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Non-Redfield C : N ratio of transparent exopolymeric particles in the northwestern Mediterranean Sea

Abstract—The stoichiometric model of Redfield, which describes the elemental composition of marine organic matter, is generally used to link the production of new organic matter to the uptake of nitrate. The Redfield C : N molar ratio of 6.6 is a well-established value for particulate organic matter produced in surface waters. Yet recent studies have shown that the inorganic C : N uptake ratio during nitrate-limiting conditions is >14. This non-Redfield behavior during the production of new organic matter suggests that a large standing stock of organic matter, rich in carbon, should accumulate in the euphotic zone from the spring bloom to late summer. This hypothetical pool of carbon-rich organic matter and the pool of transparent exopolymeric particles (TEP) exhibit similar seasonal distributions, which suggests that TEP may indeed be this carbon-rich pool. For this scheme to work, TEP should have a high C : N ratio.

TEP distribution from an open-ocean site in the northwestern Mediterranean Sea (DYFAMED) was monitored, and TEP C : N ratio was measured from TEP produced in the laboratory by bubbling dissolved organic matter collected in the field. We found that the TEP pool increases during the summer season and that the C : N ratio of TEP produced from naturally occurring dissolved organic matter, is well in excess of the Redfield ratio with an overall average C : N molar ratio of ~20. As a result, the production of TEP could be the main pathway of carbon overconsumption required of oligotrophic, nitrate-limiting waters, and, thus, TEP may represent an important intermediary pool in the ocean carbon cycle.

Photosynthesis within the euphotic layer of the ocean is the process by which biogenic carbon is produced from dissolved inorganic carbon, thus favoring the penetration of atmospheric carbon towards the oceans. The export of primary production from the surface water is a key component of the ocean carbon cycle. This deep carbon export, often referred to as the biological pump, is responsible for maintaining a vertical gradient of dissolved inorganic carbon (DIC) and thus is a drawdown of atmospheric carbon over the long term (Sarmiento and Siegenthaler 1992). In order to predict carbon export, the amount of DIC fixed by photosynthesis into organic carbon must be known. However, when measurements have been made of the concurrent drawdown of DIC and nitrate (Sambrotto et al. 1993; Banse 1994; Marchal et al. 1996; Copin-Montégut 2000), the amount of carbon removed from the water significantly exceeded the amount predicted based on the nitrate removal and the Redfield C : N ratio (Redfield et al. 1963). This process, defined by Toggweiler (1993) as carbon overconsumption, could be explained by the formation of a large pool of organic matter, unnoticed so far, cycling through the system with an anomalous C : N ratio. The production of such a pool may result if the overproduction of phytoplankton (i.e. carbon-rich exopolymer production) is added into the system.

The recently discovered pool of transparent exopolymeric particles (TEP) can help us to understand the observed carbon overconsumption and may force us to revise the originally accepted views of the biological pump. TEP range in size from one to hundreds of microns in diameter and are found in high concentrations in a variety of marine environments (Alldredge et al. 1993; Schuster and Herndl 1995; Mari and Burd 1998). They are formed by coagulation of dissolved organic matter (DOM) (Mari and Burd 1998; Zhou et al. 1998; Mari 1999; Passow 2000), which is known to be produced in large amounts by phytoplankton during nutrient-limiting conditions (Obernosterer and Herndl 1995). DOM produced during blooms, and especially its high molecular weight fraction, exhibits a high C : N molar ratio (from 13 to 21) due to the leakage of carbon-rich exopolymers, such as polysaccharides, from phytoplankton cells (Biddanda and Benner 1997; Kepkay et al. 1997). This production of carbon-rich DOM may lead to the formation of a large pool of DOM that is not stoichiometrically locked into the Redfield C : N ratio and accumulates in the euphotic zone from spring to late summer (Copin-Montégut and Avril 1993; Carlson et al. 1994; Williams 1995). This accumulation could be the consequence of a high net inorganic C : N assimilation ratio (i.e. >14), which in turn would require carbon overconsumption.

