simon & Pohlmann, 1998) and cryptomonads (Kozlowski & Vernet, 1995; Passow, Kozlowski & Vernet, 1995). Batch culture experiments confirm that phytoplankton are a main source of TEP (Table 2) (Kiørboe & Hansen, 1993; Passow & Alldredge, 1994; Passow, 2002).

TEP and chl. *a* concentrations are significantly correlated during the exponential growth of batch cultures or phytoplankton blooms (Passow, 2002). The relationship is specific for each individual bloom, but no general overall relationship between TEP and chl. *a* can be derived (Herndl, 1988; Berman & Viner-Mozzini, 2001), as too many other processes are interfering. During growth of a bloom, the concentration of TEP (μg Xeq. l^{-1}) can be estimated from the concentration of chl. *a* (μg l^{-1}) using the following empirical relationship:

$$\text{TEP} = \alpha(\text{chl}.a)^{\beta}$$

The exact values for α and β vary (Table 2, Fig. 5). Values of β are generally <1, suggesting that either loss processes counter-balance production and accumulation of TEP or that the specific production rate of TEP decreases as the blooms progress, supporting the hypothesis that TEP formation is a function of

Table 2
The relationship between TEP and chl. *a* during the growth phase (positive growth rates) of batch cultures, mesocosm blooms (1400 liter) and in situ blooms: TEP = α (Chl. *a*)$^{\beta}$, in μg Xeq. l^{-1} and in μg l^{-1}

Species	Sampling site	α	β	N	r^2	p	Reference
1. *C. affinis*	Batch culture	152	1.06	6	0.94	<0.001	Passow, 2002
2. *T. weissflogii*	Batch culture	221	0.68	5	0.94	<0.002	Passow, 2002
3. *N. angularis*	Batch culture	204	0.46	12	0.91	<0.001	Passow, 2002
4. *C. affinis*[a]	Batch culture	106	0.88	42	0.71	<0.001	Passow, 2002
5. *C. neogracilis*[b]	Batch culture	ND	0.96	14	0.90	<0.001	Calculated from Waite et al., 1995
6. Mixed diatoms[c]	Mesocosm 93	ND	0.33	9	0.89	<0.001	Calculated from Passow and Alldredge, 1995a
7. Dinoflagellates	Mesocosm 95	163	0.56	9	0.95	<0.001	Passow, 2002
8. *Phaeocystis sp.*	Mesocosm 96	106	0.76	12	0.91	<0.001	Passow, 2002
9. *Phaeocystis antarctica*	Ross Sea	1	3.63	71	0.66	<0.001	Hong et al., 1997
10. Diatoms[d]	East Sound 4/94	176	0.45	8	0.61	<0.1	Calculated from Kiørboe, 1996
11. Mixed diatoms[f]	Baltic Sea	282	0.33	48	0.62	<0.001	Engel, 1998

Combined data from 3 replicate cultures.
[a] calculations based on cell number not chl. *a.*
[b] TEP measured as Algenic Acid eq.
[c] *Thalassisira mendiolana* dominated.
[d] *Detonula confervacae* dominated.

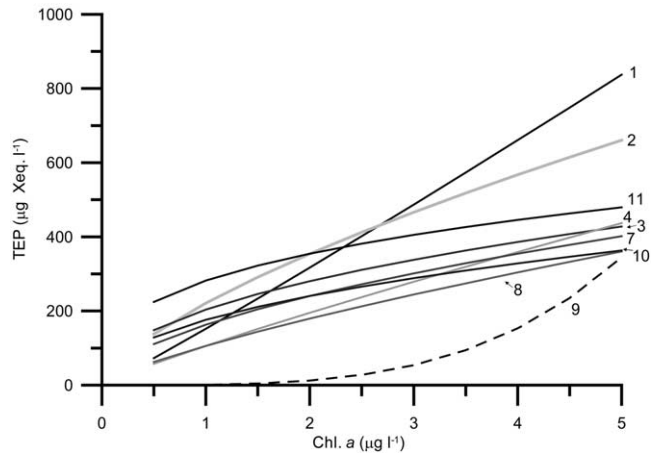

Fig. 5. TEP concentration is depicted as a function of chl. *a* during the growth period of several blooms and batch culture experiments. See Table 2 for detailed information on data sets #1–11.

growth rate rather than standing stock (Waite, Olson, Dam, & Passow, 1995). Production of TEP during a diatom and a coccolithophorid bloom grown in a mesocosm supported the hypothesis that TEP production increases as growth rates decrease (Engel, Goldthwait, Passow, & Alldredge, 2002a). Dynamics observed during a *Phaeocystis* spp. bloom observed in the Ross Sea differed from other curves ($\beta > 3$) principally, as TEP increased with increasing chl. *a* concentrations (Fig. 5). Presumably TEP were formed primarily from sloughing off from large colonies, and the sizes of the colonies were increasing as chl. *a* concentrations increased (Hong, Smith & White, 1997). In all cases at the end of the growth phase the relationship between TEP and chl. *a* disappeared, because TEP concentrations continued to increase as a result of either lysis of cells or sloppy feeding, while the chlorophyll concentrations declined.

Most EPS generated by bacteria form cell surface-bound capsules or biofilms rather than independent particles (Cowen, 1992; Costerton, Lewandowski, Caldwell, Korber, & Lappin-Scott, 1995), but bacteria have been shown to generate TEP (Heissenberger, Leppard, & Herndl, 1996; Stoderegger & Herndl, 1998; Stoderegger & Herndl, 1999). Although cultured bacteria generate large amounts of TEP (Stoderegger & Herndl, 1998; Grossart, 1999), in situ their production often appears to be insignificant (Schuster & Herndl, 1995). Generally no relationship between bacterial abundance and TEP was observed (Passow & Alldredge, 1995a; Passow et al., 2001), but during the progression of a spring bloom in the Baltic Sea such a relationship did become evident, possibly because both TEP and bacteria depended on the organic substances being released during the bloom (Mari & Kiørboe, 1996). This lack of relationship between bacterial abundance and TEP does not necessarily indicate that bacteria do not generate TEP. The interactions between bacteria and TEP are presumably complex (degradation, modification and production) so that any relationship can not be expected to be simple.

Even if bacteria do not generate significant amounts of TEP in situ, they may have an impact on the production of TEP by phytoplankton. If TEP protect phytoplankton cells from attaching bacteria, high bacterial concentrations may induce high production rates of TEP by phytoplankton (Azam & Smith, 1991; Smith, Steward, Long & Azam, 1995). Alternatively, bacteria may contribute to the generation of TEP by enzymatic hydrolysis of diatom surface mucus (Smith, Steward, Long & Azam, 1995). It has been postulated that bacterial activity stabilizes TEP, and so increases accumulation rates (Schuster & Herndl, 1995). Interactions between bacteria and phytoplankton have rarely been investigated (but see Grossart, 1999), so the relative importance of each, and the importance of their interactions for the production of TEP can not currently be evaluated.

Microorganisms appear to be the main producers of TEP both in the open ocean and in most coastal areas, but there are other organisms that generate mucoid material, which then form TEP. Thus TEP are generated in abundance by macroalgae (Ramaiah, Yoshikawa & Furuya, 2001). Zooplankton, especially copepods and euphausiids also appear to contribute to the production of TEP (Passow & Alldredge, 1999; Prieto, Sommer, Stibor & Koeve, 2001), although the mechanisms are not clear. Potentially they can generate enough turbulence to promote the formation of TEP from dissolved precursors, but they may also release precursors, which form TEP. Mucus released by corals also forms TEP (Wild, 2000).

5.3. Factors impacting the release of TEP-precursors

The release of exopolysaccharides by microorganisms depends on species, the individual physiological state and environmental growth conditions (Williams, 1990; Myklestad, 1995; Obernosterer & Herndl, 1995; Penna, Berluti & Magnani, 1999; Staats, Stal & Mur, 2000 and many others), and it appears that the release of TEP or their precursors also depends on all these factors.

In batch cultures, TEP concentration normalized to cell volume or chl. *a* varied by 1–2 orders of magnitude between different species (Table 3). The production of TEP by the coccolithophorid, *Emiliana huxleyi* and the flagellate *Rhodomonas baltica* was relatively small, whereas the prymnesiophyte *Phaeocystis antarctica* and the dinoflagellate *Gonyaulax polyedra* generated larger amounts of TEP. The diatoms tested spanned the complete range (Table 3). The range of the specific TEP production observed for one species (*Chaeoteros affinis*) was in the same order of magnitude as differences between species or taxa (Fig. 6), suggesting that physiological stage and growth conditions regulate TEP-production. TEP are generated during growth, stationary phase and senescence of some phytoplankton species, including the diatom *Chaetoceros affinis* (Passow, 2002) and the prymnesiophyte *Phaeocystis antarctica* (Hong, Smith & White, 1997). Other species (including large freshwater diatoms and colonial cyanobacteria) form free TEP only during senescence, although a cell surface mucus coat can be generated during growth (Schuster & Herndl, 1995; Grossart & Simon, 1997; Grossart, Berman, Simon & Pohlmann, 1998). TEP production by phytoplankton also varies as a function of the light regime (Hong, Smith & White, 1997), the carbon dioxide concentration (Engel, 2002), growth rate (Waite, Olson, Dam & Passow, 1995), and nutrient or trace metal depletion (Kraus, 1997). Physical factors such as the turbulence regime also impact the formation of TEP, as shear enhances the coagulation of TEP-precursors (Schuster & Herndl, 1995; Stoderegger & Herndl, 1999; Passow, 2000).

The formation of TEP as a result of bacterial activity varies with species composition, growth conditions and activity (Schuster & Herndl, 1995; Grossart, 1999; Stoderegger & Herndl, 1999), and the amount of TEP generated by macroalgae depends on light, temperature and age of the algae (Ramaiah, Yoshikawa & Furuya, 2001).

