Marine Chemistry xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

The formation of aggregates in coral reef waters under elevated concentrations of dissolved inorganic and organic carbon: A mesocosm approach

Anny Cárdenas [a,*], Friedrich Meyer [b], Hauke Schwieder [a], Christian Wild [b,c], Astrid Gärdes [a]

[a] Tropical Marine Microbiology Group, Leibniz Center for Tropical Marine Ecology (ZMT), Fahrenheitstr. 6, 28359 Bremen, Germany
[b] Coral Reef Ecology Group (CORE), Leibniz Center for Tropical Marine Ecology (ZMT), Fahrenheitstr. 6, 28359 Bremen, Germany
[c] Faculty of Biology & Chemistry (FB2), University of Bremen, Germany

ARTICLE INFO

Article history:
Received 1 August 2014
Received in revised form 5 April 2015
Accepted 7 April 2015
Available online xxxx

Keywords:
Particle aggregation
Ocean acidification
Carbon cycling
TEP
Suspended particulate matter
Algae

ABSTRACT

The transformation of dissolved organic carbon (DOC) to particulate organic carbon is the major mechanism through which large sinking organic particles are formed in aquatic systems. Global stressors, such as high concentrations of dissolved inorganic carbon (DIC) due to ocean acidification, as well as local stressors, such as high DOC concentrations due to coastal eutrophication, can significantly affect the formation and settling of aggregates and thereby the marine biogeochemical carbon cycle. Increasing aggregate formation rates can contribute to the mortality of benthic organisms in coral reef ecosystems, but relevant knowledge is scarce. Therefore, the present study addresses this issue and studies the individual and combined effects of high DIC (900 μatm) and DOC (150 μM glucose) on organic matter dynamics as well as the formation of organic aggregates in a manipulative study over 42 days using 24 mesocosms dominated by either benthic calcifying algae or by hard corals. Organic aggregates in terms of transparent exopolymer particle (TEP) concentrations and total aggregated volume were measured. Results showed lower TEP concentrations and aggregated volume under high DIC concentrations. By contrast, under DOC enrichment higher rates of aggregate formation and microbial oxygen uptake were observed. Surprisingly, the highest aggregate formation rates were observed under the combined DIC and DOC enrichment. Furthermore, benthic organisms influenced the availability of DOC resulting in higher aggregate formation in coral compared to calcifying algae mesocosms. These experiments simulate future ocean conditions in coastal ecosystems where elevated DOC concentrations could aggravate the effect of high DIC on aggregate formation. In coral reef ecosystems, this may have important consequences on benthic organisms.

1. Introduction

Coral reef decline occurs as a direct response to a single stressor or as a consequence of different global and local stressors acting simultaneously (Baker et al., 2008; Knowlton and Jackson, 2008; Szmant, 2002). Ocean acidification (OA) represents one of the most significant long-term threats to coral reefs. Experimental evidence suggests that a doubling of pre-industrial pCO_2 has reduced coral growth and calcification by up to 40% due to the reduction of aragonite formation (Hoegh-Guldberg et al., 2007). Local and regional threats generally include overfishing and land-based pollution (Moore and Best, 2001; Smith et al., 2003). These threats are generally linked to some of the main causes of coral reef degradation, such as algal overgrowth, increased disease prevalence (Bruno et al., 2003; Rosenberg et al., 2007; Voss and Richardson, 2006), bleaching (Glynn, 1993; Wiedenmann et al., 2013), and sedimentation (Devlin and Brodie, 2005; Fabricius, 2005). Elevated DOC may cause different pathologies and increase the rate of coral mortality (Kline et al., 2006; Kuntz et al., 2005). Negative effects of high DOC concentrations on coral reef health have been linked to enhanced bacterial growth rates and activities that cause coral death by oxygen depletion and accumulation of toxic substances (Gregg et al., 2013; Smith et al., 2006; Wild et al., 2010). Exogenous inputs of DOC in coral reefs are mainly derived from sewage, terrestrial run-off and marine fish farms (Fabricius, 2005; Garren et al., 2008, 2009). For instance, the global flux of riverine DOC has been calculated as high as 7.8×10^{14} g C yr^{-1} (Mantoura and Woodward, 1983). However, DOC inputs have spatial and temporal variations, being higher in areas exposed to river discharges and during the wet season when precipitation is higher and storm events are more frequent (Alongi and McKinnon, 2005; Joo et al., 2012). High concentrations of DOC can also enter the coral reef system in the form of exudates released by the benthic community, mainly from fleshy macroalgae and predominantly in the form of dissolved carbohydrates (Haas and Wild, 2010; Nelson et al., 2013; Wild et al., 2010). For instance, macroalgal blooms represent large amounts of continuous organic matter loads which can increase DOC

