Abundance and size distribution of transparent exopolymer particles (TEP) in a coccolithophorid bloom in the northern Bay of Biscay

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Abstract
The distribution of transparent exopolymer particles (TEP) was investigated during a coccolithophorid bloom in the northern Bay of Biscay (North Atlantic Ocean) in early June 2006. MODIS chlorophyll-a (Chl-a) and reflectance images before and during the cruise were used to localize areas of important biological activity and high reflectance (HR). TEP profiles along the continental margin, determined using microscopic (TEP\textsubscript{micro}) and colorimetric (TEP\textsubscript{color}) methods, showed abundant (6.1–4.4 \times 10^6 \text{L}^{-1}) and relatively small (0.5–20 \text{m}) particles, leading to a low total volume fraction (0.05–2.2 ppm) of TEP\textsubscript{micro} and similar vertical profiles of TEP\textsubscript{color}. Estimates of carbon content in TEP (TEP-C) derived from the microscopic approach yielded surface concentration of 1.5 \text{m} \mu \text{mol C L}^{-1}. The contribution of TEP-C to particulate organic carbon (POC) was estimated to be 12\% (molar C ratio) during this survey. Our results suggest that TEP formation is a probable first step to rapid and efficient export of C during declining coccolithophorid blooms.

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1. Introduction

During the last 15 years, many field studies have pointed out the importance of exopolymer substances (EPS) in natural systems (Passow, 2002; Wotton, 2004). A large fraction of EPS consists of carbohydrates that are released during and after phytoplankton blooms (Myklestad, 1995). Because of their physico-chemical characteristics, EPS are able to stick to each other and form networks of fibrils (Leppard, 1995) or colloids (Kepkay, 1994). They are thereby transferred from the dissolved to the particulate organic matter pool. Transparent exopolymer particles (TEP) merge the two properties of (1) being retained onto 0.4 \text{m} membranes and (2) being stainable by Alcian Blue, a specific dye for acidic (–COO\textsuperscript{-}) or sulphated (–O–SO\textsubscript{3}\textsuperscript{-}) reactive groups of carbohydrates (Allredge et al., 1993). Several studies indicate that TEP are natural constituents of the bulk particulate matter in marine (Passow and Allredge, 1995b; Mari and Kiorboe, 1996; Krembs and Engel, 2001; Garcia et al., 2002; Engel, 2004; Brussaard et al., 2005; Radic et al., 2005; Shackelford and Cowen, 2006; Prieto et al., 2006; Sugimoto et al., 2007) and freshwater
The release of large amounts of coccoliths, in particular E. huxleyi, coincides with those of viruses, enhancing viral infection and bloom termination associated with the decay of the bloom, when high abundances of E. huxleyi, and release of organic carbon by the cells. Because TEP have high C:N ratios (Mari, 1999; Engel and Passow, 2001; Mari et al., 2001), they are thought to contribute to particulate organic carbon (POM) rather than to the particulate nitrogen pool and can therefore increase C:N ratios of the particulate organic matter (POM).

This study investigated the contribution of coccolithophores to the TEP production, the pattern of TEP concentrations and the size distribution during a coccolithophorid bloom in the northern Bay of Biscay (North Atlantic Ocean, early June 2006). Chemical and biological parameters as well as remote sensing images are included in order to better describe phytoplankton bloom dynamics. Here, we present TEP profiles at different stations in the northern Bay of Biscay and estimate the contribution of TEP to POC.
phaeophytin concentration after acidification (HCl, 0.1 N), according to Yentsch and Menzel (1963).

