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Distributions and seasonal variations of dissolved carbohydrates in the Jiaozhou Bay, China

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ABSTRACT

Surface seawater samples were collected in the Jiaozhou Bay, a typical semi-closed basin located at the western part of the Shandong Peninsula, China, during four cruises. Concentrations of monosaccharides (MCHO), polysaccharides (PCHO) and total dissolved carbohydrates (TCHO) were measured with the 2,4,6-tripyridyl-*s*-triazine spectroscopic method. Concentrations of TCHO varied from 10.8 to 276.1 μM C for all samples and the ratios of TCHO to dissolved organic carbon (DOC) ranged from 1.1 to 67.9% with an average of 10.1%. This result indicated that dissolved carbohydrates were an important constituent of DOC in the surface seawater of the Jiaozhou Bay. In all samples, the concentrations of MCHO ranged from 2.9 to 65.9 μM C, comprising 46.1 ± 16.6% of TCHO on average, while PCHO ranged from 0.3 to 210.2 μM C, comprising 53.9 ± 16.6% of TCHO on average. As a major part of dissolved carbohydrates, the concentrations of PCHO were higher than those of MCHO. MCHO and PCHO accumulated in January and July, with minimum average concentration in April. The seasonal variation in the ratios of TCHO to DOC was related to water temperature, with high values in January and low values in July and October. The concentrations of dissolved carbohydrates displayed a decreasing trend from the coastal to the central areas. Negative correlations between concentrations of TCHO and salinity in July suggested that riverine input around the Jiaozhou Bay had an important effect on the concentrations of dissolved carbohydrates in surface seawater. The pattern of distributions of MCHO and PCHO reported in this study added to the global picture of dissolved carbohydrates distribution.

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1. Introduction

Carbohydrates are the prime products of phytoplankton photosynthesis which can be transformed into other essential components such as proteins, lipids and nucleic acids (Myklestad and Børsheim, 2007). The importance of carbohydrates is due to their ubiquitous presence in marine systems, including marine organisms, dissolved organic matter, colloids, sediments, and sinking and suspended particles (Hernes et al., 1996). In seawater, carbohydrates originate either from organisms, decomposition of organic matter, and viral lysis, or from allochthonous sources such as river runoff (Thornton, 2009), sediment resuspension, and lateral advection (Wang et al., 2006). The composition of dissolved organic carbon is far from completely characterized in many areas, but carbohydrates have been shown to constitute a large fraction of dissolved organic carbon (Benner et al., 1992; Pakulski and Benner, 1994; Myklestad et al., 1997; Bhosle et al., 1998; Pettine et al., 2001; Hung et al., 2003; Engbrodt and Kattner, 2005; Guéguen et al., 2006; Görs et al., 2007). The larger (>1000 Da) polymers in seawater are rich in carbohydrates, with the percentage of carbohydrates in this fraction varying little among samples from different locations (Aluwihare et al., 1997).

Carbohydrates are versatile molecules that serve as energy, storage, and structural components of cells. In marine systems, chemical energy is stored in the form of phytoplankton-derived carbohydrates, and this in turn provides energy to non-photosynthesizing organisms through glycolysis and respiration (Witter and Luther, 2002). Carbohydrates include monosaccharides, oligosaccharides, and polysaccharides in marine systems. Monosaccharides and oligosaccharides are primary or intermediate metabolites, or degradation products as a part of the current metabolism of the cell (Myklestad and Børsheim, 2007). Polysaccharides have been considered to play critical roles in producing biofilms and forming mucilaginous aggregates, destabilizing inorganic colloids through flocculation, and forming complexes with heavy metals (Hung et al., 2001).

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There are numerous studies on the distributions of dissolved carbohydrates and their constituent fractions in the open oceans (Handa, 1966; Pakulski and Benner, 1994; Børsheim et al., 1999; Amon and Benner, 2003; Wang et al., 2006; Myklestad and Børsheim, 2007), estuaries, or coastal and shelf regions (Burney and Sieburth, 1977; Bhosle et al., 1998; Hung et al., 2001; Witter and Luther, 2002). These researches have provided abundant information on the global distributions of carbohydrates in different marine environments. Only a few studies have focused their attention on the biochemical constituents of dissolved organic matter in the Jiaozhou Bay, a typical semi-enclosed eutrophic bay in China. Little is known about seasonal dynamics of dissolved organic carbon and carbohydrates in the bay. In this study, we determined concentrations of dissolved monosaccharides and polysaccharides in the surface water of the Jiaozhou Bay during four cruises, using the 2,4,6-tripyridyl-*s*-triazine spectrophotometric method (Myklestad et al., 1997). The objectives of this work were, 1) to track the seasonal variations in concentrations of dissolved monosaccharides and polysaccharides, and factors which might affect the variations, such as water temperature, salinity, dissolved organic carbon, and chlorophyll *a*, 2) to examine the horizontal distributions of dissolved carbohydrates, and 3) to investigate the relationships of the concentrations of dissolved carbohydrates with chlorophyll *a* and salinity.