6. Microenvironments of microbes

As particles, TEP contribute structure to the aquatic environment, creating gradients on microscale. Until recently, the environment encountered by aquatic microorganisms was perceived as being largely fluid, relatively homogeneous and governed by diffusive processes. It is now believed that, in fact, aquatic microorganisms live in an environment that is highly structured by the presence of particles that provide physical surfaces, refuge and chemical gradients for microbes (Alldredge & Cohen, 1987; Smith, Simon, Alldredge, & Azam, 1992; Blackburn & Fenchel, 1999). Therefore, the aquatic environment may be characterized as a continuum of increasing abundance of particle surfaces and gels (Azam, 1998). Aggregates, in which organisms and particles are embedded in a porous gel matrix, represent one end of this microhabitat continuum, while particle-free water represents the other extreme. In particle free water, the presence

Table 3
Production of TEP by different phytoplankton species in batch cultures (mostly non-axenic). Values in brackets are estimated from data reported in different units

Species	TEP/cell vol.Vol./vol. ($\mu m^3\ \mu m^{-3}$)	TEP/cell vol.Conc./vol.μg Xeq. μm^{-3}	TEP/chl.a μgXeq. μg^{-1}	Reference
Chaeotoceros neogracile[a]	(6.81)[b]	NV	NV	Passow and Alldredge, 1994
Chaeotoceros neogracile, Milford collect.	NV	$(36*10^{-9})$	NV	Waite et al., 1995
Chaetoceros affinis	0.05–53.83[c]	NV	NV	Kiørboe and Hansen, 1993
Chaetoceros affinis, CCMP 159	NV	$22*10^{-9}$	24–350[d]	Passow, 2002
Chaetoceros sp., NS isolate	NV	$9*10^{-9}$	4–22	Passow, 2002
Coscinodiscus sp.	NV	NV	NV	Kiørboe and Hansen, 1993
Melosira nummuloides (benthic)	NV	$2*10^{-9}$	0-70	Passow, 2002
Nitzschia angularis	(2.06)[b]	NV	NV	Passow and Alldredge, 1994
Nitzschia angularis	NV	$0.9*10^{-9}$	11–200	Passow, 2002
Nitzschia sp., isolate from SBC	NV	$25–31*10^{-9}$	1–5	Passow, 2002
Nitzschia closterium	NV	$(0.2*10^{-9})$	NV	Engel and Schartau, 1999
Skeletonema costatum	0.01–0.75	NV	NV	Kiørboe and Hansen, 1993
Skeletonema costatum, axenic	0.70-4.54	NV	NV	Kiørboe and Hansen, 1993
Stephanopyxis turris CCMP 815	NV	$26*10^{-9}$	9–3700	Passow, 2002
Thalassiosira weissflogii	(13.19)[b]	NV	NV	Passow and Alldredge, 1994
Thalassiosira weissflogii	NV	$3*10^{-9}$	63–334	Passow, 2002
Thalassiosira rotula, Meunier, NS isolate	NV	$3.6*10^{-9}$	2-5	Passow, 2002
Rhodomonas baltica	0.08–0.49	NV	NV	Kiørboe and Hansen, 1993
Emiliana huxleyi, non-calcifying strain PMC92d,	NV	$1*10^{-9}$	1–7	Passow, 2002
Tetraselmis suecia, benthic, M.Elbrächter	NV	$27*10^{-9}$	5–20	Passow, 2002
Phaeocystis antarctica	NV	NV	148–2720	Hong et al., 1997
Gonyaulax polydera (CCMP 406)	NV	$20*10^{-9}$	1–70	Passow, 2002

NS: North Sea; SBC: Santa Barbara Channel California, USA; NV: No value; TEP also appeared in batch cultures of *Cylindrotheca* fusiformis (Grossart, 1999), *Aphanizomenon* ovalisporum (Grossart, Berman, Simon & Pohlmann, 1998) and *Thalassiosira* nordenskö ldii (Passow & Wassmann, 1994), but the amount was not quantified.

[a] Name changed from *C. gracilis.*

[b] Calculated from TEP area (mm^2) per vol. cells (mm^3). Because encased volume of TEP is estimated, the volume calculations overestimate TEP (Kiørboe & Hansen, 1993).

[c] In a parallel culture maximum value reached was only 1.67 instead of 53.83.

[d] Average range of three replicate experiments, which yielded similar results.

of free fibrillar polymers changes the rheological properties and viscosity of seawater (Jenkinson, 1986) altering the flow fields experienced by cells and increasing the persistence of microzones and chemical patchiness (Jenkinson & Wyatt, 1992; Jenkinson, 1993). As TEP, the same polymers are responsible for the formation of relatively stable microhabitats in aggregates.

Besides providing physical structure to the habitat, TEP by retaining trace elements and organic rich material may also be structuring the environment chemically. TEP, like other particles or polymers may act as barriers to diffusion and create patchiness in chemical properties on scales of micrometers. The formation of such microzones would, for example, affect the chemotactic behavior of Protozoa. Colonization of TEP may also affect predation rate as the particles may provide a refuge. Although the provision of spatial structure may prove to be one of the most important ecosystem functions of TEP, this topic awaits further study.

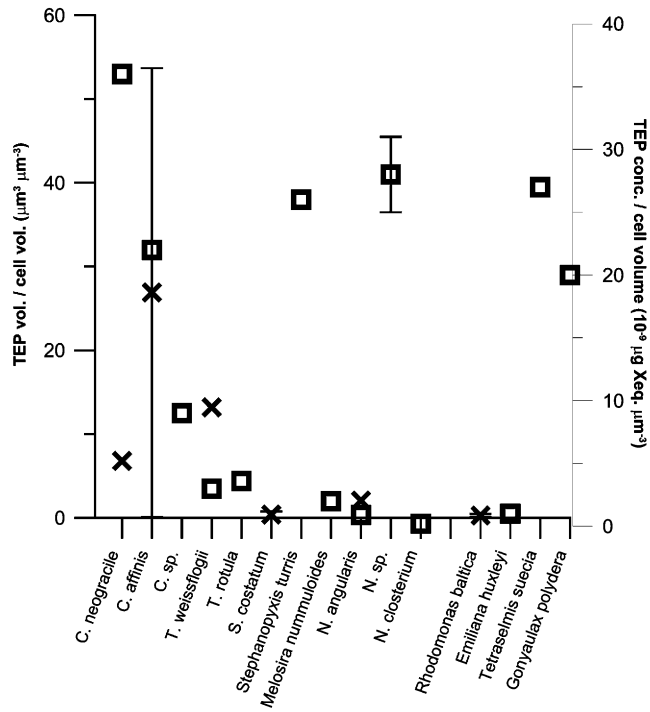

Fig. 6. Average cell specific TEP production (given as TEP volume or as xanthan equivalent per cell volume) in cultures of different phytoplankton cultures. Bars indicate the range of cell specific TEP production as measured during the growth cycle (lag, log, stationary phase). The interspecific variability of TEP-production by *Chaetoceros affinis* is as large as the interspecific variability of all species tested.

6.1. TEP as sites for attachment

As particles, TEP provide bacteria with sites for attachment (Fig. 7). The significance of TEP in providing surfaces for bacterial colonization was recognized early on and has been more thoroughly investigated than other aspects. One indication that in situ TEP exist as discrete particles, rather than as loose slimes that then formed particles on filters, was deduced from the observation that TEP are always colonized by bacteria (Alldredge, Passow & Logan, 1993; Passow & Alldredge, 1994; Mari & Kiørboe, 1996). There is one study that indicated that not all TEP-like particles are colonized by bacteria. Worm & Søndergaard (1998a) reported that not all ABSP (alcian blue stainable particles), which may include particles that are not considered to be TEP, were colonized (possibly because of their chemical composition differed or their formation had different dynamics).

The percentage of total bacteria attached to TEP varied between 0.5% and 25% (max. 89%) of all bacteria in marine (Passow & Alldredge, 1994; Schuster & Herndl, 1995; Mari & Kiørboe, 1996) and fresh waters (Worm & Søndergaard, 1998a); average values mostly ranged between 5 and 10%. In the Adriatic Sea, the fraction of attached bacteria was higher at a eutrophic station compared to a more oligotrophic station (Schuster & Herndl, 1995), but a comparison between systems gave no indication that this is a general trend.