Separation of the algal pigments was performed using a high performance liquid chromatographic (HPLC) method based on Wright and Jeffrey (1997). Between 0.5 and 3.5 L of seawater were filtered through glass fiber filters (Whatmann GF/F). The filters were stored in liquid nitrogen onboard until analysis. Extraction of the pigments was performed in a 90% aqueous aceton solution. Standard pigment mixtures were run together with the samples to allow identification and quantification of the detected pigment peaks in the chromatogram. The analysis of the diagnostic pigments for coccolithophores (19′-hexanoyloxyfucoxanthin, HexaFx) and diatoms (fucoxanthin, Fx) allowed the computation of the HexaFx:Fx ratio to assess the relative contribution of coccolithophores to the phytoplankton pool (Barlow et al., 1993, 1998). Higher values of this ratio indicate higher contributions of coccolithophores in the phytoplankton pool.

2.3. Dissolved phosphorus

Dissolved phosphate concentration was measured colorimetrically after filtration through a 0.4 μm
Nuclepore filter, using the molybdate blue method described in Grasshoff et al. (1983). The detection limit is 10 nM using a 10-cm optical cell.

2.4. Particulate organic carbon (POC)

Seawater (200–2000 mL) was filtered through precom busted (4 h, 500 °C) GF/F filters. The samples were stored at −20 °C until analysis. Within 3 months after the cruise, the filters were dried overnight at 50 °C prior to analysis. POC was determined using a Fisons NA-1500 elemental analyser after carbonate removal from the filters by HCl fumes overnight. Four to five standards of certified reference stream sediment (STSD-2) from the Geological Survey of Canada, together with 3–4 blank filters, were used for the calibration. POC was sampled down to 80 m for stations 4 and 4b, 100 m for station 1, 120 m for station 1bis, 150 m for stations 7 and 8 and down to 540 m for station 2 (of which only the uppermost 150 m are presented). No data were obtained for 30, 40 or 60 m at station 1 because of technical problems during the analysis.

2.5. Transparent exopolymer particles (TEP)

2.5.1. Colorimetric determination of TEP (TEPcolor)

Triplicates of 5–250 mL each were filtered (<200 mbar) onto 25 mm Nuclepore membrane filters (0.4 μm pore size) for the colorimetric determination of TEP (TEPcolor), according to Passow and Alldredge (1995a). The filters were stained with 0.5 mL Alcian Blue (Alldredge et al., 1993) and stored frozen at −20 °C and analysed within 6 weeks. Prior to spectrophotometric analysis (787 nm in a 1 cm path-length cell), the filters were soaked for 2 h in 80% H2SO4. Light absorbance was corrected for the adsorption of Alcian Blue on blank filters. TEPcolor is given in relative units, i.e. in % of the highest absorbance at each station (Table 1).

### Table 1

Maximum values in the upper 160 m of some parameters for each station.

<table>
<thead>
<tr>
<th>Stations</th>
<th>Date</th>
<th>Z1% (m)</th>
<th>Chl-a max (μg L⁻¹)</th>
<th>POC max (μM)</th>
<th>TEPcolor (Abs) per L of SW</th>
<th>Area TEPmicro (μm² mL⁻¹)</th>
<th>Abund. TEPmicro (mL⁻¹)</th>
<th>Conc. TEPmicro (ppm)</th>
<th>TEP-Cmicro (μmol CL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2006-05-31</td>
<td>30</td>
<td>1.49</td>
<td>11.7</td>
<td>4.10</td>
<td>11.6</td>
<td>43.71 × 10²</td>
<td>2.22</td>
<td>5.25</td>
</tr>
<tr>
<td>1bis</td>
<td>2006-06-09</td>
<td>37</td>
<td>0.89</td>
<td>17.3</td>
<td>21.72</td>
<td>4.9</td>
<td>15.40 × 10¹</td>
<td>0.98</td>
<td>2.05</td>
</tr>
<tr>
<td>2</td>
<td>2006-06-01</td>
<td>31</td>
<td>2.01</td>
<td>14.8</td>
<td>31.67</td>
<td>2.8</td>
<td>9.67 × 10³</td>
<td>1.08</td>
<td>1.57</td>
</tr>
<tr>
<td>3</td>
<td>2006-06-01</td>
<td>1.47</td>
<td>n.d.</td>
<td>7.55</td>
<td>3.2</td>
<td>6.86 × 10³</td>
<td>0.33</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2006-06-01</td>
<td>26</td>
<td>1.46</td>
<td>16.0</td>
<td>1.79</td>
<td>3.2</td>
<td>6.23 × 10³</td>
<td>1.30</td>
<td>1.63</td>
</tr>
<tr>
<td>4bis</td>
<td>2006-06-08</td>
<td>27</td>
<td>1.33</td>
<td>8.17</td>
<td>24.1</td>
<td>2.02 × 10³</td>
<td>1.47</td>
<td>2.42</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2006-06-07</td>
<td>26</td>
<td>1.43</td>
<td>24.6</td>
<td>4.93</td>
<td>37.3</td>
<td>18.92 × 10³</td>
<td>0.87</td>
<td>1.85</td>
</tr>
<tr>
<td>8</td>
<td>2006-06-06</td>
<td>34</td>
<td>0.8</td>
<td>14.6</td>
<td>2.10</td>
<td>11.3</td>
<td>6.13 × 10³</td>
<td>0.47</td>
<td>0.68</td>
</tr>
</tbody>
</table>

