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Summer nutrient dynamics and biological carbon uptake rate in the Changjiang River plume inferred using a three end-member mixing model

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article info

Article history: Received 25 December 2013 Received in revised form 28 September 2014 Accepted 30 September 2014 Available online 12 October 2014

Keywords: Water mixing River plume Nutrients Biological carbon uptake rate Primary production Changjiang River Estuary

ABSTRACT

A three end-member (Changjiang River Plume, CRP; Outer-shelf Surface Water, OSW; and Outer-shelf Deep Water, ODW) mixing model based on quasi-conservative temperature and salinity was adopted to identify the relative contribution of different water masses to nutrient inventory and to estimate biological nutrient uptake in the plume-impacted area by considering the difference between the modelpredicted and ambient concentration of nutrients up to a depth of PZD₁₀ (photic zone depth to 10% of surface photosynthetically active radiance (PAR)). The end-member composite suggested that the mixing of CRP and OSW was the main process regulating nutrient dynamics and phytoplankton growth, while the correlation of ODW with ΔP indicated that the outcropped upwelling water contributed to the replenishment of P leading to Chl a accumulation to some extent. The ratio Δ DIN: Δ P: Δ Si:excess O₂ in the euphotic zone where excess $O_2 > 10$ µmol L⁻¹ was estimated to be $28 \pm 9:1:33 \pm 13:145 \pm 71$.

A simple box model was used to evaluate biological carbon uptake rate in the euphotic zone based on nutrient deviation, Redfield ratio (6.6 C:1 DIN), and residence time of nutrients, assuming that the Changjiang River was the unique source of nutrients in the quasi-static box. The biological carbon uptake rates derived from the DIN, P and Si deviation were 465, 344, and 626 mg C m⁻² d⁻¹, respectively; these values were comparable to the POC flux (486 \pm 275 mg C m $^{-2}$ d $^{-1}$) derived from sediment trap. This finding suggested that the Changjiang River Plume was responsible for phytoplankton growth and subsequent high POC flux out of the euphotic zone. Furthermore, the community respiration rate was estimated to be 634 mg C m⁻² d⁻¹ based on the integrated ¹⁴C-based gross primary production of 1260 mg C m⁻² d⁻¹ and the net community production of 626 mg C m⁻² d⁻¹ in the euphotic zone of the region.

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1. Introduction

The Changjiang River (Yangtze River), the third largest river in the world in terms of water discharge, has delivered large amounts of nutrients to the East China Sea (ECS) ([Zhang, 1996](#page--1-0)), leading to high primary productivity and fish production in the past [\(Ning](#page--1-0) [et al., 1995](#page--1-0)). However, since the 1980s, anthropogenic activities have led to problems such as an increase in agricultural drainage and sewage effluent, causing excess nutrient enrichment and subsequent severe environmental problems such as harmful algae blooms (HAB) and seasonal hypoxia at the bottom in the Changjiang

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River estuary and adjacent ECS ([Li et al., 2007; Zhou et al., 2003\)](#page--1-0). Thus, estuarine nutrients dynamics and estimation of biological carbon uptake dominated by physical and biological processes, have been recognized as crucial factors for evaluating the contribution of estuary to global carbon production and sequestration ([Cai et al.,](#page--1-0) [2004; Han et al., 2012; Hung et al., 2000; Lohrenz et al., 1999; Zhang](#page--1-0) [et al., 2007](#page--1-0)).

In the Changjiang River estuary, nutrient dynamics along a salinity gradient were complicated because of the exchange of multiple water masses [\(Chen, 2009; Gong et al., 1996](#page--1-0)), especially under relatively stable estuarine hydrodynamic conditions in summer [\(Liu et al., 2000;](#page--1-0) [Sun et al., 2004; Wang et al., 1983, 2002, 2011; Zhang, 1996\)](#page--1-0). [Zhang](#page--1-0) [et al. \(2007\)](#page--1-0) reported that the distribution pattern of nutrients was mainly controlled by the exchange of Changjiang River water, Taiwan Warm Current (TWC), and Kuroshio Water (KW). [Wong et al. \(1998\)](#page--1-0) found excess nitrate in mesosaline waters (salinity $<$ 30.5) at depths

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of 10–15 m in the ECS in summer 1992, suggesting that primary production was likely regulated by the phosphate availability in the river plume. The coastal upwelling water with a nutrient ratio being close to the Redfield ratio might alleviate the phosphorus deficiency in the upper ocean by supplying $PO_4^{\,3-}$ ([Chen et al., 2004\)](#page--1-0). However, little is known about the relative contributions of different water masses such as river plumes, upwelling water, and oceanic water in a river plume area to the nutrient inventory and nutrient uptake of phytoplankton on the shelf of ECS. The non-conservative decreases in nutrients or dissolved inorganic carbon (DIC) along the salinity gradient were often accompanied by a high phytoplankton standing stock or high primary production in other large continental shelf– river systems ([Cai et al., 2004; Cao et al., 2011; Lohrenz et al., 1999\)](#page--1-0), but few studies have quantified the nutrient drawdown and biological carbon uptake in response to nutrient inputs from the riverine runoff in the plume-impacted areas.

