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Behavior and fluxes of particulate organic carbon in the East China Sea

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Abstract

To better understand carbon cycling in marginal seas, particulate organic carbon (POC) concentrations, POC fluxes and primary production (PP) were measured in the East China Sea (ECS) in summer 2007. Higher concentrations of POC were observed in the inner shelf and lower POC values were found in the outer shelf. Similar to POC concentrations, elevated uncorrected POC fluxes (720–7300 mg C m^{-2} d^{-1}) were found in the inner shelf and lower POC fluxes (80–150 mg C m^{-2} d^{-1}) were in the outer shelf, respectively. PP values (~ 340–3380 mg C m^{-2} d^{-1}) had analogous distribution patterns to POC fluxes, while some of PP values were significantly lower than POC fluxes, suggesting that contributions of resuspended particles to POC fluxes need to be appropriately corrected. A vertical mixing model was used to correct effects of bottom sediment resuspension and the corrected POC fluxes ranging from 41 ± 20 to 956 ± 443 mg C m^{-2} d^{-1}, which were indeed lower than PP values. The results suggest that 49–93 % of the POC flux in the ECS might be from the contribution of resuspension of bottom sediments rather than from the actual biogenic carbon sinking flux. While the vertical mixing model is not a perfect model to solve sediment resuspension because it ignores biological degradation of sinking particles, Changjinag plume (or terrestrial) inputs and lateral transport, it makes significant progress in both correcting resuspension problem and in assessing a reasonable quantitative estimate in a marginal sea.

1 Introduction

Continental margins only account for 8 % of the surface area of the ocean, but they contribute approximately 30 % of global primary production (Liu et al., 2000). Walsh (1989) proposed that continental shelf regimes were an important organic carbon source to the open ocean because marginal seas have elevated phytoplankton primary production and higher particulate organic carbon (POC) inventories as compared to those in the open ocean. Thus, marginal seas are believed to crucially influence marine carbon biogeochemical cycling (Liu et al., 2010 and references therein). Indeed, one of the major objectives of the international research project Land-Ocean Interaction in the Coastal Zone (LOICZ) is to quantify the exchange of carbon between continental shelves, marginal seas, and the open ocean.

The East China Sea (ECS) is among the largest marginal seas on the earth and has a high primary production (0.3 to 1.5 $gC\,m^{-2}\,d^{-1}$) in coastal areas, particularly during the summer months (Gong et al., 2003). According to previous reports, the ECS has been regarded as an important sink (10–30 $MtC\,yr^{-1}$, 1 Mt = 10^{12} g) for atmospheric CO_2 based on measurements of CO_2 air-sea exchange (Tsunogai et al., 1999; Peng et al., 1999; Wang et al., 2000; Shim et al., 2007; Chou et al., 2009a,b). Model-estimated organic carbon burial on the broad ECS shelf and that transported offshore ranges from 7–10 and 2–12 $MtC\,yr^{-1}$, respectively (Chen and Wang, 1999; Liu et al., 2006, 2010). While these estimations show large uncertainties, the net imbalance of organic carbon fluxes in the ECS amounts to approximately 10–20 $MtC\,yr^{-1}$. Although fluxes of particles and POC have been estimated in the ECS and adjacent areas (Hung et al., 1999, 2003; Hoshika et al., 2003; Oguri et al., 2003; Iseki et al., 2003; Guo and Zhang, 2005; Zhu et al., 2006), direct measurements of POC fluxes in the ECS coastal region are very limited (Iseki et al., 2003; Guo et al., 2010).

There is no simple means to estimate POC fluxes in the marginal seas due to strong sediment resuspension, lateral transport or dense shelf water cascading, although several methods (carbon budget, vertical flux and box model) have been used (Smith and Hollibaugh, 1993; Falkowski et al., 1994; Oguri et al., 2003; Hoshika et al., 2003). Most importantly, recent studies showed that POC fluxes (measured by moored sediment traps, 300 ~ 5000 $mg\,C\,m^{-2}\,d^{-1}$, Iseki et al., 2003) were sometimes higher than PP in the ECS (500 ~ 2500 $mg\,C\,m^{-2}\,d^{-1}$, Gong et al., 2003, 2006; Liu et al., 2010). As mentioned above, the ECS has highest PP during the summer (Gong et al., 2003, 2006), therefore, the possible factors to result in POC fluxes being higher than PP could be sediment resuspension, fluvial particles or lateral transport because dense shelf water cascading (mainly happens in winter) in summer is unlikely in this case. To better exclude resuspended POC of the sediments in the marginal seas, we measured POC concentrations and fluxes and used a vertical end-member mixing model to appropriately calibrate the POC flux. Additionally, we also measured PP to constrain the corrected POC flux in the ECS.

2 Sampling and analytical methods

Seawater samples (32 stations) were collected aboard the R/V *Ocean Researcher I* in the ECS from July 1 to 11, 2007 (Fig. 1). Temperature was recorded using a SeaBird model SBE9/11 plus conductivity-temperature-depth (CTD) recorder and salinity was determined with an Autosal salinometer. Transmissometer data (TM%) was recorded by the transmissometer attached to the CTD. Seawater samples were collected using 20-L X-Niskin bottles (General Oceanic Inc. USA) from different depths (2, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 90, 110, 150 m) for measurements of Chlorophyll *a* (Chl *a*) and particulate organic carbon (POC) concentrations. The Chl *a* samples were collected by filtering 500 mL of seawater through a GF/F filter and stored at −20 °C until analysis. Concentration of Chl *a* on the GF/F filter was determined according to standard procedures using a Turner Designs 10-AU-005 fluorometer by the non-acidification method (Gong et al. 2000). Sub-samples (0.5 ∼ 2 L for the inner and middle shelves and 4 ∼ 6 L for the outer shelf) for total suspended matter (TSM) were filtered through pre-weight GF/F filters (after pre-combusted at 500 °C for 6 h). After measuring TSM concentrations, these GF/F filters were used to determine POC concentrations (Hung et al., 2005, 2007). Sinking particles (7 stations) were collected at 20 m (S18, S19, S29, S5) (inner shelf region), 30 m (S28) (middle shelf region), 100 m (S26) and 120 m (S10) (outer shelf region) (Fig. 1 and Table 1) by a drifting sediment trap array, which consisted of six 6.8 cm diameter cylindrical plastic core tubes with honeycomb baffles covering the trap mouths (Santschi et al., 2003; Hung et al., 2009a, 2010). The array was attached to an electricsurface buoy with a global positioning system (GPS) antenna (TGB-500, TAIYO, Japan). The trap tubes, filled with filtered seawater (Sparkling

