



Biogeochemical characteristics of suspended particulate matter in deep chlorophyll maximum layers in the southern East China Sea

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Abstract. Continental shelves and marginal seas are key sites of particulate organic matter (POM) production, remineralization and sequestration, playing an important role in the global carbon cycle. Elemental and stable isotopic compositions of organic carbon and nitrogen are thus frequently used to characterize and distinguish POM and its sources in suspended particles and surface sediments in the marginal seas. Here we investigated suspended particulate matter (SPM) collected around deep chlorophyll maximum (DCM) layers in the southern East China Sea for particulate organic carbon and nitrogen (POC and PN) contents and their isotopic compositions ($\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$) to understand provenance and dynamics of POM. Hydrographic parameters (temperature, salinity and turbidity) indicated that the study area was weakly influenced by freshwater derived from the Yangtze River during summer 2013. Elemental and isotopic results showed a large variation in $\delta^{13}\text{C}_{\text{POC}}$ (-25.8 to -18.2‰) and $\delta^{15}\text{N}_{\text{PN}}$ (3.8 to 8.0‰), but a narrow molar C/N ratio (4.1 – 6.3) and low POC/Chl *a* ratio ($< 200 \text{ g g}^{-1}$) in POM, and indicated that the POM in DCM layers was newly produced by phytoplankton. In addition to temperature effects, the range and distribution of $\delta^{13}\text{C}_{\text{POC}}$ were controlled by variations in primary productivity and phytoplankton species composition; the former explained $\sim 70\%$ of the variability in $\delta^{13}\text{C}_{\text{POC}}$. However, the variation in $\delta^{15}\text{N}_{\text{PN}}$ was controlled by the nutrient status and $\delta^{15}\text{N}_{\text{NO}_3^-}$ in seawater, as indicated by similar spatial distribution between $\delta^{15}\text{N}_{\text{PN}}$ and the cur-

rent pattern and water masses in the East China Sea; although interpretations of $\delta^{15}\text{N}_{\text{PN}}$ data should be verified with the nutrient data in future studies. Furthermore, the POM investigated was weakly influenced by the terrestrial OM supplied by the Yangtze River during summer 2013 due to the reduced sediment supply by the Yangtze River and north-eastward transport of riverine particles to the northern East China Sea. We demonstrated that the composition of POM around DCM layers in the southern East China Sea is highly dynamic and largely driven by phytoplankton abundance. Nonetheless, additional radiocarbon and biomarker data are needed to re-evaluate whether or not the POM around the DCM water depths is influenced by terrestrial OM in the river-dominated East China Sea.

1 Introduction

Stable isotopes of organic carbon and nitrogen ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) and molar carbon to nitrogen (C/N) ratios are natural tracers frequently used to identify the source and fate of terrestrial organic matter (OM) in the estuarine and marine environments (Meyers, 1994; Hedges et al., 1997; Goñi et al., 2014; Selvaraj et al., 2015). This approach is based on the significant difference in $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N ratios between different end-members (e.g. terrestrial and marine), and the assumption that only a physical mixing of OM from compo-

sitionally distinct end-members occurs in these marginal settings (Thornton and McManus, 1994; Hedges et al., 1986). Quantifying the relative contributions of end-members using mass balance models thus requires known and constant elemental and isotopic values of end-members and major sources of OM in the study region (e.g. Goñi et al., 2003). Therefore, application of mixing models for the discrimination of OM sources requires clearly identified representative values for local OM sources. However, in most cases, end-member values of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and molar C/N ratios are represented by “typical” numbers, such as ca. -20 and -27‰ for $\delta^{13}\text{C}$ of marine phytoplankton and terrestrial plants (Kandasamy and Nagender Nath, 2016, and references therein), respectively, but without measuring discrete end-member values in real, local or regional OM source materials. For example, a number of earlier studies failed to measure isotopic values of marine phytoplankton despite using end-member mixing models to distinguish marine versus terrestrial OM in surface sediments (e.g. Kao et al., 2003; Wu et al., 2013), or these numbers were simply represented by values of particulate organic matter (POM) in surface waters in the studied system (e.g. Zhang et al., 2007) or elsewhere from other ocean basins (e.g. Hale et al., 2012). It is known that stable isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) and molar C/N ratios of POM in estuarine and marine areas are representative of primary production-derived OM when POM are mostly derived from phytoplankton biomass (Gearing et al., 1984). Since phytoplankton are the main primary producer of marine OM, the elemental and isotopic compositions of phytoplankton should therefore be considered while studying the dynamics of POM in the marine water column.