Given that the seasonal distributions of TEP in a eutrophic area (Mari and Burd 1998) and C-rich DOM (Williams 1995) are similar, it has been suggested that C-rich DOM is the source of TEP (Mari and Burd 1998). As a result, one can hypothesize that, from the spring bloom and throughout the summer season, phytoplankton produces large amounts of C-rich DOM, which coagulates and gives rise to the pool of TEP that decomposes when nutrients increase to prebloom concentrations. This scenario implies that primary production is not limited to the production of biomass but also includes extracellular products such as C-rich DOM and TEP. Therefore, the biological consumption of atmospheric carbon may have been underestimated because the production of C-rich DOM and TEP has, effectively, been excluded from measurements of primary production. The objectives of this study were to examine the seasonal distribution of TEP, to determine whether their accumulation in summer is a common phenomenon in both eutrophic and oligotrophic waters, and to measure the TEP C : N molar ratio to test the hypothesis that TEP production is the byproduct of carbon overconsumption.

Water column characteristics—The field study was carried out in the vicinity of the France-JGOFS station in the northwestern Mediterranean Sea (DYFAMED site, 43°25′N, 07°52′E), where both the accumulation of C-rich DOM (Copin-Montégut and Avril 1993) and carbon overconsumption (Copin-Montégut 2000) have been observed. Seawater samples were collected at DYFAMED from the layer of fluorescence maximum with 30-liter Niskin bottles at monthly

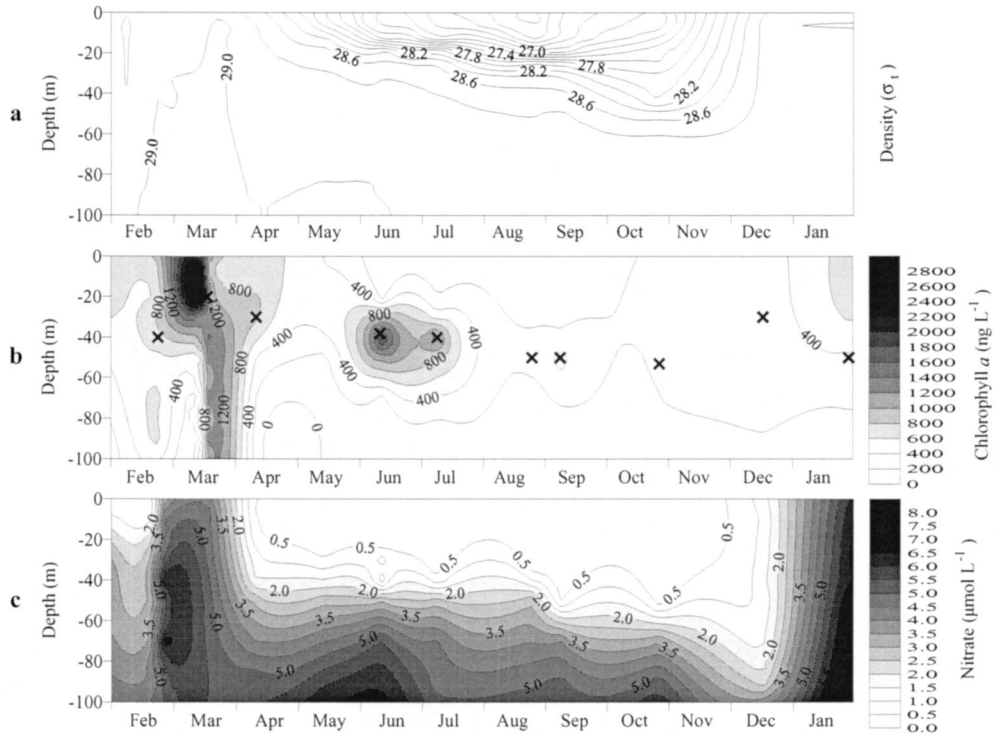


Fig. 1. Seasonal variations in the water column of (A) density, (B) Chl *a* concentration with position of the sampling depths for TEP determination (crosses), and (C) nitrate concentration.

intervals (from February 1999 to January 2000). Sampling depths were determined from the CTD casts. The concentrations of nitrate (NO_3^-) were measured by an autoanalyzer. Chlorophyll *a* concentrations were measured by high-performance liquid chromatography pigment analysis.

The water column was strongly stratified from May to November, with a pycnocline around 20 m (Fig. 1a). The seasonal distribution of Chl *a* (Fig. 1b) was characterized by a spring bloom in the beginning of March (up to 3 μg chl L^{-1} in the surface mixed layer). An increase in Chl *a* concentration (up to 1.2 μg chl L^{-1}) was also observed during June at the pycnocline layer. The nitrate concentrations (Fig. 1c) decreased from the beginning of the spring bloom and remained low until late autumn, with maximum concentrations in the surface mixed layer of 0.5 μM.

