



# Apparent enhancement of $^{234}\text{Th}$ -based particle export associated with anticyclonic eddies



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## ABSTRACT

It is increasingly recognized that mesoscale eddies play an important role in modulating the variability of ocean biogeochemistry. It is commonly believed that contrary to cyclonic eddies, anticyclonic eddies are characterized by downwelling at their core regime, which may suppress particle export. Here, by considering submesoscale domains we demonstrate that particle export might be alternatively enhanced in anticyclonic eddies on the basis of a study carried out in the oligotrophic northern South China Sea basin. We examined particle fluxes associated with three coherent anticyclonic eddies using the naturally occurring radionuclide  $^{234}\text{Th}$ . When applying a 1D steady-state model,  $^{234}\text{Th}$  and its derived particulate organic carbon (POC) fluxes in all three eddy cores were 1.9- and 1.6-fold higher, respectively, relative to those in the non-eddy region. However, an eddy-resolving circulation numerical model showed complex submesoscale circulations associated with the anticyclonic eddy. Notably, dynamic interactions occurred at submesoscales that might induce advection into the eddy core from the edge, where the  $^{234}\text{Th}$  deficit was elevated owing to higher particle production and export, probably stimulated by upwelling at the edges. We suggest therefore that enhanced particle fluxes derived from the 1D model along the vertical horizon at eddy cores only appeared to be changes, and that horizontal advection between the eddy core and edge should be taken into consideration in the flux estimation. Indeed, by integrating the  $^{234}\text{Th}$  deficit among multiple profiles in the entire anticyclonic eddy system, we derived an average  $^{234}\text{Th}$  flux of  $938 \text{ dpm m}^{-2} \text{ d}^{-1}$  at the 100-m horizon, equivalent to a POC flux of  $3.69 \text{ mmol Cm}^{-2} \text{ d}^{-1}$ . This export level was 1.6-fold higher than that from the reference sites.

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## 1. Introduction

Mesoscale eddies are ubiquitous features in the ocean and it is increasingly recognized that they play an essential role in ocean biogeochemistry (Benitez-Nelson et al., 2007; Buesseler et al., 2008; Chelton et al., 2011; Klein and Lapeyre, 2009; McGillicuddy et al., 1998; Oschlies and Garcon, 1998). There are three types of eddy identified in the ocean: cyclonic, anticyclonic, and mode-water eddies (McGillicuddy et al., 2007). The current understanding is that cyclonic or cold eddies may induce nutrient injection from the depths into the euphotic zone associated with isopycnal uplift, which stimulates primary production (PP) and ultimately enhances the downward particle flux. By contrast, it is inferred that anticyclonic or warm eddies have a minor biogeochemical effect because of the general downward displacement of isopycnals therein (McGillicuddy et al., 1998). At the Bermuda Atlantic Time-

series Study site (BATS,  $31.83^\circ \text{ N}$ ,  $64.17^\circ \text{ W}$ ), anticyclonic eddies even suppress spring blooms (Sweeney et al., 2003). Hansen et al. (2010) reported that algal blooms are delayed by  $\sim 2$  weeks owing to anticyclonic eddies in the Norwegian Sea. Moutin and Prieur (2012) showed that dissolved organic carbon (DOC) was higher in the upper 500 m of three anticyclonic eddies in the Mediterranean Sea than at non-eddy stations. Lasternas et al. (2012) attributed DOC accumulation to an increase in algal cell mortality and lysis rate in the early stage of anticyclonic eddy development in the Canary Eddy Corridor of the Northeast Atlantic Ocean. The authors suggested that such a DOC-enhanced microbial loop process would imply a reduction in the downward particulate organic carbon (POC) flux. A modeling study in the South China Sea (SCS) also showed that the export flux in anticyclonic eddies was 31% lower relative to the basin mean, in contrast to a 41% enhancement in cyclonic eddies (Xiu and Chai, 2011). However, it should be noted that the assessment of POC fluxes in the above mentioned studies were based on single station measurements, inferences, or

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numerical modeling. Direct observations of POC fluxes with reasonably good spatial resolution have thus far been rare.

