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Distribution of transparent exopolymer particles (TEP) in the northeast Atlantic Ocean and their potential significance for aggregation processes

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Abstract

The abundance of transparent exopolymer particles (TEP) was determined in the northeast Atlantic Ocean (40–55°N, ~20°W) during several cruises from June to November 1996. An accumulation of TEP in the water column was observed at bloom and post-bloom sites along a 20°W transect in June/July (maximum concentration: 124 μg Gum Xanthan equivalents (Xeq.) l^{-1}), but concentrations were uniformly low (mean concentration: 28.5 ± 10.2 μg Xeq. l^{-1}) during autumn at the BIOTRANS site (47°N, 20°W). TEP concentrations in the open northeast Atlantic were considerably lower than previously published values from coastal sites. However, during June/July TEP:Chl *a* (weight/weight) ratios were comparable to values at coastal seas. It is suggested that phytoplankton production modulates TEP concentration in the open ocean as it does in coastal systems. TEP contributed significantly to the organic carbon pool as derived from the ratio TEP-C:POC, in summer (mean percentage: 17 ± 7.5; w/w), as well as in autumn (mean percentage: 18 ± 11, w/w). The potential influence of TEP on particle coagulation rates in the northeast Atlantic was assessed from estimates of their influence on particle stickiness and on particle volume concentrations. This indicated that TEP may be essential for initiating particle aggregation at low biomass concentrations, typical for open ocean sites.

Keywords: Transparent exopolymer particles; TEP; Aggregation; Stickiness; Atlanic ocean

1. Introduction

Transparent exopolymer particles (TEP) are very special compared to the bulk of particles in pelagic systems, such as plankton, debris or clays. First, TEP originate from dissolved precursors (Mopper et al., 1995; Passow, 2000). These precursors are exopolymeric carbohydrates, mainly polysaccharides, that contain acidic sugars. Through divalent cation bridging and/or ester–sulfate bonding between the anionic ends of the acidic sugars, the polysaccharide chains can align to form polysaccharide aggregates, which eventually become large enough to be retained on 0.4 μm filters. Determined by the polysaccharide specific stain Alcian Blue, a cationic copper phthalocyanine dye that complexes carboxyl ($-COO^-$) and half-ester sulfate (OSO_3^-) reactive groups of acidic polysaccharides, the polysaccharide aggregates become microscopically

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visible and are defined as TEP (Alldredge et al., 1993). Because the amount of Alcian Blue adsorption is directly related to the weight of the polysaccharides (Ramus, 1977; Engel and Passow, 2001), TEP can be quantified colorimetrically as shown by Passow and Alldredge (1995).

The origin of exopolysaccharide precursors in seawater is manifold, but their concentration often increases during phytoplankton blooms and especially when phytoplankton become nutrient limited (Mari and Burd, 1998; Corzo et al., 2000; Engel et al., 2002a). The exudation of polysaccharides by nutrient starved phytoplankton cells is therefore interpreted as the result of a cellular carbon overflow, when primary production proceeds while biomass synthesis is limited (Wood and Van Valen, 1990). The increase of TEP at the end of phytoplankton blooms has been shown to mirror this overconsumption of carbon, shifting the carbon to nitrogen ratio of particulate organic matter (POM) far beyond the common expectation of the Redfield ratio (C:N $\sim$6.6, Redfield et al., 1963) (Engel et al., 2002a, 2003). Thus, TEP establish a bridge between the dissolved organic matter and the POM pool and influence the biogeochemical composition of particles qualitatively by a selective enrichment of carbon. Beyond this, TEP are potentially important for biogeochemical fluxes in the sea, because they influence the sedimentation mode of particles. Because of their high abundance and surface reactivity, TEP scavenge trace elements (e.g. Fe and Th) (Quigley et al., 2002; Guo et al., 2002) and are the key agents for increasing the coagulation efficiency of physical aggregation processes (Logan et al., 1995; Engel, 2000).

Although much work has been done to identify these extraordinary features of TEP in process studies, the knowledge about the abundance and distribution of TEP in the open ocean is still rather poor. The primary aim of this paper is to give new data on the spatial and temporal distribution of TEP in the northeast Atlantic Ocean and to discuss the potential importance of TEP for aggregation processes and the biogeochemical composition of particles in this open ocean region.

2. Materials and methods

Samples for TEP were collected on a transect along 20°W during Meteor cruise M36/2 in June and July 1996 and within a grid of 180×180 nautical miles around the JGOFS site BIOTRANS during the Meteor cruises M36/5 and M36/6 in September–November 1996 (Fig. 1). Seawater samples were harvested from the upper water column with a CTD/Niskin-bottle rosette, transferred to 250 ml PE bottles and preserved with formalin (1% final concentration). The preservation of samples with formalin does not interfere with the TEP analysis, as was shown by Passow and Alldredge (1995). Within 3 months after sampling TEP were determined in the home laboratory according to the spectrophotometric