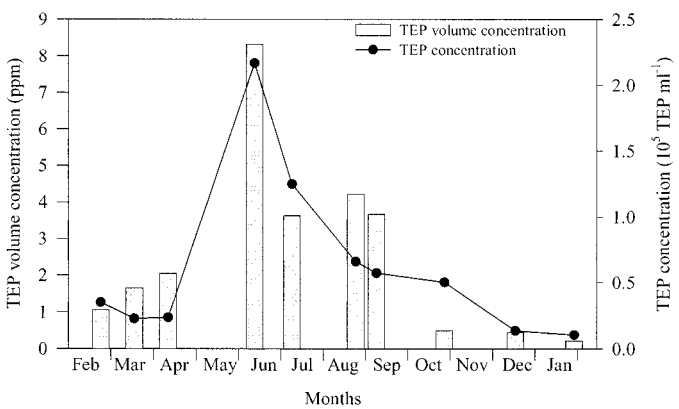


Fig. 2. Seasonal variations of TEP abundance and TEP volume concentration at the fluorescence maximum.

TEP seasonal distribution—In situ TEP size spectra were determined from semipermanent slides of TEP prepared according to the method described by Passow and Alldredge (1994). All samples were prepared fresh and within 2 h after sampling. For each slide, TEP were counted and sized at three successive magnifications (respectively, 125, 250, and 500×) by use of a compound light microscope. The equivalent spherical diameter (ESD) of each TEP was calculated by measuring of its cross-sectional area with a semiautomatic image-analysis system. Counts were combined and classified according to their ESD.

TEP occurred at all sampling occasions and concentrations varied between 0.1×10^5 and 2.2×10^5 TEP ml^{-1} (Fig. 2). TEP concentrations were low ($<0.3 \times 10^5$ TEP ml^{-1}) until the beginning of April and then increased abruptly subsequent to the spring bloom, with the highest concentrations observed at the beginning of June. TEP concentration then declined until the end of January to reach values similar to those observed before the spring bloom. TEP volume concentration varied between 0.2 ppm and 8.3 ppm (Fig. 2) and increased by a factor of six from nonlimiting to limiting nitrate conditions (late March to June). The TEP pool began to increase right after the spring bloom, and TEP volume concentrations remained high throughout summer (from June to September).

The seasonal distribution of TEP at the DYFAMED station was similar to that observed by Mari and Burd (1998)

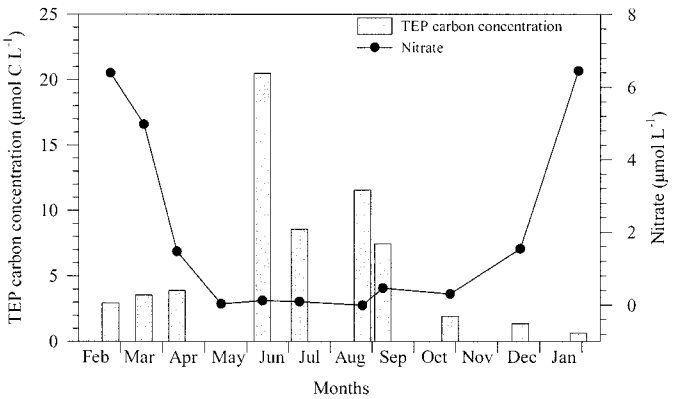


Fig. 3. Seasonal variations at the fluorescence maximum of TEP carbon concentration, compared with the annual pattern of NO_3 concentration. TEP carbon concentrations were calculated from the carbon-size relationship (Mari 1999) and field TEP size spectra.

at a coastal station in the southern Kattegat—i.e., TEP accumulated during summer. The difference in the range of TEP volume fraction between DYFAMED (from 0.2 ppm to 8.3 ppm) and the Kattegat (from 3 ppm to 100 ppm, at the pycnocline layer) reflects a difference of trophic regimes between the two sites and is consistent with the observation that the abundance of TEP tends to increase along productivity gradients (Schuster and Herndl 1995).