No overall relationship between bacterial abundance and TEP concentration was observed, when samples of different origins and types were compared. However, the surface density of bacteria colonizing TEP decreased with size of TEP (Passow & Alldredge, 1994; Schuster & Herndl, 1995; Berger, Hoch, Kavka, & Herndl, 1996; Mari & Kiørboe, 1996; Worm & Søndergaard, 1998a), according to the relationship

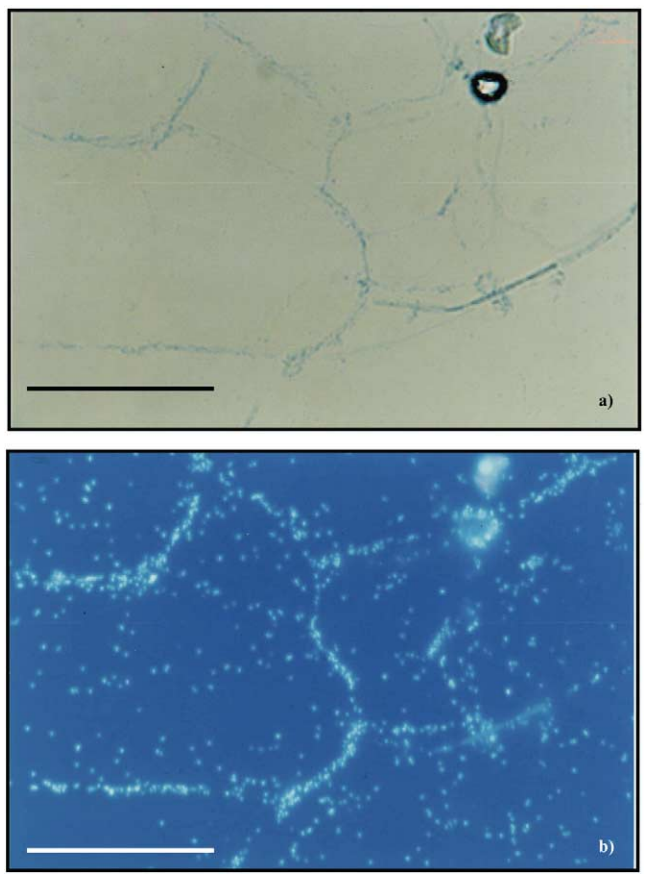

Fig. 7. (a) String and robe-like TEP in natural seawater made visible by staining with alcian blue. (b) DAPI staining of bacteria reveals that many of the bacteria are attached to TEP.

$$N = \alpha d^{-\beta},$$

where N is the bacterial density on TEP (number μm^{-2} TEP), and d is the equivalent spherical diameter of TEP in μm (Table 4, Fig. 8). As $\beta > 0$, this distribution could indicate that smaller TEP are older, thus allowing more time for their colonization. However, the importance of aggregation in TEP formation is not consistent with the concept that smaller TEP are generally older. An alternative explanation might be that the smaller TEP are denser (Schuster & Herndl, 1995). As well as varying with size, the density of bacteria colonizing TEP varies by an order of magnitude between sites; a single 5 μm particle was colonized at densities ranging from 0.08 to 0.7 bacteria per μm^{-2} (Table 4). Data from a time series study suggest that bacterial density on TEP peaks, when both bacterial and TEP concentrations are maximal, e.g. at the time of the decline of a spring bloom.

6.2. Aggregates as microhabitats

Aggregates represent the best-studied microenvironments within the pelagic environment. The mucus matrix and the fractal nature of aggregates reduces diffusion and changes advective flow through aggregates, thus allowing the development of chemical gradients and microzones within the aggregates (Gotschalk &

Table 4
Bacterial density on TEP is a function of the size of TEP and can be described by $N = \alpha\, d^{-\beta}$, where N = bacterial abundance per μm^2 TEP, and d = equivalent spherical diameter of TEP. These values were calculated assuming spherical TEP. Bacterial density on 5 μm and 100 μm-TEP are reported for easy comparison

Locations	α	β	Bacterial density (μm^{-2})		Reference
			5 μm-TEP	100 μm-TEP	
1. Coastal Pacific	1.36	0.78	0.39	0.04	Passow and Alldredge, 1994
2. Adriatic	0.28	0.70	0.09	0.01	Schuster and Herndl, 1995
3. Adriatic	0.30	0.82	0.08	0.007	Schuster and Herndl, 1995
4. Kattegat time series	0.25–1.68[a]	0.35–1.00[a]			Mari and Kiørboe, 1996
4a. [b]Pre-bloom 3/3	0.26	0.38	0.14	0.05	Mari and Kiørboe, 1996
4b. [b]Post-bloom 6/4	1.53	0.72	0.48	0.06	Mari and Kiørboe, 1996
5. River Danube	NV	NV	0.70	NV	Berger et al., 1996
6. Experimental	0.58	1.06	0.1	0.004	Schuster and Herndl, 1995

The relationship estimated from ABSP-data given in Worm and Søndergaard, 1998a) are lower, with $\alpha = 0.05$ and $\beta = 0.37$
[a] Range of values measured during the spring bloom between March and April.
[b] Maximum and minimum densities found during the time series investigation in the Kattegat.

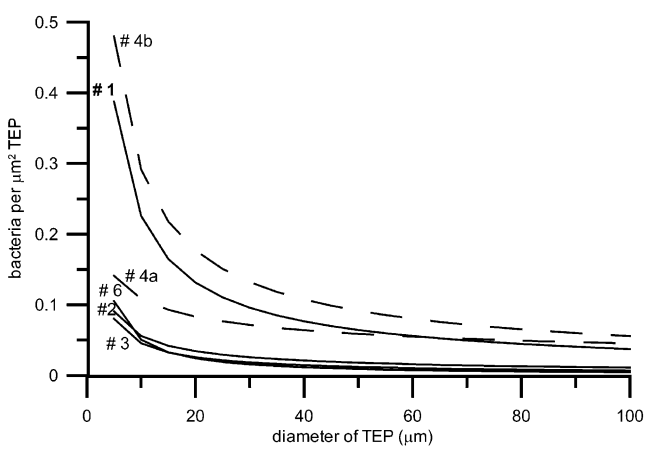

Fig. 8. Bacterial surface density of TEP as a function of TEP size. For details on data sets # 1–7 see Table 4.

Alldredge, 1989; Brzezinski, O'Bryan & Alldredge, 1997; Ploug, Kuehl, Buchholz-Cleven, & Jorgensen, 1997; Ploug & Grossart, 2000). The formation of microhabitats impacts all concentration-dependent processes. Consequently nutrient uptake rates, grazing rates and dissolution rates differ within aggregates compared to the surrounding seawater (Alldredge and Gotschalk, 1989; Kaltenbock & Herndl, 1992; Passow & Engel, pers. com.). Bacterial productivity is elevated within aggregates (Herndl, 1988; Smith, Simon, Alldredge & Azam, 1992; Grossart & Simon, 1993; Muller-Niklas, Schuster, Kaltenbock, & Herndl, 1994; Grossart, Berman, Simon & Pohlmann, 1998; Grossart & Simon, 1998a) and the composition of the bacterial community within aggregates differs from that in the surrounding seawater (Delong, Wu, Prezelin, & Jovine, 1994). As sinking aggregates may generate a large plume in their wake, they also create micropatches in the surrounding seawater (Kiørboe, Ploug, & Thygesen, 2001; Kiørboe & Thygesen, 2001).

7. Cycling of solutes and trace elements

Biogeochemical cycling of elements in marine systems results from complex interactions between dissolved and particulate matter. The cycling of metals, toxins and trace metals depends largely on the presence of polysaccharides, because of the large affinity of dissolved organic substances and trace elements to surface-active exopolymers (Tye, Jepsen, & Lick, 1996). Between 40 and 90% of trace compounds can be scavenged by adsorption onto marine colloids (Buffle, Wilkinson, Stoll, Filella & Zhang, 1998). In association with TEP these trace substances may accumulate in the surface micro-layer (Asetzu-Scott & Passow, pers. com.), they may aggregate, sediment, or be filtered by suspension feeders; whereas in solute form, they are distributed by water movement alone. Moreover, the impact of such trace elements on organisms differs if they occur sorbed to TEP rather than in their free form. Sorbed toxins are less harmful and trace elements required for growth, less available.

7.1. Cycling of thorium

To date very little work has been carried out on the role of TEP for the cycling of trace elements other than ^{234}Th. The transport of ^{234}Th is largely determined by its affinity to exopolymers (Niven, Kepkay & Boraie, 1995; Dunne, Murray, Balistrieri, Passow & Alldredge, pers.comm.) and the binding capacity of acidic polysaccharides to ^{234}Th or other metals is larger than that to any known mineral sorbent (Quigley, Santschi, Hung, Guo, & Honeyman, 2002). Model, experimental and field results, all indicate that coagulation and colloidal pumping is of primary importance for their removal (Burd, Moran & Jackson, 2000; Quigley, Santschi, Guo & Honeyman, 2001; Dunne et al., pers.comm.). Initially ^{234}Th is predominately scavenged in the colloidal size fraction, and desorption is minimal (Quigley, Santschi, Guo & Honeyman, 2001). During the colloidal pumping phase $>$90% of the ^{234}Th is transferred into the particle phase, suggesting that ^{234}Th may be a good proxy for the removal of surface-active organic matter by colloidal pumping (Quigley, Santschi, Guo & Honeyman, 2001). The significant sorption of ^{234}Th to TEP does, however, diminish usage of ^{234}Th as a proxy for flux (Dunne et al., pers.comm.).

8. Aggregation

The finding that exopolymers can exist as particles has also changed our understanding of the mechanisms promoting aggregation. Aggregation of particles is important for particle dynamics (McCave, 1984) and especially large phytoplankton blooms are frequently terminated by aggregation (Kranck & Milligan, 1988; Alldredge & Gotschalk, 1989). Aggregation theory has been well developed by the colloidal chemistry and aerosol communities and has been applied with varying success to predicting aggregation rates in the ocean (McCave, 1984; Jackson, 1990; Hill, 1992; Riebesell & Wolf-Gladrow, 1992; Jackson, 1995a; Jackson, 2001) for reviews see Alldredge and Jackson (1995) and Jackson and Burd (1998). According to coagulation theory, aggregation rate is dependent upon the size distribution and abundance of colliding particles, the intensity of mechanisms responsible for collisions between particles, and the probability that particles will stick together once they have collided, which is quantified as the stickiness coefficient, α. An alpha (α) of 1 implies that all collisions between particles result in sticking, whereas an $\alpha = 0.1$ implies that only 10% of collisions result in the particles adhering.

Using models based on aggregation theory, the abundance of solid particles in the ocean had appeared too low accurately to predict the high abundance of aggregates observed in nature (McCave, 1984; Hill, 1992), until the presence of TEP was recognised (Alldredge, Passow & Logan, 1993). In fact, TEP was discovered during an experiment on the aggregation of phytoplankton, where one diatom species was subject to a known laminar shear (Passow, Alldredge & Logan, 1994). Theoretical considerations had

predicted the first visible aggregates (>0.5 mm) would appear about 24 h after the onset of the experiment. Unexpectedly, the first visible aggregates appeared within 20–30 min of the start of the experiment, also the decrease in the concentration of unaggregated diatoms remained too low to account for the presence of large aggregates. Other particles, not easily visible under the light microscope had to be present, if aggregation theory was to be correct.

