

Original Articles

Amino sugars as indicator of organic matters source and diagenesis in the surface sediments of the East China Sea

Chengzhe Ren^{a,b}, Huamao Yuan^{a,b,c,*}, Jinming Song^{a,b,c,*}, Liqin Duan^{a,c}, Xuegang Li^{a,b,c}, Ning Li^{a,c}, Bu Zhou^{a,b}

^a Key Laboratory of Marine Ecology and Environmental Sciences, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, PR China

^b University of Chinese Academy of Sciences, Beijing 100049, PR China

^c Function Laboratory of Marine Ecology and Environmental Sciences, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266237, PR China



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ABSTRACT

Amino sugars (AS) were investigated to study the source, reactivity and bacterial contribution of organic matters (OM) in surface sediments of the East China Sea (ECS) both in summer and autumn in 2016, within and after the algae bloom, respectively. The content of AS was 0.48–7.23 $\mu\text{mol}/(\text{g dw})$ with a higher concentration in near-shore than that in offshore area and lower concentration in summer than that in autumn, which on average made up $3.65 \pm 1.66\%$ of TOC and $4.49 \pm 1.98\%$ of TN in the ECS surface sediments. The low average ratio of glucosamine/galactosamine (GlcN/GalN) (1.16 ± 0.15) indicated a major bacterial source of AS pool of the investigated area. Higher GlcN/GalN (1.30 ± 0.15 in summer and 1.21 ± 0.09 in autumn) and muramic acid (Mur) ($8.8 \pm 3.8 \text{ nmol}/(\text{mg C})$ in summer and $20.5 \pm 10.3 \text{ nmol}/(\text{mg C})$ in autumn) and together with lower GlcN/Mur (29 ± 8 in summer and 16 ± 4 in autumn) content in nearshore than those in offshore area (GlcN/GalN: 1.11 ± 0.14 in summer and 1.09 ± 0.13 in autumn; Mur: $5.2 \pm 1.7 \text{ nmol}/(\text{mg C})$ in summer and $10.4 \pm 5 \text{ nmol}/(\text{mg C})$ in autumn; GlcN/Mur: 36 ± 9 in summer and 34 ± 11 in autumn) indicated more plankton detritus and a more labile nature of OM, and also relatively higher fresh bacteria contribution to OM in nearshore area, which was consistent with the higher concentrations of Chl-*a* in corresponding surface water. The transformation of plankton to bacteria source of OM from summer to autumn was revealed by the increased total hydrolysable amino sugars (THAS) and Mur concentration, C- and N-normalized yield of THAS, and also the decreased ratios of GlcN/GalN and GlcN/Mur in sediments in autumn. The correlation between Mur in sediments and Chl-*a* in surface water suggested that the real-time settling plankton detritus was one of the major food sources for benthic bacteria in summer but contributed little in autumn. Based on Mur, the relatively fresh bacteria OM contribution to TOC were 13.1% in summer and 28.5% in autumn. In summary, the composition of AS in the ECS surface sediments showed a major bacteria origin of OM and the bioavailability decreased from nearshore to offshore and also from summer to autumn. As the algae bloom decline, the flux of plankton detritus decreased and the OM source transformed from plankton to bacteria.

1. Introduction

Continental marginal seas are important sites for the production, transformation and burial of organic matters (OM). A large number of organic materials produced in the euphotic zone are transported into sediment, becoming an important food supply for benthic community, and the burial of OM represents the major link between the “active” surface pools of carbon in the oceans, in the atmosphere, on land, and in marine sediments, and carbon pool that cycle on geologic time scales. (Dauwe and Middelburg, 1998; Burdige, 2007; Lomstein et al., 2009).

Comparing with deep sediment, the surface sediment has a close connection with the biosphere, and the source and reactivity of its OM has a great influence on the marine carbon cycle. However, how much OM is consumed, transported and transformed remains among the greatest unknowns in coastal and continental environments.

During decomposition, biomolecules undergo major transformations, which reduce our ability to molecularly characterize the detrital OM (Hedges et al., 2000). As a result, most approaches for characterizing OM origin, composition, transformation, and diagenetic state, rely on the quantification of specific biomolecules and biomarkers

* Corresponding authors at: Key Laboratory of Marine Ecology and Environmental Sciences, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, PR China.