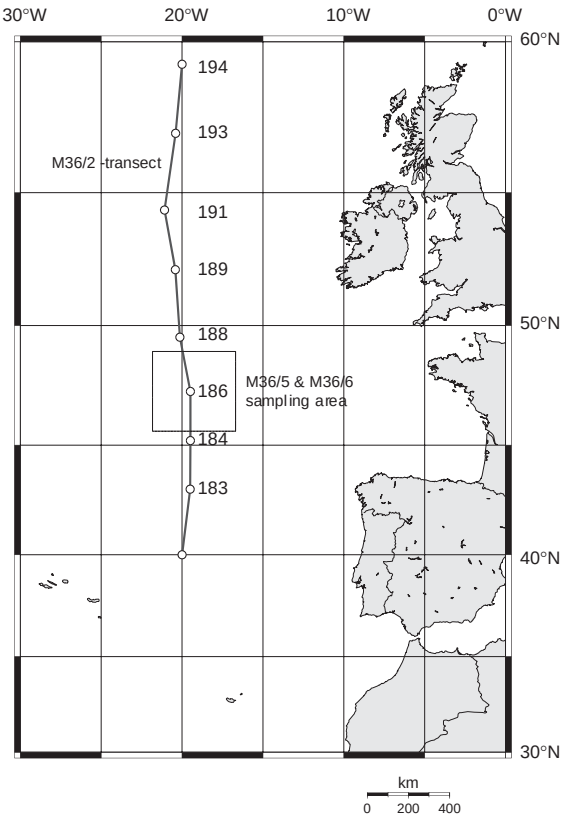

Fig. 1. Map showing the sampling sites in the Northeast Atlantic. Stations along the 20°W transect (M36/2) are indicated by numbers. Sampling during the M36/5 and M36/6 cruises was carried out within the box around 47°N, 20°W.

method of Passow and Alldredge (1995). Briefly, 100–200 ml samples were filtered onto 0.4 μm Nuclepore filters, stained with 500 μl of an aqueous solution of Alcian Blue (0.02% w/w at pH 2.5) and rinsed with distilled water. Each filter was soaked for at least 2 h with 6 ml of 80% H_2SO_4 in order to dissolve the particulate matter and then the solution was measured at 787 nm in a 1 cm cuvette. All filters were prepared in at least two replicates. The acidic polysaccharide Gum Xanthan was used as a standard. The detection limit of the measurements was 5 μg Gum Xanthan equivalents (Xeq.) l^{-1} and the standard deviation of replicate samples was $<10\%$. At four stations (M36/2, St. 188, 189, 191, 193) the total volume concentration of particles between 2 and 60 μm equivalent spherical diameter was determined with the Coulter Counter (Coulter Multisizer II) from replicate 2 ml subsamples. The Coulter Counter detects and sizes particles suspended in seawater such as cells, lithogenic particles or debris, but cannot quantify gel particles such as TEP (Alldredge et al., 1993). The total volume concentration of Coulter Counter detectable particles will be denoted as solid particles volume (SV) and hence does not include the volume of TEP. Dilution of seawater samples was not necessary as coincidence of particles at the aperture remained $<5\%$.

POC, PON, Chl *a* and nitrate data were provided by the German JGOFS data management (http://www.ifm.uni-kiel.de/jgofs/dm/parametr.htm). Further information on Chl *a* and nitrate data from the M36/5 are given by Schiebel et al. (2001), and on POC, PON, Chl *a* and nitrate data during M36/2 by Kähler and Koeve (2001).

3. Results

3.1. TEP distribution along a 20° W transect

As described by Körtzinger et al. (2001), the JGOFS Meteor cruise M36/2 traversed different vernal situations along the 20°W transect, with early bloom conditions at the northernmost stations merging into a bloom and a post-bloom situation south of 50°N and again into a non-bloom situation further south. Accordingly, nutrient concentration declined from north to south (Fig. 2a), while chl *a*, POC and PON concentrations increased, yielding highest concentrations at the bloom stations 188 and 189 (Fig. 2a and b). Depth profiles of TEP in the upper water column