TEP carbon concentration—TEP size distributions at the DYFAMED site were used along with the well-defined carbon-size relationship $TEP\text{-}C = 0.25\ r^{2.55}$ (pg C TEP^{-1}), where *TEP-C* (pg C) is the carbon content of a given TEP particle with a radius r (μm) (Mari 1999), to estimate the TEP carbon pool. The use of the TEP carbon-size relationship (obtained from TEP produced in the laboratory by coagulation of diatom exudates, by use of a bubble adsorption column) to predict naturally occurring TEP-C concentration presupposes that field and laboratory produced TEP have similar carbon content. Comparison between expected TEP carbon concentration from the carbon-size relationship (Mari 1999) and measured TEP carbon concentration inside the bubbling column showed that the model explains ~75% of the observed particulate organic carbon (POC) concentration ($POC_{measured} = 0.87\ POC_{expected} + 0.01$; $r^2 = 0.75$; $n = 18$). This suggests that the carbon content of TEP produced from naturally occurring DOM is of the same range as that of TEP produced from exudates of diatoms.

Estimated carbon concentrations in the TEP pool ranged from 0.6 to 20.5 μmol C L^{-1} (Fig. 3). TEP carbon concentrations were low (<4 μmol C L^{-1}) from February to April and increased up to 20.5 μmol C L^{-1} from April to June. TEP-C concentrations remained high throughout summer (12.0 ± 5.9 μmol C L^{-1}; mean ± SD) and declined at the beginning of the fall, to reach concentrations similar to those observed before the summer accumulation. The accumulation of the TEP pool during summer (in terms of abundance, volume, and carbon concentration) coincided with N-limiting conditions.

During a study in the northwestern Mediterranean Sea, Copin-Montégut and Copin-Montégut (1983) reported POC concentrations in the surface layer ranging from 3.6 to 16.2 μmol C L^{-1}, the highest value being recorded in May. Under the assumption that these values are typical for this area, it suggests that the TEP pool at DYFAMED may represent up to 70% of the total POC when TEP formation is high, down to ~20% when TEP formation is low.

TEP C : N ratio—TEP produced by bubbling DOM (Zhou et al. 1998; Mari 1999) from GF/C-filtered seawater were used for TEP C : N ratio determination. Seawater samples collected at DYFAMED were filtered at a low and constant vacuum pressure (<150 mbar) through 125-mm diameter Whatman GF/C filters (nominal pore size 1.2 μm). The filtrate was added to a bubble adsorption column of borosilica glass (200 cm high and 10 cm diameter) and bubbled with Ultra Zero Grade Air ($CO + CO_2 < 1$ ppm). The gas flow rate was 100 ml min^{-1}. Bubbles were produced by a glass frit of 10 to 20 μm pore size. The glass frit was fitted online with a 0.1-μm air filter and a trap that contained molecular sieves for removal of organic impurities and moisture. Between each experiment, the glass frit was soaked in 35% HCl and was rinsed three times with Milli-Q water. Samples for C : N ratio measurements were collected in the middle of the column after 1, 3, and 5 h of bubbling and were immediately filtered for TEP determination and for measurements of particulate carbon and nitrogen concentrations by use of a Leco-900 CHN-analyzer. A series of five aliquots of increasing volume, typically 100–500 ml, were filtered onto 25 mm Whatman GF/F filters (nominal pore size 0.7 μm) precombusted at 550°C for 2 h. After filtration the filters were dried at 60°C for 24 h and then frozen for later analysis.

On the basis of the following arguments, we believe that particulate carbon measured is nonliving POC. Considering that the DIC concentration at DYFAMED is about 2.2 mol m^{-3} (Copin-Montégut 2000), that the water content of a wet GF/F filter is 210 μl, and that the particulate carbon concentration measured was, on average, ~50 μg C $filter^{-1}$ (range 3–204 μg C $filter^{-1}$), DIC would add an average of ~0.07% (range 0.02%–1.15%) to the measured carbon concentration. Additionally, because the GF/C-filtered seawater was bubbled with a carbon-free gas, one would expect the DIC concentration to decline during the bubbling. Thus, a DIC concentration of 2.2 mol m^{-3} inside the bubbling column can be considered as a maximum. Finally, because the seawater used to form TEP was filtered onto a GF/C filter prior to bubbling, one can expect that most of the particulate inorganic carbon was removed and, thus, that the only significant source of inorganic carbon in the bubbling column was DIC. Therefore, we consider that the concentration of particulate carbon measured is very close to POC.