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Clear Polypropylene filter, nominal size 0.5 µm), were deployed for short scale deployment (3–8 h). Sinking particles were filtered through pre-combusted (500 °C, 6 h) quartz filters (Whatman QMA). The swimmers caught on the filters were observed using a microscope and carefully removed using forceps. POC concentrations in both suspended and sinking particles were measured using an elemental analyzer (Elementa, Germany) after filters were HCl-fumed. The analytical uncertainty (one sigma error) for POC was 2–5 % for duplicate measurements. Selected samples contained two quartz filters; the second was treated as a POC blank ranging from 0.8 to 2.0 µmol per 25 mm quartz filter. The POC flux was extrapolated to 24 h (= 1 day) on the assumption that the POC flux at night was the same as that during the day. According to Hung et al. (2010), POC fluxes in the East China Sea and the oligotrophic water of the northwest Pacific Ocean did not show a significant difference in POC fluxes between night time and day time. We thus feel confident that diurnal variability in POC fluxes, if it exists, is small compared to other sources of error in our measurements. Trapping efficiency of the floating sediment traps in the ECS and the oligotrophic water, based on the $^{234}Th/^{238}U$ disequilibrium model of Hung et al. (2004), ranged between 75 % (Li, 2009) and 80 % (Hung and Gong, 2007), respectively.

Primary production (PP) was determined by the ^{14}C assimilation method (Parsons et al., 1984; Gong et al., 1999, 2003). Briefly, water samples for the PP measurements were prescreened through a 200-µm mesh and dispensed into acid-cleaned polycarbonate carboy (10 L, Nalgene). Each subsample was inoculated with 10 µCi $NaH^{14}CO_3$ before incubation. TheP^B-E (photosynthetic-irradiance) curve at each sampling depth was determined using a seawater-cooled incubator illuminated for two hours with artificial light PP at each depth could then be calculated with the parameters from the P^B-E curve. The detailed procedures can be found in Gong et al. (2003).

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3 Results

3.1 Hydrographic settings and distributions of Chl *a*, POC and TSM in the ECS

The surface distribution of temperature, salinity, Chl *a* concentration and POC concentrationsin the ECS in July2007 are shown in Fig. 2a–d. Sea surface temperatures (SST) at all stations were above 23 °C with lower SST in the coastal and inner shelf regions and higher SST in the outer shelf (Fig. 2a). Surface salinity gradually increased from the coastal area toward the shelf edge (Fig. 2b). Distributions of surface Chl *a* concentrations ranged from 0.3 to 8.9 mg m^{-3}. Chl *a* concentrations in the outer shelf were low and increased moving landward towards the Chinese coast and the Changjiang Estuary (Fig. 2c), becoming the highest (> 5 mg m^{-3}) in the Changjiang Diluted Water (CDW). The higher Chl *a* was supported by nutrient-rich water (Gong et al., 2006; Hung et al., 2010). Distributions of surface POC concentrations varied between 40 and 450 µg L^{-1} in the ECS. High concentrations (200–450 µg L^{-1}) of POC were observed in costal surface waters (e.g. CDW, S19, S19A, S29 and S18), followed by the middle shelf (80–160 µg L^{-1}), and generally decreased towards the shelf, with the lowest values (40–70 µg L^{-1}) found in the outer shelf (Fig. 2d) with the exception high POC values (72–140 µg L^{-1}) in the southern ECS (e.g. stations 1 and 2A).

Vertical distributions of Chl *a*, POC and TSM concentrations in the inner and middle shelves (e.g. S18, S19, S29, S5, S28) and outer shelf (e.g. S10 and S26) are shown in Fig. 3a–f, respectively. In the inner shelf (e.g. stations 18, 19 and 29), elevated Chl *a* concentrations (2–5 mg m^{-3}) were apparent in the surface layer. In contrast to the high Chl *a* concentration in the inner shelf (e.g. stations 10 and 26), the outer shelf had low phytoplankton biomass (surface Chl *a* concentration < 0.4 mg m^{-3}) (Fig. 3a, b). An interesting phenomenon is that at stations 5, 10, 26 and 28, maximum Chl *a* concentrations were always observed above the depth of the euphotic zone (Table 1) and decreased with increasing depth. Elevated POC concentrations were generally observed near surface or subsurface waters and decreased with water depth at most stations in the inner and middle shelves (Fig. 3c, d).Vertical profiles of POC reflected in elevated

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Chl *a* patterns in the inner shelf and outer shelf, while at stations 18, 29, 26, POC concentrations at the lower depths were higher than at shallow depths, implying lateral transport or sediment resuspension at greater depth. Similarly, vertical profiles of TSM showed similar patterns as POC profiles (Fig. 3e, f). One can easily see that TSM concentrations at lower depths were higher than at more shallow depths, suggesting that sediment resuspension and/or lateral transport of TSM are remarkable features in the ECS. Alternatively, the Changjiang plume flows predominantly to the northeast (Beardsley et al., 1985; Chao, 1991; Lei et al., 2003) during the summer according to literature, therefore, the Changjiang River may bring fluvial particles to the inner shelf (i.e. coastal region).