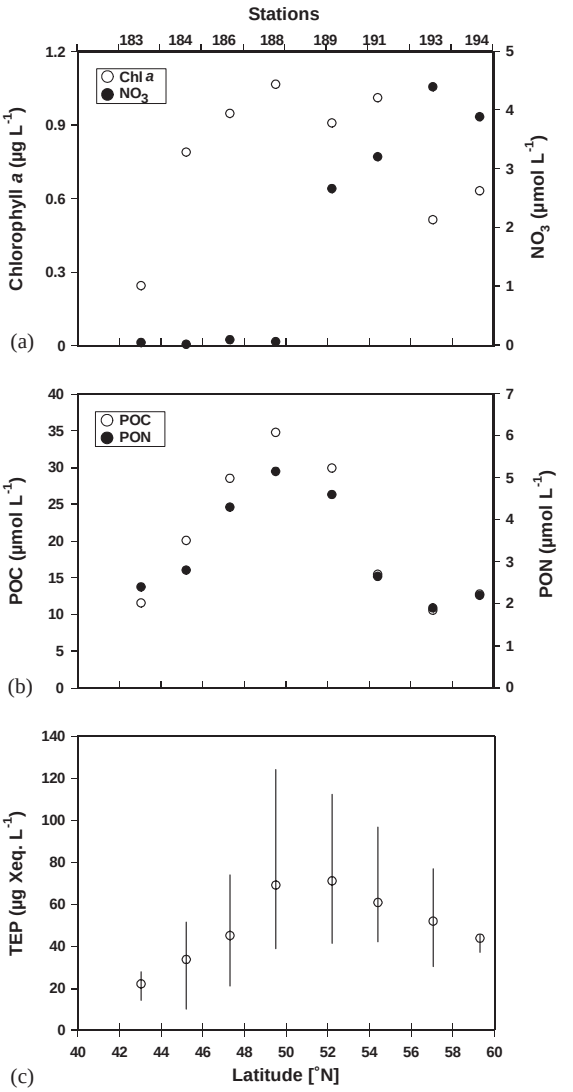

Fig. 2. Concentrations of chl *a* and NO_3 (a), and of POC and PON (b) in the surface waters (5 m) indicate that the M36/2 cruise traversed post-bloom, bloom and early bloom regions while heading towards the north. High variability of TEP concentrations within the upper 70 m was observed at the bloom stations as indicated by the bars ranging from minimum to maximum values (c), symbols denote average concentration of 4–6 sampling depths.

were determined at eight locations along the transect. The accumulation of TEP in the water column was evident from the difference between the highest and lowest concentrations in each depth profile and mirrored the rise and decline of the bloom along the transect (Fig. 2c). Little variation of TEP concentration with depth was determined before and after the bloom (st. 194 and st. 184, respectively), while distinct depth maxima occurred at the bloom stations (st. 188 and st. 189, respectively), where decreasing nutrient concentration denoted the transition from a bloom to a post-bloom situation. An overall pattern of decreasing TEP concentrations with depth was observed (Fig. 3).

3.2. TEP abundance at the BIOTRANS site

Relatively low and uniform TEP concentration of $28.5 \pm 10.2\,\mu g\,Xeq.\,l^{-1}$ (number of stations = 43, number of samples = 80) were determined within the upper 50 m at the BIOTRANS site in September and October (Fig. 4). Here, TEP concentration was uncorrelated with Chl *a* ($r^2 = -0.25$, $n = 50$; range: 0.07–0.59 µg Chl $a\,l^{-1}$) or nitrate ($r^2 = 0.31$, $n = 50$; range: 0–6.7 µmol $NO_3\,l^{-1}$) concentrations. At the two stations sampled at the beginning of November, TEP concentration had increased significantly to a mean value of $42.6 \pm 17\,\mu g\,Xeq.\,l^{-1}$.

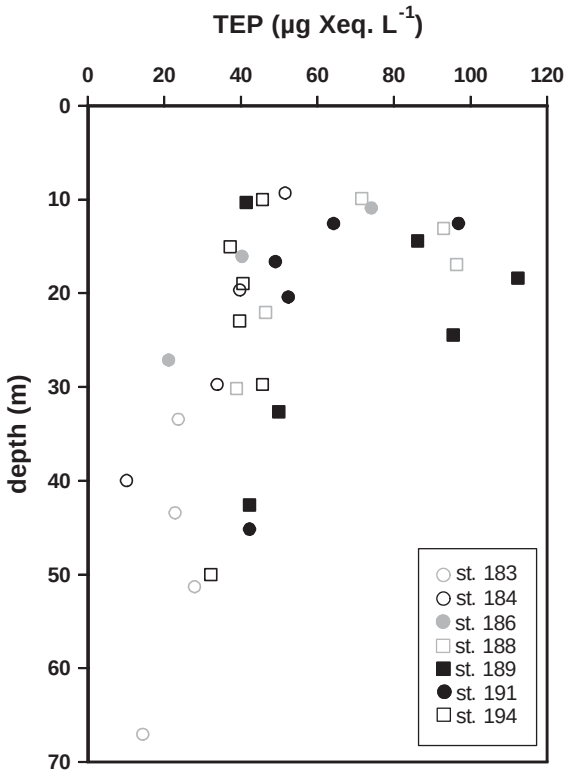

Fig. 3. General depth distribution of TEP, composite plot of all data collected during M36/2.

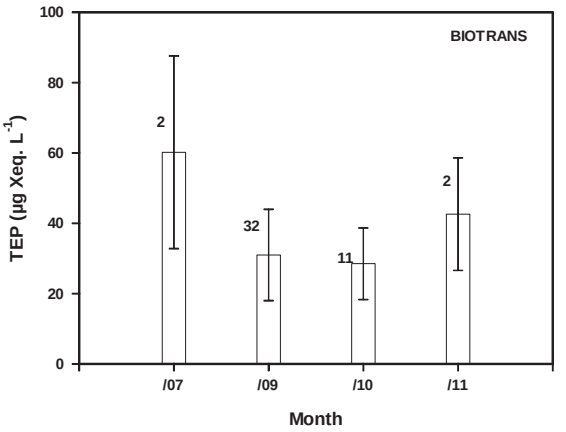

Fig. 4. Temporal changes in mean TEP concentration (±1SD) at the BIOTRANS site in 1996. Number of stations are given next to bars.