POC and particulate organic nitrogen (PON) due to bacterial biomass on the GF/F filters were calculated from bacterial abundance, under the assumption of a carbon content of 12.4 fg/cell for oceanic heterotrophic bacteria and a C : N ratio of 6.4 (Fukuda et al. 1998). Total bacterial abundance was determined for each bubbling experiment in 5-ml samples filtered onto 0.2-μm black polycarbonate filters after staining with 0.1 μg ml^{-1} 4′,6′-diamidino-2-phenylindole (Porter and Feig 1980). Bacteria were counted in 10 fields on each slide at 1,000× magnification in an epifluorescence

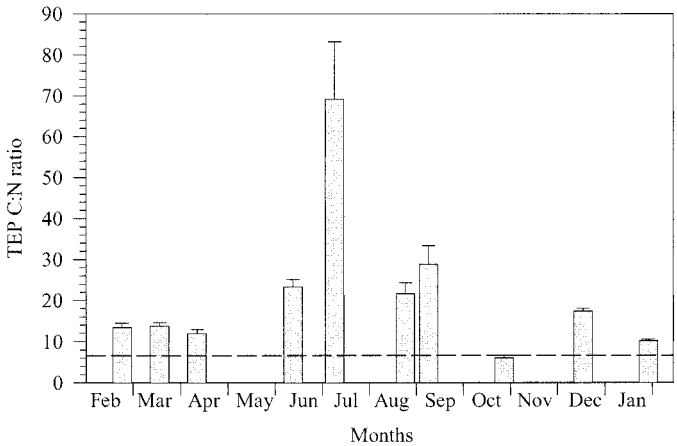


Fig. 4. Seasonal variations of TEP C : N ratios. The error bars indicate SE. The broken line represents the Redfield C : N ratio of 106 : 16.

microscope. The fraction of bacteria retained onto GF/F filters was estimated from bacterial counts (1) inside the bubbling column and (2) after filtration onto GF/F filters. TEP C : N ratios were calculated in terms of POC : PON corrected for bacterial carbon and nitrogen. We estimated that bacterial biomass represented between 0.6% and 9.8% of the POC (3.3 ± 2.9%; mean ± SD) measured inside the column. Although organisms other than bacteria may occur in the 0.7 μm (GF/F) to 1.2 μm (GF/C) size class, we detected only cells that appeared to be heterotrophic bacteria.

The C : N ratio of TEP before and after the summer period (Fig. 4) was, on average, twice the Redfield value (11.6 ± 0.4; mean ± SE; $n = 102$), and increased abruptly after the spring bloom, remaining high throughout summer (37.7 ± 5.2; mean ± SE; $n = 47$), with an overall average C : N ratio of 19.9 ± 1.9 (mean ± SE; $n = 149$). The summer increase in TEP C : N ratio coincided with the low nitrate concentration observed in the surface mixed layer.

During a previous study in the northwestern Mediterranean Sea, Copin-Montégut and Copin-Montégut (1983) reported C : N ratios for the total standing stock of particulate organic matter (POM) in the surface layer as high as 12.7 during summer. As an attempt to explain the non-Redfield behavior of POM observed, they suggested that carbonaceous compounds without nitrogen (i.e., TEP) might be more abundant when dissolved nitrogen is deficient. Furthermore, during a time-series study of sediment traps deployed at DYFAMED, Marty et al. (1994) reported a summer increase in POC flux at 200 m (with the highest value recorded during the June–July period) and observed that the C : N ratio of POM in trap samples was highest in July (C : N = 9.6). The period when both the increase in POC flux and the high C : N ratio of POM in trap samples were observed coincides with the accumulation of the TEP pool and the increase of TEP C : N ratio. This suggests that TEP, or at least the fraction of the TEP that combines with other particles to form mixed aggregates, may be found in sediment traps and contribute to the flux of sinking particles.

The relatively high C : N ratios reported for POM found in sediment traps (Marty et al. 1994) and for the total standing stock of POM (Copin-Montégut and Copin-Montégut 1983) when nitrogen is deficient further suggest that variations in the C : N of TEP could modify the C : N of both sinking and standing POM and, thus, that TEP can act as important regulators of the C : N ratio of total organic matter.

TEP source and redefinition of the TEP pool—TEP-C concentrations were compared with dissolved organic carbon (DOC) recorded during a previous study at the DYFAMED site. TEP-C concentrations were equivalent to ~5% of surface water DOC (Copin-Montégut and Avril 1993) during the spring bloom and up to ~25% of DOC during summer. In other systems, 20%–30% of oceanic DOM is high-molecular weight (HMW) dissolved organic matter—i.e., molecules >1,000 Da (Carlson et al. 1985; Benner et al. 1992; Amon and Benner 1994)—and the HMW fraction is carbohydrate rich (Benner et al. 1992). HMW DOM and C-rich DOM (Williams 1995) could represent the same fraction of the DOM. The average C : N ratio of TEP equals that of the HMW DOM produced by marine phytoplankton (Biddanda and Benner 1997; Kepkay et al. 1997), which suggests that TEP are formed from colloidal precursors exuded by phytoplankton. Because TEP and HMW DOM (or C-rich DOM) represent the same fraction of the DOM, have the same elemental composition, and have similar seasonal distributions, it is reasonable to assume that the polysaccharidic fraction of the HMW DOM is the source of TEP. This suggests that TEP appear in a continuum of size from molecules >1,000 Da to particles of hundreds of microns.

