Variability in sinking fluxes and composition of particle-bound phosphorus in the Xisha area of the northern South China Sea

Yuan Dong[a], Qian P. Li[a,*], Zhengchao Wu[a], Jia-Zhong Zhang[b]

[a] *State Key Laboratory of Tropical Oceanography, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China*
[b] *Ocean Chemistry and Ecosystems Division, Atlantic Oceanographic and Meteorological Laboratory, National Oceanic and Atmospheric Administration, Miami, FL 33149, USA*

ABSTRACT

Export fluxes of phosphorus (P) by sinking particles are important in studying ocean biogeochemical dynamics, whereas their composition and temporal variability are still inadequately understood in the global oceans, including the northern South China Sea (NSCS). A time-series study of particle fluxes was conducted at a mooring station adjacent to the Xisha Trough in the NSCS from September 2012 to September 2014, with sinking particles collected every two weeks by two sediment traps deployed at 500 m and 1500 m depths. Five operationally defined particulate P classes of sinking particles including loosely-bound P, Fe-bound P, $CaCO_3$-bound P, detrital apatite P, and refractory organic P were quantified by a sequential extraction method (SEDEX). Our results revealed substantial variability in sinking particulate P composition at the Xisha over two years of samplings. Particulate inorganic P was largely contributed from Fe-bound P in the upper trap, but detrital P in the lower trap. Particulate organic P, including exchangeable organic P, $CaCO_3$-bound organic P, and refractory organic P, contributed up to 50–55% of total sinking particulate P. Increase of $CaCO_3$-bound P in the upper trap during 2014 could be related to a strong El Niño event with enhanced $CaCO_3$ deposition. We also found sediment resuspension responsible for the unusual high particles fluxes at the lower trap based on analyses of a two-component mixing model. There was on average a total mass flux of 78 ± 50 mg m^{-2} d^{-1} at the upper trap during the study period. A significant correlation between integrated primary productivity in the region and particle fluxes at 500 m of the station suggested the important role of biological production in controlling the concentration, composition, and export fluxes of sinking particulate P in the NSCS.

1. Introduction

Phosphorus (P), an essential element for phytoplankton growth, plays an important role in marine ecosystem dynamics and eventually controls the productivity of the ocean over geological time scales (Tyrrell, 1999). Being a particle active species in seawater, dissolved inorganic phosphorus (DIP) is readily scavenged out of seawater by settling particles in the coastal environments (Ruttenberg and Berner, 1993). In the open ocean, DIP is incorporated into organic matter by phytoplankton and the fixed organic phosphorus is subsequently exported out of the euphotic zone by particles sinking to the deep ocean (Benitez-Nelson et al., 2007). As concentration of DIP is often very low in the surface ocean, remineralization of sinking particulate organic phosphorus (POP) and subsequent upwelling of the regenerated phosphate in the thermocline are thus important mechanisms for sustaining phytoplankton production and the associated biological carbon pump (Bjorkman and Karl, 2003; Honjo et al., 2008).

Particulate phosphorus can be partitioned into organic and inorganic forms in the ocean due to their different consumption pathways. In the North Pacific Ocean, a large fraction of the settling particulate P was actually found in the sinking biogenic organic matter (e.g., Yoshimura et al., 2007), which is in contrast to the coastal waters where particulate inorganic phosphorus (PIP) often dominated sinking P fluxes (Faul et al., 2005; Lyons et al., 2011). The predominance of compounds derived from phytoplankton and zooplankton affects phosphorus composition of sinking particles, as the amount of sinking particulate materials below the euphotic zone would be constrained by primary productivity above (Benitez-Nelson and Buesseler, 1999; Francois et al., 2001). Variations in the inorganic-to-organic ratios of sinking particulate P should reflect the change of water column biogeochemistry (Sekula-Wood et al., 2012). It is therefore crucial to identify and quantify the various forms of inorganic and organic P in sinking particles and their associated export fluxes in order to fully understand the dynamic of P cycle in the ocean.
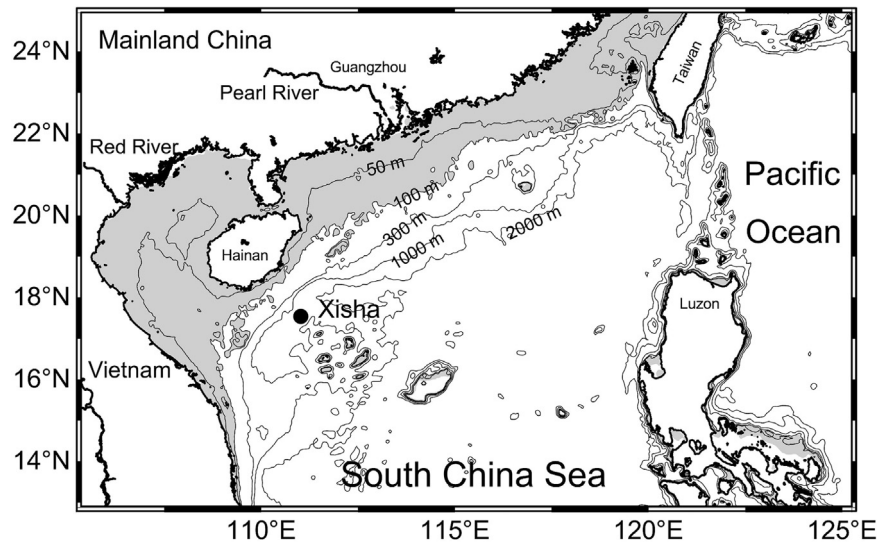

Fig. 1. Topography of the northern South China Sea (NSCS). Black dot is the Xisha (XS) station where mooring sediment traps were deployed with thin lines showing the bathymetry and the shaded area representing the NSCS continental shelf.

