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Dissolved organic carbon in the South China Sea and its exchange with the Western Pacific Ocean

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ABSTRACT

Based on a large and high quality dataset of total organic carbon (TOC, an approximation of dissolved organic carbon) collected from three cruises in spring, fall and winter in 2009–2011, we examined the distribution of TOC and its seasonality in the oligotrophic regime of the Northern South China Sea (NSCS) as well as its exchanges with the West Philippine Sea (WPS) in the Northwest Pacific Ocean through the Luzon Strait, the only deep channel linking the South China Sea (SCS) and the Pacific Ocean. Surface TOC concentration in the slope and basin areas of the NSCS varied from 65 to 75 μmol L^{-1} with relatively high values in the northeast part (southwest of Taiwan Island) in spring, and in the eastern parts of the NSCS during fall and winter. The TOC inventory in the upper 100 m of the water column ranged from 6.0–7.5 mol m^{-2} with a similar distribution pattern as the surface TOC concentration. There were two most significant differences in the TOC profiles between the SCS and the WPS. One was in the upper 200 m, where more TOC was accumulated in the WPS; the other was in the intermediate layer at ~1000–1500 m, where the gradient of TOC concentration was still persistent below 1000 m in the SCS, a feature which did not exist in the WPS. At this intermediate layer, there also appeared an excess of TOC in the SCS as compared with that in the WPS. The TOC concentration below 2000 m in the SCS was identical to that in the Northwestern Pacific, both of which were ~40 μmol L^{-1} without significant difference among stations and seasons, suggesting that this deep water TOC was homogeneously distributed in the deep SCS basin owing to the fast replenishment of the deep water from the WPS. We adopted an isopycnal mixing model to derive the water proportion contributed respectively from the SCS and Kuroshio along individual isopycnal plane and examined the impact of the Kuroshio intrusion on the TOC in the NSCS. The upper 100 m TOC inventory in the NSCS was overall positively correlated with the Kuroshio water fraction, suggesting that the Kuroshio intrusion enhanced the TOC inventory thereby significantly influencing TOC distribution in the NSCS. Following the sandwich structure of water exchange through the Luzon Strait, with an inflow in the surface and deep layer but an outflow from the SCS in the intermediate layer, we conducted a first order estimation of the TOC transport fluxes based on the reported cross strait volume transport. The TOC transport flux was -107.1 ± 54.6, 54.7 ± 15.0 and -16.4 ± 13.1 Tg C yr^{-1} at the upper, intermediate and deep layer, respectively. Note that the positive sign means that the flux was from the SCS to the WPS. By integrating the three-layers, the total net transport flux of TOC through the Luzon Strait would be -68.8 ± 58.0 Tg C yr^{-1}. Because of the great spatial–temporal variability of the water flow across the Luzon Strait, these first order TOC flux estimates were subject to large uncertainty. Nevertheless, because the SCS is featured by higher DOC production, the exchange of these fluxes with the open ocean interior where DOC would have experienced more degradation would have important implications for both the microbial community in the ocean interior and overall carbon cycle in the SCS.

1. Introduction

Located in the continuity between the land and the ocean, ocean margins exchange waters and material with major ocean basins in a very dynamic and interactive way. Such exchange remains as a hard question both in terms of physical dynamics and biogeochemistry

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(Huthnance et al., 2009 and references therein). Observational and modeling studies of water exchange between the marginal seas and the open ocean have been carried out at several locations including the Middle Atlantic Bight (Biscaye et al., 1994) the US western shelf (Jahnke et al., 2008) and the South China Sea (SCS; Tian et al., 2006; Qu et al., 2006; Hsin et al., 2012). These studies all point towards the complexity in mechanisms and fluxes of these water mass exchanges in time and space. It is even more challenging to resolve the material exchanges because many chemical constituents often exert large gradients between the ocean margin and the ocean interior induced by the difference in sources and the consumption in between. Dai et al. (2013) recently propose a new framework, the Ocean-dominated Margin (OceMar) characterized by dynamic interactions with the open ocean, which may provide non-local CO_2 sources thereby modulating the CO_2 fluxes in OceMars.

The SCS is the largest marginal sea of the Pacific Ocean, which exchanges with the West Philippine Sea (WPS) in the Northwestern Pacific Ocean through the Luzon Strait, the only deep water channel with a maximal sill depth of ~2200 m (Dai et al., 2009 and references therein). The water exchange across the Luzon Strait exhibits a "sandwich-like" flow pattern, with an inflow from the WPS in the upper and deeper layers but an outflow to the WPS in the intermediate layer (Chao et al., 1996; Li and Qu, 2006; Qu et al., 2006; Tian et al., 2006; Gan et al., 2006). The rapid replenishment of the SCS deep water from the WPS is maintained by fast ventilation with the shallower intermediate water, as well as a persistent net outflow at an intermediate depth (Chao et al., 1996; Chen et al., 2001; Li and Qu, 2006). Such a unique circulation pattern makes the SCS a perfect site to examine ocean margin–open ocean interactions.