Chlorophyll *a* (Chl *a*) concentration in seawater is often used as an index of phytoplankton biomass (Cullen et al., 1982). The deep chlorophyll maximum (DCM) layer, which contributes significantly to the total biomass and primary production in the whole water column (Weston et al., 2005; Sullivan et al., 2010), is approximately equal to the subsurface biomass maximum layer (e.g. Sharples et al., 2001; Ryabov et al., 2010). The formation of maximum chlorophyll concentration at the DCM layer has been explained by several mechanisms: the differential zooplankton grazing with depths (Riley et al., 1949; Lorenzen, 1967; Pilati and Wurtsbaugh, 2003), adaption of phytoplankton to light intensities or to increased concentration of nutrients (Nielsen and Hansen, 1959; Gieskes et al., 1978; Hickman et al., 2012), chlorophyll accumulation by sinking detritus of phytoplankton (Gieskes et al., 1978; Karlson et al., 1996), decomposition of chlorophyll by light (Nielsen and Hansen, 1959), and wind-driven nitrate supply and nitrate uptake in seasonally stratified shelf seas (Hickman et al., 2012; Williams et al., 2013). The DCM layer is common in both coastal and open oceans, occurring at relatively shallow depths (1–50 m) in coastal seas, but at greater depths (80–130 m) in the open ocean (Cullen et al., 1982; Gong et al., 2015), and often variable in time and space (Karlson et al., 1996). For example,

the DCM layers were reported at depths of 30–50 m across the shelf in the southern East China Sea (ECS) during summer from 1991 to 1995 (Gong et al., 2010). Hence, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and molar C/N ratios of POM in the DCM layers of the continental shelf waters should reflect the $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and molar C/N ratios of phytoplankton (Savoye et al., 2003, 2012; Gao et al., 2014).

The East China Sea is one of the largest marginal seas in the world, receiving huge quantities of freshwater ($905.1\text{ km}^3\text{ yr}^{-1}$; Dai et al., 2010) and organic C (2.93 Tg C yr^{-1} , $\text{Tg}=10^{12}\text{ g}$; Qi et al., 2014) from the Yangtze River (Changjiang). Nutrient-rich freshwater inputs in turn stimulate the water column productivity in coastal waters compared to the open ocean. Annual primary production over the entire shelf of the East China Sea is high relative to other marginal seas and was estimated to be 85 Tg C yr^{-1} in 2008 (Tan et al., 2011). Several studies have been carried out on the physical, chemical and biological aspects of the East China Sea, including distributions of seasonal currents (e.g. Gong et al., 2010), chemical hydrography and nutrient distribution (Chen, 1996, 2008), and phytoplankton species composition in the water column (e.g. Zheng et al., 2015; Jiang et al., 2015). Likewise, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and molar C/N ratios of POM have been determined for a limited number of transects across the East China Sea (e.g. Wu et al., 2003, 2007a) as well as in a wide area of the western North Pacific marginal seas (Chen et al., 1996). Nonetheless, studies on elemental ratios and stable isotopic compositions of POM in DCM layers in the continental shelf of the East China Sea, especially along the indirect transport pathway of the Yangtze-derived terrestrial material to the Okinawa Trough (Chen et al., 2017), are poorly studied. A recent study in the northern East China Sea investigated elemental and isotopic compositions of POM in the surface, DCM and bottom layers on both seasonal and inter-annual timescales (Gao et al., 2014); however, there was minimal attention given to biogeochemical processes associated with the DCM. Here, we investigate $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and molar C/N ratios of suspended POM around the DCM layer in the continental margin of the East China Sea, in particular the area south of the Yangtze estuary, aiming (1) to comprehend the sources of POM in DCM layers and (2) to understand the factors controlling $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ dynamics in DCM layers of the southern East China Sea.