The thickness of the photic zone refers to the depth at which 1% of the incoming PAR is measured (Z1%). Chl-a max (μg L⁻¹) and POC max (μM L⁻¹) represent the highest levels of Chl-a and POC per profile. The values of the maximum of absorbance at each station (normalized per liter of seawater) are quoted as TEPcolor (Abs) for the colorimetric determination of TEP (TEPcolor). The following columns present the maxima of total area (μm² mL⁻¹), abundance (mL⁻¹) and carbon content estimate (μmol CL⁻¹) of the TEPmicro, n.d., parameter not determined.

* Stations located within the HR patch.
$N = a d^\delta p$ by $\delta = \beta + 1$. Spectral slopes were used to describe the TEP size distribution, an increase in $\delta$ being due to an increase of the fraction of large TEP. The volume concentration is defined here as the mean volume of the particles that belong to a size class in the sample; changes of this quantity indicate some changes in the dynamics of particles due to aggregation/disaggregation processes.

2.5.3. Estimation of TEP carbon concentration (TEP-C)

TEP-C content (TEP-C$_{\text{micro}}$, $\mu$M) was assessed by the microscopic approach assuming that the volume of TEP is proportional to $r^D$, where $r$ is the equivalent spherical radius in $\mu$m and $D$ the fractal dimension associated with the size distribution of particles. Therefore TEP-C$_{\text{micro}}$ was determined from TEP size spectra according to Mari (1999). For each sample, $D$ was deduced from the spectral slope, $\delta$, according to the semi-empirical relationship (Burd and Jackson, unpublished data, as referred to in Mari and Burd, 1998)

$$D = (64 - \delta)/26.2$$

(1)

Thus, TEP-C$_{\text{micro}}$ was derived from the histogram distribution, according to

$$\text{TEP-C}_{\text{micro}} = \frac{a}{12} \sum n_i r_i^D,$$

(2)

where $n_i$ is the concentration of TEP in the size class $i$ and $r_i$ the mean equivalent spherical radius of this size class. The constant, $a = 0.25 \times 10^{-6} \mu$g C, was determined by Mari (1999).

Fig. 2. Vertical profiles of temperature and phosphate concentration (PO$_4$) in the upper 160 m over the continental shelf (stations 1, 1bis, 4, 4bis, 7 and 8) and over the slope (stations 2, 3, 5 and 6). Grey symbols represent the revisited stations; PO$_4$ concentrations were similar at the revisited stations 1bis and 4bis (superposed dots). For this figure and the following ones, the organization of the stations on the chart follows the geographic localization of the stations (stations 8, 7, 4 and 1 are located on the shelf and stations 5, 2, 6 and 3 are located on the slope), as represented in the inner box showing station names and the bathymetry of the area.
3. Results

3.1. Hydrography

Vertical distributions of temperature revealed that sea-surface temperatures ranged between 13.0 and 14.0°C during the first leg (stations 1–5) and increased up to 14.9°C during the second leg (stations 6, 7, 8, 4bis and 1bis) (Fig. 2). They also show that the upper water column over the continental shelf can be divided into 3 distinct parts: (i) a thin surface mixed layer of 10 m, (ii) an intermediate layer displaying a strong vertical gradient and (iii) a homogeneous cold deep layer below 60 m (11.4°C).

