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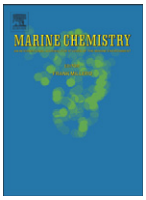

Vertical change in the composition of marine humic-like fluorescent dissolved organic matter in the subtropical western North Pacific and its relation to photoreactivity

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ABSTRACT

The vertical change in the composition of marine humic-like fluorescent dissolved organic matter ($FDOM_M$) and its controlling factors were examined in the subtropical western North Pacific. Fluorescence intensity and molecular weight distribution were measured on the hydrophobic fraction of $FDOM_M$ (O-$FDOM_M$) fractionated with ODS solid phase extraction. Although the same vertical trends with low fluorescence intensity in surface waters and high in deep waters were observed both for bulk $FDOM_M$ and O-$FDOM_M$, the contribution of O-$FDOM_M$ to bulk $FDOM_M$ decreased with depth. A sunlight irradiation experiment of deep seawater revealed that the fluorescence intensity of O-$FDOM_M$ as well as bulk $FDOM_M$ tended to decrease, whereas the contribution of O-$FDOM_M$ to $FDOM_M$ increased from 42% to 62% throughout the irradiation experiment. This suggests that the hydrophobic fraction is more refractory to photoirradiation than a hydrophilic one and that the difference of photo-lability results in the vertical change of the contribution of O-$FDOM_M$ to $FDOM_M$. Molecular weight (MW) distributions of O-$FDOM_M$ were measured by high-performance size exclusion chromatography. O-$FDOM_M$ was composed of three MW fractions throughout the samples examined and the compositional change was noted with an increase in the high MW fraction with depth. The photoirradiation experiment of deep seawater sample clearly showed that a high MW fraction was more susceptible than a low MW fraction of O-$FDOM_M$. The present study strongly suggests that $FDOM_M$ is composed of some fractions with different photoreactivity, and that photoirradiation is the main factor controlling the compositional change in $FDOM_M$ with depth. The fate of each fraction of $FDOM_M$ after photoirradiation is presumably one of the key processes in the biogeochemical cycle of marine DOM.

1. Introduction

Marine dissolved organic matter (DOM) is one of the major organic carbon reservoirs on the earth's surface (Hedges, 1992) and plays important roles in the biogeochemical cycle of the ocean. Marine DOM has been considered to be mainly derived from photosynthetic production by phytoplankton, whose organic matter is mainly composed of labile biomolecules such as carbohydrates, proteins and lipids. However, uncharacterized and bio-refractory organic matter account for a major part of oceanic DOM (Benner, 2002). These very disparate properties have provoked interest in the diagenesis and transformation of phytoplankton organic matter toward bio-refractory DOM and have produced a considerable number of studies during the past few decades (Lara and Thomas, 1995; Amon and Benner, 1996; Hama et al., 2004; Yoshimura et al., 2009).

Marine humic substances are known to be one of the main components of bio-refractory DOM (Thurman, 1985). Since they have a specific fluorescent property, their distribution and dynamics have recently been assessed as marine humic-like fluorescent DOM (marine humic-like FDOM: $FDOM_M$) using high-sensitivity and high-precision fluorescence analyses (e.g., Coble et al., 1998; Yamashita and Tanoue, 2008; Omori et al., 2010). In the pelagic ocean, where few effects of terrestrial humic substances are expected, vertical profiles characterized by low fluorescence intensity at the surface layer and high intensity at the deeper layer were commonly observed (Mopper et al., 1991; Chen and Bada, 1992; Hayase and Shinozuka, 1995; Yamashita and Tanoue, 2008; Omori et al., 2010). The $FDOM_M$ profile significantly differs from the general distribution patterns of DOM with concentrations high in the surface layer and low in the deep layer. Thus, the factors controlling the vertical distribution of $FDOM_M$ are unique. It is considered that the low value of $FDOM_M$ in the surface layer is due to photobleaching by sunlight (Chen and Bada,