3.2 Relationships between POC and Chl *a* (TSM) and C/N ratios in the ECS

Concentrations of POC and Chl *a* showed a strong positive correlation in the ECS (Fig. 4a), suggesting that production of POC may be directly related to marine phytoplankton production. Our POC/Chl *a* value ($64\,g\,g^{-1}$) is in agreement with previous investigations in the northern East China Sea ($13 \sim 94\,g\,g^{-1}$, Chang et al., 2003; $70\,g\,g^{-1}$, Hung et al., 2009b), and the Gulf of Mexico, and the Bay of Bengal (~ 36–$144\,mol\,g^{-1}$, Khodse et al., 2009). A good correlation (POC/TSM = $0.93\,\mu mol\,mg^{-1}$) between POC and TSM (except for data marked by the blue circle) was also observed, as shown in Fig. 4b. Zhu et al. (2006) also reported similar positive relationship (POC/TSM = $0.74\,\mu mol\,mg^{-1}$) between POC and TSM in the inner shelf of the ECS in October and November, but they did not find a good relationship between POC and TSM in the middle shelf. Moreover, a significant correlation between POC and PN was obtained, as shown in Fig. 4c, where the slope is approximately 5.9, close to Redfield ratios. Figure 4d shows a good relationship (some data away from the correlation line) between POC/TSM and the reciprocal of TSM suggesting that the constituents of TSM are a mixture of two end members: one consisting of high POC content and low TSM, and the other consisting of low POC content and high TSM.

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3.3 Spatial variation of uncorrected POC fluxes and PP in the ECS

Uncorrected elevated POC fluxes (720–7300 $mg\,C\,m^{-2}\,d^{-1}$) during the summer were found in the inner shelf (e.g. S5, S18, S19, and S29) and gradually decreased towards the middle shelf (200 $mg\,C\,m^{-2}\,d^{-1}$ at S28) and then the outer shelf (80–150 $mg\,C\,m^{-2}\,d^{-1}$ at S10 and S26) (Table 1). Similarly high POC fluxes (100–3000 $mg\,C\,m^{-2}\,d^{-1}$ in the inner shelf (e.g. station PN 12, surveyed by a group of Japanese scientists in the ECS) and ~ 50–3000 $mg\,C\,m^{-2}\,d^{-1}$ in the outer shelf (e.g. station PN8, surveyed by a group of Japanese scientists in the ECS) were also reported by Iseki et al. (2003), but they did not have summer POC flux data in the ECS.

Distribution of PP in the ECS is similar to uncorrected POC flux pattern with higher PP (1897–3377 $mg\,C\,m^{-2}\,d^{-1}$) in the inner shelf (S18, S19 and S29, except for S5 with PP ~ 337 $mg\,C\,m^{-2}\,d^{-1}$) and lower PP (440–1153 $mg\,C\,m^{-2}\,d^{-1}$) in the outer shelf (S10 and S26). Most of measured PP values in this study were analogous to previously reported PP by Gong et al. (2003) and Liu et al. (2010). The lower PP at S5 could be caused by high total suspended matter (TSM > 1 ~ 2 $mg\,L^{-1}$, e.g. a light effect), nutrient limitation or strong vertical mixing (e.g. water un-stabilization). On the whole, one may see that some of POC fluxes are significantly higher than PP (Table 1), suggesting that POC measured by sediment traps might be overestimated. Therefore, in the later section, we will use a vertical mixing model to exclude the possible influences from non-biogenic flux in later section.

3.4 Using a vertical particle mixing model to correct POC flux

As mentioned above, some of uncorrected POC fluxes were much higher than those of primary production, suggesting that bottom sediment resuspension could be likely associated with the elevated POC fluxes in the ECS. First, we used a vertical particle mixing model derived by Morris et al (1987) to obtain two end member values: one with high POC content and low total suspended matter (TSM), and the other with low POC content and high TSM (Bloesch, 1994). The two end member mixing model is shown

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in Eq. (1) (Bale and Morris, 1998).

$$C = (S_0(C_0 - C_s))/S + C_s \tag{1}$$

where C is the observed POC concentration (%) in the mixture, S_0 is the total weight of surface phytoplankton ($mg\,L^{-1}$), S is the total weight of observed suspended particles ($mg\,L^{-1}$), C_0 is the POC concentration of phytoplankton (%), C_s is the POC concentration of surface sediment (%). The data of C_s and C_0 can be obtained according to the observed parameters C and S by plotting suspended POC concentrations against the reciprocal of observed suspended particle concentration, TSM (Fig. 5). Linear relationships between POC and TSM in the CDW, CUW and KW all show significant correlations with lowest p values (< 0.001, Fig. 5), suggesting that POC content is mainly controlled by the mixing of two end members thus attesting to the utility of this mixing model (Morris et al., 1987; Bale and Morris, 1998). The slope in Fig. 5 is equal to $S_0(C_0 - C_s)$ and the intercept on the y-axis (Cs) estimates a value for the POC value of the resuspended particles. The estimated POC concentrations in the surface sediments (Cs) ranged from −0.9 to 2.1 % (Table 2). The measured POC values in the surface sediments in the ECS in this study ranged from 0.08 to 0.61 % (an average value = 0.30 ± 0.16 %). Because the derived values of C_s in the CDW are much higher than published data (Table 2), herein the average C_s values (data from previous studies and this study, see Table 2) are used to represent the POC content of the surface sediments rather than using the derived C_s values. With the C_s data, we assume a reasonable surface phytoplankton weight ($S_0 = 0.5\,mg\,L^{-1}$) to solve the C_0 values. The statistical data of intercept and slope in different water masses (CDW, CUW and KS) are shown in Table 3. The predicted C_0 (phytoplankton POC concentration) values in different water masses ranged from 13.4 to 23.5 (%), which are in agreement with the published phytoplankton culture data (*Thalassiosirawessflogii* (POC = 10.2–15.8 %); *Skeletonema sp.* (POC = 10.7–14.8 %); *Chaetocerosaffinis* (POC = 8.1–16.8 %), Tseng, 2010). In comparison, both derived C_0 and C_s in the ECS are in agreement with previously reported data by Sheu et al. (1995), Kao et al. (2003) and Tseng (2010). The results demonstrate

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that our interpretation using a two end-member mixing model to describe particle mixing in the East China Sea seems to give reasonable results.

