Continental Shelf Research 168 (2018) 1–10

Contents lists available at ScienceDirect

Continental Shelf Research

journal homepage: www.elsevier.com/locate/csr

Distribution and characteristics of inorganic nutrients in the surface microlayer and subsurface water of the Bohai and Yellow Seas

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ARTICLE INFO

Keywords:
Nutrients
Distribution
Surface microlayer
Enrichment
Yellow Sea
Bohai Sea

ABSTRACT

Concentrations and diurnal variations of inorganic nutrients (dissolved inorganic nitrogen (DIN), phosphate (PO_4-P) and silicate (SiO_3-Si)), as well as chlorophyll a (Chl-a) were determined in the subsurface water (SSW) and surface microlayer (SML) of the Bohai and Yellow Seas in summer 2015. The concentrations of DIN, SiO_3-Si and Chl-a (except for PO_4-P) in the SML were respectively correlated with their concentrations in the SSW, indicating that a major source of substances in the SML could be transported from the SSW. The enrichment factor (EF) was defined as the ratio of the concentration in the SML to that in the corresponding SSW. There was little difference in concentrations of PO_4-P between the SML and the SSW samples by nonparametric difference test ($P > 0.05$). DIN, SiO_3-Si and Chl-a (except for PO_4-P) were found to be enriched in the SML relative to the SSW, with average EFs of 2.45, 1.18 and 2.37, respectively. No connection was identified between nutrients EFs and wind speed for our entire data. DIN, SiO_3-Si, PO_4-P and Chl-a concentrations in the SSW and the SML exhibited strong diurnal variations at an anchor station.

1. Introduction

Nutrients are an important material basis for the marine biogeochemical cycle, which affects the growth of marine phytoplankton and marine primary productivity (Tyrrell, 1999). The concentrations and ratios of nutrients (nitrogen, phosphorus, silicon) in seawater play a crucial role in the population dynamics and community structure of phytoplankton (Hodgkiss and Ho, 1997; Flynn, 2002; Maguer et al., 2004). Nitrogen and phosphorus are two essential nutrients for photosynthesis of phytoplankton in marine systems, although silicate and some trace metals such as iron also play an important role (Chai, 1995; Falkowski et al., 1998; Shen et al., 2006). Nitrogen is the basic element of certain organic molecules, including protein, phospholipid and chlorophyll, and also controls the primary productivity and carbon output in ocean. Phosphorus is the main component of plants' cytomembranes and nucleic acid (Schachtman et al., 1998). Nitrogen and phosphorus are described as biomimetic elements due to the influence of biological growth (Sinem et al., 2012). Silicon contributes to the formation of the skeletons of diatoms and radiolarian (Martin-Jézéquel et al., 2000; Sinem et al., 2012). In recent years, increasing the inputs of nutrients has a significant impact on coastal ecosystems, such as the increase in biomass of primary producers, causing oxygen consumption, changing species composition and biodiversity (Jung et al., 2017). Given the unique impact on marine ecosystems, such as frequent harmful algal blooms and increased phytoplankton biomass, it becomes an essential task to further understand nutrients in marginal seas.

The sea surface microlayer (SML) is the top 1000 μm (or 1 mm) of the ocean surface. It is the boundary layer where all exchange occurs between the atmosphere and the ocean (Cunliffe et al., 2013; Liss and Duce, 1997). Compared with the subsurface water, the SML has unique chemical physical, and biological properties and is normally enriched with various organic and chemical substances (Yang, 1999; Liss and Duce, 1997). A wide range of matter, such as carbohydrates (Wurl et al., 2011; Henrichs and Williams, 1985), amino acids (Yang et al., 2009), dissolved inorganic nitrogen (Yang et al., 2009), hydrocarbons (Hardy, 1982) and chlorophyll *a* (Yang et al., 2009; Chen et al., 2016) are normally enriched in the SML compared with the underlying seawater. Given the SML has a unique position at the air–sea interface and links the hydrosphere with the atmosphere, the SML plays a very important role in the biogeochemical cycle.

Previous studies have been conducted on the biogeochemistry of nutrients in oceans. Chen (2008) conducted a comprehensive and

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https://doi.org/10.1016/j.csr.2018.09.001
Received 5 February 2018; Received in revised form 4 August 2018; Accepted 3 September 2018

systematic analysis of nutrients distribution in the South and East China Seas. Many studies also provided information on the transport of nutrients (Wang, 1999; Wang et al., 1999) and seasonal variations along 35°N transect (121–125°E) in the Yellow Sea (Wang, 2000). However, the concentration and enrichment of nutrients in the SML have rarely reported in the literature. In the present work, our aims were to examine concentrations and diurnal variations of nutrients in the SML and the SSW in the Bohai and Yellow Seas, to evaluate the sources and the enrichments of nutrients in the SML.

2. Materials and methods

2.1. Study area

The Bohai Sea, located in the north of Shandong Peninsula and the south of Liaodong Peninsula, is a semi-enclosed sea area (average depth = 18.7 m; total area = 7.7×10^4 km^2). By region, the Bohai can be divided into the Bohai Bay, the Liaodong Bay, the Laizhou Bay and the Central Bohai. Affected by the East Asia monsoons, tides and riverine inputs, the biogeochemical environment of the Bohai is extremely complex.