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1992; Hayase and Shinozuka, 1995). The depth distributions within the mesopelagic layer are similar to those of apparent oxygen utilization (AOU), indicating that $FDOM_M$ is produced in situ concomitant with the microbiological degradation of organic matter that consumes dissolved oxygen (Hayase and Shinozuka, 1995; Yamashita et al., 2007; Yamashita and Tanoue, 2008). That accordingly suggests that bacterial activity is responsible for the main production process of $FDOM_M$. Experimental studies using bacterial populations without phyto- and zooplankton confirmed the bacterial production of $FDOM_M$ (Kramer and Herndl, 2004; Shimotori et al., 2009).

Although photoirradiation has been recognized as the major factor diminishing the fluorescence intensity of $FDOM_M$ in the surface layer (Chen and Bada, 1992), most previous studies have measured only the fluorescence intensity of intact seawaters. $FDOM_M$ likely consists of heterogeneous components (Thurman, 1985), each of which is expected to display a different reactivity to photoirradiation. Skoog et al. (1996) indicated that humic substances in coastal areas were composed of two fractions that exhibited different susceptibility to photoirradiation; one was bleached exponentially and another was resistant to photobleaching. In order to understand the dynamics of $FDOM_M$ and its relation to the biogeochemical cycle, it is necessary to elucidate the chemical characteristics and dynamics of each component of $FDOM_M$.

It has been shown that the chemical and biological reactivity of DOM varies considerably depending on molecular weight (MW) (e.g., Amon and Benner, 1996; Hama et al., 2004; Stedmon et al., 2007; Helms et al., 2008; Dalzell et al., 2009). Studies of the relationship between the photoreactivity and MW of colored DOM (widely used as an index of humic-like substances in fresh and coastal waters) showed that the MW decreased due to photoirradiation (e.g., Mopper and Kieber, 2002; Helms et al., 2008), and that the higher MW fraction was more susceptible to photoirradiation than the lower MW one (Lepane et al., 2003; Lou and Xie, 2006). However, for pelagic waters where an autochthonous source likely represents the major components, the relationships between MW of marine DOM and photoirradiation have not yet been elucidated.

Some studies showed that bio-refractory DOM in deep seawater was partly degraded by sunlight irradiation into carbon monoxide and low MW, biologically labile organic matter (Kieber et al., 1990; Mopper et al., 1991), indicating that photoirradiation is one of the most important factors in the carbon cycles. Humic substances are also directly mineralized to carbon dioxide and/or carbon monoxide (Granéli et al., 1996; Bertilsson and Bergh, 1999). During photoirradiation experiments of bacteria-derived FDOM, however, no significant decrease in dissolved organic carbon (DOC) concentration was observed although the fluorescence intensity decreased (Kramer and Herndl, 2004). This finding suggests that photobleached $FDOM_M$ would survive over a substantial period of time. The "inverse" profiles of $FDOM_M$ and DOC (the lowest fluorescence intensity but the highest concentration for DOC in the surface layer) often lead some to conclude that $FDOM_M$ is not an important constituent in the ocean surface layer (Nelson et al., 1998). To elucidate the role of $FDOM_M$ in the ocean carbon cycle, accurate information on its chemical characteristics in relation to photoreactivity would be most useful, though only a few attempts have been made in this respect.

In the present study, we measured profiles of the MW distribution of hydrophobic $FDOM_M$, which was fractionated by hydrophobic solid phase extraction, in the subtropical western North Pacific along 137°E, using high-performance size exclusion chromatography (HPSEC). A sunlight irradiation experiment was carried out and changes in the MW composition throughout the experiment were determined to assess the deciding factor among vertical differences in the MW composition of hydrophobic $FDOM_M$. Vertical changes in the compositional ratios of hydrophobic and hydrophilic $FDOM_M$ were also examined. Moreover, we discussed the importance of $FDOM_M$ and photobleached $FDOM_M$ in the oceanic carbon cycle.