4. Discussion

4.1. Abundance of TEP in the northeast Atlantic

So far, field measurements of TEP have almost exclusively been carried out in coastal regions. There, mean TEP concentrations in the range 100–3000 $\mu g\,Xeq.\,l^{-1}$ have been reported (see Passow, 2002, for review), generally much higher than the values determined for the northeast Atlantic during this study. However, because of higher nutrient concentrations and shallower mixing depths, phytoplankton biomass is usually higher at coastal sites too. For a better comparison, the ratio between TEP concentration and phytoplankton abundance is considered here, taking Chl *a* as an indicator of phytoplankton biomass. Average TEP:Chl *a* ratios (w/w) in the upper water column

ranged between 49 and 104 $\mu g\,Xeq.\,\mu g^{-1}$ during the summer transect in 1996 and varied around 61 $\mu g\,Xeq.\,\mu g^{-1}$ at the BIOTRANS site in autumn. The former values are comparable to mean TEP:Chl *a* ratios determined for the Ross Sea ($\sim 85\,\mu g\,Xeq.\,\mu g^{-1}$) (Hong et al., 1997) and are only a little lower than ratios determined during a phytoplankton bloom at a coastal site in the sub-Arctic Pacific (125–144 $\mu g\,Xeq.\,\mu g^{-1}$) by Ramaiah et al. (2001) or for the central Baltic Sea during summer ($130 \pm 50\,\mu g\,Xeq.\,\mu g^{-1}$) by Engel et al. (2002b). This indicates that at least during the productive season and relative to phytoplankton biomass, the magnitude of TEP production in the open northeast Atlantic is comparable to coastal seas.

During autumn, TEP concentration did not follow changes of the two main indicators for biological productivity, nitrate and chlorophyll, and stayed rather constant over time. This indicates either that the phytoplankton community in autumn did not produce a significant amount of TEP or that TEP were degraded rapidly. There are only few and conflicting observations of the biodegradability of TEP. Exopolymers released by phytoplankton under nutrient limitation can be rather resistant to bacterial decomposition (Obernosterer and Herndl, 1995). Degradation experiments with TEP produced by diatoms showed that even after 1 month, TEP were not completely degraded by bacteria (Engel and Grossart, unpublished results). On the other hand, bacteria can also produce refractory TEP (Stoderegger and Herndl, 1999). The likely fate of refractory TEP is removal from the water column by aggregation with sinking particles. Because particle abundances in autumn are low, aggregation is less likely and refractory TEP should prevail in the upper waters for a longer time.

4.2. Relationship between TEP and POC

The carbon content of TEP (TEP-C) depends on the origin of TEP precursors and has so far been observed to vary between 39% (w/w), as determined for TEP that was produced during a bloom of the coccolithophorid *Emiliania huxleyi,* and 88% (w/w), as measured for a culture of the diatom *Coscinodiscus wailesii* (Engel et al., 2003; Engel and Passow, 2001). For estimating TEP-C from TEP of diatom origin, Engel and Passow (2001) gave a conversion factor of $f' = \Delta C/\Delta TEP = 0.75$. With this factor they estimated a mean TEP-C concentration of $40 \pm 13\,\mu g\,l^{-1}$ for the M36/2 samples and $27 \pm 1.0\,\mu g\,l^{-1}$ for the samples collected during M36/5. In order to obtain an improved conversion factor that covers a broader range of samples and concentrations, a recalculation for f' was performed here, using data from 47 determinations of TEP-C by the method of Engel and Passow (2001); including TEP produced during an *E. huxleyi* bloom ($n = 11$, Engel et al., in press), TEP produced by various diatoms species ($n = 26$, Engel and Passow, 2001, omitting the two highest values) and by a mixed culture of *Chaetoceros decipiens* and *Thalassiosira pseudonana* ($n = 10$, unpublished data). Regression analysis yielded $f' = 0.63 \pm 0.03$ ($n = 47$, $r^2 = 0.80$, $p < 0.001$). Because this conversion factor is still biased by a large number of values derived for TEP of diatom origin, it can again be only an approximation for natural TEP-C. Hence, assuming a carbon content of TEP of 63% (w/w), TEP-C accounted for approximately $33.6 \pm 16\,\mu g\,C\,l^{-1}$ during the transect M36/2 in June/July, which is equivalent to $18 \pm 7\%$ of the measured POC concentrations. TEP-C was significantly lower at the BIOTRANS site in autumn with $19 \pm 8\,\mu g\,C\,l^{-1}$, but the ratio TEP-C:POC was in a similar range ($18 \pm 11\%$). Because TEP have high C:N ratios (Engel and Passow, 2001; Mari et al., 2001), they contribute to POC rather than to PON. Thus, the relatively uniform TEP concentrations observed at the BIOTRANS region in autumn provided a background concentration of POC and may partly explain the offset in the linear regression of POC vs. PON (Fig. 5).