E-mail addresses: yuanhuamao@qdio.ac.cn (H. Yuan), jmsong@qdio.ac.cn (J. Song).

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(Bourgoin and Tremblay, 2010). As the only Nitrogen-bearing carbohydrates, amino sugars (AS) are ubiquitous in marine environment. Chitin (poly- β -1,4-N-acetyl-D-glucosamine), a biopolymer of Glucosamine (GlcN), is widely occurred in marine planktons, and the production of chitin can provide up to 10% of heterotrophic bacteria production (Kirchman and White, 1999). Heterotrophic bacteria are a dominant source and play an important role in the composition and chemical characteristics of marine organic matter (Kaiser and Benner, 2008). AS such as GlcN, galactosamine (GalN), mannosamine (ManN) and muramic acid (Mur) are abundant in bacteria (Benner and Kaiser, 2003). The composition of AS is varied in different kinds of organisms. For example, planktons that contain chitin material have a high GlcN/GalN (> 8), but on the contrary, bacteria have a low GlcN/GalN (< 3) in general (Benner and Kaiser, 2003; Niggemann and Schubert, 2006). Mur only exists in peptidoglycan, which is the main component of bacteria cell wall, and the reactivity of Mur is relatively high (Kawasaki and Benner, 2006; Lomstein et al., 2009), making Mur a good indicator of relative fresh bacteria OM (Moriarty, 1977; Kaiser and Benner, 2008; Niggemann and Schubert, 2006; Lomstein et al., 2009; Bourgoin and Tremblay, 2010). Such properties of AS make it a good indicator of plankton and bacteria, which is helpful for differentiating the source and evaluating the relative reactivity of organic matter in surface sediment.

The East China Sea (ECS) is one of the largest marginal seas in the world, which has moderately high primary production about $108\text{--}997\text{ mg m}^{-2}\text{ d}^{-1}$ with a mean value of $425\text{ mg m}^{-2}\text{ d}^{-1}$ (Gong et al., 2003). As a typical marginal sea, ECS both receive terrestrial and marine organic matters and meanwhile, algae bloom frequently outbreaks, leading to an intense seasonal change of transportation, transformation and diagenetic states of organic matters. However, these changes and states of organic matters are still not fully understood. In the present study, AS distribution and composition were analyzed to evaluate the sources, diagenetic changes and different degradation behaviors of OM and also to provide quantitative estimates of the bacterial contributions to OM in surface sediments of the ECS.

2. Materials and methods

2.1. Sampling area

According to the spatial distributions of the grain size in sediments, the middle and outer shelf of the ECS is mainly covered by sands, while the inner shelf is characterized by a belt of muddy sediments, which extends from the mouth of the Changjiang River to southwest along Zhejiang-Fujian coast (Mckee et al., 1983) (Fig. 1).

The major currents of the ECS include the Changjiang Diluted Water (CDW), the Zhejiang-Fujian Coastal Current (ZFCC), the Taiwan Warm Current (TWC) and the Kuroshio Current (KC). Most suspended matters from CJR are transported southward by ZFCC in winter and blocked by TWC, which leads to the deposition of suspended matters and forms the belt of mud area within 75 m isobath (Chao, 1990; Chuang, 1985).

2.2. Sample collection and pretreatment

Surface sediments were sampled by a box collector onboard the R/V *Kexue-3* during June 5–12th and September 23th–October 1th, 2016. The surface 2 cm sediments were collected and stored in aluminum boxes at $-20\text{ }^{\circ}\text{C}$. About 200 mL of surface water were filtered through $0.45\text{ }\mu\text{m}$ cellulose acetate membrane for Chl-*a* analysis. Prior to filter, the membrane was pretreatment by 1 mL saturated Magnesium Chloride. The membrane was encased in aluminum foil and stored in $-20\text{ }^{\circ}\text{C}$. In laboratory, the sediments were freeze-dried and grounded. During the determination of TOC, TN, $\delta^{13}\text{C}$ and AS, two parallel samples were determined for each 10 samples, and the relative standard errors were below 10%.