* Corresponding author.
E-mail address: anny.cardenas@zmt-bremen.de (A. Cárdenas).

http://dx.doi.org/10.1016/j.marchem.2015.04.002
0304-4203/

concentrations up to 1000 μmol L^{-1} (Kline et al., 2006). Coral reefs are thus profoundly impacted by any activity linked to macroalgal overgrowth, as is the case of inorganic nutrient enrichment and overfishing (Smith et al., 2006).

Although DOC is the most dominant form of organic carbon in most marine ecosystems, large sinking particles constitute a biologically important, though often small, percentage of the total organic carbon (Alldredge, 2000; Verdugo et al., 2004). In coral reef waters, the particulate fraction may be trapped by coral mucus and is mainly remineralized by benthic bacterial communities in order to fuel new production (Huettel et al., 2006; Wild et al., 2004, 2005). However, high levels of suspended particulate matter directly affects light penetration and sedimentation rates and may subsequently promote coral mortality (Fabricius, 2005; Fabricius et al., 2003; Fichez et al., 2005; Garren and Azam, 2012).

The formation of large sinking particles from DOC generally involves acidic polysaccharide gel-like particles termed transparent exopolymer particles (TEPs) (Azetsu-Scott and Passow, 2004; Engel et al., 2004b; Passow, 2002). Abiotic TEP formation requires TEP-precursors present in some DOC pools, and depends on turbulence, ion density and concentration of inorganic colloids (Alldredge et al., 1993; Logan et al., 1995; Passow, 2002). However, TEP can also be directly produced from cell exudates of numerous organisms, particularly from phytoplankton cells as well as macroalgae, coral and bacteria (Gärdes et al., 2012; Passow, 2000; Ramaiah et al., 2001; Wotton, 2004).

Local and global stressors may significantly alter biogeochemical carbon cycling. For instance, declines in pH due to DIC enrichment cause changes of TEP properties and abundance, presumably because of alterations in total alkalinity (TA). This can lead to higher downward carbon exportation (Mari, 2008; Passow, 2012). Mesocosm experiments examining phytoplankton blooms under elevated DIC show an increased CO_2 uptake and subsequent TEP exudation of phytoplankton cells (Egge et al., 2009; Engel, 2002; Engel et al., 2004a), which can stimulate particle aggregation and acceleration of sedimentation (Gärdes et al., 2011; Logan et al., 1995; Mari, 2008) However, there are no studies focused on understanding particle aggregation under high DIC in coral reef environments.

DOC drives the microbial loop and further transformations into large aggregates. For example, anthropogenic activities can result in high loads of organic matter in coastal ecosystems, and these are often related to large quantities of particulate organic matter in the form of large suspended particles (Garren et al., 2008, 2009; Sarà et al., 2004). Experimental evidence also suggests increases in aggregate formation in eutrophic coastal waters, most likely due to the increased phytoplankton growth and subsequent DOC release (Degobbis, 1989; Kiorboe et al., 1998; Linley and Field, 1982). However, there is no evidence supporting the effects of high DOC on aggregate formation in coral reef systems, despite its importance in coral mortality related to increased sedimentation (Anthony, 1999; Anthony and Fabricius, 2000; Fabricius, 2005).

This study explores the individual and combined effects of elevated DIC and DOC concentrations on aggregate formation processes in the overlying water column in coral reef mesocosms. Furthermore, it intends to compare the effect of these stressors working on two groups of key players in coral reefs specifically, benthic calcifying algae and hard coral communities. Since aggregates and TEP always reach high concentrations in elevated nutrient scenarios of eutrophication, such as after phytoplankton blooms or upwelling events (Kiorboe et al., 1998; Passow and Alldredge, 1995b), higher concentrations of TEP and higher aggregate formation in DIC and DOC treatments were expected.