The classification of organic matter as dissolved and particulate, based on the operational criterion of size, already leads to confusion for conventional particles and is particularly questionable when one tries to define the highly dynamic pools of HMW DOM and of TEP (Kirchman et al. 1991; Mari and Burd 1998). As a consequence, we argue that the definition of this pool of carbon-rich organic matter should be extended to include both size fractions and that TEP should be redefined (without any consideration of size) as one single pool of transparent exopolymeric products.

Potential implications for the biological pump model and the water column stoichiometry—The measured C : N ratios of TEP are consistent with the net DIC : NO_3 assimilation ratios reported at the DYFAMED station during N-limiting conditions (Copin-Montégut 2000). To explain the carbon overconsumption, Toggweiler (1993) suggested that a large pool of organic matter with an anomalous C : N ratio should increase by 15–50 μmol C L^{-1} from spring bloom to late summer. We have shown here that the pool of TEP probably increased by ~17 μmol C L^{-1} during the same period and that TEP have an overall average C : N ratio of ~20. Both of these findings suggest that the TEP pool is indeed a product of carbon overconsumption and overproduction. As a consequence, the C : N ratio of POM is not an accurate index of the total organic matter produced and, thus, cannot be used to link the production of new organic matter to the removal of nitrate.

At this point, two main questions are raised by the introduction of TEP as a C-rich pool of POM to prime the biological pump. What mechanisms cause the formation and the

accumulation of TEP? How can the observed uptake and measured C : N ratios be reconciled with Redfield stoichiometry—i.e., what process(es) drive(s) the C : N ratio back to Redfield values? A way to reconcile the observed high C : N uptake ratio and water column stoichiometry is that the TEP pool is respired back to the atmosphere before it reaches the aphotic zone. This implies that TEP should sink slower than the rate of bacterial degradation. Since TEP are highly hydrated polysaccharidic particles likely to present a density close to that of seawater, they are supposed to sink very slowly unless they combine with other particles. Furthermore, enzymes released by bacteria attached to marine aggregates may render the aggregates soluble (Smith et al. 1992). All TEP are colonized by bacteria and the fraction of TEP-attached bacteria can represent up to 25% of the total bacterial population (Passow and Alldredge 1994; Mari and Kiørboe 1996). The ectoenzyme-mediated mineralization by bacteria may solubilize TEP and the resulting DOM may enter the microbial loop and/or coagulate to reform TEP. This ''aging'' of TEP as bacteria increase in number may in turn selectively remove organic carbon and regulate the C : N ratio of total organic matter, hence, returning the ratio back to values similar to that predicted by Redfield stoichiometry (Kepkay et al. 1997).

The exchanges between the pools of TEP and C-rich DOM could present a dynamic steady-state mainly controlled by the intensity of DOM production and bacterial activity, i.e. both pools should accumulate in the water column during nutrient-limiting conditions if the microbial loop cannot metabolize the excess DOM produced or solubilize the TEP formed (Mari and Burd 1998). Therefore, the nutritional status and the mixing regime of surface waters may control the relative importance of bacterial mineralization versus TEP formation for the transfer of carbon from DOM to POM. The seasonal distributions of nitrate (Fig. 1c), TEP (Fig. 2), C : N ratios (Fig. 4), and C-rich DOM (Copin-Montégut and Avril 1993; Carlson et al. 1994; Williams 1995) are all consistent with the central role that TEP play in the degradation and recycling of DOC.

We suggest that TEP could be the key intermediary during the breakdown of organic carbon in surface waters as the biological pump is primed for carbon transfer to the deep ocean. However, the significance of TEP for the vertical export of carbon will closely depend on the potential fate of these particles (i.e. aggregation-sedimentation processes, bacterial mineralization, and consumption by particle grazers or filter feeders). Because these pathways process organic matter in different ways, the relative importance of each of them will determine the efficiency of the biological pumping of TEP carbon out of the euphotic zone.

