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Dynamics of transparent exopolymeric particles and their precursors during a mesocosm experiment: Impact of ocean acidification

Guillaume Bourdin [a, b], Frédéric Gazeau [a, b], Marie-Emmanuelle Kerros [a, b], Sophie Marro [a, b], Maria Luiza Pedrotti [a, b, *]

[a] Sorbonne Universités, UPMC Univ Paris 06, UMR 7093, LOV, Observatoire océanologique, F-06230, Villefranche/mer, France
[b] CNRS, UMR 7093, LOV, Observatoire océanologique, F-06230, Villefranche/mer, France

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ABSTRACT

The dissolution of anthropogenic atmospheric CO_2 in seawater is suspected to exert a strong pressure on biological processes as well as on carbon and nutrient cycles. Transparent exopolymeric particles (TEP) are polysaccharide particles, formed by aggregation of polymers exuded by phytoplankton and strongly involved in organic matter sedimentation. A mesocosm experiment was performed from February to March 2013 in the coastal waters of the Northwestern Mediterranean Sea, a region characterised by low-nutrient low-chlorophyll (LNLC) levels. We aimed to determine the effect of ocean acidification on the organic carbon pool of TEP produced by a natural phytoplankton community. The experiment was conducted in nine mesocosms of 50 m^3 deployed for 12 days, and subjected to seven partial pressures of CO_2 (pCO_2) levels: one control level in triplicate and six elevated levels between 450 and 1250 μatm. The use of different analytical methods allowed the assessment of TEP density, volume concentration and size distribution as well as both TEP and TEP precursors carbon content. TEP contributed vastly to the particulate organic carbon pool (~62%), and were mainly produced by small-sized phytoplankton such as pico- and nanophytoplankton. TEP precursors carbon content represented three times the carbon content of particulate TEP, showing that this pool has to be considered in experiments focused on the environmental control of TEP production. There was no evidence that TEP and TEP precursors were dependent on pCO_2. These parameters exhibited clear temporal dynamics, with tight links to community composition, nutrient availability and other environmental parameters.

1. Introduction

During the last 150 years, human activities have led to a dramatic release of carbon dioxide (CO_2) in the Earth's atmosphere through the combustion of fossil fuels and land-use change. The accumulation of anthropogenic CO_2 in the atmosphere increases radiative forcing, thereby warming the atmosphere and ocean. Furthermore, oceans act as carbon sinks, absorbing one fourth of the atmosphere's anthropogenic carbon dioxide through physico-chemical processes (Le Quéré et al., 2014). The dissolution of atmospheric CO_2 in seawater ("ocean acidification") is suspected to have important effects on biological processes as well as on carbon and nutrient cycles (Gattuso et al., 2011).

By reducing pH, the availability of carbonate ions, and the saturation state of the major shell-forming carbonate minerals (e.g. $\Omega_{aragonite}$) as well as by increasing the concentration of bicarbonate ions (Gattuso et al., 2011), ocean acidification is projected to have major impacts not only at the species level but on entire ecosystems (Hoegh-Guldberg and Bruno, 2010). The responses of plankton species to ocean acidification are shown to be very different depending on the organism, its trophic level and its ability to assimilate carbon (Rost et al., 2008). Phytoplankton productivity represents half of the world's primary production (Field, 1998), and is responsible for organic matter export to the deep ocean (biological pump). Primary productivity and organic matter export are potentially affected in various ways by carbonate chemistry changes induced by ocean acidification (Riebesell and Tortell, 2011). The observed complexity of plankton responses to elevated CO_2 could lead to shifts in the dominance of species and therefore influence marine productivity and biogeochemical cycles through an

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* Corresponding author. Sorbonne Universités, UPMC Univ Paris 06, UMR 7093, LOV, Observatoire océanologique, F-06230, Villefranche/mer, France.
E-mail address: pedrotti@obs-vlfr.fr (M.L. Pedrotti).

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Table 1
Initial (day 0) and average (±SD) environmental conditions during the mesocosm experiment in the Bay of Villefranche in winter 2013. Partial pressure of CO_2 (pCO_2; μatm), temperature (T; °C), dissolved inorganic nitrogen and phosphate concentrations (DIN and DIP respectively; nmol L^{-1}) as well as chlorophyll a (chl a; μg L^{-1}) concentrations are presented.

	Initial					Mean				
	pCO_2	T	chl *a*	DIN	DIP	pCO_2	T	chl *a*	DIN	DIP
OUT	354	13.2	0.95	n/a	10.3	366 ± 9	13.2 ± 0.1	0.81 ± 0.10	1306 ± 12	12.9 ± 3.1
C1	378	13.3	1.22	167	9.8	359 ± 13	13.2 ± 0.1	1.04 ± 0.20	233 ± 9	9.1 ± 1.3
C2	347	13.2	1.10	118	12.0	356 ± 15	13.2 ± 0.1	0.96 ± 0.13	364 ± 9	9.0 ± 2.1
C3	350	13.2	1.12	110	8.9	353 ± 13	13.2 ± 0.1	1.01 ± 0.11	139 ± 9	8.8 ± 1.2
P1	494	13.2	1.16	135	10.2	458 ± 27	13.2 ± 0.1	0.99 ± 0.20	118 ± 10	9.1 ± 0.9
P2	622	13.2	1.16	133	8.9	491 ± 78	13.2 ± 0.1	0.99 ± 0.13	330 ± 9	9.3 ± 1.4
P3	691	13.2	1.15	n/a	8.5	547 ± 103	13.2 ± 0.1	0.99 ± 0.12	323 ± 8	8.2 ± 0.8
P4	744	13.3	1.21	72	11.5	542 ± 145	13.2 ± 0.1	0.95 ± 0.18	358 ± 10	9.4 ± 1.3
P5	932	13.2	1.19	134	15.2	728 ± 181	13.2 ± 0.1	1.04 ± 0.15	188 ± 10	9.4 ± 2.4
P6	1249	13.2	0.94	159	8.3	949 ± 258	13.2 ± 0.1	0.96 ± 0.10	165 ± 9	8.6 ± 1.2