2 Study area

The East China Sea (Fig. 1) is the largest river-dominated marginal sea in the north-western Pacific region (Chen et al., 2017). The ECS shelf is wide ($> 500\text{ km}$), but relatively shallow ($< 130\text{ m}$) with an average water depth of 60 m (Gong et al., 2003; Liu et al., 2006). The Yangtze River (Fig. 1), with a catchment area of more than $1.94 \times 10^6\text{ km}^2$ (Liu et al., 2007), is the main source of freshwater and sediment to the continental shelf. It is the fifth largest river in terms of water

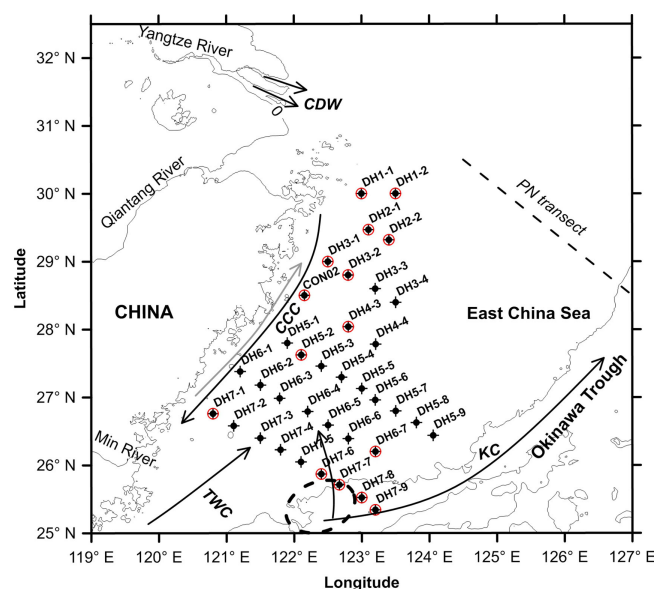


Figure 1. Map showing the locations of suspended particulate matter (SPM) collected around the deep chlorophyll maximum (DCM) layer from the East China Sea during summer (22 June–21 July) 2013 for the present investigation. Also shown is the modern current pattern in the East China Sea. Red circles mark the SPM samples that were collected from the water depths either below or above but mostly contiguous to the DCM layer. CDW – Changjiang Diluted Water, CCC – China Coast Current, TWC – Taiwan Warm Current and KC – Kuroshio Current. The dashed ellipse represents the center of Kuroshio upwelling, occurring due to an abrupt change in the bottom topography, in the north-east of Taiwan Island (Wong et al., 2000). Also shown is the PN transect, a cross-shelf transect in the East China Sea in which particulate organic matter dynamics is relatively well studied.

discharge ($900 \text{ km}^3 \text{ yr}^{-1}$) and the fourth largest river in terms of sediment discharge (470 Mt yr^{-1}) in the world (Milliman and Farnsworth, 2011).

In addition to the huge inputs of nutrients (dissolved inorganic nitrogen, DIN: $61.0 \pm 13.5 \times 10^9 \text{ mol yr}^{-1}$ for the interval of 1981–2006; Chai et al., 2009) and sediments from the Yangtze River, the ECS is characterized by a complex circulation pattern that is largely driven by the seasonally reversing East Asian monsoon winds (He et al., 2014; Chen et al., 2017). The surface circulation in the shelf is characterized by the south–north China Coastal Current (CCC) in the west, northward-moving Taiwan Warm Current (TWC) in the central part and the north-eastward-flowing Kuroshio Current (KC) in the east (Fig. 1) (Liu et al., 2006). The Changjiang Diluted Water (CDW) is a mixture of Yangtze River freshwater and the East China Sea shelf water and is characterized by a low salinity (< 30 , Umezawa et al., 2014). Owing to a huge amount of freshwater discharge from the Yangtze into the ECS, it is thought that the CDW is the main component of CCC (Fig. 1). Because of the East Asian monsoon, where there is a strong north-east monsoon in winter and

a weaker south-west monsoon in summer, the CDW flows southward along the coastline of mainland China as a narrow jet in winter (Chen, 2008; Han et al., 2013), whereas the same spreads mainly to the north-east in summer (Isobe et al., 2004). The TWC is a mixture of the warm water from the Taiwan Strait and intruding saline Kuroshio water; the latter is thought to be the most dominant source of heat and salt to the ECS (Su and Pan, 1987; Zhou et al., 2015). In addition, Kuroshio Subsurface Water (KSSW) is upwelled in the north-east off Taiwan Island due to an abrupt change in seafloor topography at the ECS outer shelf (dashed ellipse in Fig. 1) (Su et al., 1990; Sheu et al., 1999). The upwelled, oxygen-undersaturated KSSW is characterized by low temperature, high salinity and high nutrients (Liu et al., 1988; Wong et al., 1991). The water exchange rate between the ECS water and Kuroshio water was estimated to be about $22\,000 \pm 9000 \text{ km}^3 \text{ yr}^{-1}$, which is approximately 25 times the amount of Yangtze run-off into the ECS (Li, 1994; Sheu et al., 1999). Furthermore, Kuroshio water accounts for up to 90 % of the shelf water in the ECS (Chen, 1996; Sheu et al., 1999).

