



Sources, behaviors and degradation of dissolved organic matter in the East China Sea



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ABSTRACT

Concentrations of dissolved organic carbon (DOC), dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON) and its major compound classes—total hydrolysable amino acids (THAA) were measured at 4 cross-shelf transects of the East China Sea in July 2011. Surface concentrations of DOC, DIN, DON and THAA at the nearshore stations were mostly in excess of those found at the offshore sites, indicating either substantial autochthonous production or allochthonous inputs from the Changjiang River. The vertical distributions of DOC, DON and THAA showed similar trends with higher values in the surface layer, whereas the elevated concentrations of DIN were observed in the bottom layer. Major constituents of THAA presented in the study area were glycine, serine, alanine, glutamic acid, aspartic acid and valine. The mole percentages of neutral amino acids increased from surface water to bottom water, whereas acidic and hydroxy amino acids decreased with the water depth. Concentrations of DOC and THAA were negatively correlated to the Δ DIN values (the difference between the real concentration and theoretical concentration), respectively, indicating the coupling relation between dissolved organic matter (DOM) remineralization and nutrient regeneration in the water column. The C/N ratios in the water column exhibited different characteristics with elevated values appearing in the surface and bottom layers. Box and whisker plots showed that both degradation index (DI) values and THAA yields displayed a decreasing trend from the surface layer to the bottom layer, implying increasing degradation with the water depth. Our data revealed that glycine and alanine increased in relative abundance with decreasing DI, while tyrosine, valine, phenylalanine and isoleucine increased with increasing DI.

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1. Introduction

Dissolved organic matter (DOM) in the ocean is one of the largest dynamic reservoirs of organic carbon and nitrogen on Earth (Hedges and Oades, 1997). To date, our understanding of the sources, compositions, and reactivity of DOM in the ocean is still very limited (Amon et al., 2001). According to biological availability, the DOM can be classified operationally into three categories: labile DOM (LDOM), semi-labile DOM (SLDOM) and recalcitrant DOM (RDOM) (Carlson and Ducklow, 1995; Jiao et al., 2010). However, the large majority of marine DOM have not been described at the molecular level (Bronk, 2002), because of analytical limitations. DOM is composed of a suite of organic compound classes with turnover times ranging from seconds, hours, days,

years to millennia (e.g., Cherrier et al., 1996; Coffin et al., 1993; Fry et al., 1996; Hopkinson and Vallino, 2005; Williams and Druffel, 1987). Dissolved organic carbon (DOC) is the carbon component of DOM and it plays a critical role in the marine biogeochemical cycle (Hedges, 1992). More than 90% of the global ocean DOC is recalcitrant, and has a lifespan from months to millennia, with an average age of 4000–6000 years (Lechtenfeld et al., 2014).

Dissolved organic nitrogen (DON) is a main source of reactive nitrogen in the surface ocean, and the dominant pool of fixed nitrogen especially when inorganic nutrients are depleted (Letscher et al., 2013). DON can be used directly by phytoplankton and bacteria to fulfill at least a part of their nitrogen requirements (Bronk and Glibert, 1993; Veuger et al., 2004), but in most situations they are degraded to release inorganic nutrients as bacteria consume DOC during growth (Connolly et al., 1992; Wotton, 1994). The chemical identity of DON is key to understanding its sources, transformations and the degradation mechanisms. DON is a wide spectrum of compounds, including urea, amino acids, amino sugars, nucleic acids, and complex macromolecules such as humics (Antia et al., 1991; Bronk, 2002). Amino acids, as the main

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component of the DON, are the building blocks of proteins, the largest reservoir of organic nitrogen in most organisms. Their natural occurrence and geochemical behavior in marine plankton (e.g., Cowie and Hedges, 1996), sinking particles (e.g., Cowie and Hedges, 1992; Ittekkot et al., 1984; Lee et al., 2000; Wu et al., 2007a), DOM (e.g., Amon et al., 2001; Yamashita and Tanoue, 2003; Davis et al., 2009; He et al., 2010) and sediments (e.g., Bourgoin and Tremblay, 2010; Gupta, 2001; Henrichs and Farrington, 1984; Peter et al., 2012) have been intensively studied. Generally, amino acids account for roughly 50% of the bacterial nitrogen demand (Keil and Kirchman, 1991; Middelboe et al., 1995) and 25% of the bacterial carbon demand in estuarine and coastal areas (Middelboe et al., 1995). The contributions of amino acid carbon to organic carbon and amino acid nitrogen to organic nitrogen and relative proportion of individual amino acids are useful indicators of decomposition and transport in the marine environment (Cowie and Hedges, 1994; Dauwe and Middelburg, 1998; Dauwe et al., 1999; Keil et al., 2000 and references therein). During diagenesis in seawater and marine sediments, the proportion of the individual amino acids changes in a characteristic way and can therefore be used as a proxy for diagenetic processes (Dauwe and Middelburg, 1998; Dauwe et al., 1999).

The East China Sea (ECS) is a highly dynamic area that receives materials of various origins (Su and Yuan, 2005). The primary source of freshwater to the ECS is terrestrial runoff, and approximately 90% of terrestrial materials entering are derived from inputs from the Changjiang River (Zhou et al., 2010). The rich supply of nutrients contributes to the high primary productivity in the Changjiang Estuary and its adjacent sea. Previous studies have demonstrated both conservative and non-conservative behaviors for different materials including dissolved inorganic nitrogen (DIN), DOC and DON in the Changjiang Estuary and the ECS (e.g., Hung et al., 2003; Zhang et al., 2007; Zhu et al., 2014). However, the biogeochemical behaviors of DOM in the ECS are still poorly understood because they involve complex interactions among hydrogeologic, oceanic, and biochemical processes. To date, only few studies have focused on the behaviors and degradation of DOM in this area (Hung et al., 2003; Zhu et al., 2014). The aims of this study were to determine the concentrations, compositions and distributions of DOC, DIN, DON and total hydrolysable amino acids (THAA) in the surface water and water columns of the ECS, to assess the behaviors of DOC, DON and DIN along the cross-shelf transects, and to evaluate the sources and degradation state of DOM using THAA characteristics, such as the C/N ratio, THAA yields and the degradation index (DI).