alteration of organic matter fluxes (Fiorini et al., 2011). This broad range in sensitivities to ocean acidification can be partially attributed to CO_2 concentration mechanisms (CCMs) that are present in many plankton groups. These mechanisms are known to have variable species-specific efficiencies (Reinfelder, 2011; Rost et al., 2008). The increase in CO_2 concentration has been shown to affect growth, primary production and phytoplankton species composition when conducted at the community level. During a mesocosm experiment in the coastal North Sea, Riebesell et al. (2007) showed an increase in the uptake of dissolved inorganic carbon (DIC) by phytoplankton at elevated pCO_2. During this experiment, the excess of carbon consumption was not used to increase biomass but was released via exudation, and probably accounted for the 4-fold increase in transparent exopolymeric particle (TEP) concentrations.

TEP are polysaccharide particles, formed by aggregation of polymers exuded by phytoplankton (Alldredge et al., 1993). They can represent a major fraction of particulate organic carbon (POC), and contribute significantly to organic matter exports to the deep ocean (marine snow; Engel and Passow, 2001; Mari et al., 2001). TEP play a major role in phytoplankton post-bloom cells flocculation and sedimentation (Engel et al., 2004b; Logan et al., 1995; Passow et al., 1994). These particles also provide substrate and are a major source of organic matter for the attached bacterial community (Pedrotti et al., 2009; Simon et al., 2002). Furthermore, a recent study showed that TEP colloidal precursors (p-TEP) represent a significant part of the organic carbon pool being three times more abundant than the particulate form (Villacorte et al., 2009).

Exudation of polysaccharides is highly correlated to primary production rates, and is therefore, influenced by nutrient availability, light, temperature, and carbonate chemistry (Engel et al., 2011). At the cellular level, CO_2 is still consumed even if nutrients limit phytoplankton biomass production (Toggweiler, 1993). This carbon overconsumption represents up to 50% of the carbon assimilated during photosynthesis and is eliminated by exudation in the water column (Baines and Pace, 1991; Engel et al., 2004a). Considering the major role played by TEP and p-TEP in the carbon cycle, especially in oligotrophic areas (Bar-Zeev et al., 2011), it is of the utmost importance to determine their response to ocean acidification in order to better project the overall impact of ocean acidification on the oceanic biological pump.

To date, available studies reported very contrasting effects of ocean acidification on TEP production and aggregation. First, Engel (2002) and Riebesell et al. (2007) showed a direct relationship between CO_2 uptake and TEP production during a mesocosm experiment in the coastal North Sea, and further suggested a increase of TEP production with elevated pCO_2. Furthermore, at the same site, Engel et al. (2004a) showed that TEP production (normalised to the cell abundance) increased at elevated pCO_2 and Engel et al. (2014b) showed a higher peak of TEP concentration under elevated pCO_2. In contrast, still in the same site of the coastal North Sea, Egge et al. (2009) and Engel et al. (2014a) showed an absence of pCO_2 effects on TEP production rate, while MacGilchrist et al. (2014) suggested that, in the offshore Atlantic Ocean environmental parameters such as community structure, nutrient availability, and phytoplankton growth events play a key role in the response of TEP production to ocean acidification. A low pH has been also reported to influence TEP aggregation by modifying particle structure and density and could alter vertical exports of organic carbon to the deep ocean (Dogsa et al., 2005; Mari, 2008). In addition, elevated CO_2 appears to alter the size distribution of TEP (Pedrotti et al., 2012). The diversity of TEP sensitivities to elevated pCO_2 is a result of complex interactions between environmental and biological variables, involved in TEP production and aggregation, but also involved in TEP consumption and disaggregation.

The impact of ocean acidification on marine plankton communities has been widely investigated in mesotrophic to eutrophic conditions (see Riebesell and Tortell, 2011 for a review), but so far, very rarely in low nutrient low chlorophyll (LNLC) areas. Because extracellular exudation is enhanced by nutrient limitations (Baines and Pace, 1991; Beauvais et al., 2003), it appears crucial to investigate the effect of ocean acidification in oligotrophic areas such as the Mediterranean Sea. These regions are expanding as a consequence of global warming (Moutin et al., 2012; Polovina et al., 2008) and are dominated by pico- and nanoplankton species. These pico- and nanoplankton species are known to produce large amounts of TEP (Mari et al., 2001; Passow, 2002a, 2002b) which influence significantly POC exports (Lomas and Moran, 2011). Additionally, these phytoplankton groups were reported to be possibly favoured by elevated pCO_2 (Brussaard et al., 2013; Hare et al., 2007). For instance, Fu et al. (2007) showed an increase in *Synechococcus* photosynthetic rates with elevated pCO_2.

The objectives of the this study were i) to describe the temporal variability of TEP and p-TEP abundances and carbon contents, ii) to evaluate the potential importance of TEP and p-TEP in relation to other organic carbon pools (e.g. particulate organic carbon and ultraphytoplankton groups) under nutrient limiting conditions and iii) to assess the effect of elevated pCO_2 on TEP and p-TEP (colloidal precursors) dynamics. In order to achieve these objectives, a mesocosm experiment was conducted in coastal waters of the North-western Mediterranean Sea, characterised by LNLC conditions. This study was carried out in the framework of the European project MedSeA (Mediterranean Sea Acidification in a changing climate: http://medsea-project.eu). In addition to TEP and p-TEP, various variables, such as ultraphytoplankton organic carbon pools