In this study, a three end-member mixing model was used to examine the nutrient drawdown due to biological uptake within the euphotic zone. The ambient nutrient concentration was compared with the nutrient concentration predicted by considering the conservative mixing of three water masses alone. Subsequently, a simple box model was adopted to estimate the biological carbon uptake rate in the euphotic zone, based on nutrient drawdown and nutrient residence time.

2. Material and methods

2.1. Sampling collection

A cruise was conducted from 18 July to 14 August 2006 (R/V: China Marine Surveillance 49). Seventy-five stations were visited in the ECS (Fig. 1). At each station, temperature and salinity were measured with a Sea Bird model 9/11 conductivity–temperature depth (CTD) recorder. Water samples for measuring concentrations of nutrients, chlorophyll a (Chl a) and dissolved oxygen were collected with Niskin bottles attached to the CTD rosette. In our study, the euphotic zone was defined as the water depth (PZD_{10}) above 10% of the surface photosynthetically active radiance (PAR).

2.2. Chemical analysis

For analyzing the nutrients in seawater, seawater samples were filtered through 0.45-μm cellulose acetate membranes, and then, 0.3 ml 35 g/L HgCl₂ solution was added in each 100 ml sample for further analysis [\(Kattner, 1999\)](#page--1-0). Concentrations of nutrients $(NO₃^-$, $NO₂^-$, $NH₄^+$, $PO₄^{3-}$ and $SiO₃^{2-})$ were determined by performing a Continuous Flow Analysis (CFA) using Skalar San⁺⁺ system in laboratory with colorimetric methods described by [Grasshoff et al.\(1999\).](#page--1-0) The detection limits (precision values in parentheses) of NO_3^- , NO_2^- , NH_4^+ , PO_4^3 ⁻ and SiO_3^2 ⁻ were 0.20 $(\pm 0.7\%)$, 0.05 ($\pm 8.6\%$), 0.05 ($\pm 15\%$), 0.03 ($\pm 10\%$) and 0.07 (\pm 6.0%) μmol L $^{-1}$, respectively. Dissolved oxygen was measured by Winkler titration method [\(Grasshoff et al., 1999\)](#page--1-0). To measure chlorophyll a content, 100–250 ml seawater samples were filtered on a GF/F filter and stored at -20 °C until analysis. Chl a samples were extracted with 10 ml 90% acetone at -20 °C and measured using a Turner Designs 10-AU fluorometer according to the fluorometric acidification procedure ([Holm-Hansen et al., 1965](#page--1-0)).

3. Results

3.1. Surface distribution of nutrients

Surface dissolved inorganic nitrogen (DIN: NO_3^- , NO_2^- , NH_4^+), PO_4^{3-} and SiO_3^{2-} concentrations were generally high in the west and low in the east and exhibited a clear gradient offshore [\(Fig. 2\)](#page--1-0). Surface nutrient exhibited a tongue-like shape at the river mouth, consistent with distribution pattern of salinity [\(Fig. 2\)](#page--1-0). For example, at estuarine station M5-1 with salinity being approximately zero, DIN, PO_4^{3-} and SiO_3^{2-} were up to 100, 1.59 and 114 μ mol L⁻¹. respectively, while DIN, PO_4^{3-} and SiO_3^{2-} at the offshore station M4-13 were 0.62, 0.35 and 1.22 μ mol L⁻¹, respectively [\(Fig. 2\)](#page--1-0).

High nutrient concentrations were observed at estuarine station M5-9 with a salinity of 0.18, near a sewage outfall in Shanghai, where DIN, PO_4^{3-} and SiO_3^{2-} were 136, 2.14, and 112 μ mol L⁻¹, respectively ([Fig. 2](#page--1-0)).

Two typical transects (M1 and $123^{\circ}E$), which were influenced by different water masses such as Taiwan Warm Current, the Changjiang River Plume and the outer shelf Kuroshio Water, were selected to present the vertical distributions of temperature, salinity, nutrients, and oxygen saturation. In transect M1, there was an obvious invasion of the relatively saline ($>$ 31) and cold ($<$ 23 °C) water, in which nutrient concentrations were relatively high (13.2–16.0 µmol L^{-1} for DIN, 0.61–1.06 μmol L⁻¹ for PO₄³⁻, 16.1–24.3 μmol L⁻¹ for SiO₃²⁻).

Chl *a* was very high (up to 48.04 mg m⁻³ in the 2 m depth at L1-8) between transect L2 and transect M1. The high Chl a area

Fig. 1. Sampling stations in the Changjiang Estuary. "A" denotes the main sewage outfall in Shanghai City. The station numbers follow the pattern of the first named station of each horizontal transect for brevity. White bordered rectangles indicate two typical transects (M1 and $123^{\circ}E$), that was selected to present the vertical profile of temperature, salinity nutrients and oxygen saturation. A cruise was conducted from 18 July to 23 August 2006.

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