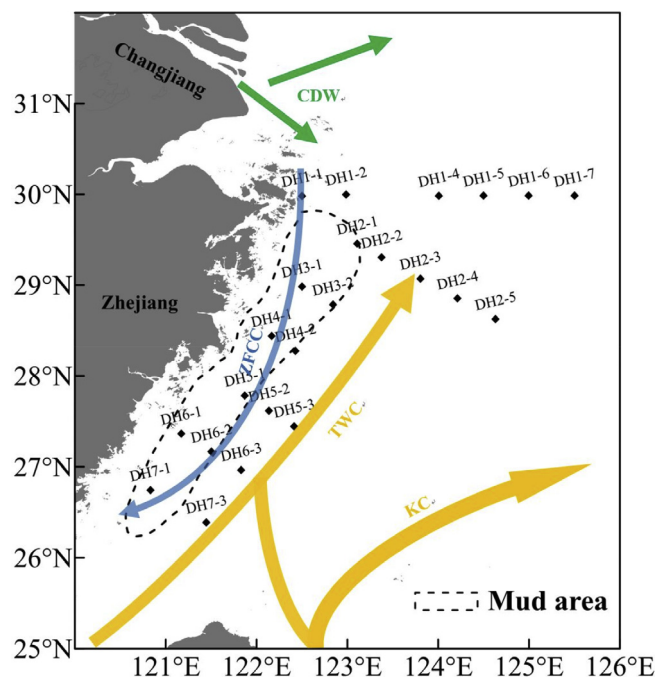


Fig. 1. Sampling area and sites of surface sediments in the East China Sea. Arrows reflect regional circulation modes, and dashed line represents the mud area. CDW, the Changjiang Diluted Water; ZFCC, the Zhejiang-Fujian Coastal Current; KC, the Kuroshio Current; TWC, the Taiwan Warm Current.

2.3. Analytical methods

2.3.1. TOC, TN, $\delta^{13}\text{C}$

Measurements of TOC, TN, and stable carbon ($\delta^{13}\text{C}$) isotopes were conducted in the third Institute of Oceanography, State Oceanic Administration of China. TOC and TN of sediment samples were analyzed using a Vario El-III elemental analyzer, following the method of Hu et al. (2014). Briefly, sediment samples were grounded in an agate mortar after being dried, and then soaked in 1 M HCl at room temperature for 1 d to remove carbonates. After rinsing with Milli-Q water several times and drying in a vacuum freeze drier, the carbonate free samples were measured for the TOC and TN concentrations. Replicate analysis of well-mixed samples provided a standard deviation of 0.01% for the TOC and TN concentrations ($n = 5$). The $\delta^{13}\text{C}$ analysis was performed on inorganic carbon-free sediments, using a Thermo DeltaPlus XL continuous flow mass spectrometer. The values of $\delta^{13}\text{C}$ were expressed in a standard delta notation relative to Pee Dee Belemnite (PDB). The average standard deviations of $\delta^{13}\text{C}$ based on the replicated analysis were 0.1‰ ($n = 5$).

2.3.2. AS

Amino sugars (GlcN, GalN, ManN, and Mur) were pretreated and determined following the procedure of Zhang and Amelung (1996) and Zhu et al. (2014). The freeze-dried and grounded sediment sample (100 mg) was hydrolyzed with 6 M HCl (10 mL) in a closed ampoule bottle (filled with N_2 gas) for 7 h at $105\text{ }^{\circ}\text{C}$. After cooling, the sample was centrifuged to remove particulate matters. The hydrolysate was adjusted to pH 7 with KOH solution and centrifuged to remove precipitate. The supernatant was passed through solid-phase extraction (SPE) columns (Supelclean™ ENVI-Carb™ Plus SPE cartridges and accessories were obtained from Sigma-Aldrich Chemie GmbH or Carl Roth GmbH (Karlsruhe, Germany)) to remove salts. All the desalted products were evaporated under a stream of N_2 and converted to GC-amenable derivatives for analysis. The derivatization procedure was followed by Guerrant and Moss (1984). The AS of sediment samples were finally analyzed with a gas chromatograph-mass spectrometry

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