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Photoreactivity of dissolved organic matter from macroalgae

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HIGHLIGHTS

- We tested photoreactivity of macroalgal DOM using artificial sunlight.
- A part of macroalgal DOM is directly mineralized by sunlight.
- CDOM analysis showed the shift toward less aromaticity and low molecular weight.
- EEM-PARAFAC analysis showed generation of degradation products.
- Irradiation for sunlight would accelerate decomposition of macroalgal DOM.

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ABSTRACT

A large fraction of primary production of macroalgae is released as dissolved organic matter (DOM), and it constitutes a part of the coastal DOM pool. Since photochemical decomposition could be involved in the dynamics of marine DOM, we observed the time course of macroalgal DOM exposed to artificial sunlight. During 24 h of irradiation at 400–765 W m^{-2}, concentrations of dissolved organic carbon constantly decreased and 72%–77% of the initial concentration remained, suggesting that macroalgal DOM is mineralized by solar radiation in comparison with the DOM of other marine organisms such as phytoplankton and bacteria. A shift in organic composition was evaluated using analyses of absorption and fluorescence spectra. We found a decrease in the absorption coefficient at 270 nm, suggesting molecular destruction of phenolic compounds. In addition, increases in slope value and ratio could imply a shift towards lower-sized compounds with low aromaticity. The fluorescence analysis showed an increase in humic-like peak in the region with shorter wavelengths. Since it would reflect an accumulation of degradation products with lower molecular weight and less aromaticity, the results of the fluorescence analysis were consistent those of the absorption spectra analysis. The mineralization and molecular shift suggest that sunlight exposure accelerates the decomposition of macroalgal DOM in coastal environments.

1. Introduction

Macroalgal communities are one of the most highly productive communities on the Earth's surface (Alongi, 1998; Yokohama et al., 1987; Cebrian, 1999). Such a high productivity implies the importance of macroalgae in coastal ecosystems, and their roles in food webs (Kwak and Zedler, 1997; Valiela et al., 1997; Estes et al., 1998), export of organic matter (Harrold et al., 1998), and habitat provision (Bologna and Steneck, 1993) have been discussed in detail. In addition, macroalgae release 20%–40% of their photosynthetic products as dissolved organic matter (DOM); production of DOM has been addressed as another function of macroalgae in marine ecosystems in various studies (Khailov and Burlakova, 1969; Sieburth, 1969; Abdullah and Fredriksen, 2004; Wada et al., 2007).

The ecological roles of DOM in marine ecosystems would depend on its decomposition process. A part of marine DOM is called labile DOM, and bacteria utilize it within hours to days (Cherrier et al., 1996; Keil and Kirchman, 1999). Despite its small contribution to the bulk DOM pool (Davis and Benner, 2007), labile DOM acts as a major energy source for microbial food webs because of its short turnover time (Koshikawa et al., 1999; Hagström et al., 1984).

Abbreviations: DOM, dissolved organic matter; DOC, dissolved organic carbon; CDOM, chromophoric dissolved organic matter; FDOM, fluorescent dissolved organic matter; EEM, excitation–emission matrix; PARAFAC, parallel factor analysis.

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Other components such as semi-labile and refractory DOMs constitute a major part of marine DOM (Carlson et al., 1994; Carlson and Ducklow, 1995; Ogawa and Tanoue, 2003). Since those fractions are resistant to bacterial mineralization, they contribute to transportation, sequestration, and reservation processes of organic carbon in marine environments (Ogawa and Tanoue, 2003; Carlson, 2002). A previous study on the decomposition process of macroalgal DOM demonstrated its refractory property for marine bacteria on the basis of a dark incubation experiment (Wada et al., 2008).

Bacterial decomposition is definitely important in determining the fate of marine DOM, but another process, photodecomposition, also has a significant effect on DOM dynamics. Considering that macroalgal habitats are mainly spread in a shallow region where sunlight reaches the bottom layer, DOM released by macroalgae should be particularly exposed to strong solar radiation. Photodecomposition would cause not only mineralization but also a shift in the chemical composition because of the generation of degradation products (Corin et al., 1996). In case of natural marine DOM, photodegradation products tend to be more biologically labile than its parent materials (Kieber et al., 1989), suggesting that decomposition would be affected by sunlight. However, the photo-reactivity of the macroalgal DOM has been rarely studied.

In order to study photo-reactivity, analysis of chromophoric DOM (CDOM) would be useful because many researchers have reported the photo-reactivity of CDOM (e.g., Andrews et al., 2000 and Shank and Evans, 2011). On the basis of shifts in absorption coefficient and slope values, decreases in molecular weight and aromaticity in the photodecomposition process of marine DOM were evaluated (Helms et al., 2013; Weishaar et al., 2003). Since some components of CDOM would have fluorescent property, analysis of fluorescent DOM (FDOM) has been used to characterize CDOM (Wada et al., 2007; Coble, 1996; Yamashita et al., 2008; Coble et al., 2014). Fluorescence signature provides a detailed composition of DOM, and previous studies have shown that macroalgal DOM contains a humic-like fluorophore (Wada et al., 2007; Wada and Hama, 2013). Since the release of humic-like materials has been observed in a variety of macroalgal species (Wada et al., 2007; Wada and Hama, 2013; Fogg and Boalch, 1958; Craigie and McLachlan, 1964), focus on the humic-like materials may be an effective approach in understanding the chemical alteration of macroalgal DOM. Considering that humic-like materials are subjected to photodecomposition (Osburn et al., 2009), analysis of FDOM would be useful in monitoring the shift (e.g., changes in aromaticity and molecular weight) in DOM molecules due to solar radiation.

