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Composition and bioavailability of dissolved organic matter in different water masses of the East China sea

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ABSTRACT

The degradation of dissolved organic matter (DOM) is affected by ocean currents, but this influence is poorly understood in the East China Sea (ECS), a dynamic shallow continental shelf characterized by several discrete water masses. This study investigates dissolved organic carbon (DOC), nitrogen (DON) and total dissolved amino acids (TDAA) in different water masses of the ECS. Bioassay experiments were also conducted to determine the labile fraction of DOM. Carbon-normalized yields of TDAA [TDAA (%DOC)] as well as the degradation index (DI) was used to investigate the diagenetic state of organic matter in different water masses. Generally, DOM concentration decreased from the Coastal Current Water (CCW), to the Shelf Mixed Water (SMW), to the Taiwan Warm Current Water (TWCW), and to the Kuroshio Current Water (KCW). DOM in CCW is relatively labile due to inputs from phytoplankton production, while that in the TWCW exhibits low bioavailability, which may be related to nutrient limitation leading to low productivity. The long residence time of the KCW resulted in a high degree of biodegradation associated with nutrient regeneration. Intrusion of nutrient-rich KCW may contribute to the high primary productivity in shelf water, while complex hydrodynamic processes and stratification may control DOM availability in SMW.

1. Introduction

River-influenced ocean margins are highly dynamic systems. Continental shelf and adjacent slope waters account for only 10–20% of the global ocean surface area, yet contribute 25–50% of total marine primary production (Walsh, 1988). As a transport route of materials from land to the open ocean, river-influenced ocean margins play a pivotal role in the global carbon cycle (Gattuso et al., 1998; Walsh, 1991). In the past two decades, this region has attracted considerable attention due to the enigma associated with its function as a carbon source or sink (Bauer et al., 2013; Chen and Wang, 1999; Smith and Hollibaugh, 1993; Tsunogai et al., 1999).

The source and transformation of dissolved organic matter (DOM) in river-influenced ocean margins is complex due to the intricate hydrodynamic processes involved. Ocean currents with different physical, chemical and biological signatures interact in a dynamic manner and often greatly influence processes occurring in this region, including those associated with the bioavailability of DOM. Investigation of the bioavailability and diagenetic state of DOM in river-influenced ocean margins can contribute to a better understanding of the regional carbon cycle.

Based on the timeframe of its microbial utilization, DOM in the ocean can be classified into three categories: labile DOM (L-DOM), with a turnover time of hours to days, semi-labile DOM (S-DOM), with a turnover time of weeks to months, and refractory DOM (R-DOM), with a turnover time of years to decades (Carlson and Ducklow, 1995; Davis and Benner, 2007). The source of DOM is likely related to primary productivity (Bo et al., 1995), but along ocean margins this relationship remains unclear. The L-DOM fraction derived from plankton production can provide the fuel for bacterial growth and respiration (Amon and Benner, 1998; Benner and Opsahl, 2001). This fraction cannot be measured directly, and is traditionally quantified using bioassay experiments (Sondergaard and Middelboe, 1995; Vittor et al., 2009). Dissolved organic carbon (DOC), the carbon component of DOM, plays an important role in marine carbon biogeochemical cycles (Hedges, 1992). In turn, dissolved organic nitrogen (DON) is the main source of reactive nitrogen in the surface ocean (Letscher et al., 2013), and in most instances DON is degraded to release inorganic nutrients as DOC is consumed by bacteria (Connolly et al., 1992; Wotton, 1994). Identification of DOM at the molecular level can improve our understanding of

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this dynamic carbon and nitrogen pool. Due to analytical limitations, however, < 11% of DOM can be characterized at the molecular level (Benner, 2002). Amino acids (AA) are bioactive molecules in the DOM fraction that can be rapidly utilized, and can be used to estimate the degree of degradation of organic matter (OM) (Benner, 2003; Davis and Benner, 2007). The DOC- and DON- normalized yields of AA as a biochemical indicator have been widely applied to characterize the bioavailability of DOM in the estuarine (Zhang et al., 2015), shelf (Shen et al., 2016), ocean (Kaiser and Benner, 2012; Kim et al., 2017) and polar region (Davis and Benner, 2005; Shen et al., 2017). The amino acid degradation index (DI), developed by Dauwe and Middelburg (1998) to investigate the diagenesis of sediments is calculated based on the % molar composition of individual AA and has been previously applied to evaluate the degree of DOM degradation (Davis et al., 2009; Kaiser and Benner, 2009; Yamashita and Tanoue, 2003).

The East China Sea (ECS), one of the largest continental shelves in the world is a highly dynamic system. It receives large inputs of nutrients and organic matter from the Changjiang (Yangtze) River and is affected by several currents that lead to the high primary productivity in the Changjiang Estuary and its adjacent sea. The ECS is mainly influenced by the Kuroshio Current Water (KCW), the Taiwan Warm Current Water (TWCW), the Coastal Current Water (CCW) which includes the Zhejiang-Fujian Coastal Current (ZFCC) and Changjiang Diluted Water (CDW), and Shelf Mixed Water (SMW) formed by mixing of other water masses (Zhao et al., 2013) (Fig. 1). Studies of nutrients in the ECS reveal spatial linkages among terrigenous inputs, water mass migration, primary production and remineralization processes, which cause problems of eutrophication and hypoxia (Chen, 2000; Tseng et al., 2011; Zhang et al., 2007; Zhu et al., 2011). These processes also impact the properties and mineralization of DOM (Wei et al., 2014). Previous studies were conducted using bioassay experiments to investigate the effects of different currents on the organic matter (Gan et al., 2016; Hung et al., 2003). Because of the dynamic nature of water masses, however, a single incubation is insufficient to describe the full scenario. Furthermore, incubation experiments can only quantify bulk carbon (C), and thus mask the underlying transformation of DOM. It is thus critical to evaluate the bioavailability and transformation of DOM in different water masses of the ECS at the molecular level.