The Yellow Sea surrounded by the mainland of China and Korean peninsula is an epicontinental sea, which is located on the west margin of the North Pacific and has an average depth of 44 m and a total area of 38×10^4 km^2. The Yellow Sea is divided into the South Yellow Sea (SYS) and the North Yellow Sea (NYS) by the Shandong Peninsula. The west is characterized by the Lubei and Subei Coastal Currents; the center, by the Yellow Sea cold-water masse in summer, and the east, by a warm, highly saline current called Yellow Sea Warm Current (Su, 1998).

In recent years, with the rapid economic and social development and the influx of exogenous nutrients, eutrophication and increased primary productivity have produced in part of coastal waters of the Bohai and Yellow Seas.

2.2. Seawater sampling

Both the SML and SSW samples were collected at 51 grid stations on the R/V "*Dong Fang Hong 2*" in the Bohai and Yellow Seas in summer 2015. The detailed locations of the collected samples are shown in Fig. 1. A screen sampling method was used to collect the SML samples (Garrett, 1965). The screen sampler was made of a 16-mesh stainless steel which stretched over a 40 × 40 cm^2 stainless steel frame. The screen sampler was dipped into the sea until completely submerged and then slowly lifted from the sea surface. The seawater and surface film material entrapped by the mesh spaces were allowed to drain into a sample bottle. The diameter of mesh wires and the size of mesh determined the specific thickness of SML samples. During the sampling, the SML typically ranged in size within 200 ± 10 μm (Garrett, 1965; Carlson, 1982; Momzikoff et al., 2004; Lechtenfeld et al., 2013). The subsurface samples (about 3 m) were collected with 12 L Niskin bottles attached onto a conductivity–temperature–depth (CTD) rosette. The environmental and hydrographic conditions of the sampling stations were determined using a ship-board CTD apparatus.

2.3. Nutrient and Chl-a analyses

The seawater samples were immediately filtered through Whatman GF/F filters. The filtrate was stored at − 20 °C for automatically analysis using the Auto Analyzer AA3 according to the process described by Strickland and Parsons (1972). DIN was calculated as the sum of nitrate (NO_3–N), nitrite (NO_2–N) and ammonia (NH_4–N). NO_3–N and NO_2–N were measured by the standard diazo-azo method, NH_4–N by the indophenol blue method; SiO_3-Si and PO_4-P by the standard molybdenum blue method. The detection limit for determining NO_3–N/NO_2–N, NH_4–N, PO_4–P, SiO_3–Si was 0.015 μmol/L, 0.040 μmol/L, 0.024 μmol/L and 0.030 μmol/L, respectively. The standard deviation for determining was ± 0.022 μmol/L for NO_3–N/NO_2–N, ± 0.05 μmol/L for NH_4–N, ± 0.012 μmol/L for PO_4–P and ± 0.051 μmol/L for SiO_3–Si.

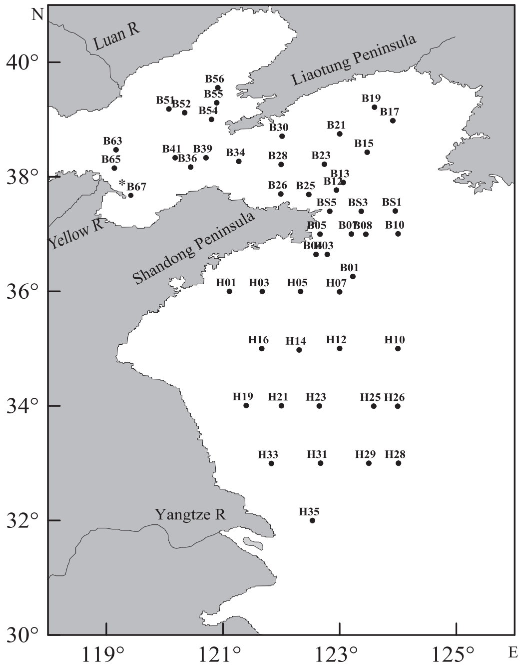

Fig. 1. Locations of sampling stations in the Bohai and Yellow Seas during summer cruise.

For Chl-a analysis, the samples were obtained by filtering 300 mL seawater through 47 mm Whatman GF/F filters. Chl-a retained on the filter was extracted with 10 mL 90% acetone for 24 h under cool, dark conditions and then measured fluorometrically with an F-4500 Fluorometer (Hitachi, Japan) based on the method described by Lorenzen (1967). The precision of triplicate measurements for each sample was better than 7%.

2.4. Enrichment factor (EF)

The enrichment of substance in the SML can be evaluated by enrichment factor (EF).

$$EF = C_M/C_S$$

where C_M is the concentration of any substance in the SML, and C_S is its concentration in the SSW. EF > 1.0 indicates that the constituent is selectively enriched, whereas EF ≤ 1 indicates that it is depleted in the SML. The enrichment probability in the SML was defined as the ratio of samples number with EF > 1.0 to total number. Because concentration distributions of nutrients in the SSW and the SML did not suit for the Gaussian distribution, the non parametric Wilcoxon in SPSS statistics packages was used for significant analysis. The difference was significant when $P < 0.05$.

3. Results and discussion

3.1. Distribution of Chl-a and nutrients in the SML and the SSW

As the main pigment of phytoplankton, Chl-a can be used as an indicator of phytoplankton biomass (Cullen, 1982). The distribution of Chl-a concentrations is affected by phytoplankton blooms, river discharges, tides, upwelling (Tang et al., 2004; Hu et al., 2003; Chen et al., 2001). Normally, high nutrients in water are accompanied by high Chl-a concentrations, such as the upwelling areas and estuaries. Nutrients are the basis of phytoplankton growth and can directly regulate and