Concentrations of phytoplankton-sized TEP are in the same range as phytoplankton, thus dramatically increasing the potential collision frequency of particles (Passow, Alldredge & Logan, 1994; Logan, Passow, Alldredge, Grossart & Simon, 1995). Moreover, because the presence of TEP enhances the effective stickiness of the particle population (Dam & Drapeau, 1995; Engel, 2000), the adhesion success of collisions is also increased by the presence of TEP. Some models predict that the addition of TEP does not increase overall aggregation rates significantly, if their stickiness is similar to that of solid particles (Jackson, 2001), whereas other models suggest that an increase in particle number alone would be sufficient to enhance aggregation rates appreciably (Hill, 1992). The presence of TEP also presumably increases the overall aggregation rates by creating more, larger particles and by increasing overall stickiness (Jackson, 1995b). Individually, neither small solid particles nor TEP reach great depths as their sinking velocities are so small, that the particles are remineralized before reaching the deep ocean. However, when incorporated into aggregates both particle types will exhibit fast sinking speeds and subsequently high sedimentation rates, even at depth.

8.1. Aggregation of phytoplankton

Observational evidence confirms that the formation of aggregates at the decline of diatom blooms is frequently controlled by TEP (Logan, Passow, Alldredge, Grossart & Simon, 1995). The following scenario describes the aggregation dynamics of many marine diatom blooms (Passow & Alldredge, 1994): Diatoms (e.g. *Chaetoceros affinis* and *C. neogracilis*) release dissolved TEP-precursors into the water during growth (Kiørboe & Hansen, 1993; Passow, 2002). As the development of the bloom progresses the concentrations both of TEP formed from the released precursors, and of the phytoplankton increase, until aggregation dominates particle dynamics (Passow, Alldredge & Logan, 1994). The peak values of the average size and the total quantity of TEP are attained simultaneously during the aggregation phase, which terminates the blooms either in nutrient-replete or nutrient-deplete conditions (Fig. 9a). Combined stickiness may decrease (Dam & Drapeau, 1995) or increase (Engel, 2000) as the bloom progresses. In agreement with the coagulation model (Jackson, 1990), aggregation comes to dominate the particle dynamics, once particle concentrations reach a critical concentration (Dam & Drapeau, 1995). Aggregation driven by TEP is non-selective, implying that all categories of particle present in the water become incorporated into aggregates (Crocker & Passow, 1995). Blooms driven by this type of dynamic are the most commonly observed in marine environments and in large marine mesocosm experiments (Alldredge & Gotschalk, 1989; Riebesell, 1991; Passow, Alldredge & Logan, 1994; Passow & Alldredge, 1995a; Grossart & Simon, 1997).

A large diatom spring bloom observed in East Sound (off Washington, USA) was an example of a bloom, which did not aggregate, presumably because very little TEP was available (Kiørboe et al., 1996). This bloom was dominated by the large single-celled species *Thalassiosira mendiolana*. TEP concentrations were low compared to phytoplankton standing stocks, presumably either because TEP production by this particular species is low, or because of the filtration activity of appendicularians, which were abundant at the time (Hansen, Kiørboe, & Alldredge, 1996). The overall stickiness of all particles >20 μm was very low ($\alpha = 0.05$) and the stickiness of T. *mendiolana* cells in particular was near zero. This low stickiness of the particles explains why no diatom aggregates were observed by divers and none appeared in sediment traps. Aggregation rates were extremely slow and had no visible effect on size frequency distribution of particles.

TEP can also be generated during senescence of phytoplankton; either when a cell associated mucus

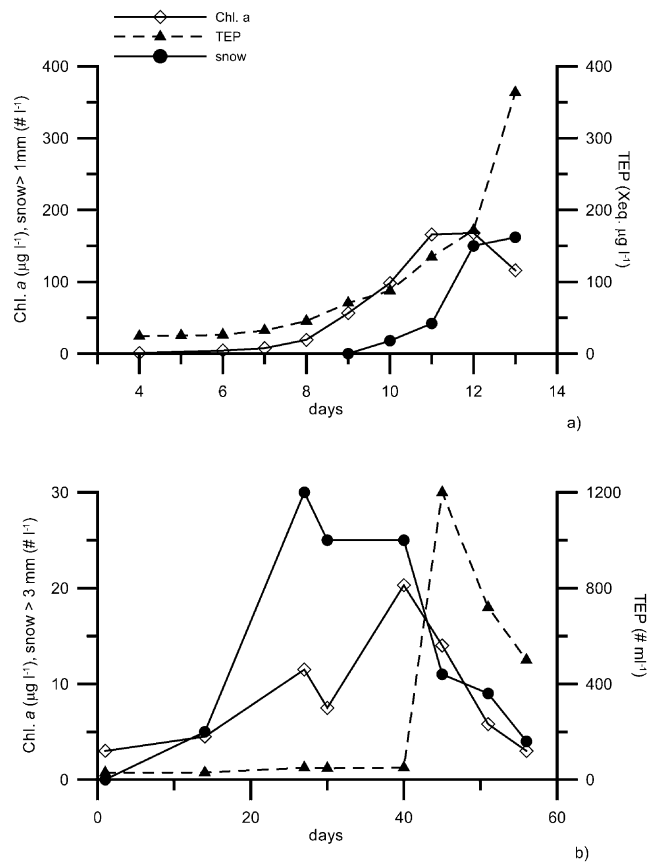

Fig. 9. The temporal patterns of the concentrations of chl. *a*, TEP and large aggregates (snow) during phytoplankton blooms may exhibit different dynamics. (a) During the progression of a spring bloom grown in a mesocosm, TEP increased simultaneously with chl. *a*, whereas the abundance of large aggregates lagged by 1–2 days (redrawn from Alldredge, Gotschalk, Passow & Riebesell, 1995; Passow & Alldredge, 1995a). (b) During a summer bloom in a large fresh water lake large aggregates appeared simultaneously with the increase in the phytoplankton, whereas TEP were formed at senescence (redrawn from Grossart & Simon, 1998b).

layer (cell surface layer, colony matrix) disintegrates or from cell internal material as a result of lysing of cells or sloppy feeding. The formation of detrital aggregates is also driven by TEP. Examples include blooms dominated by diatom species that formed a thin mucus layer on their cell surface during exponential growth (Schuster & Herndl, 1995), which is sloughed off at senescence thus triggering an aggregation event (Grossart & Simon, 1997; Grossart & Simon, 1998b). As these diatoms also aggregated during growth (because of their high cell surface stickiness, see below), two aggregation events were observed and peak concentrations of TEP occurred after the peak concentrations in phytoplankton and flocks had passed. During blooms dominated by colony forming cyanobacteria (Grossart & Simon, 1997; Grossart, Berman, Simon & Pohlmann, 1998), TEP concentrations remain low during growth and the large mucus flocks, which appear formed by growth and not by aggregation. At senescence, when these flocks decayed, free TEP are released into the water (Fig. 9b). In this case, the increased TEP concentration at senescence did not lead to the formation of large aggregates, presumably because concentrations of solid particles were too low. The formation of TEP from the colony matrix of disintegrating *Phaeocystis* follows a similar dynamic to that of colony forming cyanobacteria, but sedimentation of detrital aggregates was observed

after the disintegration of colonies (Passow & Wassmann, 1994; Riebesell, Reigstad, Wassmann, Noji & Passow, 1995; Hong, Smith & White, 1997). The aggregation of a diatom bloom dominated by *Skeletonema costatum* in a microcosm provided an example for the formation of TEP at an advanced stage of senescence (Engel, 1998). This particular bloom flocked two and a half weeks after the bloom had peaked, when diatom concentrations had declined by 80% (from 10^4 to $0.2*10^4$ l^{-1}). TEP concentrations increased drastically during the late senescence of this bloom, 18 days after the peak of the bloom had passed and nitrate was limiting growth. The overall stickiness of particles increased from $\alpha < 0.2$ during early senescence to unity later on (Engel, 1998). The formation of bacterial/detrital aggregates also ended a decaying dinoflagellate bloom grown in a mesocosm (Passow, 2002). It is questionable whether natural blooms ever reach such an advanced stage of senescence, or whether this was a consequence of the artificial conditions in micro- and macrocosms.

Phytoplankton will aggregate in the absence of TEP, if diatoms that have sticky cell wall coatings are dominant (especially pennate diatoms and fresh-water species) (Logan, Passow, & Alldredge, 1994b; Crocker & Passow, 1995; Schuster & Herndl, 1995; Waite, Olson, Dam & Passow, 1995; Grossart & Simon, 1997; Waite, Gallager, & Dam, 1997). The stickiness of *Nitzschia closterium*, for example, is dependent on cell wall stickiness and not on TEP; no differences in α were observed between three cultures of *Nitzschia closterium*, although normalized TEP concentrations ranged from 20–135 pg Xeq. per cell (Engel, 1998). As originally assumed for phytoplankton aggregation in general (Smetacek, 1985), such species aggregate as a result of increased stickiness of their cell surface (Kiørboe & Hansen, 1993). Aggregates formed by species with sticky cell walls consist of dense globules of cells, with very little matrix material (Hansen & Kiørboe, 1997). Aggregation based on cell wall associated stickiness, is highly species specific, as the cells aggregate predominantly with themselves (Crocker & Passow, 1995). The first of two aggregation events observed during a summer bloom in Lake Constance, was driven by sticky cells (Fig. 9b) (Grossart & Simon, 1997). The aggregation of a *Skeletonema costatum* bloom was also explained by the stickiness and size frequency distribution of cells alone (Kiørboe, Lundsgaard, Olesen & Hansen, 1994). However, TEP was not measured and the effect of TEP may have been implicitly included in the calculations. The determination of stickiness of solid particles is overestimated and may even reach values >1, if the presence of TEP is ignored (Engel, 2000). Aggregation in the absence of TEP was also postulated for a bloom in an upwelling area of Benguela (Kiørboe et al., 1998). However, the absolute amount of TEP, rather than the volume of TEP normalized to other particles was compared to stickiness in that study and thus the impact of TEP on the aggregation was hard to judge.