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References

ALLDREDGE, A. L., U. PASSOW, AND B. E. LOGAN. 1993. The abundance and significance of a class of large, transparent organic particles in the ocean. Deep-Sea Res. **40:** 1131–1140.

AMON, M. W., AND R. BENNER. 1994. Rapid cycling of high-molecular-weight dissolved organic matter in the ocean. Nature **369:** 549–552.

BANSE, K. 1994. Uptake of inorganic carbon and nitrate by marine plankton and the Redfield ratio. Global Biochem. Cycles **8:** 81–84.

BENNER, R., J. D. PAKULSKY, M. MCCARTHY, J. I. HEDGES, AND P. G. HATCHER. 1992. Bulk chemical characteristics of dissolved organic matter in the ocean. Science **255:** 1561–1564.

BIDDANDA, B., AND R. BENNER. 1997. Carbon, nitrogen, and carbohydrate fluxes during the production of particulate and dissolved organic matter by marine phytoplankton. Limnol. Oceanogr. **42:** 506–518.

CARLSON, C. A., M. L. BRANN, T. H. MAGUE, AND L. MAYER. 1985. Molecular weight distribution of dissolved organic matter in seawater determined by ultrafiltration: A reexamination. Mar. Chem. **16:** 155–171.

———, H. W. DUCKLOW, AND A. F. MICHAELS. 1994. Annual flux of dissolved organic carbon from the euphotic zone in the northwestern Sargasso Sea. Nature **371:** 405–408.

COPIN-MONTÉGUT, C. 2000. Consumption and production on scales of a few days of inorganic carbon, nitrate and oxygen by the planktonic community: Results of continuous measurements at the Dyfamed Station in the northwestern Mediterranean Sea (May 1995). Deep-Sea Res. **47:** 447–477.

———, G., AND B. AVRIL. 1993. Vertical distribution and temporal variation of dissolved organic carbon in the North-Western Mediterranean Sea. Deep-Sea Res. **40:** 1963–1972.

———, AND G. COPIN-MONTÉGUT. 1983. Stoichiometry of carbon, nitrogen, and phosphorus in marine particulate matter. Deep-Sea Res. **30:** 31–46.

FUKUDA, R., H. OGAWA, T. NAGATA, AND I. KOIKE. 1998. Direct determination of carbon and nitrogen contents of natural bacterial assemblages in marine environments. Appl. Environ. Microbiol. **64:** 3352–3358.

KEPKAY, P. E., J. F. JELLET, AND S. E. H. NIVEN. 1997. Respiration and the carbon-to-nitrogen ratio of a phytoplankton bloom. Mar. Ecol. Prog. Ser. **150:** 249–261.

KIRCHMAN, D. L., Y. SUSUKI, C. GARSIDE, AND H. W. DUCKLOW. 1991. High turnover rate of dissolved organic carbon during a spring phytoplankton bloom. Nature **352:** 612–614.

MARCHAL, O., P. MONFRAY, AND N. R. BATES. 1996. Spring-summer imbalance of dissolved inorganic carbon in the mixed layer of the northwestern Sargasso Sea. Tellus **48:** 115–135.

MARI, X. 1999. Carbon content and C:N ratio of transparent exopolymeric particles (TEP) produced by bubbling exudates of diatoms. Mar. Ecol. Prog. Ser. **183:** 59–71.

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———, AND A. BURD. 1998. Seasonal size spectra of transparent exopolymeric particles (TEP) in a coastal sea and comparison with those predicted using coagulation theory. Mar. Ecol. Prog. Ser. **163:** 63–76.

———, AND T. KIØRBOE. 1996. Abundance, size distribution and bacterial colonization of transparent exopolymeric particles (TEP) during spring in the Kattegat. J. Plankton Res. **18:** 969–986.

MARTY, J. C., E. NICOLAS, J. C. MIQUEL, AND S. W. FOWLER. 1994. Particulate fluxes of organic compounds and their relationship to zooplankton fecal pellets in the northwestern Mediterranean Sea. Mar. Chem. **46:** 387–405.

OBERNOSTERER, I., AND G. J. HERNDL. 1995. Phytoplankton extracellular release and bacterial growth: Dependence on the inorganic N:P ratio. Mar. Ecol. Prog. Ser. **116:** 247–257.

PASSOW, U. 2000. Formation of transparent exopolymer particles, TEP, from dissolved precursor material. Mar. Ecol. Prog. Ser. **192:** 1–11.