The primary productivity in the ECS is limited by nitrogen in summer, but light in winter (Chen et al., 2001; Chen and Chen, 2003). With the highest primary production during summer, annual primary production showed distinct spatial and temporal variations of 155, 144 and $145 \text{ g C m}^{-2} \text{ yr}^{-1}$ in the north-western ECS, south-eastern ECS and the entire ECS, respectively, in 1998 (Gong et al., 2003). The primary productivity has, however, decreased by 86 % between 1998 and 2003 due to a large number of impoundments in the drainage basin of Yangtze River (Gong et al., 2006).

3 Materials and methods

3.1 Sample collection

To investigate the biogeochemical characteristics of POM in the DCM layer of the southern East China Sea, suspended particles around the DCM water depths (10–130 m; Table 1) were collected from 36 stations along 7 transects across the continental shelf by the *Science 3* cruise during summer (22 June–21 July) 2013 (Fig. 1). At each site, the physical properties of the water column were recorded by a conductivity–temperature–depth (CTD) rosette (Seabird, SBE911+) fitted with a Seapoint chlorophyll fluorometer to detect the fluorescence maximum (see Table S1 in the Supplement for the whole dataset). Seawater was collected using the rosette of Niskin water bottles attached to the CTD frame, and then stored in 5 L PVC bottles. All PVC bottles had been soaked in 0.1 M HCl and then cleaned by distilled water. The volume of each water sample was measured by graduated cylinder before filtration. Suspended particles were obtained by filtering 4.1–19.1 L of seawater collected around the fluorescence maximum layer through $0.7 \mu\text{m}/47 \text{ mm}$ What-

Table 1. Summary statistics of elemental and isotopic compositions, as well as C / N and POC / Chl *a* ratios, of suspended particulate matter (SPM) around DCM layers in the southern East China Sea ($n = 36$). Chl *a* is the converted value using the linear relationship between measured Chl *a* and chlorophyll fluorescence. SD = standard deviation.

	Sampling depth (m)	SPM (mg L ⁻¹)	POC (μg L ⁻¹)	PN (μg L ⁻¹)	δ ¹³ C _{POC} (‰)	δ ¹⁵ N _{PN} (‰)	C / N molar	POC / Chl <i>a</i> (g g ⁻¹)
Minimum	10	1.7	20.4	4.4	-25.8	3.8	4.1	33.3
Maximum	130	14.7	263.0	52.8	-18.2	8.0	6.3	303.3
Mean	45	4.4	85.5	17.7	-23.0	6.1	5.6	100.3
SD	21	2.7	49.5	9.9	1.5	1.0	0.5	51.8

man glass fiber filters (GF/F), which were wrapped in aluminium foil. The filtration was under an ultimate pressure of 0.08 MPa to avoid the rupturing of phytoplankton cells (Steinman et al., 2017). All filters had been pre-combusted at 450 °C for 4 h in a muffle furnace to remove the background carbon and pre-weighed to determine the concentration of suspended particulate matter (SPM). After filtration, filters were folded without rinsing, wrapped again in aluminium foil and then immediately stored at -20 °C in a freezer on-board before they were brought back to the laboratory for further analysis.

3.2 Determination of SPM concentration and analyses of Chl *a*, POC, PN, δ¹³C and δ¹⁵N

In the laboratory, filters with suspended particles were freeze-dried and then dried in an oven at 50 °C for 48 h. The weight difference between the dried filter and the same filter before the filtration was used to calculate the weight of SPM. Five SPM samples (DH1-2, DH2-1, DH3-1, DH7-1 and DH7-7; Fig. S1) from water depths ranging between 20 and 50 m were randomly selected for the measurement of chlorophyll *a* (Chl *a*) concentration. Chlorophyll *a* was extracted using 90 % acetone and then determined spectrophotometrically according to Lorenzen (1967) and Aminot and Rey (2000). Briefly, the absorbance of sample extraction was measured at 665 and 750 nm against a 90 % acetone blank before (E665_o, E750_o) and after (E665_a, E750_a) acidification with 1 % HCl by the UV-Vis spectrophotometer (UV 1800, Shimadzu). Chl *a* concentration (μg L⁻¹) was calculated as follows: Chl *a* = $11.4 \times 2.43 \times ((E665_o - E750_o) - (E665_a - E750_a)) \times V_e / L \times V_f$, where V_e and V_f were the volumes of sample extraction and filtered seawater (mL), respectively, and L was the cuvette light path (cm) (Aminot and Rey, 2000).