In the present study, we performed photodecomposition experiments by using macroalgal DOM and monitored the time courses of dissolved organic carbon (DOC) concentrations and spectral properties of CDOM and FDOM. Then, we evaluated the dynamics of macroalgal DOM on the basis of photoreactivity.

2. Materials and methods

2.1. Collection of macroalgal DOM

The study site was located in Oura Bay in Shimoda City, southern part of Izu Peninsula, Japan (Fig. 1). The mean water depth was about 8 m, and there is a thick kelp forest of *Ecklonia cava* (Yokohama et al., 1987). We conducted a bag-covering experiment in December 2011 and May 2013 to collect DOM derived from *E. cava* on the basis of our previous study (Wada et al., 2007). Briefly, we used a transparent bag to cover all the blades of an individual *E. cava* with ambient seawater, and the open end of the bag was tied at the stipe by scuba divers. The samples were covered with the bags for 48 and 30 h in December 2011 and May 2013, respectively. Next to a sample bag (with *E. cava*), two additional bags were filled with ambient seawater without *E. cava* to obtain control

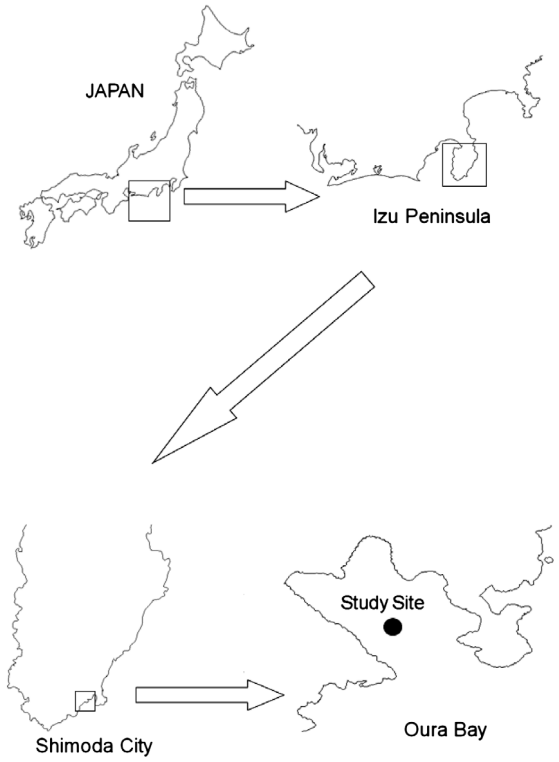

Fig. 1. Location of the study site.

samples. At the start and end of the experiment, divers used 100-ml glass syringes to collect water samples through the sampling valve of the bags. We collected triplicate samples for each bag, and the seawater samples were filtered through a precombusted glass fiber filter (Whatman, GF/F) immediately after collection. All the seawater samples were recovered after the experiments, and we filtered the seawater samples using the GF/F filter after measuring the seawater volume in the bags. The filtrates were stored at −20 °C until the photodecomposition experiment, and the blades of *E. cava* were dried at 60 °C until their weights were constant in order to measure their dry weight.

2.2. Photodecomposition experiment

To eliminate the effect of bacterial activity, the samples were filtered through capsule filters with a pore size of 0.2 μm (Millipore, Steripak-GP10 Filter Unit and Whatman, Polycap 150TC in December 2011 and May 2013, respectively) after thawing. For the samples obtained in December 2011, the filtrates were divided into twelve 200-ml acid-cleared quartz bottles, and they were irradiated using a sunlight simulator (Atlas, SUNTEST XLS$^+$) at 23 °C. Light intensities were set at 400 and 765 W m^{-2} for 4 bottles, and another 4 bottles were stored in the dark at 23 °C. The intensity at 765 W m^{-2} is similar to that on daytime in summer around our study area (data not shown). At each subsampling time (0, 2, 4, and 24 h), we collected a single bottle under each light condition (dark, 400, and 765 W m^{-2}) for analyses of DOC concentration and fluorescence spectra. For the samples obtained in May 2013, we conducted the decomposition experiment, but the light conditions used were dark and 765 W m^{-2}. The filtrates were divided into eighteen 200-ml quartz bottles, and duplicate bottles were collected at each subsampling time (0, 2, 4, 7, 12, and 24 h) for the samples irradiated at 765 W m^{-2}. For the sample under the dark condition, we collected a single bottle at each subsampling time. The samples were stored at −20 °C until