2. Materials and methods

2.1. Study area

The ECS is a marginal sea of the Western Pacific, with an average water depth of about 72 m. It has a wide continental shelf in the west and deep groove in the east, so it possesses the characteristics of shallow water and deep sea. The hydrographic characteristics of this region are greatly affected by the water masses, including the nutrient rich and low salinity Changjiang Diluted Water (CDW) along the Chinese coast, the warm and nutrient poor Kuroshio Surface Water (KSW) and the cold and nutrient rich Kuroshio Subsurface Water (KSSW) on the eastern boundary of the shelf, the Jiangu Coastal Current (JCC) and the Zhejiang-Fujian Coastal Current (ZFCC) on the western side and the warm and nutrient poor Taiwan Warm Current (TWC) invading from the middle shelf (Su, 1998) (Fig. 1). Because of the effects of monsoons and the changing scale of the Changjiang River runoff, the circulation of water masses is varied seasonally in the ECS. During summer, southwest winds prevail, and the CDW extends to the northeast towards the Tsushima/Korea Straits, but in winter it flows southwest within a narrow band adjacent to the Chinese coast (Beardsley et al., 1985; Liu et al., in press). Monthly Changjiang River discharge data (1970–2013) at Datong hydrological gauging station suggested that there

were significant seasonal variations in river discharge with the highest value ($12.9 \pm 2.7 \times 10^{10} \text{ m}^3/\text{month}$) observed in July and the lowest value ($2.61 \pm 0.53 \times 10^{10} \text{ m}^3/\text{month}$) found in January (Wang et al., in press).

2.2. Sample collection

The cruise was conducted aboard the R/V “Dong Fang Hong 2” in the ECS from 7 to 16 July, 2011. Locations of 28 sampling stations at 4 transects are shown in Fig. 1. The biogeochemical changes that occur during substance transport from river to ocean are poorly understood, and here we attempt to elucidate some of these transformations along the cross-shelf transects of the ECS. These transects were chosen to provide broad geographic coverage as well as to evaluate potential differences in the influence of the Changjiang River discharge. Three transects (D, F and P) were investigated from the Changjiang Estuary to the outer shelf area, which were under the direct impact of the Changjiang River discharge. In contrast, transect E characterized by decreasing river inputs was considered as representative of an oceanic reference. Surface water samples (<5 m) and the profile samples (at transects D and P) in different depths were collected using 12 L Niskin bottles mounted to a Seabird CTD Rosette (General Oceanics Co.). The environmental and hydrographic conditions of the sampling stations, including the location, surface seawater temperature, salinity and water depth are described in Table 1.

After collection, the samples were immediately filtered through Whatman GF/F glass fiber filters (precombusted at 500 °C for 5 h). The filtrate was stored in acid rinsed glass vials at -20 °C for the analyses of dissolved amino acids. Seawater for nitrogen species analyses was collected into preconditioned 60 mL high density polyethylene bottles and immediately frozen upright at -20 °C . Samples for DOC analyses were collected in precombusted 20 mL glass vials and preserved at 4 °C after adding two drops of 12 mol L^{-1} HCl. Materials collected on the filter were used for analyses of chlorophyll *a*. Samples for determination of bacterial abundance were pre-filtered with a $20\text{ }\mu\text{m}$ pore size net and preserved with formaldehyde (3.4% final concentration) and kept in sterile 50 mL screw-cap plastic bottles in the dark at 4 °C . After being brought to the land laboratory, the samples were analyzed immediately.

2.3. Analytical methods

Amino acids were determined using the *o*-phthalaldehyde-3-mercaptopropionic acid derivatization method and separated by high performance liquid chromatography (HPLC) with fluorescence detection (Chen et al., 2013; Lindroth and Mopper, 1979). Samples for THAA measurements were hydrolyzed with 6 mol L^{-1} HCl inside flame sealed ampules at 110 °C for 22 h under N_2 , and then the hydrolysate was evaporated, and the dried hydrolysate was redissolved in Milli-Q water for derivatization before HPLC analysis. The HPLC was a Waters system (e2695) equipped with a quaternary pump, an online degasser, an autosampler, a column heater and a fluorescence detector (e2475). The derivatives of 14 standard amino acids (Sigma-Aldrich) including aspartic acid (ASP), glutamic acid (Glu), serine (Ser), histidine (His), glycine (Gly), threonine (Thr), arginine (Arg), alanine (Ala), tyrosine (Tyr), valine (Val), methionine (Met), phenylalanine (Phe), isoleucine (Ile), leucine (Leu) were separated on an Agilent ZORBAX Eclipse AAA column ($150 \times 3.0\text{ mm}$, $5\text{ }\mu\text{m}$) with a column temperature of 35 °C . The eluent consisted of two components: eluent (A) was 0.05 mol L^{-1} sodium acetate (pH 7.2), and eluent (B) was prepared by mixing 0.1 mol L^{-1} sodium acetate, acetonitrile and methanol solutions with a volume ratio of 45:45:10 and then titrated with glacial acetic acid to pH 7.2. Amino acid derivatives were separated with a linear binary gradient starting with 90% A to 85% A at 6 min, then 63% A at 16 min and 45% A at 30 min. After 30 min the system was returned to 90% A and equilibrated for 3 min. The concentrations of the

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