Prior to the measurement of POC and PN contents and their stable isotope values (δ¹³C_{POC} and δ¹⁵N_{PN}) in SPM samples, a half of each filter was placed in a culture dish and 3 mL of 1 N HCl was then added into the dish by a dropper. These were allowed to react for 16 h to remove inorganic carbon (mainly carbonate). The de-carbonated sample was dried at 50 °C for 48 h in an oven for HCl evaporation. Then a half of the de-carbonated filter (i.e. a quarter

of the original filter, ~ 11 mm) was then punched and placed in tin capsules for further analysis. The POC and PN contents and their δ¹³C_{POC} and δ¹⁵N_{PN} compositions were measured at the Stable Isotope Facility of University of California Davis in the USA, by using an elemental analyser (EA) (Elementar Analysensysteme GmbH, Hanau, Germany) interfaced to a continuous flow isotope ratio mass spectrometer (IRMS; PDZ Europa 20-20, Sercon Ltd., Cheshire, UK). During the isotope (δ¹³C_{POC} and δ¹⁵N_{PN}) analyses, different working standards (bovine liver, glutamic acid, enriched alanine and nylon 6) that were compositionally similar to the samples were used and were calibrated against NIST Standard Reference Materials (IAEA-N1, IAEA-N2, IAEA-N3, USGS-40 and USGS-41). The standard deviation was 0.2 ‰ for δ¹³C and 0.3 ‰ for δ¹⁵N. Isotopic values were presented in standard δ-notation as per mille deviations relative to the conventional standards, i.e. VPDB (Vienna Pee Dee Belemnite) for carbon and atmospheric N₂ for nitrogen, that is $\delta X (\text{‰}) = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \times 10^3$, where $X = ^{13}\text{C}$ or ^{15}N , $R = ^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$, R_{sample} and R_{standard} are the heavy (^{13}C or ^{15}N) to light (^{12}C or ^{14}N) isotope ratios of sample and standard, respectively (e.g. Selvaraj et al., 2015).

Lorrain et al. (2003) cautioned that the measurement of PN and δ¹⁵N after freezing increases the uncertainty of δ¹⁵N and, in combination with the concentrated HCl treatment, leads to a loss of PN and alteration of the δ¹⁵N signature. Therefore, PN content and δ¹⁵N values in the current study may have some bias due to de-carbonation. Nonetheless, a similar methodological approach has been adopted by Wu et al. (2003) while investigating suspended particles along the PN transect in the East China Sea (Fig. 1) and by Hung et al. (2007) while studying the suspended particles in the entire East China Sea. For instance, the range of δ¹⁵N values (~ 3.8–8.4 ‰) obtained in the present study is comparable to the range of δ¹⁵N values (ca. 0.7–9.4 ‰) obtained by Wu et al. (2003) for the entire water column. In addition, precision for δ¹³C and δ¹⁵N decreases for samples containing less than 100 μgC and 20 μgN, respectively. Among 36 filters analysed for the present study, only 5 (3) filters contain less than 100 μgC (20 μgN).