The smaller temperature gradient on the continental slope suggests input of a cold, deeper water mass in the upper 25–35 m, which corresponds to the photic zone (see below). This induced a mixing of the upper layer of the water column. Between the two legs, warming of the surface layer deepened the vertical temperature gradient down to 50 m depth at the stations 1bis and 4bis. Salinity stayed within a narrow range of 35.5–35.6 down to 800 m depth at the deepest station 6 (data not shown).

Dissolved phosphate concentration was on average $0.49 \pm 0.04 \mu M$ (average ± standard deviation; $n = 7$) at 150 m depth, while PO$_4$ was depleted in surface waters (Fig. 2). Compared to the slope, the continental shelf was more PO$_4$ depleted, and the concentrations in the upper 10 m ranged between 0.01 and 0.05μM. Higher surface concentrations of phosphate were observed for the shelf-break (0.08–0.16μM), where the surface layer only occasionally fell below 0.05μM (station 6) during the second leg (Fig. 2).

3.2. Chlorophyll-a and reflectance

Satellite images showed surface Chl-a concentrations (Fig. 1a and c) and several HR patches (Fig. 1b and d) distributed inshore of the 200 m isobath, the bathymetric...
boundary between the open ocean and the continental shelf of the northern Bay of Biscay, in June 2006. The comparison of MODIS (Fig. 1a and c) and reflectance (Fig. 1b and d) images revealed changes in phytoplankton biomass in the southern HR patch (stations 4, 7 and 8) between the two legs. An overall decline in surface Chl-a concentration was observed between the two periods at the revisited stations. At stations 4bis, 7 and 8 this decline was associated with an increase in reflectance.

Sea-surface Chl-a concentration ranged between 0.5 and 2.0 μg L⁻¹ (Fig. 3). The highest concentration was determined at station 2, where the concentration in the photic zone (ranging between 25 and 37 m depth based on light measurements) exceeded 1.5 μg L⁻¹. The vertical profiles over the continental shelf showed higher Chl-a concentration at intermediate depth situated between 20 and 40 m, which decreased strongly down to 80 m. At stations 1bis and 4bis, 9 days and 6 days, respectively, after the initial visit, Chl-a concentrations in surface waters decreased, respectively, by 0.6 and 0.2 μg L⁻¹. As inferred from Chl-a concentration and pigment composition (Fig. 3), the mixed phytoplankton community was dominated by coccolithophores at stations 1, 2 and 3.

3.3. POC

The highest concentrations of POC were observed within the upper 20 m of the water column, ranging between 10 and 15 μM and reaching up to 25 μM at station 7 (Fig. 4). Concentrations were lower than 2.5 μM below 20 m depth, except for station 1, where a concentration of 7.7 μM was determined a few meters above the sea-bottom, which may be linked to resuspension of sediments. At station 4bis, POC concentration in the water column was significantly less than at other stations. No significant difference in POC concentration was observed between station 1 and 1bis.

Fig. 4. Particulate organic carbon (POC) concentration (μmol CL⁻¹) (black dots) and TEP-Cμm estimates (μmol CL⁻¹). Grey symbols represent the revisited stations (1bis and 4bis). Stations 3, 5 and 6 were not sampled for POC; stations 3 and 5 were not sampled for TEP-C.
3.4. Concentration and size distribution of TEP

3.4.1. TEP<sub>color</sub>

The vertical profiles of relative TEP<sub>color</sub> absorbance exhibited strong variations, achieving maximum values (100%) in the surface or subsurface layer (Fig. 5). A general decrease of absorbance was observed from surface to depth, showing similar vertical distribution patterns as Chl-a and POC. The lowest absorbance (normalised for 1 L of seawater) was observed in the deepest samples and ranged between 9% and 14.5% below 150 m (not shown). In contrast, the upper 40 m exhibited more variable values.