As TEP are generated primarily by phytoplankton, phytoplankton aggregates are prominent, but TEP aggregate all types of non-phytoplankton particles, e.g. clays and detrital matter, as well. The occurrence of a mucus matrix in natural aggregates and data from sediment traps confirm direct observational evidence that in marine systems TEP are essential for the aggregation of most natural phytoplankton blooms and other small solid particles. These particles are removed from suspension by TEP (Passow et al., 2001), cleaning the water as was envisioned long before their discovery (Smetacek, 1985; Smetacek & Pollehne, 1986). TEP play no role in the formation of marine snow, which is formed by mechanisms other than by aggregation, e.g. marine snow formed from feeding structures of zooplankton, although TEP may be enriched in larvacean houses as a result of feeding activities (see below).

8.2. Contribution of TEP to aggregates

A polysaccharide matrix has been found to surround and connect composite particles in all marine and lake aggregates investigated (Rieman, 1989; Alldredge, Passow & Logan, 1993; Cowen & Holloway, 1996; Grossart, 1996; Holloway & Cowen, 1997; Alldredge, Passow & Haddock, 1998). Most of this material stains with alcian blue suggesting that the mucus matrix consists predominantly of TEP. Diatom aggregates are very rich in TEP (Passow, Alldredge & Logan, 1994; Passow & Alldredge, 1995a; Grossart & Simon,

1997), but TEP-rich flocks can also occur during both dinoflagellate blooms (Alldredge, Passow & Haddock, 1998) and cyanobacterial blooms (Grossart & Simon, 1997). Dinoflagellate snow and some lake snow appear additionally to consist of amorphous, transparent mucus material that is not TEP (Logan, Grossart & Simon, 1994a; Alldredge, Passow & Haddock, 1998). The relative inclusion of TEP and solid particles within aggregates represents a further example of the apparently variable behavior of TEP. An experiment with artificially generated aggregates generated from a natural population dominated by filamentous cyanobacteria, suggested that compared to the source material, TEP was strongly enriched within aggregates (Engel, Meyerhöfer & von Bröckel, 2002b), whereas I have observed no enrichment of TEP in aggregates generated artificially from cultured diatoms (unpublished data).

The amount of TEP in aggregates varies widely between 0.1 and 50 μg Xeq. per aggregate and increases with the aggregate volume (1–1000 mm^3). No statistically significant differences have been found between different types of aggregates, although aggregates consisting of miscellaneous debris contained relatively little TEP (Alldredge, Passow & Haddock, 1998). The solid volume of particles other than TEP included in marine snow-sized aggregates (>0.5 mm) is <5%, and is often <<1% of the aggregate volume (Alldredge & Gotschalk, 1988; Logan & Alldredge, 1989; Alldredge & Crocker, 1995). The contribution of TEP to aggregate volume can be estimated in different ways. A direct comparison conducted on aggregates generated artificially from enriched seawater laden with filamentous cyanobacteria, suggested that the volume fraction of TEP in those aggregates was highly variable but comprised the major part of the particle volume, with a median volume ratio of TEP to solid particles of 18 (Engel, Meyerhöfer & Von Bröckel, 2002b). This implies that the volume of a median aggregate of diameter $d = 0.5$ mm consisted of just 2.4 % and 4 % of solid particles and TEP, respectively, whereas because of fractal scaling the respective numbers would be 0.06% and 1% of the volume of a larger aggregate ($d = 5$ mm).

Using the carbon density of 17.4 g carbon per dm^3 of TEP derived from free TEP (Engel & Passow, 2001), a volume fraction of about 0.3% TEP in aggregates can be estimated based on the relationship between TEP and aggregate size. In lake snow, the fraction of the total area of solid particles that consisted of TEP was, on average, 8%, as estimated microscopically (Grossart, 1996), which would suggest that TEP contribute ~0.4% of the total volume. Estimates derived from changes in sinking speed of diatom aggregates at a halocline suggested that 0.5–2% of the aggregate volume must be occupied by TEP to retard sinking and cause the observed rates of aggregate accumulation at the halocline (Alldredge & Crocker, 1995). Model calculations based on measured sinking speed of particle-free TEP, suggest that diatom aggregates will be positively buoyant, if the TEP volume fraction is at least 0.5–5 times the solid particles volume fraction (Azetzu-Scott & Passow, unpublished data). These estimates suggest that the volume fractions of solid particles and TEP each appear to be on the order of 0.5–5%, emphasizing that aggregates consist mostly of water. Thus aggregates may be envisioned to consist of widely spaced solid particles that are connected by polysaccharide fibrils that form a polymer network (Heissenberger & Leppard, 1996). If solid particles were spaced evenly within aggregates, their average separation would be ≥4–10 cell diameters.

Besides acting as the glue, the TEP matrix effects the sinking velocities of aggregates. The relative proportion of TEP compared to solid particles determines sinking speed of aggregates. Aggregates formed by *Nitzschia closterium*, which contained a relatively higher proportion of TEP showed lower sinking velocities, than TEP-poor aggregates of the same size and type (Engel & Schartau, 1999).

8.3. Large mucus events

In most areas of the world oceans, mucopolysaccharides do not accumulate to macroscopic proportions, although a seasonal build-up over the summer has been observed (Mari & Burd, 1998). However, large accumulations of mucopolysaccharides regularly occur after *Phaeocystis* spp. blooms in the North Sea (Lancelot, Billen, Sournia, Weisse, Colijn, Veldhuis et al., 1987) and in the Adriatic during the summer

(Stachowitsch, Fanuko, & Richter, 1990; Herndl, 1992). Possibly the production of TEP is so high compared to the presence of solid particles, that large amounts of TEP remain in the water column, escaping sedimentation. Low concentrations of inorganic nutrients may retard bacterial degradation. TEP may then accumulate forming large carpets of mucus, which do not sink. The accumulation of mucopolysaccharide-rich marine snow can lead to anoxia at the sediment surface with associated consequences for the benthos (Ott & Herndl, 1995), but even moderate concentrations, such as those found in all coastal systems can have dramatic effects. TEP-rich marine snow loaded with inorganic sediments can, for example, lead to the death of coral recruits (Fabricius & Wolanski, 2000; Wild, 2000).

8.4. Aggregation in fresh and marine waters

The contribution of TEP to the aggregation of phytoplankton blooms, is the best-studied aspect of TEP. Although some cultured marine diatoms aggregate in the absence of TEP because of the stickiness of their cell walls, this mechanism appears to be rare in marine waters, and all marine aggregates investigated to date have had a TEP-matrix. Lake snow appears to more commonly consist of aggregates formed by sticky cells and in lakes and brackish waters TEP are frequently generated only during the senescent phase of the phytoplankton blooms, although generation of TEP during the growth phase of fresh water diatoms has also been observed (Table 5). The temporal relationship between phytoplankton standing stock, TEP and aggregation differs significantly between both scenarios (Fig. 9). Differences in the species composition and the cation concentration could be responsible for such a difference between fresh and marine waters. Both aggregation mechanisms, however, cause changes in the size distribution of solid particles, which in turn have profound effects on both on the food web and on the flux of particles.

9. Flux of particles

The importance of TEP for sedimentation is twofold. Firstly TEP influences the sedimentation of non-TEP particles by aggregating them and secondly TEP themselves contribute directly to the flux of carbon. The fractionation between material that is degraded in the upper ocean and material that sediments to depth depends on the relation between the degradation and the sedimentation rates, so any changes in the average sinking velocity will result in different sedimentation rates. Aggregation increases the average sinking velocity of particles.

9.1. Flux of solid particles

Most marine particles settle as marine snow-sized aggregates ($\geq$0.5 mm) (Alldredge & Gotschalk, 1988; Alldredge & Gotschalk, 1989; Diercks & Asper, 1997). Sedimentation events following the aggregation of large blooms especially, contribute to the total annual flux (Asper, 1987; Passow, 1991; Silver & Gowing, 1991; Lampitt, Hillier, & Challenor, 1993). All three studies, which have measured sedimentation rates of TEP directly, have confirmed the co-sedimentation between TEP and solid particles (Passow et al., 2001; Reigstad et al., pers.comm.). High sedimentation rates of POC or biogenic silica following phytoplankton blooms were always found to be associated with peak sedimentation rates of TEP during a two-year study off California (Passow et al., 2001). As expected, no correlation between sedimentation rates of TEP and POC or dry weight was observed when larvacean feeding structures or foraminifera shells dominated flux. But inorganic particles, like clays, also sank out rapidly as a component of TEP-rich aggregates. The sedimentation of inorganic particles in TEP-rich aggregates was also observed in the Indian Ocean (Kumar, Sarma, Ramaiah, Gauns & de Sousa, 1998). In a subarctic fjord annual sedimentation rates of TEP and POC both peaked during two spring blooms dominated by *Phaeocystis pouchetii* and at the decline of a