The northern South China Sea (NSCS) (Fig. 1), one of the world's largest semi-enclosed seas, is influenced by seasonal monsoons, upwelling/mixing, river discharges, internal waves, and eddies (Liu et al., 2002). Although DIP in the surface NSCS was very low, phytoplankton community was generally limited by nitrogen due to low nitrogen-to-phosphorus ratios of the surface seawater (Wu et al., 2003). P-limitation of primary production was found in the summer when the outflows of P-deficit riverine waters mixed with the oligotrophic NSCS waters (Yin et al., 2004; Xu et al., 2008). Export fluxes of particulate organic materials including POP at the base of the euphotic zone of the NSCS were higher in the winter-spring but lower in the summer-fall (Chen et al., 2008), due to seasonal variability of productivity (Wei et al., 2011). Vertical distributions of sinking particulate P in the NSCS were influenced by both primary production and P adsorption on mineral clays (Ho et al., 2009). One previous study has shown that POP was ~57% of the total particulate phosphorus (TPP) at 1000 m of the NSCS but detailed P speciation was lacking, not to mention the temporal variations of different P forms and their associated fluxes (Liebezeit, 1991).

In this paper, we report a time-series study of particle fluxes by sediment trap measurements from September 2012 to September 2014 at a mooring station of Xisha (named XS hereafter) in the western NSCS. The Xisha area was characterized by higher particulate organic carbon fluxes compared to the central NSCS (Ma et al., 2011). There was on average 65% of sinking particles at Xisha originating from Taiwan by advective transport and deposition, with relatively less contribution by the nearby Red River (Liu et al., 2014). Using a sequential extraction method (SEDEX) (Ruttenberg, 1992; Zhang et al., 2010), we quantified five classes of sinking particulate P from sediment trap samples, including loosely-bound P, Fe-bound P, CaCO$_3$-bound P, detrital apatite P, and refractory organic P. Based on these data, we examined the temporal variability of the particulate P concentration and composition, as well as the associated export P fluxes at XS. Our goals are to address the mechanisms responsible for long-term change of sinking particulate P and to understand the role of sinking particles on biogeochemical cycling of P in this high-productive marginal sea.

2. Material and methods

2.1. Descriptions of the study site, sediment trap moorings, and seawater samplings

The time-series mooring station (XS) is located at 17° 24.5′ N, 110°

55.0′ E with a bottom depth of 1690 m (Fig. 1). During the winter monsoon, a deepening mixed layer of ~60 m is typically found at XS (Fig. 2A). Nutrient profiles at XS are similar to the oligotrophic central NSCS (Li et al., 2015), with phosphate of < 0.1 μm, nitrate plus nitrite of < 1 μm and silicate of < 1.5 μm at the surface (Fig. 2B). Water column at XS is generally stratified in the summer with reduced nutrient supply leading to low productivity. Discrete samples were collected by SeaBird SBE 9/11 CTD aboard R/V *Shiyan III* during November 2013 with nutrients measured at lab by a Seal AA3 autoanalyzer (Bran-Luebbe, GmbH) and the surface low-level phosphate by a highly sensitive long-path spectrophotometry method (Li et al., 2008; Li and Hansell, 2008).

Two sediment traps (Nichiyu Giken Kogyo, SMD-26S) were deployed at the XS station from September 2012 to September 2014 at the depths of 500 m and 1500 m, respectively. Sample collection was made twice a month and each sample measures a 14–16 days accumulative flux (lower trap sampling was not performed after January 2014). The sediment trap had a collecting area of 0.5 m^2 and sampling cups were filled with particle free seawater (0.45 μm filtration) containing 3.3 g/L HgCl$_2$ to prevent microbial decomposition of organic matter. Particle samples were stored in polyethylene bottles at 4°C until further analyses. Larger zooplankton (such as foraminifers) was removed once the trap samples returned to the lab. The sample was then ground to < 125 μm and oven dried for 24 h before final dry-weight determination. Total mass flux (TMF in unit of mg m^{-2} d^{-1}) of the sinking particles was obtained when the dry-weight was divided by the collecting area and the exposure time. Flux of each particulate P composition was estimated by multiplying P mass concentration with TMF.

2.2. Procedure of sequential extraction of particulate P from sediment trap samples

We used a modified five-step sequential extraction method (SEDEX) by Zhang et al. (2010) to separate various forms of P in the sediment trap samples: (1) loosely-bound P including adsorbed inorganic P and exchangeable organic P, (2) Fe-bound inorganic P, (3) CaCO$_3$-bound P that is the calcium-phosphate minerals of the apatite group including authigenic carbonate fluorapatite, biogenic apatite, CaCO$_3$ associated apatite, (4) detrital apatite P, and (5) refractory organic P (Ruttenberg, 1992). Soluble reactive phosphorus (SRP) and total dissolved phosphorus (TDP) of the extracted supernatant during each step were measured by methods in Section 2.3.