Recently, Hung et al. (2003) estimated that the 'Alginic Acid equivalent' carbon content of acid polysaccharides (APS), which they determined by slightly modifying the method of Passow and Alldredge (1995), accounted for 0.9–3.3% of POC in the Gulf of Mexico. Alginic acid is a polysaccharide, which is entirely composed of acidic sugars. Because Alcian Blue reacts with acidic

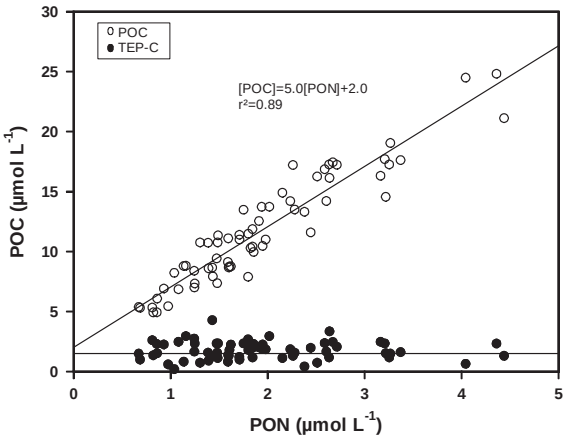

Fig. 5. Estimated carbon content of TEP (TEP-C) related to PON concentration. Mean TEP-C concentration ($1.5\,\mu mol\,l^{-1}$) explained 74% of the background POC (y-intercept), as calculated by linear regression of POC vs. PON. Samples ($n = 65$) were taken in autumn at the BIOTRANS site (cruises M36/5 and M36/6).

sugars, an 'Alginic Acid equivalent' carbon content can be interpreted as the carbon content of the acidic sugars (monomers) within the polysaccharide. To date the acidic sugar content of TEP is not known, but since the neutral sugar composition of TEP is similar to that of polysaccharides released by marine phytoplankton (Mopper et al., 1995; Aluwihare and Repeta, 1999), it can be suggested that the acidic sugar fractions are of comparable magnitude also. For example, 20% of the total sugar content of polysaccharides released by *E. huxleyi* are represented by the acidic sugar D-galacturonic acid (De Jong et al., 1979). Bacterial exopolysaccharides have a higher acidic sugar content (20–50%, Kennedy and Sutherland, 1987), but contribute only a small amount to TEP in the ocean (Stoderegger and Herndl, 1999). Hence, the estimates for the 'Alginic Acid equivalent' carbon content of APS given by Hung et al. (2003) would explain only a minor fraction of the carbon content of polysaccharides contained in TEP.

TEP-C in this study was estimated from Alcian Blue adsorption using a conversion factor, which was obtained from direct measurements of TEP-C after Engel and Passow (2001). The method of Engel and Passow (2001) has been shown to give consistent results with the method of Mari (1999), who also determined the carbon content of TEP directly, but enumerated and sized TEP by microscopy. Since it is known that mucoid substances formed from algal exudates contain not only carbohydrates but also small amounts of proteinaceous material and lipids (Decho, 1990), the total carbon content of TEP may be larger than the carbon content of carbohydrates contained in TEP. Because the relationship between Alcian Blue adsorption and carbon content of TEP varies between different phytoplankton species, it cannot be fully ruled out that the chosen mean conversion factor over- or underestimates TEP-C at the field stations considered here.

4.3. TEP effect on aggregation rates

The abundance of TEP increases bulk particle volume concentration and hence collision rates between particles, which is the prerequisite for aggregation to occur. Moreover, TEP raise the bulk stickiness of particles. Engel (2000) computed the relationship between the stickiness (α) of bulk particles and the ratio of TEP to Chl *a* and obtained: $\alpha_1 = 6.38 \times 10^{-4}$(TEP:Chl *a*) -3.3×10^{-3}. With this relationship and the concentrations of Chl *a* and TEP during M36/2, values for α between 0.03 and 0.08 are obtained (Table 1). These values are quite low and comparable to the stickiness of cells in healthy cultures (Kiørboe and Hansen, 1993). However, Engel (2000) determined the stickiness only for senescent phytoplankton, where the Chl *a* content of cells was quite low and the TEP:Chl *a* ratio consequently rather high (range 250–3800 $\mu g\,Xeq.\,\mu g^{-1}$). Since phytoplankton cells are only a fraction of particles that aggregate, it can be assumed that the ratio between TEP and the total volume of Coulter Counter detectable particles (TEP:SV) is more independent from the relative abundance of phytoplankton or the physiological state of cells and thus a better indicator for the coagulation efficiency of bulk particles. Therefore, the relationship between α and TEP:SV $\mu g\,Xeq.\,\mu l^{-1}$ was recalculated from the data of Engel (2000), using

Table 1
Estimated mean stickiness (α) of particles within surface waters along the transect 20°W

Station	TEP:Chl a	Stickiness		TEP:SV	Stickiness	
	Mean ($\mu g\,\mu g^{-1}$)	Mean (α_1)	Range (α_1)	Mean ($\mu g\,\mu l^{-1}$)	Mean (α_2)	Range (α_2)
183	83	0.05	0.03–0.08	—	—	—
184	54	0.03	0.02–0.05	—	—	—
186	58	0.03	0.02–0.06	73	0.07	0.04–0.11
188	64	0.04	0.03–0.06	90	0.08	0.07–0.11
189	73	0.04	0.02–0.08	117	0.11	0.06–0.18
191	49	0.03	0.02–0.04	106	0.10	0.06–0.12
193	104	0.06	0.04–0.11	—	—	—
194	79	0.05	0.04–0.06	—	—	—

Calculation: $\alpha_1 = 6.38 \times 10^{-4}$(TEP:Chla)$-3.3 \times 10^{-3}$ (Engel, 2000), $\alpha_2 = 9.1 \times 10^{-4}$(TEP:SV) recalculated from Engel (2000) ($r^2 = 0.95$, $n = 8$).
Mean values were calculated from 4 to 6 sampling depths within the upper 70 m of the water column.