Secondly, with the two end member values (C_s and C_0), we can use the Eq. (2) (see below) reported by Bloesch (1994), to estimate the ratio of resuspended particles to total sinking particles in the ECS.

$$R/T = (C_t - C_0)/(C_s - C_0) \quad (2)$$

where R represents the fraction of resuspended particles (mg L^{-1}, dry weight, dw) collected by a sediment trap, T: total entrapped sinking particles (mg L^{-1}, dw) collected by a sediment trap, C_t: organic fraction of observed sinking particles (%). With C_t, C_0, C_s, the ratio (R/T) of resuspended particles to entrapped sinking particles can be estimated from the Eq. (2). Consequently, the corrected POC flux can be calculated based on Eq. (3).

$$\text{Corrected (Corr.) POC flux} = \text{uncorrected POC flux} \times (1 - R/T) \quad (3)$$

The detailed data of R/T, uncorrected and corrected POC fluxes are summarized in Table 4. The predicted R/T in trapped particles the ECS ranged from approximately 49 % to 93 % with higher values in the inner shelf and lower values in the outer shelf suggesting that sediment resuspension is ubiquitous phenomenon in the ECS. The results are similar to the estimated resuspension ratios (70 ~ 94 %) in the Yellow Sea and the East China Sea (Guo et al., 2010). The corrected POC fluxes (41 ± 20 ~ 82 ± 38 mg C m^{-2} d^{-1}) in the outer and middle shelves gradually increased to 300 ± 151 ~ 956 ± 443 mg C m^{-2} d^{-1}, which are all lower than the PP values (Table 5) in the ECS, revealing that appropriate corrections for constraining POC fluxes in marginal seas are necessary.

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4 Discussion

4.1 Spatial POC variation and possible POC flux impact in the ECS

The good correlations between POC and Chl *a* (or TSM) are found in the most regions of the ECS, but there are some data (i.e. the data in the blue circle in Fig. 4a, b and d) away from the correlations. It is reasonable to predict that in situ phytoplankton species composition and abundance are mainly responsible for production of POC, thus result in good correlations among these parameters in the ECS. For example, Chang et al., (2003) reported strong spatial variation of carbon : Chl *a* values in the ECS with low values in the inner shelf and high values in the middle (or outer) shelves using the POC-Chl *a* regression (inner POC/Chl *a* : middle POC/Chl *a* = 13 : 93 g g^{-1}) and phytoplankton cell volume (inner POC/Chl *a* : middle POC/Chl *a* = 18 : 67 g g^{-1}). Chang et al. (2003) also suggested that carbon : Chl *a* variations are due to phytoplankton species difference and phytoplankton cell abundant. For example, *Skeletonema costatum* (followed by *Synechococcus* spp.), *Synechococcus* spp. (followed by *Pseudosolenia calcar-avis*) and *Trichodesmium* spp. (followed by nanoflagellates) are the main phytoplankton group contributing autotrophic carbon in the inner (75 % of autotrophic carbon), middle (79 % of autotrophic carbon) and outer (80 % of autotrophic carbon) shelves, respectively. Therefore, the insiders in the dotted circle in Fig. 4a, b and d could be the results of different phytoplankton species composition and cell abundance.

Particle resuspension is known in the shelf to play a major role in transporting carbon, but in the vicinity of large rivers, plumes containing fluvial particles can also influence POC fluxes. However, it is difficult to evaluate the contribution of fluvial POC from the Changjiang River without a suitable tracer such as aluminum in both suspended and sinking particles (Hsu et al., 2010). Alternatively, we can estimate the contribution of phytoplankton carbon to total carbon in the inner shelf using previously reported autotrophic carbon based on cell volume measurements (Chang et al., 2003). The phytoplankton carbon level in the inner shelf was 143 mg C m^{-3} and accounted for 47.7 % of POC concentration (~ 300 mg C m^{-3}, the detailed information can be found in Chang et al., 2003). Nevertheless, other factors, such as dead phytoplankton cells, zooplankton, resuspended particles, and fecal pellets are likely sources of POC in the water column. The result suggests that the Changjiang plume carrying fluvial particles in the water column of the inner shelf approximately contributes < 50 % to measured POC concentration.

As mentioned above, POC sources are mainly from in situ phytoplankton (also zooplankton) production, detritus, terrestrial input, and fluvial carbon. Recently, hypoxia zone (dissolved oxygen concentration < 62.5 µM) has been noticed in the estuarine and coastal regions of the East China Sea (Chen et al., 2007; Wang, 2009; Zhu et al., 2011), but the mechanisms for the occurrence of oxygen depletion is still unclear. Our data support the contention that high organic matter fluxes may consume oxygen in the near bottom waters off the Changjiang Diluted Water regions during the summer, as was reported by Chen et al. (2007) and Zhu et al. (2011). In other words, the very high POC fluxes in the inner shelf during the summer could be caused by the Changjiang River discharge (e.g. phytoplankton growth supporting by numerous nutrients, Gong et al., 2003, 2006) and/or resuspension of surface sediments (Table 1).

4.2 Sensitivity of the vertical particle mixing model

Two parameters, C_s and C_0, will affect the ratio of resuspended particles to total sinking particles in the Eq. (2). If we use the predicted C_s (C_s^1 in Table 2) and a fixed C_t and C_0, to estimate the R/T, the variation of R/T ranges from 4 % to 9 % suggesting that R/T is not significantly affected by C_s. However, some of derived C_s values are negative in the KW (Table 2), suggesting unreasonable extrapolation of the mixing model. For example, if we exclude the highest value (POC = 36.8 %) at station 14, the intercept (i.e. derived C_s) will be positive (0.36 %) which is similar to the POC value in the surface sediment in the ECS. Furthermore, some of derived Cs, mainly from the CDW, are higher than the observed POC values in the surface sediments of the ECS suggesting that discharge of suspended particles (with low carbon high TSM) of the Changjiang River could significantly affect the results besides bottom sediment resuspension (Zhu

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et al., 2006; Guo et al., 2010). These results illustrate that the derived C_s values need appropriate adjustment by field observed POC data in the sediments.

If we use a given C_0 ($S_0 = 0.25$, about 50 % of uncertainty) and a fixed C_t and C_s, to estimate the R/T, the variation of R/T ranges from 3 % to 51 % (on average: 28 %). If we change C_0 to ($S_0 = 0.75$) and fix C_t and C_s, the variation of R/T ranges from 4 % to 51 % (on average: 29 %). The results suggest that C_0 is more sensitive than C_s. If we use $S_0 = 0.5\,\mathrm{mg\,L^{-1}}$ to estimate R/T, then the predicted C_0will be 13.4 % to 21.9 % which are very close to the phytoplankton culture data (10–17 %, Tseng, 2010). Overall, the vertical mixing model is a simple approach to effectively constrain the effect of resuspended particles on POC flux, but it is not a perfect tool.