Table 5
Occurrence of TEP during phytoplankton blooms

Observation time	Location	Dominating species	References
Temporal pattern 1a: TEP increases appreciably both during growth and senescence of phytoplankton blooms			
Spring bloom 93	Lake Constance, Germany	Diatom: *Stephanodiscus* and flagellate: *Rhodomonas*	Grossart and Simon, 1997
Mesocosm Spring 93	Inoculum from SBC, USA	Diatoms: *Chaetoceros, Thalassiosira, Nitzschia, Schröderella, Leptocylindrus,*	Passow and Alldredge, 1995a
Mesocosm fall 95[a]	Inoculum from SBC, USA	Naked dinoflagellates and phototrophic protists	Passow, 2002
Summer bloom 95	Kattegat	NV (usually mixed, flagellates, diatoms, dinoflagellates)	Mari and Burd, 1998
Mesocosm spring 96[a]	Inoculum from SBC, USA	*Phaeocystis sp.*	Passow, 2002
Antarctic summer 94	Ross Sea	*Phaeocystis antarctica*	Hong et al., 1997
Temporal pattern 1b: TEP increases appreciably during growth and the bloom ends because of aggregation and sedimentation			
Spring bloom 92	SBC	Diatoms: *Chaetoceros*	Passow et al., 1994
Temporal pattern 2: TEP increases appreciably only at senescence of phytoplankton blooms			
Spring bloom 95	Kattegat	NV (usually *Skeletonema costatum*)	Mari and Burd, 1998
Summer bloom 93	Lake Constance, Germany	Diatoms *(Dinobryon, Melosira, Fragellaria, Diatoma, Tabellaria*)	Grossart and Simon, 1997
Fall bloom 93	Lake Constance, Germany	Diatoms (*Dinobryon, Fragellaria*) & cyanobacteria (*Microcystis)*	Grossart and Simon, 1997
Fall 95	Lake Kinneret, Israel	Cyanobacteria (*Aphamizomenon*)	Grossart et al., 1998

NV = no values; SBC = Santa Barbara Channel.
[a] All mesocosm experiments were conducted like the one in 93, for methods see (Alldredge, Gotschalk, Passow & Riebesell, 1995).

flagellate bloom (Reigstad et al. pers.comm.). No other peaks in sedimentation of POC or TEP were observed, suggesting that in this area TEP were responsible for all sedimentation events. No significant sedimentation was observed during a third study conducted in East Sound, Washington, USA where TEP concentrations remained consistently low throughout the spring bloom (Kiørboe et al., 1996); an observation that is consistent with the hypothesis that TEP are necessary for the sedimentation of small solid particles.

Two additional studies corroborate that TEP are responsible for the sedimentation of phytoplankton blooms. Firstly, a high flux of particulate organic matter was observed to coincide with the disappearance of TEP in the euphotic zone at the decline of a spring phytoplankton bloom in a fresh water lake (Logan, Passow, Alldredge, Grossart & Simon, 1995). Secondly the high sedimentation rates subsequent to the decline of a bloom dominated by *Phaeocystis pouchetii*, also coincided with the disappearance of TEP in the upper water layer, suggesting that TEP-detrital aggregates were responsible for the continuing high sedimentation rate after phytoplankton had disappeared (Riebesell, Reigstad, Wassmann, Noji & Passow, 1995).

9.2. Flux of TEP

The appearance of TEP and TEP-like mucus in sediment traps (Newton, Lampitt, Jickells, King & Boutle, 1994; Passow et al., 2001; Reigstad et al. pers. comm.) suggest that an important fraction of TEP, which had been generated during the blooms, was sedimenting in aggregates. As the carbon content of TEP is at times in the same order of magnitude as that of phytoplankton (Mari, 1999; Engel & Passow, 2001), this loss of carbon via sedimentation of TEP is significant. During a 2-year study in the Santa Barbara Channel sedimentation rates of TEP at 500 m ranged between 10 and 100 mg Xeq. m^{-2} d^{-1} (Passow et al., 2001). Based on the conversion introduced by Engel and Passow (2001), these latter sedimentation rates are equivalent to the sedimentation of 7–70 mg TEP-derived carbon m^{-2} d^{-1}, implying that sedimentation of TEP-C contributed roughly 30% to the POC flux. In a North Norwegian Fjord, TEP sedimentation rates at 40 and 100 m reached 490 and 280 mg TEP-carbon m^{-2} d^{-1}, respectively, during a one-year study (Reigstad, 2002; Reigstad et al. pers.comm.). As for solid particles, sedimentation rates of TEP decreased appreciably with depth.

Moreover, the sedimentation of TEP may represent a mechanism for the selective sedimentation of carbon to depth, without a concomitant loss of nitrogen. During seasons of high productivity, dissolved organic carbon accumulates in the euphotic zone without the respective accumulation of dissolved organic nitrogen (Copin-Montégut & Avril, 1993; Carlson, Ducklow, & Michaels, 1994). The formation and sedimentation of carbon-enriched TEP may explain this carbon over-consumption (Sambrotto, Savidge, Robinson, Boyd, Takahashi, Karl et al., 1993; Toggweiler, 1993; Körtzinger, Koeve, Kähler, & Mintrop, 2001). Because TEP are enriched in carbon relative to nitrogen (Engel & Passow, 2001) a selective increase in the formation rate of TEP resulting from rising carbon dioxide concentrations (Engel, 2002) potentially decouples the pumping of carbon and nitrogen (Engel, Goldthwait, Passow & Alldredge, 2002a). The formation and sedimentation of TEP may thus function as a feed-back mechanism counteracting rising atmospheric carbon dioxide concentrations by enhancing the sequestration of excess carbon to deeper water.

10. Food-web structure

Which fraction of primary produced particles sinks to depth, also depends on the type of food web present (Rivkin, Legendre, Deibel, Tremblay, Klein, Crocker et al., 1996). Particles may be utilized by bacteria or grazed by eukaryotes. Very little is known about the impact of TEP on the feeding relationships, or on the microbial loop, and the quantitative significance of TEP for these respective pathways can not yet be addressed.

10.1. Grazing by eukaryotes

Marine heterotrophs feed on particles within a specific size ranges, so changes in the size distribution of available food particles will alter food-web structure and dynamics. As free exopolymer material, TEP and their precursors can be ingested directly and utilized as food by small filter feeding protozoan (Sherr, 1988; Shimeta, 1993; Tranvik, Sherr, & Sherr, 1993) and Appendicularia (Flood, Deibel, & Morris, 1992). Appendicularia remove TEP from seawater at rates typical for grazing on colloids (Deibel, pers. com.). Because new TEP are formed from colloidal matter at levels similar to their removal, such grazing activity does not result in a rapid decrease of TEP concentrations. It remains unclear if TEP are ingested and actually utilized by Appendicularia, or if TEP are only accumulated and retained in the house, which is discarded when clogged (Deibel, pers. com.). Feeding on TEP and similar particles, which form from polymers allows dissolved material to enter the food web (Kepkay, 2000).

Copepods did not actively ingest free TEP in the absence of other food particles (Prieto, Sommer, Stibor & Koeve, 2001). And the presence of free polysaccharides appears to depress the feeding rates of copepods on diatoms, either because their feeding was inhibited (Malej & Harris, 1993), or possibly because the microaggregates formed by the polysaccharides, provide an additional food source and so reduces the additional intake of cells. If TEP are associated with diatom cells, they may be grazed by copepods, as copepods ingested beads that were coated with polysaccharides (Decho & Moriarty, 1990).

The presence of TEP was observed to provide additional food for *Euphausia pacifica*, as TEP- rich microaggregates ($<$50 μm) of bacteria, detritus and organisms $<$5 μm were grazed readily at rates similar to diatom cells (Passow & Alldredge, 1999). Thus, whereas free TEP and TEP precursors may inhibit grazing by copepods, TEP- microaggregates will provide a link between the microbial loop and the traditional food web by enabling large zooplankton to ingest bacteria-sized particles. Traditionally, the microbial loop and the food chain are connected by the grazing activity of macrozooplankton, e.g. copepods, which graze on large ciliates (microzooplankton), which in turn feed on nanoflagellates and bacteria. In the presence of TEP bacteria-sized organisms are utilized directly by macro or megazooplankton via the formation of micro-aggregates and the utilizable food supply of these animals is increased. Moreover, the direct utilization of bacteria by large heterotrophs represents a short cut in the food web, increasing the potential production of biomass at the top level by decreasing the number of trophic transfers. This is significant for estimates of ocean productivity, because transfer efficiencies and number of trophic levels frequently provide the basis for such calculations.

Euphausiids (Dilling, Wilson, Steinberg, & Alldredge, 1998), larval stages of metazoans (Bochdansky & Herndl, 1992) and fish (Grossart, Berman, Simon & Pohlmann, 1998) will all consume marine snow-sized ($>$ 500 μm) aggregates. Some copepods are also able to feed on marine snow-sized aggregates (Dilling, Wilson, Steinberg & Alldredge, 1998), but others are not (Bochdansky & Herndl, 1992; Kiørboe, 2000). Euphausiids also mechanically fragment the aggregates (Dilling & Alldredge, 2000), thus changing their size distribution, sinking speeds and availability for potential consumers.

10.2. Bacterial utilization

Bacteria utilize TEP, but the quantitative importance of microbial degradation is controversial. Bacteria modify the molecular structure of labile compounds producing refractory DOM (Ogawa, Amagai, Koike, Kaiser, & Benner, 2001), but the relative importance of microbial hydrolysis is still to be evaluated. Temporal distribution patterns and size-frequency distributions of TEP imply that it is coagulation of TEP rather than bacterial degradation that is the major pathway whereby TEP are lost. A relatively low degradation rate of most natural TEP was also postulated based on the relationship between bacterial colonization density and size of TEP (Mari & Kiørboe, 1996). Conversely, it is argued that the relative loss rate of TEP by degradation and grazing must be similar in magnitude to that of POC (Passow et al., 2001), because

the percentage of TEP from the euphotic layer, retrieved from sediment traps at 500 m is similar to that of POC (2–3%) and much lower than that of biogenic silica (50%). A five-fold decrease in the carbon associated with polysaccharides between surface- and deep water, corroborates that a major fraction of this material is recycled in the upper ocean (Kepkay, 2000).