Table 2
Estimated half-lifes ($t_{1/2}$) of particle concentration within the mixed layer (at depths 15–17 m) at bloom and post-bloom stations in the North Atlantic (M36/2)

Station	Stickiness (α_2)	SV (ppm)	TEP_Vol. (ppm)	$t_{1/2}$ SV (days)	$t_{1/2}$ SV + TEP_Vol. (days)	$t_{1/2}$ SV_{*2} + TEP_Vol. (days)
186	0.04	0.91	1.46	105	40	29
188	0.08	1.13	3.49	44	11	8.6
189	0.17	0.61	4.07	38	4.9	4.3
191	0.06	0.84	1.90	80	25	19

Calculations were performed according to Eq. (2) for the assumptions: (1) only solid particles that can be determined with the Coulter Counter aggregate ($t_{1/2}$ SV), (2) Solid particles and TEP aggregate ($t_{1/2}$ SV + TEP_Vol.), (3) the SV was twice as much before the cruise M36/2 but the amount of TEP was the same (SV_{*2} + TEP_Vol.). The shear rate was set to $G = 0.84\,s^{-1}$. For SV_{*2} and SV_{*2} + TEP_Vol_{*2}, $t_{1/2}$ is simply half the value of $t_{1/2}$ SV and $t_{1/2}$ SV + TEP_Vol., respectively.

the TEP-corrected α' (see Engel, 2000, for details), and yielded: $\alpha_2 = 9.1 \times 10^{-4}$ (TEP:SV) ($r^2 = 0.95$, $n = 8$). With this second formula, values for α in the range 0.04–0.18 were obtained, with the highest stickiness in the TEP maximum at the bloom station 189. These values are still low compared to stickiness values determined for coastal sites, e.g. α ranged 0–0.45 at the coastal Baltic Sea during the spring bloom (Engel, 1998) and yielded values of up to 0.4 for a diatom bloom in the Benguela upwelling current (Kiørboe et al., 1998), but are comparable to estimates for the open ocean used in model calculations (Kriest and Evans, 1999). However, particle concentration and size, rather than stickiness, are the most sensitive parameters for predicting aggregation rates (Hill, 1992). Initial aggregation of similar sized particles can be approximated by an exponential function after Kiørboe and Andersen (1990):

$$C_t = C_0 e^{-(7.82\alpha\Phi G/\pi)t}, \quad (1)$$

where α is the stickiness, Φ is the volume concentration of particles (ppm), G the fluid shear rate (s^{-1}) and C_0 and C_t the particle concentrations at times 0 and t, respectively. As a first order approximation of aggregation dynamics during the June/July bloom 1996, the time needed to reduce particle concentration through coagulation by half ($t_{1/2}$) was derived from Eq. (1) using the estimated α_2 values (Table 2) and a shear rate of $0.84\,s^{-1}$ after Kriest and Evans (1999)

$$t_{1/2} = \frac{\ln 2\pi}{7.82\alpha_2\Phi G}. \quad (2)$$

This approximation indicated that during the bloom, M36/2 aggregation of particles would

operate on timescales of weeks to months, even at the bloom station 189, and hence would be negligible compared to the timescales of biological growth and decay ($t_{1/2}$ SV, Table 2).

To estimate now the influence of TEP on aggregation rates, the volume concentration of TEP was included in Φ. Therefore, the volume concentration of TEP was calculated from TEP-C assuming a carbon density of 1.74×10^{-2} kg l^{-1} (after Engel and Passow, 2001) and yielded a range of 0.76–4.1 ppm for stations 186–191. These estimated TEP volume fractions are, again, quite low compared to data from coastal seas, which range between 7 and 44 ppm (Engel and Passow, 2001) but can be as high as 310 ppm in the coastal Baltic Sea (Mari and Burd, 1998). However, for the northeast Atlantic the estimated volume fractions of TEP are still 2–7 times higher than the volume fraction of particles determined with the Coulter Counter. Hence, even these low amounts of TEP increase the total volume fraction of particles sufficiently to reduce $t_{1/2}$ drastically, e.g. from 38 days to 4.9 days at the TEP maximum at St. 189 ($t_{1/2}$ SV + TEP_Vol., Table 2).

It is questionable, whether these half-life values are already sufficient for marine snow formation to occur and to promote pulsed sedimentation 'events'. Logan et al. (1995) observed that $t_{1/2}$ values were on the order of 1 day prior to the occurrence of large aggregates. May this be a possible value for the northeast Atlantic? Körtzinger et al. (2001) calculated that about 50% of the seasonal new production between stations 188 and 189 had already been exported at the time of the M36/2 cruise. Assuming that the volume concentration of particles in the mixed layer was two times higher (SV_{*2}) before M36/2 samples were taken, and ignoring TEP, $t_{1/2}$ would still have exceeded 2 weeks and not be sufficient to promote marine snow formation. Even if TEP was included in aggregation processes ($t_{1/2}$ SV_{*2} + TEP_Vol., Table 2) and was twice as high also, a value for $t_{1/2}$ on the order of 1 day would not have been achieved, although in the latter scenario $t_{1/2}$ reduces to appreciable 2.4 days at station 189. Because cell growth in the euphotic zone is limited by nutrient availability, the maximum SV that can be sustained in an area is finite. In contrast, TEP production can proceed under nutrient limitation and could be an important mechanism to increase particle concentration in the open ocean.