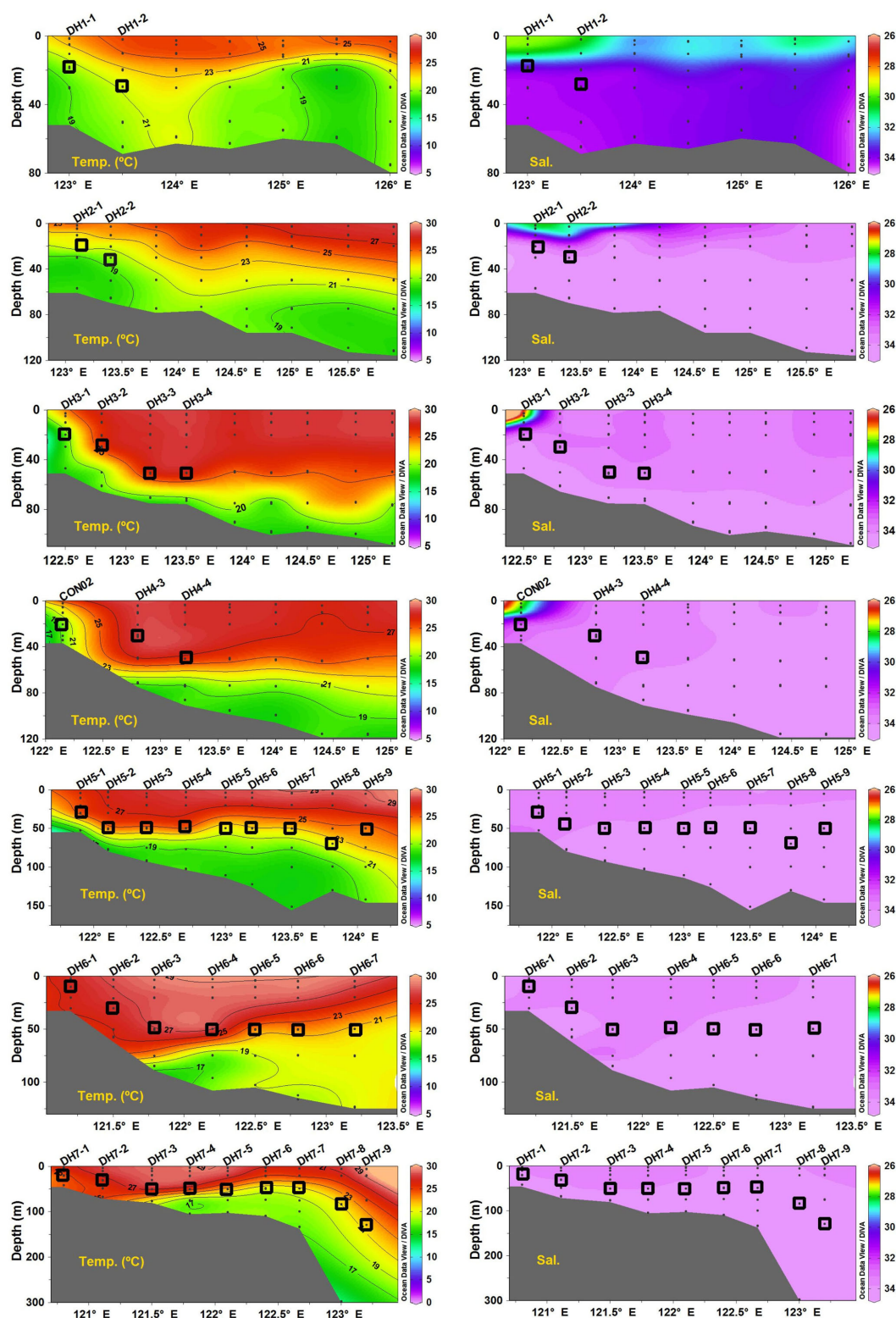


Figure 2. Vertical distributions of temperature and salinity along seven transects across the southern East China Sea during summer 2013. Note that there is an obvious thermally stratified water column during the collection of suspended particles in the study area.

4 Results and interpretations

4.1 Hydrographic characteristics and chlorophyll *a*

4.1.1 Temperature and salinity

Figure 2 illustrates the vertical distributions of temperature and salinity along seven transects across the ECS. Water temperature in the upper 300 m varied from 15 to 30 °C, with distinct thermal stratification of the water column across the entire study area (Fig. 2). The temperature decreases when depth increases and the highest temperature (~ 30 °C) seen mostly in the surface water and the lowest temperature (5 °C) was observed in stations DH7–8 and DH7–9 at water depths of 850 and 800 m, respectively (Fig. 2 and Table S1). Temperature at sampling depths of SPM ranged from 19.1 to 28.2 °C, showing a general decreasing trend from the inner to outer shelf in each transect (Fig. 2).