4.3 Possible carbon export in the outer shelf of the ECS

Taking into account this cavity, we found nonetheless that the POC flux in the ECS have been constrained by the vertical mixing model. However, as discussed above, suspended particle discharge from the Changjiang River may affect the POC flux calculation in the inner shelf. So, herein we only attempt to estimate POC export in the outer shelf (i.e. Stations 10 and 26). The POC buried in the sediment of Stations 10 and 26 (i.e. the outer shelf) is approximately 9 and 5 $\mathrm{mg\,C\,m^{-2}\,d^{-1}}$, respectively (Tseng, 2010). The remineralization carbon in the outer shelf is approximately 6 $\mathrm{mg\,C\,m^{-2}\,d^{-1}}$, according to organic phosphorous remineralization to carbon ratio (Fang et al., 2007). As a result, the POC exports in the outer shelf of the ECS are roughly 26 and 33 $\mathrm{mg\,C\,m^{-2}\,d^{-1}}$, respectively. The carbon export rate (i.e. e ratio = POC flux /PP = $0.04 \pm 0.02 \sim 0.10 \pm 0.05$, Table 5) in the outer shelf is similar to that in the oligotrophic ocean, when compared to other investigations (Hung and Gong, 2007, e ratio = 0.05 ~ 0.11 in the oligotrophic Kuroshio water; Guo et al., 2010, e ratio = 0.18 in the middle shelf of the ECS). Particles can be carried out the ECS in the bottom turbid layer to remote regions (Hoshika et al., 2003) and/or enter the open ocean interior or partly deposited near northern Okinawa Trough (Fig. 1).

Besides the carbon export in the outer shelf of the ECS, we also find that higher carbon export rate (e ratio = 10–50 % for CDW and 89 % for CUW) in the CDW and CUW regions. The higher carbon export rate in the CDW regions is mainly caused by strong phytoplankton primary production because of high nutrient supply from the Changjiang River and/or partly from the Changjiang plume carrying fluvial particles. The high e-ratios in this study are similar to the reported values in the middle Yellow Sea and in the upwelling region off Zhejiang by Guo et al. (2010). While the nutrient supply in the CUW is not pronounced, the question arises as to why the carbon export rate is so high? Possible explanations are: (1) PP is limited by light intensity (due to high suspended particles, TSM $> 1 \sim 2\,\text{mg}\,\text{L}^{-1}$), (2) nutrient limitation in the surface layer or (3) strong vertical mixing (e.g. water un-stabilization). Regardless of the POC flux values in the inner shelf, one will ask another question: where is the carbon going? This study indeed provides quantitative POC flux data, but it is difficult to compare it with direct evidence. Another possible transport pathway in the inner shelf would be south, along the coast, with eventual burial in the southern Okinawa Trough (Liu et al., 2000). According to Berelson (2002), the average settling velocity of particles in the ocean ranges from 100 to $300\,\text{m}\,\text{d}^{-1}$. Given that the water depth in the ECS ranges from 30 to 200 m, particles would settle in a day or less. In other words, particles are being transported, undergo continuous sinking and resuspension in the bottom turbid layer (Hoshika et al., 2003) or to the bottom of sediments. Tsai (1996) also reported that when tidal currentsflow eastward in the southern ECS, the suspended particulate matter flux is elevated, revealing that tidal currents are an important mechanism for transporting particles from marginal seas to the open ocean. Therefore, we suggest that lateral POC transport is driven by the interactions of surface sediment resuspension with tidal currents, or contour currents or via isopycnal diffusion. Apparently, fine particles did not accumulate in the middle shelf (Kao et al., 2003), suggesting that these fine particles were transported elsewhere.

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4.4 Comparing short-time measurements of POC fluxes and PP values with long-time estimates of ^{234}Th-derived POC fluxes and satellite-derived PP

In this study, one may ask questions if short-time (hours ~ day) measurements of sediment trap measured POC fluxes and C-14 incubation PP values are reliable? First, sediment traps are often used to measure POC flux directly, despite possible biases by hydrodynamic and biological effects (Gardner, 1980; Gardner et al., 1983; Lee et al., 1988; Karl and Knauer, 1989). Furthermore, Marty et al. (2009) reported that short-term fluctuations of POC fluxes were quite obvious with a diel periodicity: higher POC fluxes during night period and lower POC fluxes during day period. However, Li (2009) investigated POC fluxes using a time-series (4, 8, 12 and 24 h) of trap deployments in the East China Sea and found no significant difference in POC flux between night and day. Hung et al. (2010) also reported that daytime POC fluxes (08:00 a.m. to 05:00 p.m.) at 120 m and 150 m in the outer shelf of the ECS off northeastern Taiwan in 2008 were $46 \pm 7\,\mathrm{mg\,C\,m^{-2}\,d^{-1}}$ and $48 \pm 8\,\mathrm{mg\,C\,m^{-2}\,d^{-1}}$, respectively. Night time POC fluxes (12:00 a.m. to 09:00 a.m.) at the same depths were $53 \pm 9\,\mathrm{mg\,C\,m^{-2}\,d^{-1}}$ and $44 \pm 7\,\mathrm{mg\,C\,m^{-2}\,d^{-1}}$, respectively. The inconsistent field observations may reflect the fact that POC fluxes are affected by both physical and biological processes simultaneously. Moreover, the trapping efficiency of sediment traps is variable and it may also give additional uncertainties to our estimate of the POC fluxes in the ECS.

Besides sediment traps, ^{234}Th has been increasingly used as a tracer to estimate POC flux due to its timescales (weeks to month) in surface water (Coale and Bruland, 1985; Santschi et al., 2006) based on calculation of the product of the POC/^{234}Th ratio in sinking particles and the ^{234}Th flux. Although both methods have their uncertainties (see review in Buesseler et al., 2006, 2007; Hung and Gong, 2010; Hung et al., 2012), recent studies have shown that both methods are complementary means for estimating POC flux in the upper ocean in different marine environments including the East China Sea, the Kuroshio, the South China Sea, the Gulf of Mexico, the oligotrophic northwestern Pacific Ocean (Hung and Gong, 2007; Li, 2009; Hung et al., 2004, 2010; Wei et al., 2011). The POC fluxes measured by sediment traps and ^{234}Th approaches in the Kuroshio, the Gulf of Mexico, and the South China Sea are in good agreement if the ratio of POC/^{234}Th is appropriately selected. These results support that our short-time sediment trap method is reliable.