3.4.2. Concentration and size distribution of TEP<sub>micro</sub>

The microscopic determination of TEP allowed for their enumeration and classification into size classes, based on their equivalent spherical diameter (ESD). The size frequency distribution of TEP showed a dominance (>90%) of particles smaller than 20 μm (ESD) in surface waters. Fig. 6 is a three-dimensional representation of the vertical distribution of TEP<sub>micro</sub> volume concentration (in μm<sup>3</sup> mL<sup>-1</sup> μm<sup>-1</sup>) as a function of the size of particles in the water column. The larger particles ranged between 20 and 30 μm and were abundant in the upper part of the water column. Their concentration strongly decreased with depth to become insignificant below 80 m. The coincidence of abundant large and small particles in the first 30 m (i.e. the upper mixed layer) can be considered as the result of the assembly of larger particles from smaller ones by aggregation. Therefore, the snapshot of this station 8 likely represents the different steps of the formation of TEP from their small precursors, formed by coagulation of phytoplankton exudates, to larger particles formed by the aggregation of the bulk colloidal material.

In accordance with the distribution of TEP<sub>color</sub>, TEP<sub>micro</sub> abundance was higher in surface waters, down to 40 m depth, ranging between $2.1 \times 10^3$ mL<sup>-1</sup> and $43.7 \times 10^3$ mL<sup>-1</sup> at stations 2 and 1, respectively (Fig. 7). At greater
depth the distribution was relatively uniform and in the lower range of surface abundances. In the HR patch (stations 4, 7 and 8), TEP micro exhibited concentrations in the range of \(3.3 \times 10^3\) to \(20.2 \times 10^3\) mL\(^{-1}\). An overall 2-fold increase of TEP micro, in association with a decrease of Chl-a concentration after 6 days, was observed at the revisited stations 4bis, where concentrations ranged between \(6.7 \times 10^3\) and \(20.2 \times 10^3\) mL\(^{-1}\). However, such an increase in TEP concentration was not observed after 9 days at stations 1 and 1bis, despite a similar decrease of Chl-a concentration.

A power-law relationship fitted the size distributions of TEP very well in all cases \((r^2 > 0.9)\) as shown in Fig. 8. The size distribution can be described by spectral slope, \(\delta\), with less negative values indicating an increase with the fraction of large particles and, potentially, TEP aggregation. In the top 40 m, \(\delta\) values ranged between \(-3\) and \(-2\) (Fig. 9). The increase of \(\delta\) in the surface layer at the revisited station 1bis suggests that aggregation of TEP had taken place after an elapsed time of 9 days. In contrast, a decrease of \(\delta\) was observed between station 4 and 4bis. Together with an increase of total TEP abundance, this could be attributed to the production of smaller TEP. The fractal dimension, \(D\), of TEP was deduced from \(\delta\), and ranged between 2.51 and 2.56.

### 3.4.3. TEP-C estimates

Surface concentration of TEP-C\(_{\text{micro}}\) ranged between 0.44 and 5.25 \(\mu\)mol CL\(^{-1}\) at stations 4bis and 1, showing higher concentrations above the thermocline (Fig. 4). Except for station 1, TEP-C\(_{\text{micro}}\) concentrations in the photic zone were found to be below 2.00 \(\mu\)mol CL\(^{-1}\). At greater depths, 0.75 \(\mu\)mol CL\(^{-1}\) was an upper limit for TEP-C\(_{\text{micro}}\) at all stations, except station 1, where the resuspension of sediment was probably responsible for higher TEP-C estimates close to the bottom. Low variability in TEP-C was observed at the revisited stations (1bis and 4bis).