Salinity in general shows an increasing trend with water depths (Fig. 2), varying from 26.9 to 34.8 with an average value of 34.6 for the entire water column. An increasing trend in salinity from the west to east is evident in all seven transects (Fig. 2). The low salinity (< 30) was constrained in the upper 10 m in four coastal stations (DH1–1, DH2–1, DH3–1, CON02; Fig. 2), wherein temperature is < 24 °C, indicating the limited influence of CDW plume in the study area. The middle salinity ($30 < S < 34.1$) was observed at a depth interval between 10 m and 30 m in stations (DH1–1, DH1–2, DH2–1, DH2–2, DH3–1; Fig. 2), but it spreads to a depth interval between the surface and 30 m in the remaining stations. High salinity was mostly prevalent at bottom depths in all stations investigated. The salinity distribution at depths of SPM sampling shows an increasing trend from the inner to outer shelf (Fig. 2) and varied from 32.7 to 34.7 with an average salinity of 34.0, indicating low influence of CDW at DCM depths in the study area.

4.1.2 Turbidity

The turbidity in the water column of the ECS varied from 0.0 to 20.9 Formazin Turbidity Unit (FTU) (Fig. 3). In the inner shelf region, the vertical distribution of turbidity shows an obvious downward increasing trend and these high turbidity stations were limited along the coast (Fig. 3). This indicates sediment resuspension from the sea floor that was probably induced by hydrodynamic forces such as tides, waves and currents in the shallow coastal region. In the outer shelf stations, the turbidity was uniformly low from the surface to the bottom. Overall, most water depths where the SPM was sampled have low turbidity (< 2.0 FTU), except for stations CON02 (4.75), DH5–1 (3.44) and DH7–1 (5.52) (Fig. 3).

4.1.3 Chlorophyll fluorescence and chlorophyll *a* (Chl *a*)

The highest chlorophyll fluorescence concentration ($18.0 \mu\text{g L}^{-1}$) was observed in surface waters at station DH3–1 and all other values were less than $8.0 \mu\text{g L}^{-1}$ (Fig. 3). The vertical profiles of chlorophyll fluorescence usually showed a clear maximum in the subsurface layer at around 20 m in near-coastal stations and 50 m in outer shelf stations (Fig. 3). The chlorophyll fluorescence in the sampling depth ranged from 0.1 to $4.1 \mu\text{g L}^{-1}$. Around 70 % of SPM sampled in this study falls in the DCM and/or contiguous to the DCM layer (open squares in Fig. 3), ideally representing the biogeochemical behaviours of POM across the DCM layer. Based on the photosynthetically active radiation (PAR), we defined the euphotic depth as a depth at which the PAR is 1 % of its value at the sea surface and photosynthesis can take place (Kirk, 1994; Ravichandran et al., 2012; Guo et al., 2014a). The euphotic depth increased from the inner shelf (20 m) to the outer shelf (100 m) region. This is consistent with average euphotic depth of 33 m calculated based on the empirical relation: $Z_{\text{eu}} = 4.605/K_d(\text{PAR})$ (Kirk, 1994), where $K_d(\text{PAR}) = 1.22 K_d(490)$ (Tang et al., 2007; Ravichandran et al., 2012) and a mean value of 0.115 for $K_d(490)$ for the East China Sea in summer was taken from Chen and Liu (2015). The presence of DCM layers near the euphotic depths suggests a close relationship between the light availability and deep chlorophyll maximum, and the OM in the SPM samples was likely to be dominated by the phytoplankton.

The linear correlation between the measured Chl *a* values and the fluorescence values obtained directly from the calibrated sensor attached with the CTD rosette is high, with $R^2 = 0.93$ (see Fig. S1 in the Supplement). This relationship was used to convert the fluorescence values into Chl *a* concentration of all the remaining SPM using the following equation: $y = 0.708x + 0.199$, where y is Chl *a* concentration and x is in situ fluorescence value. The Chl *a* concentration varied from 0.28 to $3.08 \mu\text{g L}^{-1}$. The highest value is observed in near-coastal station DH5–1, whereas the lowest value is noted in station DH7–9 located off north-east Taiwan. The converted Chl *a* values were used to calculate the POC/Chl *a* ratio (Table S1), which is discussed in Sect. 5.2.2.