The ECS is a typical shallow shelf area, which experiences complex phenomena, i.e., current mixing, river input and anthropogenic disturbances. The biogeochemistry of DOM in the ECS is poorly understood, especially the degradation of OM. In this study, shipboard experiments were conducted to characterize the compositional changes in bulk C during early diagenesis and to determine the concentrations of nutrients, DOC, DON and total dissolved amino acids (TDAA) in different water masses of the ECS. Furthermore, this study evaluates the diagenetic state and transformation of DOM in different water masses and discusses the factors affecting these processes.

2. Materials and methods

2.1. Study area and sampling

The ECS shelf region receives materials of diverse origins. Numerous rivers carry large amounts of freshwater and nutrients into the western continental shelf, especially the Changjiang River, one of the world's largest rivers. The ZFCC flows along the western boundary of the shelf, whereas the broad middle shelf region is intruded by high salinity-TWCW which flows northward through the Taiwan Strait (Fig. 1). Along the east, KCW enters the shelf region at the shelf break northeast of Taiwan. The KCW originates in the eastern coast of Luzon, Philippines, and is characterized by high salinity and nutrient-depleted waters. In contrast, CCW is characterized by low salinities and high nutrient concentrations attributed to river input. As one branch of the KCW, the TWCW has elevated temperature and salinity (Jan et al., 2002). Furthermore, the monsoon has a profound seasonal influence on water circulation patterns. From late September to early April, the strong northeast monsoon directs the Changjiang River plume and Coastal Current flow southward. The southwest monsoon prevails from May to August, and causes the plume and Coastal Current to flow northeastward.

Water samples were collected aboard the R/V "Science No.3" in late spring-early summer (May 25-June 5) and autumn (October 18-October 29) of 2014. The sampling stations are shown in Fig. 1. Nearly all sampling sites were located within the 100 m isobath. Water samples were collected with a Seabird 911 CTD rosette fitted with Niskin bottles. Samples for DOM analysis were collected from the surface, 10 m, 20 m, 30 m, 50 m and bottom depths (2 m from the bottom); they were immediately filtered through pre-combusted (450 °C for 4 h) Whatman GF/F glass fiber filters (0.7 μm pore size). After filtration, samples were stored frozen in pre-cleaned 60-ml amber glass bottles until analysis was conducted in the home laboratory.

2.2. Identification of water masses in the ECS

As indicated earlier, it is important to distinguish the various water masses in this complex and dynamic study area. The traditional method used to achieve this is based on salinity and temperature, and this method was used in the present study to cluster water types. Four water masses were identified during each cruise using the *pamk* function of the software package *fpc* in R (Li et al., 2018).

2.3. Bioassay experiments

Shipboard bioassay experiments were conducted in spring to investigate the microbial utilization and transformation of labile DOM. The two incubation sites (29.45 and 33.98 salinity), are representative of the CCW and TWCW, respectively. Polypropylene bottles (1 L capacity) were used as incubation containers, eight parts of 0.2 μm-filtered water and one part filtered through GF/C Whatman filters (1.2 μm pore size) were mixed in the containers, and then incubated onboard at ambient seawater temperatures in the dark for 12 d. Subsamples were obtained at 0 d and 12 d. Water samples were frozen (−20 °C) until laboratory analysis to determine the concentrations of DOC and amino acids. Temperature and salinity were measured using the CTD apparatus during sample collection.

2.4. Chemical analyses

Dissolved oxygen (DO) was determined following the standard Winkler titration method (Bryan et al., 1976). The apparent oxygen utilization (AOU) was calculated as the difference between the measured DO concentration and its equilibrium saturation concentration in water with the same physical and chemical properties. Concentrations of chlorophyll (Chl) *a* were determined with a fluorescence spectrophotometer (F-4500, Hitachi Co, Japan) after 90% acetone extraction, with a detection limit of 0.01 mg m^{-3} (Aminot and Rey, 2000).

Dissolved organic carbon (DOC) was measured by high-temperature oxidation using a Shimadzu TOC-V, equipped with a chemiluminescent nitrogen detector (Shimadzu TN-1), to allow for the simultaneous analysis of total dissolved nitrogen (TDN) (Spyres et al., 2000). The standard deviation of the injections was < 2%. Inorganic nutrients (nitrate, nitrite, ammonium, phosphate and silicate) were analyzed with a SEAL Analytical AACSII nutrient automatic analyzer. Each sample was measured three times in parallel, achieving a standard deviation (SD) < 3% (Strickland and Parsons, 1969). Dissolved inorganic nitrogen (DIN) was calculated as the sum of nitrate (NO_3^-), ammonium (NH_4^+) and nitrite (NO_2^-). Dissolved organic nitrogen (DON) was determined as the difference between TDN and DIN.

Amino acids were determined with an Agilent high performance liquid chromatography (HPLC) system equipped with a ZORBAX Eclipse AAA (4.6 × 150 mm, 5 μm particles) column and a fluorescence