2. Materials and methods

2.1. Sampling

Water samples were collected at 4 stations (30, 25, 20, and 15°N) along 137°E in the western North Pacific Ocean (Fig. 1) during 5 cruises of the R/V *Ryofu-Maru* and the R/V *Keifu-Maru* (Japan Meteorological Agency) from April 2006 to April 2007. Time–depth distributions of the total organic carbon (TOC) concentration and $FDOM_M$ (at a wavelength of excitation (Ex)/emission (Em) = 320/420 nm) in bulk seawater during those same cruises were previously reported (Omori et al., 2010).

Seawaters collected from each depth by the CTD rosette system were transferred to acid-cleaned polycarbonate bottles (1 l). The sampling depths were 5, 10, 25, 50, 75, 100, 125, 150 and 200 m in April 2006, with an additional 1000 m in June 2006, and 0 or 10, 25, 50, 75, 100, 150, 200, 500 and 1000 m in October 2006 and January and April 2007. Total number of samples was 165. The water samples were not filtered to avoid possible contamination during filtration (Yoro et al., 1999; Lee et al., 2008; Omori et al., 2010). Samples of seawater were immediately frozen (−20 °C) after sampling, and we performed chemical measurements in the lab after the cruise; the samples were stored frozen in dark for three to six months, until the measurements.

2.2. Extraction

Solid-phase extraction (SPE) was performed to prepare the DOM samples for HPSEC analysis using octadecylsilyl (ODS) cartridges (C18

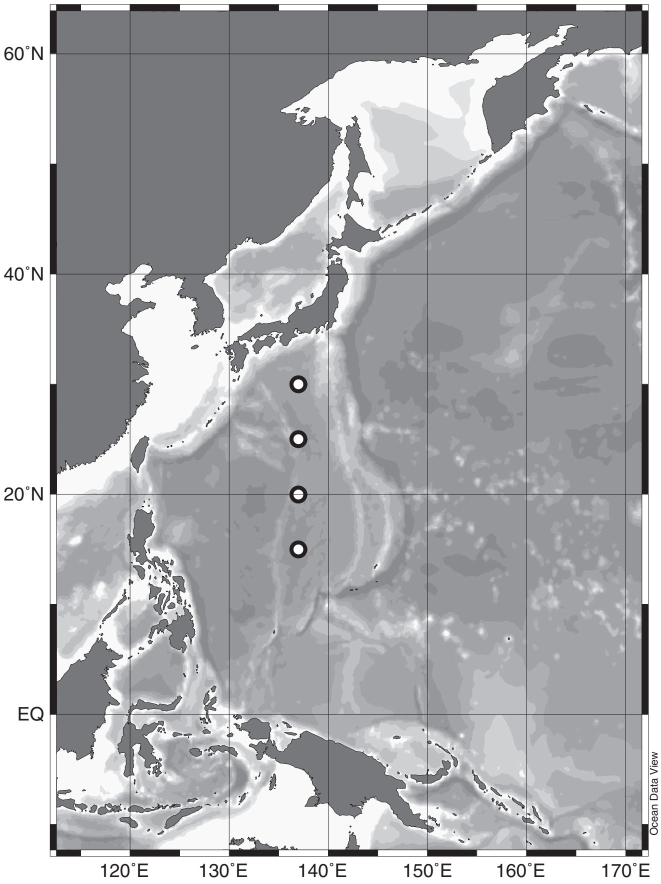

Fig. 1. Sampling stations in the subtropical western North Pacific during 5 cruises conducted aboard vessels of the Japan Meteorological Agency; KS06-04 (April 2006), RF06-06 (July 2006), RF06-10 (October 2006), KS07-01 (January 2007) and KS07-04 (April 2007). KS and RF cruises were made by the R/V *Keifu-Maru* and R/V *Ryofu-Maru* conducted by the Japan Meteorological Agency, respectively. Latitudes of sample sites (dots in this figure) were 30, 25, 20 and 15°N along 137°E.