## 4. Discussion

### 4.1. Relationship between bloom development and biological parameters

Based on remote sensing images (Fig. 1) and vertical profiles of nutrients (Fig. 2) and Chl-a (Fig. 3), the coccolithophorid bloom investigated in our study can be split into two distinctive regions: (i) a southern part associated with higher Chl-a and lower reflectance, where coccolithophores were in the initial stage of the bloom (stations 1, 2, 3 and 6) and (ii) a northern part where increased reflectance rather suggested that the coccolithophorid bloom had reached a stationary phase (stations 4, 5, 7 and 8).

The surface waters of the study area were characterized by the formation of a seasonal thermocline at 50 m depth on the continental shelf and a general warming by 1 °C during the course of the cruise (10 days). Over the shelf-break (stations 2, 3 and 5), the temperature below the thermocline decreased continuously with depth, suggesting the mixing of the upper layer with a deep
cold nutrient-rich water mass. A significant ($r^2 = 0.82$, $n = 96$, $p < 0.0001$) correlation was observed between phosphate consumption and temperature, indicating a strong control of hydrodynamics on phytoplankton activity (Wollast and Chou, 2001). The northern Bay of Biscay is characterized by intermittent inputs of nutrient-rich deep water to the photic layer promoted by internal waves (Huthnance et al., 2001), enhancing and sustaining localized biological activity in spring (Joint et al., 2001). In the Bay of Biscay, two diatom blooms usually occur during phytoplankton succession in spring and fall, but diatoms remain in the phytoplanktonic community during the spring bloom (Joint et al., 2001). Prymnesiophytes, to which coccolithophores belong, are an important component of the phytoplanktonic community in this area, especially in spring, and persist at low densities over the whole annual cycle (Joint et al., 2001). The accumulation of coccoliths, the minute calcite discs produced by this species, modifies the optical properties of surface seawater leading to high reflectance so that high reflectances are traditionally associated with coccolithophorid blooms (Balch et al., 1996). The spatial distribution of localized HR patches on satellite images (Fig. 1b and d) suggested the development of a coccolithophore-dominated bloom during our study, as reported by Holligan et al. (1983, 1993a, 1993b), the GREPMA (1988), and Brown and Yoder (1994) in the North Atlantic. The most common species that is known to produce such important blooms is *E. huxleyi* (Brown and Yoder, 1994).

Surface distributions of Chl-$a$ and PO$_4$ suggest that phytoplankton production has led to inorganic phosphate depletion in surface waters. Dissolved silicates (data not shown) remained below 2 $\mu$M in surface waters, probably because of the uptake of this nutrient by diatoms (Egge and Aksnes, 1992). Such a situation likely triggers coccolithophores at the period of high irradiance (Tyrrell and Merico, 2004), whose requirements for inorganic phosphorus are relatively low, because their reliance on alkaline phosphatase allows them to use organic phosphorus (Riegman et al., 2000).
4.2. TEP concentrations observed in the field