———, AND A. L. ALLDREDGE. 1994. Distribution, size and bacterial colonization of transparent exopolymer particles (TEP) in the ocean. Mar. Ecol. Prog. Ser. **113:** 185–198.

PORTER, G. K., AND Y. S. FEIG. 1980. The use of DAPI for identifying and counting aquatic microflora. Limnol. Oceanogr. **25:** 943–948.

REDFIELD, A. C., B. H. KETCHUM, AND F. A. RICHARDS. 1963. The influence of organisms on the composition of sea-water, p. 26–77. *In* M. N. Hill [ed.], The sea, v. 2. John Wiley & Sons.

SAMBROTTO R. N., AND OTHERS. 1993. Elevated consumption of carbon relative to nitrogen in the surface ocean. Nature **363:** 248–250.

SARMIENTO, J. L., AND U. SIEGENTHALER. 1992. New-production and the global carbon cycle, p. 317–332. *In* P. G. Falkowski and A. D. Woodhead [eds.], Primary productivity and biogeochemical cycles in the sea. Plenum.

SCHUSTER, S., AND G. J. HERNDL. 1995. Formation and significance of transparent exopolymeric particles in the northern Adriatic Sea. Mar. Ecol. Prog. Ser. **124:** 227–236.

SMITH, D. C., M. SIMON, A. L. ALLDREDGE, AND F. AZAM. 1992. Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution. Nature **359:** 139–141.

TOGGWEILER, J. R. 1993. Carbon overconsumption. Nature **363:** 210–211.

WILLIAMS, P. J. LE B. 1995. Evidence for the seasonal accumulation of carbon-rich dissolved organic material, its scale in comparison with changes in particulate material and the consequential effect on net C/N assimilation ratios. Mar. Chem. **51:** 17–29.

ZHOU, J., K. MOPPER, AND U. PASSOW. 1998. The role of surface-active carbohydrates in the formation of transparent exopolymer particles by bubble adsorption of seawater. Limnol. Oceanogr. **43:** 1860–1871.

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Multispectral in situ measurements of organic matter and chlorophyll fluorescence in seawater: Documenting the intrusion of the Mississippi River plume in the West Florida Shelf

Abstract—We performed multispectral, in situ fluorescence measurements of detrital colored organic matter (COM) and chlorophyll *a* (Chl *a*) in surface waters of the West Florida Shelf using the Wet Labs spectral absorption and fluorescence instrument (SAFIre). Continuous underway measurements allowed simultaneous mapping of the dispersal pattern of riverine organic material and Chl *a* on the shelf. We used two fluorescence emission ratios to differentiate between riverine and marine COM. The data showed unusually high concentrations of COM offshore. These were attributed to an offshore extension of the Mississippi River plume. Comparisons between in situ Chl *a* concentrations measured with the SAFIre and Chl *a* values obtained from the sea-viewing wide field-of-view sensor (SeaWiFS) satellite data using OC4 and MODIS algorithms showed that, although both algorithms overestimated Chl *a*, MODIS performed better than OC4, particularly in areas with high COM concentrations. Analysis of the relationship between Chl *a* and COM concentrations within the study area showed regional variability probably caused by differences in river source.

Accurate determinations of marine chlorophyll *a* (Chl *a*) and colored dissolved organic matter (CDOM) concentrations using satellite color-sensor data are essential for our understanding of the global carbon cycle and its implications in modifying world climate. CDOM is a major impediment to accurately estimating Chl *a* concentrations in coastal regions from satellite ocean color sensors (Carder et al. 1989; Müller-Karger et al. 1989). The major source of CDOM in coastal waters is river runoff of terrigenous organic matter. Away from continental margins, the effect of rivers declines and CDOM is mostly composed of material produced in the oceans. Phytoplankton growth (Carder et al. 1989; Siegel and Michaels 1996) and zooplankton grazing (Momzikoff et al. 1994) produce new CDOM, whereas photodegradation is the major destructive pathway (Kouassi and Zika 1990; Kieber et al. 1989). These in situ processes result in changes in CDOM concentrations and could alter its optical properties. Understanding these changes has obvious implications in the study of the carbon cycle and in the determination of Chl *a* concentrations from satellite color sensors.

Several spectroscopic techniques can be used to study the optical properties of CDOM. Studies using high-resolution fluorescence spectroscopy demonstrate that CDOM fluorescence excitation and emission maxima (Ex_{max}-Em_{max}) are de-