Dissolved organic carbon (DOC) is the biggest organic carbon reservoir in the ocean, and is a critically important component in oceanic carbon cycling (Siegenthaler and Sarmiento, 1993). Ocean margins generally produce more organic carbon than they respire, and can significantly contribute organic carbon to fuel microbial metabolism in the deep open ocean (Dai et al., 2009 and references therein). However, our understanding of the DOC interaction between the marginal sea and open ocean is very limited. Our prior research has revealed that the intermediate outflow exports 3.1 ± 2.1 Tg C yr^{-1} of DOC from the SCS. Such export of excess DOC to the adjacent open ocean may represent an important pathway to sequestrate carbon within the SCS and a critically important carbon source of the interior Pacific Ocean, which would significantly contribute to fueling microbial metabolism in the Pacific Ocean Interior (Dai et al., 2009).

The present study will further such studies on the interactions between the SCS and WPS by reporting the full spectrum of DOC exchanges through the Luzon Strait based on a large and high quality dataset of total organic carbon (TOC, an approximation of DOC). Data were collected during three cruises that covered a large portion of the Northern SCS (NSCS). At the upper layer, we adopted an isopycnal mixing model (Du et al., 2013) to quantify the influence of the Kuroshio intrusion on the TOC inventory. At the intermediate and deep layers, the net exchange fluxes of TOC across the Luzon Strait were estimated based on the water mass exchange fluxes and TOC concentration gradients. Additionally, this study was aimed at better defining the seasonality of TOC within the SCS basin area, which has not been reported previously.

2. Materials and methods

2.1. The study area

The basin-scale surface currents in the SCS are driven to a significant extent by monsoons that result in a cyclonic circulation gyre during the northeast monsoon and an anti-cyclonic gyre during the southwest monsoon. As a consequence, the SCS basin is effectively isolated from terrestrial inputs and a wide area of the SCS basin is oligotrophic. Within this oligotrophic basin, both the biomass and primary productivity are believed to be dominated by the nutrient supply modulated by the strength of the seasonally reversing East Asian Monsoon (Liu et al., 2002, 2013). In winter, increased wind speed stimulates photosynthesis through strong mixing that entrains the nutrient-rich subsurface water to the upper layer; while in summer, the upper water column is highly stratified, which results in a reduction in biological productivity. Recently, Du et al. (2013) quantify that the degree of the Kuroshio intrusion into the SCS also significantly impacts the upper SCS nutrient inventory.

2.2. Sampling and analysis

TOC samples were collected during winter (Dec., 2009–Jan., 2010), fall (Oct.–Nov., 2010) and spring (Apr.–Jun., 2011) covering nearly the entire NSCS basin and the Luzon Strait. We focused on a region from 111 to 120°E and from 18 to 22°N, roughly the 200 m isobaths in the zonal direction (Fig. 1). In this study, we considered only stations with water depth >200 m, where TOC concentration was not significantly influenced by terrestrial sources.

Samples were collected in duplicate using acid cleaned 12 L Niskin bottles attached to the CTD rosette as previously described (Dai et al., 2009). Samples were not filtered and were stored in precombusted EPA vials at −20 °C until analysis. Here, we used TOC as an approximation of DOC given the fact that particulate organic carbon (POC) concentrations based on our parallel study represented on average only ~4% of TOC (Cai et al., 2015). TOC was measured using a Shimadzu TOC-V analyzer. A four-point calibration curve was obtained by injecting working solutions of potassium hydrogen phthalate, which was freshly prepared every two days. TOC concentration was determined by subtracting the running blank from the average peak area of the samples (injected 3–4 times) and dividing the subtraction by the slope of the calibration curve. The running blank was determined as the average of the peak area of the Milli-Q water acidified with H_3PO_4. Low carbon water and deep sea water, provided by Dr. Hansell's laboratory at the University of Miami, were used for quality assessment of our measurements. The coefficient of variation on the analysis of our replicate measurements was ~2%. The standard deviation of our long term replicate measurements on the reference deep sea water was ± 0.8 μmol L^{-1}, which was used as an index of our analytical precision.

2.3. Isopycnal mixing model

In order to quantify the impact of the Kuroshio intrusion on the TOC inventory in the NSCS, a well validated isopycnal model (Du et al., 2013) was adopted. Using this model, we calculated the mixing ratios contributed by the different water masses along the isopycnal plane. The model assumed that the isopycnal mixing rate was much faster than the diapycnal mixing rate and so the effect of diapycnal mixing could be negligible. Within the SCS, we estimated the isopycnal mixing rate of TOC to be 6.0×10^{-3} mmol m^{-2} s^{-1}, which was three orders of magnitude larger than the diapycnal mixing rate of $\sim 1.0 \times 10^{-6}$ mmol m^{-2} s^{-1}.

Details of the application of the isopycnal mixing model are introduced by Du et al. (2013). For any in situ observed water parcel shown in the T–S diagram in Fig. 2a, the proportional contributions of SCS and the Kuroshio along the individual isopycnal surface can be calculated (Eq. (3)) based on the conservation of salinity or potential temperature (Eqs. (1) and (2)):