Microscopic enumeration and sizing of TEP micro (Table 1) showed abundant \( (6.13 \times 10^2 \text{mL}^{-1} \text{ to } 4.4 \times 10^4 \text{mL}^{-1}) \) relatively small (0.5–20 \( \mu \text{m} \) ESD) particles leading to a low total volume concentration of TEP (0.05–2.2 ppm) (not shown). The fractal scaling of TEP (D), deduced from the spectral slope (\( \delta \)), was close to the value of 2.55 proposed by Mari and Burd (1998) for naturally occurring TEP. These concentrations agree with previous estimates (0.76–4.1 ppm) in the NE Atlantic mixed layer (Engel, 2004) and were in the lower range (3–310 ppm) of earlier observations in a coastal diatom bloom of the Baltic Sea (Mari and Burd, 1998). Small variations of the spectral slope (\( \delta \)) with depth and between stations suggest only minor changes in the size distribution of particles. Hence, TEP aggregation can hardly be assessed from size distributions in this study. Together with the observed increase in total TEP micro abundance at revisited stations, the dominance of small particles may point towards TEP production at the time of our study, rather than to massive aggregation, which may occur in later phases of phytoplankton blooms. Concentrations of TEP micro in coastal regions range from \(<100 \text{ to } 3000 \mu \text{gXeqL}^{-1}\) (Passow, 2002). For an open ocean transect in the NE Atlantic surface water TEP micro concentration ranged from 40 to \(120 \mu \text{gXeqL}^{-1}\) in the top 20 m (Engel, 2004), and vertical patterns of TEP distribution were similar to those reported in Fig. 5. The upper and lower boundaries of TEP-C concentration provided by Engel (2004) lead to estimates between 30 and 89 \( \mu \text{gCL}^{-1}\) and are thus in agreement with our values determined by TEP micro (Fig. 4). Previous measurements conducted in the study area in June 2004 revealed TEP color concentrations similar to those determined by Engel (2004) (up to \(120 \mu \text{gXeqL}^{-1}\)).

4.3. Contribution of TEP-C to POC

The relative contribution of the TEP-C to POC was estimated for each depth by the molar ratio of TEP micro to POC in the water column that ranged between 1.5% and 68%. TEP micro accounted for 12% of POC in the photic zone and was slightly lower than our estimate for the photic zone in the same area during an earlier cruise to this study site (June 2004), where \(26 \pm 4\%\) was observed (TEP-C micro:POC, mean \( \pm \) confidence interval at 95%, \( n = 31 \) (Harlay et al., in prep.). The contribution of TEP-C to POC during this coccolithophorid bloom is in the range reported in previous studies, which indicated a contribution of TEP-C to POC ranging between 17% and 54% (Mari, 1999; Engel and Passow, 2001; Engel, 2002). Statistically, no significant changes were detected after 9 days at station 1.

4.4. TEP production and carbon cycling

The decoupling from inorganic nutrient of carbon production by carbon over-consumption (Engel et al., 2002; Schartau et al., 2007) suggests that the flux of particulate carbon might be enhanced when TEP is produced, rendering coccolithophores good candidates for the export and sequestration of carbon. Several studies have shown that the balance between TEP and solid particles, such as cells, co-determines the efficiency of particle coagulation and formation of macroscopic aggregates (Logan et al., 1995; Engel, 2000; Kahl et al., 2008). Particle aggregates are a major vehicle for organic matter export to the deep ocean. Coccolithophores potentially enhance the efficiency of organic matter export through the addition of mineral ballast (Francisco et al., 2002; Klaas and Archer, 2002). Hence, TEP production during coccolithophorid blooms may control aggregate formation and enhance organic matter export (De la Rocha and Passow, 2007). The deposition of gelatinous detritus mixed with E. huxleyi at the seafloor has been described by Cadée (1985) for the North Sea. Based on the sinking velocity of coccoliths and coccospheres, Holligan et al. (1993b) estimated the time required for the coccolithophore optical signature to disappear from satellite images to be...
>200 d in the North Sea. However, the effective life-time of coccolithophorid blooms does not exceed 40 d after the optical signature appears (Holligan et al., 1993b). The persistence of coccolithophores in waters depleted in nutrients for 3–6 weeks and the potential production of up to 400 coccoliths per cell with a mean delay of 2–3 h per coccolith (Linschooten et al., 1991; Fernández et al., 1993) suggest that cells remain active for several weeks after the onset of the bloom. If carbon over-consumption can be applied to coccolithophorid physiology, one can suspect that the significance of coccolithophores in carbon cycling, at least of the bloom-forming species E. huxleyi, has been under-estimated. The E. huxleyi blooms could result in massive aggregation events that wash out the surface waters from detritus and particles.