For this study we used replicated mesocosms deployed with calcifying algae or hard coral communities. The following future ocean scenarios were manipulated over 42 days: Elevated DIC concentrations (DIC), elevated DOC concentrations (DOC), the combined effect of elevated DIC and DOC (combined), and a control treatment. During the course of the experiment, the following parameters were measured: DOC, TEP and suspended particulate matter (SPM) concentrations, total aggregated volume, bacterioplankton cell density and oxygen uptake.

2. Methods

2.1. Origin and preparation of organisms

The experiments were carried out at the MARine Experimental Ecology facility (MAREE) of the Leibniz Center for Tropical Marine Ecology (ZMT). Coral and algal fragments were taken from existing colonies at the MAREE. The fragmentation was done 45 days prior to the starting point of the experiments and fragments were acclimatized for 15 days. The algal species used in the experiments were *Halimeda cuneata*, *Halimeda opuntia*, *Halimeda macroloba*, *Halimeda copiosa* and *Amphiroa foliacea*. Coral species used were *Acropora millepora*, *Pocillopora damicornis*, *Seriatopora hystrix*, *Stylophora pistillata* and *Acropora muricata*.

2.2. Setup of mesocosms

Mesocosms were assembled as an open system using two-compartment tanks with a total volume of 264 L and a constant flow between compartments (Fig. S1). Mesocosms were filled with reverse osmosis and ion exchange resin (Dowex™) prepared water with the addition of artificial sea salts. Every tank contained 20 L of oolite live sand (Ocean Direct™) with a fraction size ranging from 200 μm to 1000 μm as a substrate. Of the 24 tanks, twelve were set up with algae and twelve with coral fragments, with the following conditions: 3 tanks for DIC enrichments, 3 tanks for DOC enrichment, 3 tanks for the combined treatment and 3 tanks to perform the control treatment. Every mesocosm contained between 48 and 52 fragments comprising 5 species of algae or coral. Every tank contained a protein skimmer with 10% of the water being exchanged every week to ensure complete homogenization while minimizing material accumulation. Water was sampled from the lower compartment, directly at the inflow point of the upper compartment using polypropylene beakers (sulfuric acid-cleaned and artificial seawater-leached).

2.3. Background parameters and DIC/DOC enrichment

To obtain elevated DIC conditions, CO_2 was supplied constantly via aeration with 1000 μatm CO_2 pre-mixed gas (gas mixing system, HTK Hamburg, Germany) at a flow rate of 25 L min^{-1} in the DIC and combined treatments. Control and DOC tanks were also aerated at the same flow rates in order to avoid differences in microbial and chemical activity due to bubbling although using 400 μatm CO_2. In DOC and combined treatments, DOC enrichment was achieved by adding 1.5 μM h^{-1} glucose using peristaltic pumps and a glucose stock solution of 30 mmol L^{-1} exchanged once a week. Total alkalinity was maintained constant using 40 g L^{-1} $CaHCO_3$ stock solution by peristaltic pumps. The carbonate chemistry was monitored by measuring in situ pH_{NBS}, temperature, oxygen saturation and salinity using a multi-probe, (WTW 3430, Germany). TA was measured by end-point titration using the TitroLine alpha plus Titrator (SI Analytics, Germany) using 0.5 M HCl and certified reference material (Batch 111, CRM Andrew Dickson, Scripps Institution of Oceanography). The complete carbonate system was calculated from pH_{NBS} and TA using the CO_2 Sys Excel Macro (Lewis and Wallace, 1998) with the KSO_4 constants of Dickson (Dickson, 1990) and K1 and K2 from Mehrbach et al. (1973) refitted by Dickson and Millero (1987).

2.4. Carbon pool analyses

Changes in concentration of DOC, TEP, and SPM were measured over time to follow changes in organic carbon pools during the various future ocean scenarios. For DOC analysis 20 mL of water were collected weekly

Please cite this article as: Cárdenas, A., et al., The formation of aggregates in coral reef waters under elevated concentrations of dissolved inorganic and organic carbon: A mesoco..., Mar. Chem. (2015), http://dx.doi.org/10.1016/j.marchem.2015.04.002