Secondly, short-time (hours incubation) PP experiment was conducted in the East China Sea covering all four seasons by Gong et al. (2003) and the results showed seasonal variations with elevated values in the inner shelf of the ECS and low values in the outer shelf of the ECS. For example, PP values in the southern East China Sea off the northeastern Taiwan were approximately 400 ~ 500 mg C m^{-2} d^{-1} in summer under good weather conditions. In comparison, Siswanto et al. (2009) reported that satellite-derived PP value in the southern East China Sea in summer in 2005 under non-typhoon conditions was approximately 500 mg C m^{-2} d^{-1} which is in good agreement with the PP values. Recently, Hung et al., (2010) reported that PP values estimated by the model (1283 mg C m^{-2} d^{-1}, Behrenfeld and Falkowski, 1997) and by C-14 incubation (1773 mg C m^{-2} d^{-1}, Gong et al., 2003) in the southern ECS in 2007 are quite comparable if the analytical uncertainty (20–30 %) is considered. In other words, data (POC fluxes and PP values) obtained from short-term measurements by sediment traps and C-14 incubation are comparable to long-term methods such as ^{234}Th-derived approaches and satellite-derived PP values.

5 Conclusions

This study involved direct measurement of POC fluxes and primary production in the East China Sea. It was found that some of POC fluxes were higher than primary production, suggesting that the elevated POC fluxes might be overestimated due to strong sediment resuspension and nepheloid layer transport processes. A vertical particle mixing model was used to correct effects of bottom sediment resuspension. The corrected POC fluxes in the inner, middle and outer shelves thus obtained were 300±151 ~ 956±443, 82±38 and 42±20 mg C m^{-2} d^{-1}, respectively. While the vertical

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mixing model is still not a perfect model to accurately determine sediment resupension fluxes, because it ignored biological degradation of sinking particles, terrestrial, fluvial input and lateral transport, it does result in reasonable quantitative estimates of export fluxes. It is a first step towards the development of a better model to calibrate POC flux in a high-suspended marine environment, which is needed because carbon cycling in the marginal sea is more complex than previously thought.

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Table 1. Parameters of bottom depth, euphotic zone (EZ) depth, uncorrected POC flux, and primary production (PP) in the ECS.

Water mass	Station	Bottom (m)	EZ (m)	Trap depth (m)	Uncorr. POC flux ($mg\,C\,m^{-2}\,d^{-1}$)	PP ($mg\,C\,m^{-2}\,d^{-1}$)
CDW	S18	47	15	20	3900	1897
CDW	S19	38	22	20	7300	3045
SMW	S28	60	50	30	200	600
CDW	S29	57	26	20	750	3377
CUW	S5	51	36	20	720	337
KW	S10	154	90	120	80	1153
KW	S26	118	74	100	150	442

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Table 2. POC in sediments in the ECS based on different studies and a selection of an average Cs (= (Cs^2 + Cs^3+Cs^4)/3) with a standard deviation from Cs^2, Cs^3 and Cs^4.

Water mass	Station	Cs^1 (%)	Cs^2	Cs^3	Cs^4	Avg. Cs ±1δ (%)
			(POC in surface sediment)			
CDW	S18	2.1	0.19 %	0.67 %	0.52 %	0.46 ± 0.25
CDW	S19	2.1	0.66 %	0.19 %	0.12 %	0.32 ± 0.29
SMW	S28	2.1	0.38 %	0.29 %	0.22 %	0.30 ± 0.08
CDW	S29	2.1	0.27 %	0.28 %	0.20 %	0.25 ± 0.04
CUW	S5	0.1	0.45 %	0.88 %	0.46 %	0.60 ± 0.25
KW	S10	−0.9	0.29 %	0.42 %	0.15 %	0.29 ± 0.14
KW	S26	−0.9	0.28 %	0.23 %	0.07 %	0.19 ± 0.11

[1] Model estimated values.
[2] Sheu et al. (1995).
[3] Kao et al. (2003).
[4] This study.

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Table 3. Statistical data of linear regressions of POC values versus the reciprocal of total suspended matter concentrations in the East China Sea. The unit of C_s and C_0 is %. C_0 (max) and C_0 (min) represent the minimum and maximum derived POC concentrations of phytoplankton.

Water mass	Station	Slope $S_0(C_0 - C_S)$	Intercept (C_S)	C_0 ($S_0 = 0.5$)	C_0 (max) ($S_0 = 0.25$)	C_0 (min) ($S_0 = 0.75$)
CDW	S18	10.7	0.46	23.5	44.9	16.4
CDW	S19	10.7	0.32	23.5	44.9	16.4
SMW	S28	10.7	0.30	23.5	44.9	16.4
CDW	S29	10.7	0.25	23.5	44.9	16.4
CUW	S5	6.4	0.60	13.4	26.2	9.1
KW	S10	6.9	0.29	14.1	27.9	9.5
KW	S26	6.9	0.19	14.1	27.9	9.5

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Table 4. Detailed values of Ct, R/T, uncorrected POC flux (Uncorr. POC flux) and corrected POC flux (Corr. POC flux ± uncertainty) in the different areas of the ECS.

Water mass	Station	Ct (%)	R/T (%)	Uncorr. POC flux ($mg\,C\,m^{-2}\,d^{-1}$)	Corr. POC flux ($mg\,C\,m^{-2}\,d^{-1}$)
CDW	S18	6.1	75	3900	956 ± 443
CDW	S19	2.0	93	7300	520 ± 240
SMW	S28	9.9	59	200	82 ± 38
CDW	S29	11.2	53	750	354 ± 162
CUW	S5	5.9	58	720	300 ± 151
KW	S10	7.3	49	80	41 ± 20
KW	S26	4.2	71	150	43 ± 21

Note: the uncertainty of the calculated fluxes was based on the standard deviation of three C_0 values (C_0, C_0 (min), C_0 (max)).