More importantly, no studies in light of the increasingly recognized submesoscale processes have been reported for POC export in anticyclonic eddies. We note that both observational and/or numerical modeling studies (although limited) have increasingly pointed towards the importance of considering submesoscale processes in resolving the biogeochemical impact of anticyclonic eddies. Indeed, small-scale hotspots of upwelling occur to the periphery of anticyclonic eddies, serving as a frontal zone between the eddy and the surrounding waters, owing to intensification of ageostrophic secondary circulation (Klein and Lapeyre, 2009). Model simulation further indicates that nutrient supply and PP can be alternatively stimulated by such submesoscale processes in anticyclonic eddies (Mahadevan et al., 2008). Samuelsen et al. (2012) used an eddy-resolving physical model with a particle-tracking module to show that particles tend to accumulate at the edge of an eddy.

Notwithstanding submesoscale processes, we contend that the inferred suppression of export fluxes by anticyclonic eddies should be re-examined by considering submesoscale processes. In this context, we conducted a study to examine the responses of particle export to three anticyclonic eddies using high-resolution sampling of  $^{234}\text{Th}$  as an effective tracer. We compared  $^{234}\text{Th}$ -derived export fluxes based on a 1D steady-state (SS) model and integrated fluxes that canceled the lateral variability induced by submesoscale transport. This comparison revealed that POC fluxes derived from the 1D model only appeared to be changes, and disappeared when a 3D model was applied, or that the vertical  $^{234}\text{Th}$  fluxes estimated were biased by submesoscale lateral transport of  $^{234}\text{Th}$ . We further introduced an eddy-resolving numerical model that revealed a 3D eddy structure to estimate the physical transport of  $^{234}\text{Th}$ ; this confirmed significant exchange between the eddy core and edge.

## 2. Methods

### 2.1. Study area

The SCS is the largest semi-enclosed marginal sea of the Pacific Ocean. The basin-scale circulation is mainly driven by the East Asian monsoon, which is expressed as a generally cyclonic gyre in winter and a two-gyre system in summer (Fig. 1a) comprising a cyclonic gyre north of approximately  $12^\circ\text{N}$  and an anticyclonic gyre in the south (Cao and Dai, 2011 and references therein). Eddies are frequently generated in the SCS owing to different mechanisms such as frontal instability, coastal jet separation, and/or monsoon-driven forcing (Hu et al., 2011). In the northern SCS basin, eddies are mainly formed as a result of the variation and/or instability of these circulation gyres (Wang et al., 2003) or eddy penetration through the Kuroshio from the Western Pacific Ocean (Hu et al., 2012).

The SCS is an oligotrophic mini-ocean (Du et al., 2013) with PP in the range  $16\text{--}46\text{ mmol C m}^{-2}\text{ d}^{-1}$ ; higher values usually occur in winter, when the mixed layer is deepened (Chen, 2005). Eddy activities are thus expected to be important for the biogeochemistry of the SCS basin. For example, PP could be elevated to  $>90\text{ mmol C m}^{-2}\text{ d}^{-1}$  by a cyclonic eddy in the northern SCS (Chen et al., 2007). Lin et al. (2010) found that eddies can bring coastal nutrients into the oligotrophic basin and induce an algal bloom [chlorophyll (Chl) *a* concentration as high as  $300\text{--}400\text{ ng L}^{-1}$ ].

### 2.2. Sample collection

The sampling campaign was conducted from 28 July to 7 August 2007 on board the R/V *Dongfanghong II* in the northern SCS

basin (Fig. 1b). Two transects were visited during the cruise: transect H along  $18^\circ\text{N}$ , covering all three of the anticyclonic eddies under study; and transect G along  $19^\circ\text{N}$ , located outside the eddies. Discrete water samples were collected at five depths in the upper 100 m (normally 0, 25, 50, 75, and 100 m) using 12-L Niskin bottles assembled on a CTD (Seabird SBE 911)/Rosette sampler. For the stations denoted in red in Fig. 1b, a small volume (4 L) of seawater was collected for total  $^{234}\text{Th}$  determination and another 8 L was filtered on board using a quartz microfiber (QMA) filter (25 mm,  $1.0\text{ }\mu\text{m}$ ) for particulate  $^{234}\text{Th}$  and POC analysis. Samples for biogenic  $\text{SiO}_2$  ( $\text{bSiO}_2$ ) analysis were collected only from selected stations (H06, H08, H10, H12, H14, H16, G04, G06, G08, and G10), for which 2 L of seawater was filtered through a  $1.0\text{-}\mu\text{m}$  polycarbonate membrane filter. Nutrients were sampled only for stations denoted in black in Fig. 1b.