How much TEP would have been necessary to reduce $t_{1/2}$ to 1 day at station 188–189? Solving Eq. 1 for Φ, using the same parameter values for shear and stickiness as above, and subtracting SV_{*2} as the maximum SV that can be sustained in that area, results in a total 'need' for TEP volume concentration on order of 20–47 ppm, equivalent to 30–68 μmol TEP-C l^{-1}. This amount of TEP-C would in turn have raised the molar POC:PON ratio of the seasonal new production at stations 188–189 to values of 9.8–13.5, provided the new production of SV (NP_{SV}) followed a 'Redfield ratio' of C:N of 6.6, and to 8.8–12.5, provided NP_{SV} is formed with a C:N of 5.6 as suggested by Körtzinger et al. (2001). Both estimates are well within the range of C:N ratios calculated for the export production at these sites (Körtzinger et al., 2001). At the time of M36/2 the POC:PON ratios at stations 186–191 were in the range of 4.8–7.2. A higher production of TEP at the time of export production could therefore explain the mechanism of export, i.e. physical aggregation, and could also explain an elevation of POC:PON ratios of the exported material.

To sum up, assuming that physical aggregation is initiated with similar sized particles, e.g. phytoplankton cells, the northeast Atlantic cannot sustain a volume concentration of particles sufficient to reduce $t_{1/2}$ to values that have been determined at times of marine snow formation. Unlike phytoplankton growth, TEP production is not limited by nutrient availability. Therefore, TEP production can potentially increase the bulk volume concentration of particles to such a degree that marine snow formation is likely to occur. The associated increase of POC concentration would be in good accordance with estimates for the C:N ratio of export production. When the amount of nitrate available for NP_{SV} production decreases, as the transect approaches the southern oligotrophic stations, it is obvious that the need for additional particulate material like TEP to promote aggregate formation will become higher. Because TEP do not sink by themselves and slow down the settling velocity of aggregates (Engel and Schartau,

1999), the formation of aggregates that are 'heavy' enough to sink will have a minimum requirement for solid particles. This may not be fulfilled in oligotrophic regions.

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References

Alldredge, A.L., Passow, U., Logan, B.E., 1993. The abundance and significance of a class of large, transparent organic particles in the ocean. Deep-Sea Research I 40, 1131–1140.

Aluwihare, L.I., Repeta, D.J., 1999. A comparison of the chemical characteristics of oceanic DOM and extracellular DOM produced by marine algae. Marine Ecology Progress Series 186, 105–117.

Corzo, A., Morillo, J.A., Rodríguez, S., 2000. Production of transparent exopolymer particles (TEP) in cultures of *Chaetoceros calcitrans* under nitrogen limitation. Aquatic Marine Ecology 23, 63–72.

Decho, A.W., 1990. Microbial exopolymer secretions in the ocean environments their role(s) in food webs and marine processes. Oceanography and Marine Biology: An Annual Review 28, 73–153.

De Jong, E., van Rens, L., Westbroek, P., Bosch, L., 1979. Biocalcification by the marine alga *Emiliania huxleyi* (Lohmann) Kamptner. European Journal of Biochemistry 99, 559–567.

Engel, A., 1998. Bildung, Zusammensetzung und Sinkgeschwindigkeiten mariner Aggregate. Berichte aus dem Institut für Meereskunde Kiel, Ph.D. Thesis, p. 300.

Engel, A., 2000. The role of transparent exopolymer particles (TEP) in the increase in apparent particles stickiness (α) during the decline of a diatom bloom. Journal of Plankton Research 22, 485–497.

Engel, A., Delille, B., Jacquet, S., Riebesell, U., Rochelle-Nevall, E., Terbrüggen, A., Zondervan, I. TEP and DOC production by *Emiliania huxleyi* exposed to differentCO_2 concentrations: a mesocosm experiment. Aquatic Microbial Ecology, in press.

Engel, A., Goldthwait, S., Passow, U., Alldredge, A., 2002a. Temporal decoupling of carbon and nitrogen dynamics in a mesocosm diatom bloom. Limnology and Oceanography 47, 753–761.

Engel, A., Meyerhöfer, M., v. Bröckel, K., 2002b. Chemical and biological composition of suspended particles and aggregates in the Baltic Sea in summer (1999). Estuarine, Coastal and Shelf Science 55, 729–741.

Engel, A., Passow, U., 2001. The carbon and nitrogen content of transparent exopolymer particles (TEP) in relation to their Alcian Blue adsorption. Marine Ecology Progress Series 219, 1–10.

Engel, A., Schartau, M., 1999. Influence of transparent exopolymer particles (TEP) on sinking velocity of Nitzschia Closterium aggregates. Marine Ecology Progress Series 182, 69–76.

Guo, L., Hung, C.C., Santschi, P.H., Walsh, I.D., 2002. ^{234}Th scavenging and its relationship to acid polysaccharide abundance in the Gulf of Mexico. Marine Chemistry 78 (2–3), 103–119.

Hill, P.S., 1992. Reconciling aggregation theory with the observed vertical fluxes following Phytoplankton blooms. Journal of Geophysical Research 97 (C2), 2295–2308.