Table 5. Data ofcorrected POC flux (POC flux), primary production (PP) and e-ratio (POC flux/PP) in the ECS.

Water mass	Station	Bottom (m)	EZ (m)	Trap depth (m)	POC flux ($mg\,C\,m^{-2}\,d^{-1}$)	PP ($mg\,C\,m^{-2}\,d^{-1}$)	e-ratio
CDW	S18	47	15	20	956 ± 443	1897	0.50 ± 0.23
CDW	S19	38	22	20	520 ± 240	3045	0.17 ± 0.08
SMW	S28	60	50	30	82 ± 38	600	0.14 ± 0.06
CDW	S29	57	26	20	354 ± 162	3377	0.10 ± 0.05
CUW	S5	51	36	20	300 ± 151	337	0.89 ± 0.45
KW	S10	154	90	120	41 ± 20	1153	0.04 ± 0.02
KW	S26	118	74	100	43 ± 21	442	0.10 ± 0.05

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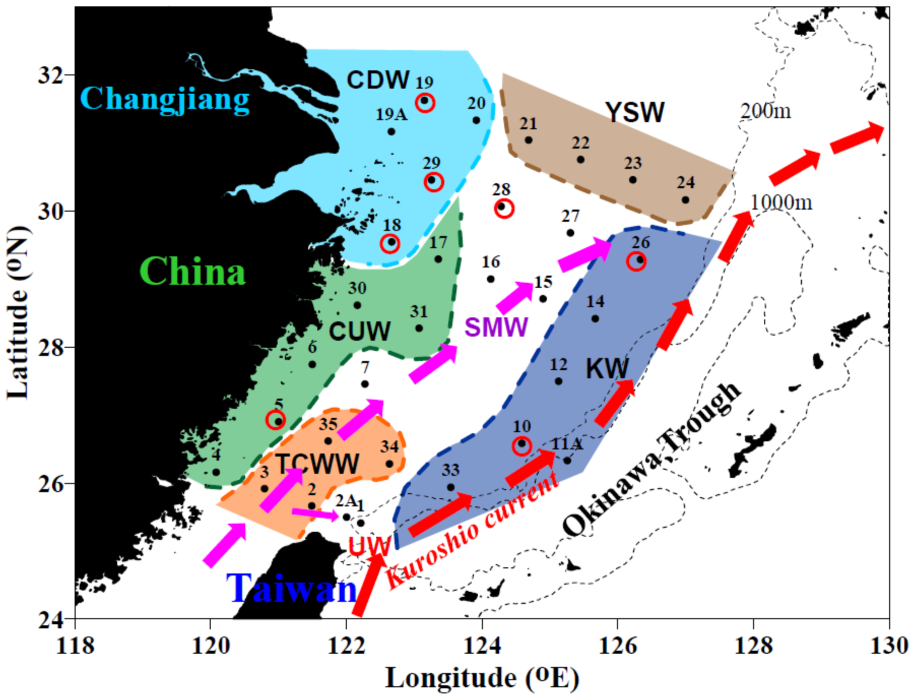

Fig. 1. Sampling locations (black dots) of hydrography in the East China Sea. The dashed band with red arrows represents the main stream of the Kuroshio Current and the pink arrows represent the Taiwan Warm Current in summer. Red-circles indicate the sediment trap deployment stations in summer 2007. CDW: Changjiang Diluted Water, YSW: Yellow Sea Water, CUW: Coastal Upwelling Water, TCWW: Taiwan Current Warm Water, UW: Kuroshio Upwelling Water, KW: Kuroshio Water, SMW: Shelf Mixing Water (after Liu et al., 2000; Kao et al., 2003; Chou et al., 2009a).

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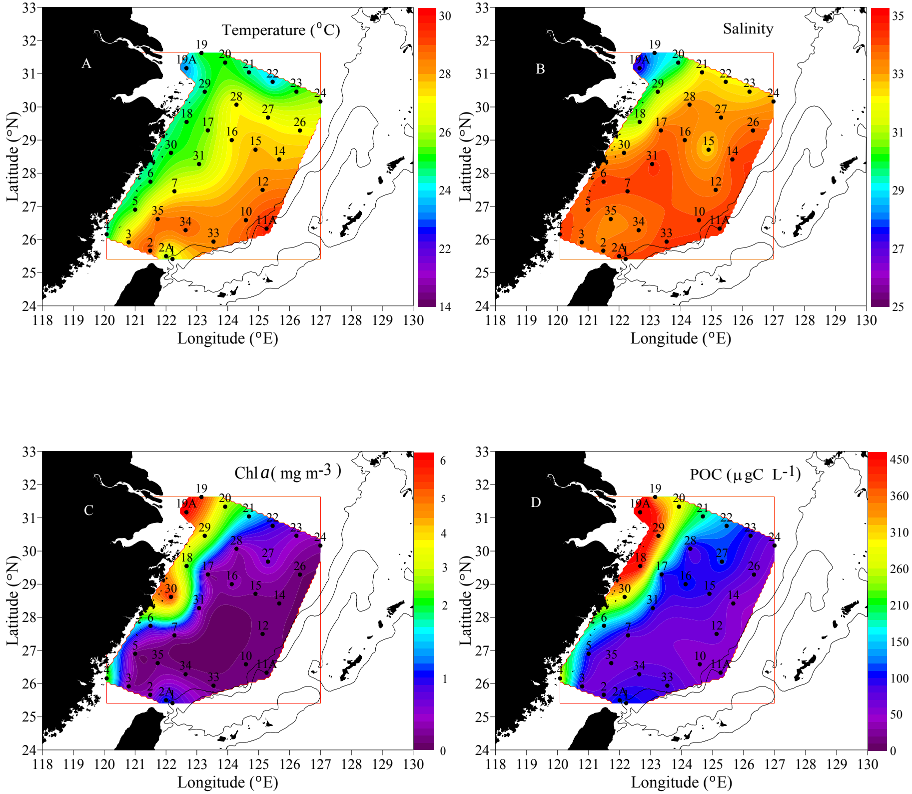

Fig. 2. Contours of surface temperature **(A)**, salinity **(B)**, chlorophyll (Chl *a*) concentration **(C)** and POC concentrations **(D)** in the East China Sea in summer 2007, respectively.