### 2.3. $^{234}\text{Th}$ analysis

We used the small-volume (4 L)  $\text{MnO}_2$  co-precipitation method for total  $^{234}\text{Th}$  analysis (Benitez-Nelson et al., 2001; Buesseler et al., 2001; Cai et al., 2006; Zhou et al., 2012). In brief,  $^{234}\text{Th}$  was co-precipitated with  $\text{MnO}_2$  formed by addition of  $\text{KMnO}_4$  and  $\text{MnCl}_2$  solutions, and was then filtered through a QMA filter (25 mm,  $1.0\text{ }\mu\text{m}$ ).  $^{234}\text{Th}$  recovery was monitored by adding  $\sim 10\text{ dpm }^{230}\text{Th}$ . All total and particulate  $^{234}\text{Th}$  samples were dried and mounted on plastic discs with two layers of aluminum foil (total density  $\sim 7.2\text{ mg m}^{-2}$ ) and one layer of Mylar film. A gas-flow proportional low-level RISØ beta counter was used for  $^{234}\text{Th}$  counting. All  $^{234}\text{Th}$  samples were counted for at least 12 h until 2500 counts were obtained. To determine the background, a second count was carried out after  $>6$  months. Total  $^{234}\text{Th}$  samples were demounted for recovery analysis of the  $^{230}\text{Th}$  spike on QMA filters after beta counting. The  $^{230}\text{Th}$  was monitored using  $^{228}\text{Th}$ , purified using iron precipitation and anion column exchange, and finally plated on a 25-mm stainless steel disc. The disc samples were counted using an alpha counter until the counting errors for both  $^{230}\text{Th}$  and  $^{228}\text{Th}$  were  $<2\%$ . All  $^{230}\text{Th}$  recovery results lay between 78% and 101%, with an average of  $89.6 \pm 2.4\%$  (mean  $\pm 1\sigma$ ,  $n = 85$ ). The  $^{234}\text{Th}$  data presented here were calibrated after recovery and decay-corrected back to the sampling time. The uncertainties for  $^{234}\text{Th}$  were propagated from counting errors associated with the first and second counts, recovery analysis, and the detection efficiency of the beta counter. The precision of the final  $^{234}\text{Th}$  value was approximately 5%. On the basis of its conservative characteristics in the open ocean, the linear relationship  $^{238}\text{U} (\text{dpm L}^{-1}) = 0.07081 \times \text{salinity}$  was applied for estimating uranium activity (Chen et al., 1986). The uncertainty derived from this equation was approximately 3%, which was also included in the calculation of  $^{234}\text{Th}$  fluxes.

### 2.4. POC and $\text{bSiO}_2$ analysis

The particulate  $^{234}\text{Th}$  samples were used for POC measurements after beta counting. The QMA filters were fumed with concentrated HCl to remove carbonate. After drying in an oven at  $50^\circ\text{C}$ , POC was determined using a PE-2400 SERIES II CHNS/O analyzer according to the JGOFS protocol (Knap et al., 1996). The procedural carbon blank was  $<0.06\text{ }\mu\text{mol L}^{-1}$  and the uncertainty for our POC data was better than 10%.  $\text{bSiO}_2$  was measured using a Technicon AA3 auto-analyzer (Bran-Lube, GmbH) after double-wet alkaline (NaOH) digestion following Ragueneau et al. (2005) and Liu et al. (2012). The procedural blank for  $\text{bSiO}_2$  was  $<0.03\text{ }\mu\text{mol L}^{-1}$  and the uncertainty was  $<10\%$ . The uncertainties for both POC and  $\text{bSiO}_2$  were considered during flux estimation.

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