Bacterial utilization of particulate polysaccharides depends heavily on their chemical composition. Compositional evidence strengthens the argument that a large percentage of TEP can not be considered to be labile. In the high molecular weight fraction of polysaccharides exuded by *Thalassiosira weissflogii*, it is the polysaccharides rich in mannose and galactose that are preferentially degraded (Aluwihare & Repeta, 1999); this suggests that those TEP that are rich in fucose (Zhou, Mopper & Passow, 1998) may be more resistant to degradation. In situ hydrolysis experiments with different polysaccharides have also suggested that rates of hydrolysis of sulfated polysaccharides (e.g. fucoidan) that are an important component of TEP, are comparatively low (Arnosti, 2000).

Direct measurements of degradation rates of TEP formed from bacterial capsular material revealed that this material is resistant to bacterial degradation over a time scale of hours to days (Stoderegger & Herndl, 1998). More rapid degradation of TEP was suggested by an experiment (Passow & Azam, unpublished), in which seawater from a large diatom bloom (Alldredge, Gotschalk, Passow, & Riebesell, 1995) was concentrated (10 l–35 ml) by vortex-flow filtration and the 0.2–0.8 μm-fraction incubated in the dark for 22 h. TEP was copiously generated during vortex flow filtration, so newly-formed uncolonized TEP were initially abundant. Free and attached bacteria, as well as TEP were enumerated at the start of the experiment and after 16 and 22 h. During the first 16 h the density of bacteria on TEP increased by an order of magnitude (0.02–0.18 bacteria μm^{-2} TEP), suggesting rapid bacterial colonization. Thereafter, the bacterial density on TEP remained constant. The concentration of total bacteria numbers increased throughout the experimental period (assuming exponential growth: $\mu = 2.6\ d^{-1}$), whereas the concentration of TEP and bacteria attached to TEP decreased. The total area of TEP decreased linearly ($r^2 = 0.99$) from 6.6 mm^2 ml^{-1} to 0.1 mm^2 ml^{-1}, suggesting there was rapid bacterial utilization of this very fresh material (degradation rate: 0.3 mm^2 TEP ml^{-1} h^{-1}). Overall, it may be assumed that bacterial degradation of some types of TEP can be an important loss pathway at least under some circumstances.

11. Carbon budget

Although most data on TEP collected to date stems from coastal areas, work in related fields suggests that these gel-like particles exist in all oceanic regions and affect the carbon cycle on global scales.

11.1. Direct contribution of TEP to the cycling of carbon: putting the pieces together

The fate of a significant fraction of primary production is to be released into the water as either dissolved or colloidal polysaccharides. Polysaccharides are the largest identifiable fraction of organic carbon in seawater and amount to the ~25 % of dissolved organic carbon (DOC) in surface waters (Benner, Pakulski, McCarthy, Hedges & Hatcher, 1992; Anon & Benner, 1994; Pakulski & Benner, 1994; Kepkay, 2000). This labile component of DOC increases especially during diatom blooms (Senior & Chevolot, 1991; Kepkay & Wells, 1992; Kepkay, Niven & Milligan, 1993; Niven, Kepkay & Boraie, 1995; Norman, Zweifel, Hopkinson, & Fry, 1995; Smith, Steward, Long & Azam, 1995). As well as phytoplankton, other important sources of DOC are protozoans, bacteria and viruses (Nagata, 2000). An appreciable fraction of these colloidal polysaccharides that are released into the water are the fibrillar material that is the precursor of TEP (Santschi et al., 1998).

A large portion of this freshly formed DOC is either removed from the euphotic zone by bacterial utilization (Azam et al., 1983) or accumulates in the near surface water until it gets mixed down below

the euphotic zone by deep winter mixing (Carlson, Ducklow & Michaels, 1994; Michaels, Bates, Buesseler, Carlson, & Knap, 1994; Nagata & Kirchmann, 1997). Any DOC that is mixed below the euphotic zone gets utilized rapidly (within 1–2 weeks). Thus even when its degradation by bacteria is delayed, the final fate of this DOC remains the same, e.g. its incorporation into the microbial loop. Another pathway that is the coagulation of colloidal DOC, which subsequently is transported downwards as particles, has also been speculated upon (Kepkay, Niven & Milligan, 1993). The abiotic formation of TEP and TEP-like particles, which sediment via marine snow, provides such an alternate pathway for the removal of DOC. The deficiencies currently observed in many carbon budgets (Michaels, Bates, Buesseler, Carlson & Knap, 1994) may be resolved if the budgets are expanded to include the formation and sedimentation of TEP.

11.2. Estimates of the amount of carbon cycling through TEP

To assess the potential quantitative importance of TEP in the carbon cycle, the fraction of carbon cycled through TEP is estimated (Fig. 10). This estimate is based on data collected during 1996 in the Santa Barbara Channel and on a variety of experimental data. Concentrations of TEP (determined colorimetrically), phytoplankton and bacteria were measured at two-week intervals at six depths in the upper 75 m, and sedimentation rates of TEP and POC (colorimetrically) were measured at 2-week intervals with a Paraflux sediment trap (Passow et al., 2001). The amount of TEP in aggregates was estimated assuming a high value of 1 aggregate/l^{-1} in the upper 20 m. Standing stocks and sedimentation rates of TEP-C were determined using a conversion factor of 0.7 μg carbon (μg Xeq.)$^{-1}$ (Engel & Passow, 2001). (Note: The directly determined value was 0.75±0.05, but a correction for non-TEP contaminants yielded a value of 0.69±0.05, which was not significantly different from the original relation. Thus here a value of 0.7 has been used for the conversions). The bacterial and phytoplankton production of TEP were calcu-

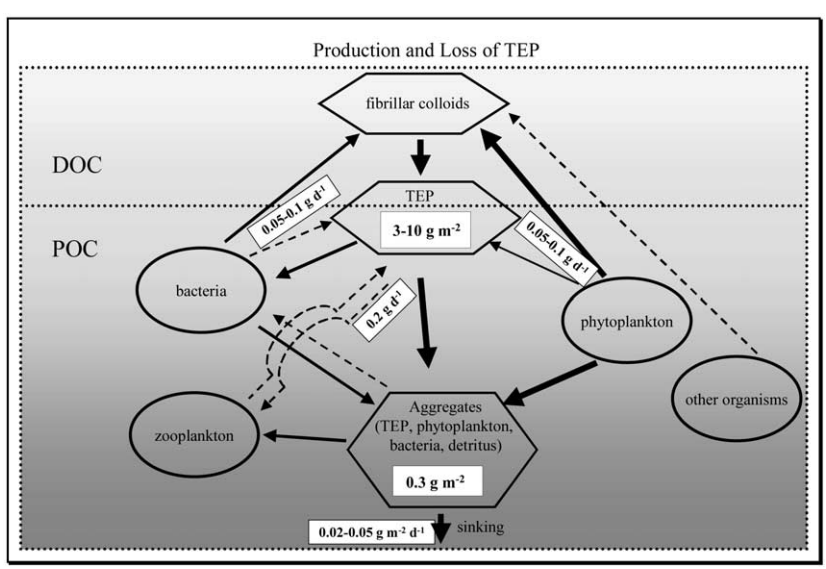

Fig. 10. Production and loss processes of TEP in the pelagic zone. TEP exist at the interface between POC and DOC and because some significant fraction of TEP is not retained on GF/F filters, TEP are only partially included in POC measurements. Both phytoplankton and bacteria release dissolved substances that form TEP. Some diatoms and possibly bacteria generate TEP directly. TEP may be degraded by bacteria or possibly grazed by filter feeding zooplankton. TEP can also form aggregates that are either grazed or sediment out of the euphotic zone. Solid, fat arrows depict known processes of general importance, solid, thin arrows signify events that are only locally or sporadically important, and the dashed arrows represent unknown pathways.

lated from the respective standing stocks and specific production rates were determined experimentally (bacteria: 4 amol TEP-C $cell^{-1}$ h^{-1}) (Stoderegger & Herndl, 1999) and (Chaetoceros sp.: 100 fg TEP-C $cell^{-1}$ h^{-1}) (Passow, 2002). A rough estimate of the grazing rate by euphausiids was calculated from their standing stocks (5 m^{-3}) (Dilling & Alldredge, 2000) and the experimentally determined estimates of grazing rate of TEP of 240 μg Xeq. d^{-1} $animal^{-1}$ which is most likely an overestimate (Passow & Alldredge, 1999). The maximal potential bacterial degradation rate of freshly formed TEP was estimated from bacterial standing stocks, and the degradation rate of the unpublished experiment introduced above. The degradation of TEP-carbon was calculated as TEP-C using the conversion of Mari (1999).

During the annual study the standing stock of TEP-C varied between 3 and 10 g C m^{-2}, with POC varying between 8 and 25 g carbon m^{-2}. Assuming an aggregate concentration of 1 aggregate l^{-1} in the upper 20 m, roughly 0.3 g carbon m^{-2} would exist in the form of TEP in aggregates. The production of TEP-C by both bacteria and phytoplankton was around 50–100 mg TEP-C m^{-2} d^{-1}. Sedimentation rates of TEP-C at 500 m were around 20–50 mg TEP-C m^{-2} d^{-1}, which was on average about 1% of the standing stock and 50% of daily production reaching 500 m depth each day. The quantitative significance of the utilization of carbon by large heterotrophs and bacteria can not yet be assessed. A presumably high estimate for the grazing rate of TEP by euphausiids was 250 mg TEP-C d^{-1} m^{-2}, but as these animals feed in migrating swarms, this rate is likely to have varied appreciably both spatially and temporally. The potential of the bacterial population to degrade fresh phytoplankton derived TEP was estimated as 1 kg TEP-C m^{-2} d^{-1}, which suggests bacterial degradation of fresh TEP was not limited by the potential degradation capacity of bacteria. However, older TEP is not degraded easily and degradation of bacterial TEP or older material is negligible on the time scale of days. These are all only order of magnitude estimates, but they provide evidence that the quantity of carbon cycled through TEP can be a significant component in overall carbon budgets. But maybe more importantly, our emerging knowledge about TEP and similar particles is changing our concepts of food webs and carbon cycling.