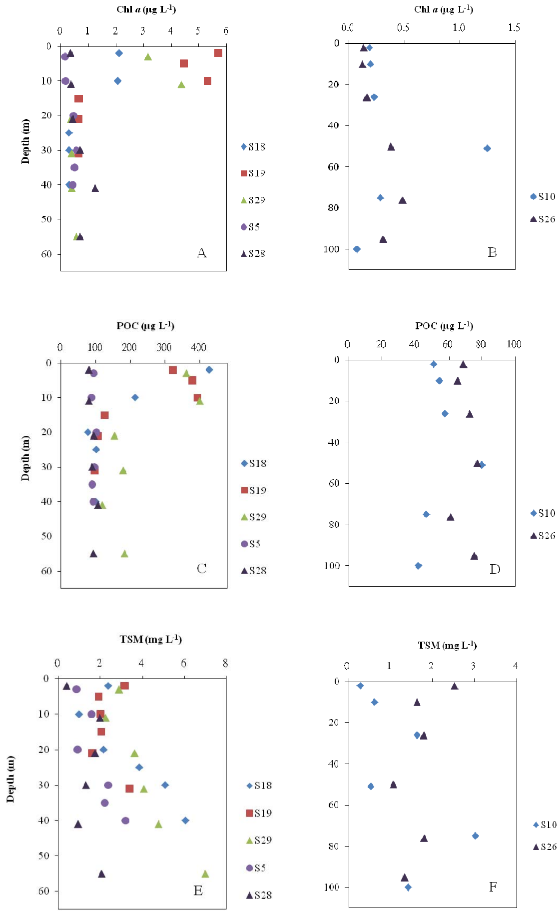

Fig. 3. Distributions of vertical Chl *a*, POC concentrations and total suspended matter (TSM) concentrations in the inner shelf (S18, S19, S29, S5, and S28) and the outer shelf (S10 and S26) of the East China Sea.

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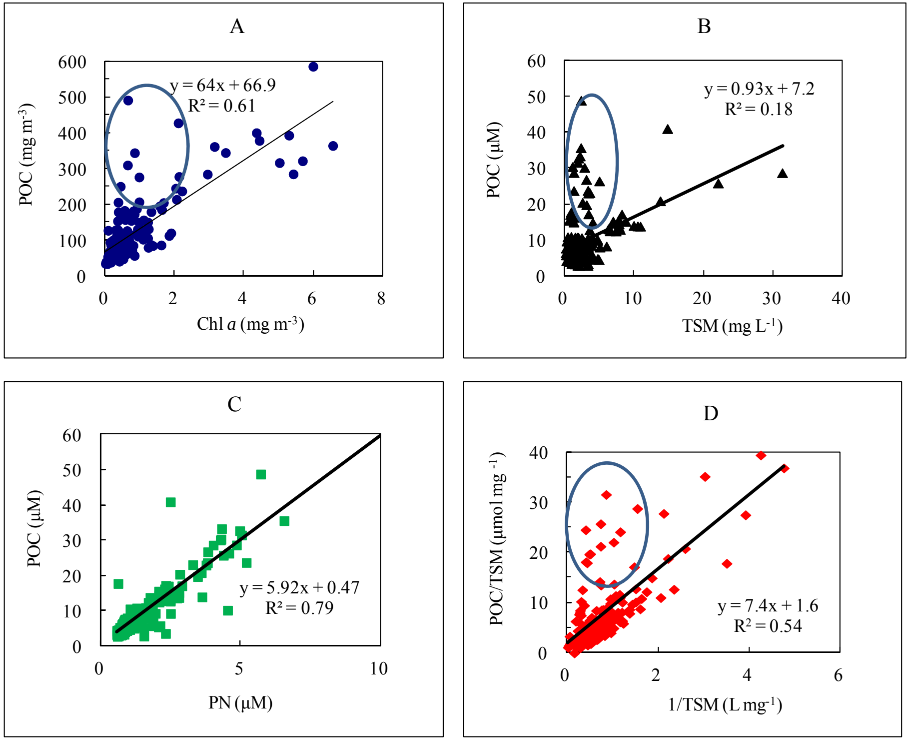

Fig. 4. (A) Relationship between POC concentrations and Chl *a* concentrations in the ECS. **(B)** Relationship between POC concentrations and TSMconcentrations in the ECS. **(C)** Relationship between POC concentrations and PN concentrations in the ECS. **(D)** Relationship between POC/TSM and 1/TSM in the ECS.

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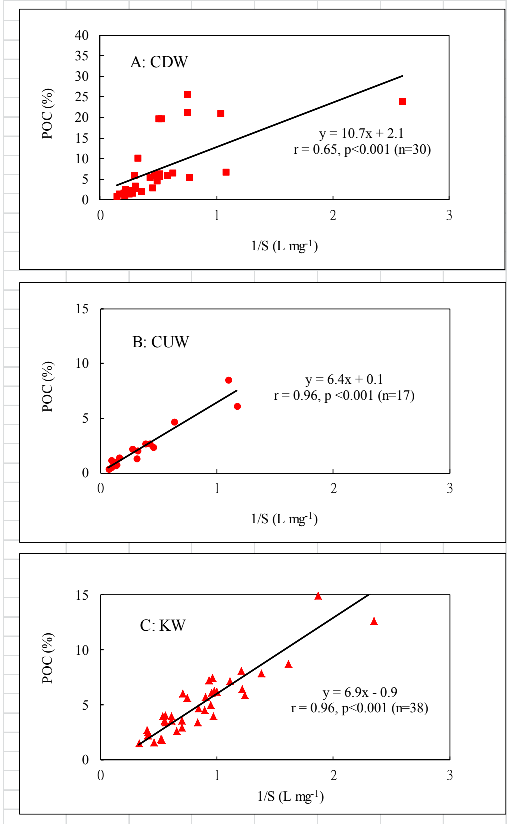

Fig. 5. (A) Relationships between POC (%) and 1/S (1/TSM) in the CDW of the ECS. **(B)** Relationship between POC (%) and 1/S in the CUW of the ECS. **(C)** Relationship between POC (%) and 1/S in the KW of the ECS.