Hong, Y., Smith Jr., W.O., White, A.M., 1997. Studies on transparent exopolymer particles (TEP) produced in the Ross Sea (Antarctica) and by *Phaeocystis antarctica* (Prymnesiophyceae). Journal of Phycology 33, 368–376.

Hung, C.-C., Guo, L., Santschi, P H., Alvarado-Quiroz, N., Haye, J.M., 2003. Distributions of carbohydrate species in the Gulf of Mexico. Marine Chemistry 81, 119–135.

Kähler, P., Koeve, W., 2001. Marine dissolved organic matter: Can its C:N ratio explain carbon overconsumption? Deep-Sea Research I 48, 49–62.

Kennedy, A.F.D., Sutherland, I.W., 1987. Analysis of bacterial exopolysaccharides. Applied Biochemistry and Biotechnology 9, 12–19.

Kiørboe, T., Andersen, K.P., Dam, H.G., 1990. Coagulation efficiency and aggregate formation in marine phytoplankton. Marine Biology 107, 235–245.

Kiørboe, T., Hansen, J.L.S., 1993. Phytoplankton aggregate formation: Observations of patterns and mechanisms of cell sticking and the significance of exopolymeric material. Journal of Plankton Research 15, 993–1018.

Kiørboe, T., Tiselius, P., Mitchell-Innes, B., Hansen, J.L.S., Visser, A.W., Mari, X., 1998. Intense aggregate formation with low vertical flux during an upwelling-induced diotom bloom. Limnology and Oceanography 43, 104–116.

Körtzinger, A., Koeve, W., Kähler, P., Mintrop, L., 2001. C:N ratios in the mixed layer during the productive season in the northeast Atlantic Ocean. Deep-Sea Research I 48, 661–688.

Kriest, I., Evans, G.J., 1999. Representing phytoplankton aggregates in biogeochemical models. Deep-Sea Research I 46, 1841–1859.

Logan, B.E., Passow, U., Alldredge, A.L., Grossart, H.-P., Simon, M., 1995. Rapid formation and sedimentation of large aggregates is predictable from coagulation rates (half-lives) of transparent exopolymer particles (TEP). Deep-Sea Research II 42, 203–214.

Mari, X., 1999. Carbon content and C:N ratio of transparent exopolymer particles (TEP) produced by bubbling of exudates of diatoms. Marine Ecology Progress Series 183, 59–71.

Mari, X., Burd, A., 1998. Seasonal size spectra of transparent exopolymeric particles (TEP) in a coastal sea and comparison with those predicted using coagulation theory. Marine Ecology Progress Series 163, 63–76.

Mari, X., Beauvais, S., Lemee, R., Pedrotti, M.L., 2001. Non-Redfield C:N ratio of transparent exopolymeric particles in the northwestern Mediterranean Sea. Limnology and Oceanography 46, 1831–1836.

Mopper, K., Zhou, J., Ramana, K.S., Passow, U., Dam, H.G., Drapeau, D.T., 1995. The role of surface-active carbohydrates in the flocculation of a diatom bloom in a mesocosm. Deep-Sea Research II 42, 47–73.

Obernosterer, I., Herndl, G.J., 1995. Phytoplankton extracellular release and bacterial growth: dependence on inorganic N.P ratio. Marine Ecology Progress Series 116, 247–257.

Passow, U., 2000. Formation of transparent exopolymer particles, TEP, from dissolved precursor material. Marine Ecology Progress Series 192, 1–11.

Passow, U., 2002. Transparent exopolymer particles (TEP) in aquatic environments. Progress in Oceanography 55, 287–333.

Passow, U., Alldredge, A.L., 1995. A dye-binding assay for the spectrophotometric measurement of transparent exopolymer particles (TEP) in the ocean. Limnology and Oceanography 40, 1326–1335.

Quigley, M.S., Santschi, P.H., Hung, C., Guo, L., Honeyman, B.D., 2002. Importance of acid polysaccharides for ^{234}Th complexation to marine organic matter. Limnology and Oceanography 47, 367–377.

Ramaiah, N., Yoshikawa, T., Furuya, K., 2001. Temporal variations in transparent exopolymer particles (TEP) associated with a diatom spring bloom in a subarctic ria in Japan. Marine Ecology Progress Series 212, 79–88.

Ramus, J., 1977. Alcian Blue: a quantitative aqueous assay for algal acid and sulfated polysaccharides. Journal of Phycology 13, 345–348.

Redfield, A.C., Ketchum, B.M., Richards, F.A., 1963. The influence of organism on the composition of sea-water. In: Hill, M.N. (Ed.), The Sea, Vol. 2. Wiley, New York, pp. 26–77.

Schiebel, R., Waniek, J., Bork, M., Hemleben, C., 2001. Planktic foraminiferal production stimulated by chlorophyll redistribution and entrainement of nutrients. Deep-Sea Research I 48, 721–740.

Stoderegger, K., Herndl, G.J., 1999. Production of exopolymer particles by marine bacterioplankton under contrasting turbulence conditions. Marine Ecology Progress Series 189, 9–16.

Wood, M.A., Van Valen, L.M., 1990. Paradox lost? On the release of energy-rich compounds by phytoplankton. Marine Microbial Food Webs 4, 103–116.