Our survey probably did not cover any massive aggregation phase of the coccolithophorid bloom because of the small size of TEP. Therefore, the contribution of TEP in coccolithophore aggregates to the vertical export was not quantified in this study. However, the deposition of gelatinous detritus over the continental slope of the Bay of Biscay has been found to occur later in the summer (de Wilde et al., 1998; McCave et al., 2001). Pigment analysis and scanning electron microscopy of particulate samples in late August 1995 showed that coccolithophores were the major contributors to this mass deposition (de Wilde et al., 1998). The carbon content of the deposited mucus layer represented 250 mmol C m\(^{-2}\) and covered an area of 50 000 km\(^2\) (de Wilde et al., 1998), comparable to the 65 000 km\(^2\) surface area of a coccolithophorid bloom at the continental margin of the Gulf of Biscay observed in June 2006. Since specific pigments are well preserved together with the carbonates, this detrital mass deposition indicates a tight coupling of particulate matter export and surface production of coccolithophores. The production of TEP observed during the present study could

Fig. 9. Spectral slope (\(\delta\)) of the TEP\(_{\text{micro}}\) size distributions. An increase of \(\delta\) corresponds to an increase of the fraction of large TEP\(_{\text{micro}}\). Grey symbols represent the values at the revisited stations 4bis and 1bis. Stations 5 and 6 were not sampled for this parameter.
constitute the first step within the process of coccolithophore aggregation, sedimentation and seafloor deposition in the Bay of Biscay.

5. Conclusions

The present study shows agreement between the vertical distribution of TEP determined with the microscopic (this study) and the colorimetric (Engel, 2004; Harlay et al., in prep.) approaches. The estimates of TEP-C obtained with the microscopic approach are comparable to those previously obtained with the colorimetric one in the Bay of Biscay (coccolithophorid bloom in June 2004, Harlay et al., in prep.) and during an offshore transect at the same latitude in the NE Atlantic Ocean (Engel, 2004). High absorbance of particles issued from the area where coccolithophores occurred, or had occurred in the past history of the water mass, has been pointed out. We suggest that during coccolithophorid blooms, the production of TEP is also occurring, as already determined for other phytoplankton groups (Passow, 2002) as a possible consequence of carbon over-consumption by this taxon. The implication of those particles for the seasonal cycling of carbon is enhanced by the physical properties of the water column. The formation of aggregates potentially contributes, through the ballast of aggregates with biogenic calcite, to efficient and rapid export of carbon out of the photic layer and important deposition over the seafloor. Carbon over-consumption by phytoplankton and the subsequent transformation of the cellular releases into TEP (Schartau et al., 2007) account for an additional sink for carbon sequestration in coccolithophorid blooms, where the efficiency of the carbon pump may not be limited to the production of biomass, as computed from variations in Chl-a concentration (e.g. Iglesias-Rodriguez et al., 2002). However, such a mechanism has been neglected in carbon inventories because of the complexity of the study of gel phases in marine environments. The significance of gel particles in the global carbon cycle may have been under-estimated, so far, and improvement in the description of these processes is required to better constrain this flux as well as the development of techniques to estimate the coupling between the surface and the seafloor.

Further effort is then needed to increase the reproducibility of both approaches for estimating TEP-C. The microscopic approach, less sensitive to coccolithophorid density and changes in TEP stability, provided a reliable estimate of the carbon content of TEP during this study. However, its use as a routine method for TEP determination during multidisciplinary studies is often discarded in favour of the colorimetric technique, which requires less labor and expertise. However, highly coloured TEP do not necessarily reflect high TEP-C (TEP-C_micro,POC of 12%) but suggest different chemical properties of their constituents. Improvement of the methods is a particular challenge for studying possible changes in polysaccharide composition of TEP in aging-bloom situations (polysaccharide diagenesis) or for directly determining TEP-C in the field, since conversion factors obtained from phytoplankton blooms can only give rough estimates in peculiar conditions.

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