2. Materials and methods

2.1. Sampling

The Jiaozhou Bay (35°58′–36°18′N, 120°04′–120°23′E) is the largest semi-enclosed water body along the South Yellow Sea (Fig. 1). It is surrounded by the city of Qingdao, and has an area of about 390 km^2 and an average water depth of about 7 m. The maximum depth is about 70 m in a narrow channel close to the mouth of the bay, which is directly affected by strong tidal currents (Zhang et al., 2006). The bay has been affected extensively by human activity, including industry, agriculture, aquaculture, and increasing harbor construction around it.

Four cruises were conducted in the Jiaozhou Bay in October 2007, January, April, and July 2008, respectively. The sample locations are shown in Fig. 1. All the seawater samples were collected from a depth about 20 cm by submerging a stoppered glass bottle, opening and closing it under water. They 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 carbohydrates. The samples for the analyses of dissolved organic carbon were preserved at 4 °C after adding two drops of saturated solution of $HgCl_2$. Materials collected on the filter were used for analyses of chlorophyll *a*. After being brought to the land laboratory, the samples were analyzed immediately.

2.2. Dissolved organic carbon and chlorophyll a analyses

Concentrations of dissolved organic carbon (DOC) were determined as total carbon by catalytic high temperature oxidation using a total organic carbon analyzer (Shimadzu TOC-V_{CPH}, Shimadzu Co., Japan) with a Pt catalyst at 680 °C. After acidification to pH 2∼3 with 2 M HCl, the samples were sparged with high purity air gas to eliminate the inorganic carbon component. Triplicates of 50 μl aliquots were injected into the furnace by the autosampler and the combusted products (carbon dioxide) were detected by the non-dispersive infrared gas analyzer. The precision was estimated as the standard deviation of the injections and was less than 2% of the mean.

Chlorophyll *a* (Chl-*a*) on the membrane was extracted with 90% acetone for 12 h in the dark at 4 °C, centrifuged for 10 min, and then measured with a fluorescence spectrophotometer (F-4500, Hitachi Co., Japan) according to Parsons et al. (1984).

2.3. Dissolved carbohydrates analyses

Monosaccharides (MCHO) and polysaccharides (PCHO) were determined by the 2,4,6-tripyridyl-*s*-triazine (TPTZ) spectrophotometric method (Myklestad et al., 1997). It involves two reactions: reduction of Fe^{3+} to Fe^{2+} by reducing sugars in the presence of base, and then Fe^{2+} is complexed by TPTZ to form a violet-colored product. Therefore, this method is easy to carry out in laboratory.

Following the procedure, at the beginning, 1 ml of seawater was mixed with 1 ml solution of potassium ferricyanide (0.7 mM) in

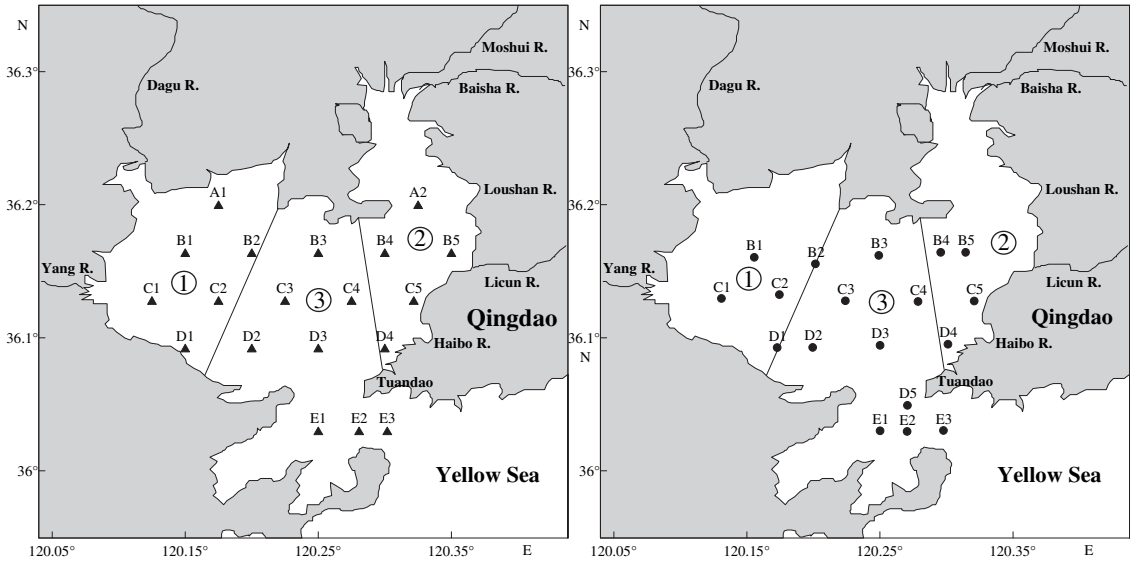

Fig. 1. Locations of the sampling stations in the Jiaozhou Bay during the cruises of October 2007 (▲), January, April and July 2008 (●) and the subdivisions of the Jiaozhou Bay (① western coast; ② eastern coast; ③ central bay).

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