11.3. Changing concepts

Twenty to thirty years ago the concept of the classical food chain or web (Steele, 1974) was expanded by the recognition of the microbial loop (Azam et al., 1983), thereby incorporating the role of organisms <5 μm in our concepts of the cycling of carbon. Past attempts to determine carbon flux simplistically as a function of primary production have consistently met with failure. So, it is now acknowledged that food web structure plays an fundamental role in regulating carbon flux (Rivkin et al., 1996). The discovery of TEP and their role in the aggregation of particles has now further improved our understanding of the biogeochemical cycling of carbon. A further expansion of the theory of particle dynamics to incorporate these particles and their complex interactions with organisms is now needed if our concepts of material cycling are to be improved. The proposed expansion of particle dynamic theory and the role of TEP within current concepts are represented schematically in Fig. 11. The aggregation web plays a central role in the formation of particles from dissolved organic carbon and in the sedimentation of organic matter. It also influences food-web structure to an unknown extent, because the characteristics of TEP that lead to the condensation of DOM and submicroscopic particles into small aggregates make these components available to the feeding of larger organisms, thus linking the microbial and classical foodwebs.

12. Conclusions and perspectives

The discovery of the high abundance of colloidal and submicron particles in seawater have changed our understanding of the dynamics of DOM (e.g. Isao, Shigemitsu, Terauchi, & Kogure, 1990; Koike, Hara, Terauchi & Kogure, 1990; Wells & Goldberg, 1991; Longhurst et al., 1992; Buffle, Filella, & Leppard,

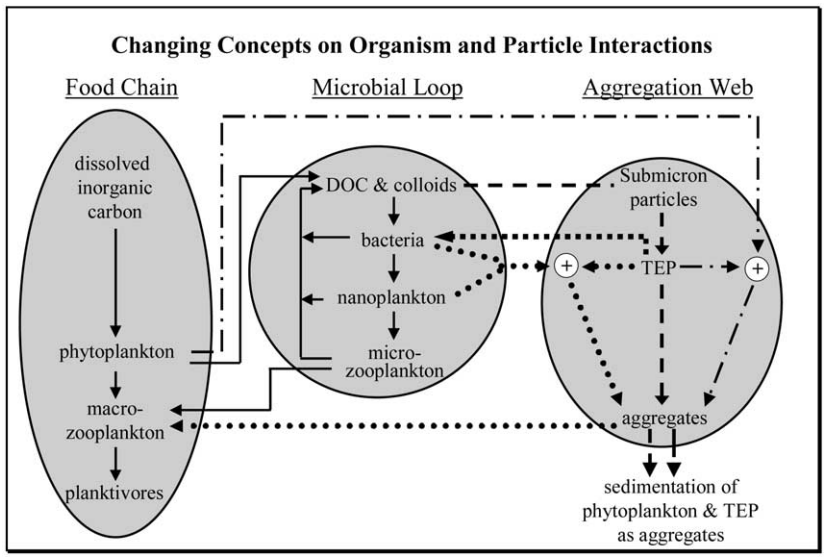

Fig. 11. Changes in the concepts of organism–particle interactions in aquatic environments, depicting the simplified food chain, the microbial loop and a newly proposed aggregation web. The food chain (or web) describes the fixation of inorganic carbon and its transfer from primary producers to successive levels of large heterotrophs. Within the microbial loop carbon is cycled between DOC, bacteria and different members of the protozooplankton. Within the aggregation web TEP binds organisms and particles, including bacteria, nanoflagellates and phytoplankton permitting the formation of aggregates. The release of DOC by phytoplankton represents a connection between the food chain and the microbial loop. Grazing by large protozoans on mesozooplankton links the microbial loop with the classical food chain. The proposed aggregation web provides a further link between the microbial loop and the food chain, because TEP aggregate the small organisms of the microbial loop into particles which are large enough to be grazed by mesozooplankton (dotted line). The proposed aggregation web describes the loss of particles from the upper water, as TEP enable the rapid sedimentation of phytoplankton and other small particles, through the formation of large, fast sinking aggregates (dash-dot line). Moreover, the sedimentation of TEP, which has formed from DOC provides a pathway (dashed line) that is an alternative to microbial degradation (cubed line) and winter mixing, for the loss of DOC from surface waters.

1994; Leppard, 1997; Nagata & Kirchmann, 1997). Colloids aggregate like particles (Wells & Goldberg, 1993; Kepkay, 1994), but act as solutes otherwise. Mucoid particles behave even more like particles, although they differ from solid particles in that they do not sink and their volume to mass ratio is variable. The distinction between particulate and dissolved substances changes meaning in light of the high abundance of colloidal and mucoid particles.

Chemically and physically TEP are a heterogeneous group of particles that exhibit the properties of gels and are generally very sticky. Their seemingly variable behavior can largely be attributed to the heterogeneity of particles classified within this group. One of the major future challenges will be to achieve more detailed and extensive characterization of the different types of TEP. Improvements in our knowledge of their chemical structure currently restricted to their monosaccharide composition will enhance our understanding of their dynamics, especially their biodegradability of TEP. Understanding the changes in physical characteristics of these gels (e.g. their rheological properties and surface charges) will also contribute greatly to our mechanistic understanding of the behavior of TEP. Knowledge from the fields of material, colloidal and medical sciences will presumably be able to contribute appreciably to this end.

Improvements in the tools whereby TEP and other mucoid particles can be characterizes will greatly improve our ability to progress our understanding of their role in the cycling of carbon and trace substances and also their role in structuring the microenvironment of microbes. A significant area for future research will be focused on the role played by TEP in carbon cycling and marine food-webs. The sedimentation

of TEP condensed from dissolved substances may be an important even dominant pathway whereby DOC may be transported into deep water. Since C:N ratio of TEP can be appreciably higher than the *Redfield*-ratio, the sedimentation of TEP-rich aggregates may be pumping carbon in excess to nitrogen to the sea floor (Engel & Passow, 2001; Engel, Goldthwait, Passow & Alldredge, 2002a).

The turnover of TEP by grazing and microbial degradation needs to be explored to evaluate the quantitative significance of TEP for such transport of carbon to the deep ocean. First results on the degradation of TEP suggest that some fractions of TEP are readily degradable, but evidence is accumulating that others are semi-resistant to microbial degradation. The effects of biological aging of TEP, and the impact of age on degradation rates, density or size of TEP, and C:N ratios of TEP need to be determined. Degradation-resistant substances may accumulate at depth at rates significant within the carbon cycle, but may not be easily detected compared to the large pool of largely unidentified carbon in the deep ocean. TEP losses through physico-chemical or photo-chemical reactions have not been investigated and offer another large area for future research efforts. Once the mechanisms driving TEP turnover have been established, more work on the abundances of TEP in those marine areas which are not dominated by diatom blooms is needed, to assess the respective quantitative significance of TEP and other mucus particles on global scales.

The function of TEP as ligands for trace elements and metals has recently begun gaining interest as the importance of acidic polysaccharides for the cycling of these substances becomes clearer (e.g. Quigley, Santschi, Hung, Guo & Honeyman, 2002). The role of exudates in the cycling of trace metals, especially Fe and the bioavailability of Fe bound to TEP offer exciting future topics for research. Very recent work on the sorption of ^{234}Th has enabled a re-evaluation of the usage of ^{234}Th as a proxy for flux and may explain some of the discrepancies between fluxes estimated from trap data and ^{234}Th profiles.

Marine microbes live in an environment that is highly structured by the presence of colloids, gel-particles and solid particles. The interactions of bacteria, phytoplankton, and protists with this organic matter continuum, and their behavioral responses to heterogeneity, create microscale ($<$1 cm) features—activity hotspots—with distinctive natures and intensities of biochemical transformations (Azam, 1998; Azam & Long, 2001; Kiørboe, Ploug & Thygesen, 2001; Kiørboe & Thygesen, 2001). By their production of particles, and their activities that change and/or degrade gels and other particles, microbes create and modify their own habitats and community structure. Recently the first tools to study microhabitats and interactions between individual microbes and their environment have been developed (e.g. microsensors, high-resolution digital vidio-imaging) and these are opening possibilities for research into interactions on microscales, and how such interactions influence the structure and functioning of marine ecosystems and biogeochemical cycles at larger scales.

The inclusion of colloids and TEP-like particles in concepts and models of food web structure as well as biogeochemical cycling add to their complexity, because these substances mediate interactions among organisms and with their surrounding. But the presence of these and similar particles are an inherent property of aquatic ecosystems, and their roles in the conversion between dissolved and particulate matter, their impact on food web structure, and their effect on the cycling of matter are too large to ignore. Their inclusion in models and concepts will consequently improve model results and our understanding of particle interactions.

Acknowledgements

During the last 8 years, countless people have contributed to the work on TEP, and I want to thank them all for adding a small piece to the big puzzle. I enjoyed working with my co-authors and I thank them for a working atmosphere that was fun and productive. Colleagues and reviewers from all over the world have shared their observations, ideas and send encouragement. I especially want to thank Bernt Zeitzschel for his continuous trust and kind nudging of me to write this review, and Alice Alldredge, who

welcomed me into her laboratory many years ago and with whom I shared many years of great research and a wonderful friendship. I also especially thank Avan Antia, Uli Bathmann, Christopher Cogan, Anja Engel, Paul Kepkay, Viktor Smetacek, Doug Wallace and two anonymous reviewers for constructive comments and discussions.

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