4.2 POC and PN

The concentration of SPM ranged from 1.7 to 14.7 mg L^{-1} with a mean value of 4.4 mg L^{-1} (Table 1). The spatial distribution of SPM showed higher values in the inner shelf region and lower values in the outer shelf region (Fig. 4), consistent with the water column turbidity (Fig. 3). The POC concentrations in the DCM layer varied between 20.4 and $263.0 \mu\text{g L}^{-1}$, with a mean value of $85.5 \mu\text{g L}^{-1}$ ($n = 36$) (Fig. 4). The PN ranged from 4.4 to $52.8 \mu\text{g L}^{-1}$, with a mean

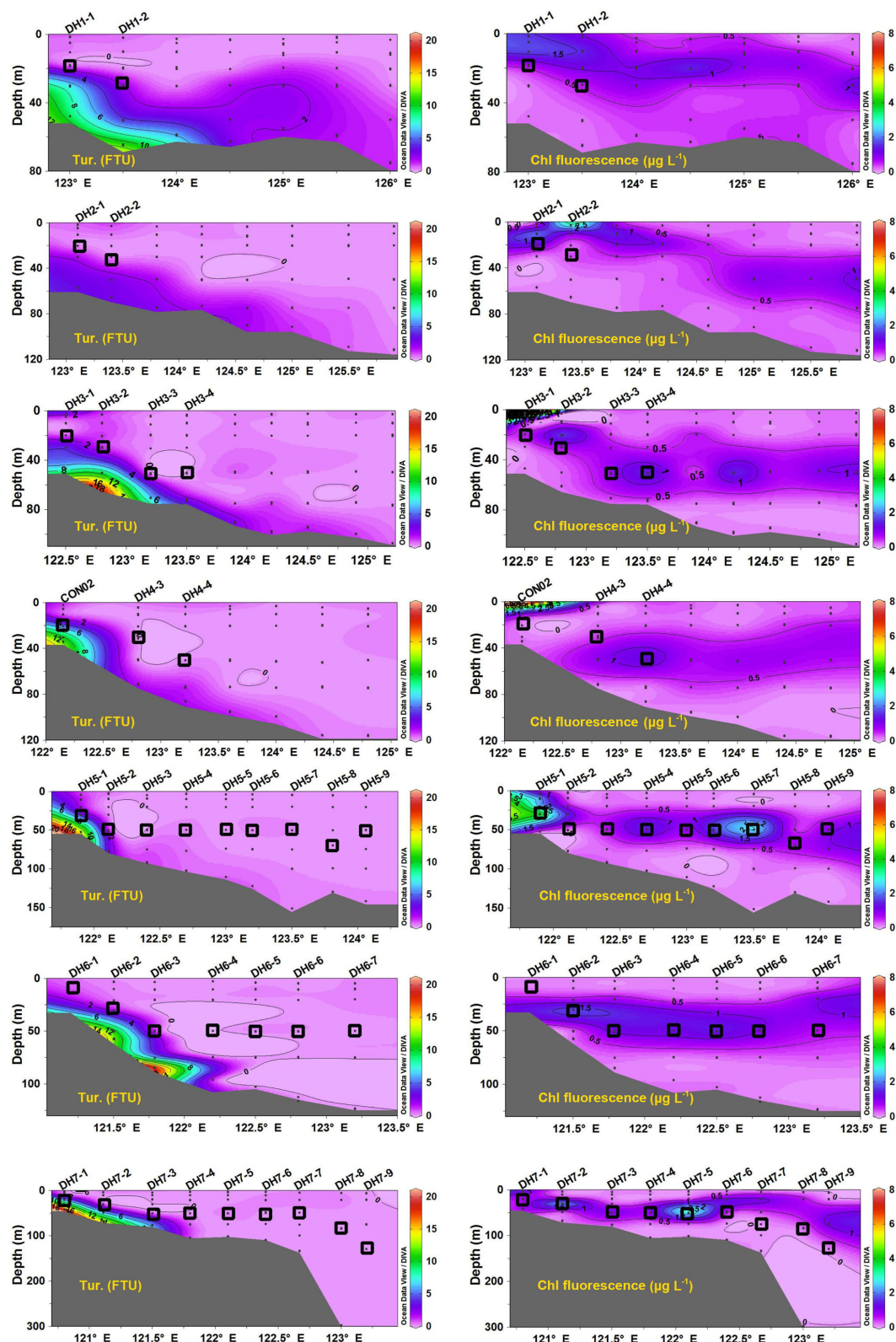


Figure 3. Vertical distributions of turbidity (Tur.) and chlorophyll fluorescence (Chl fluorescence) concentration along seven cross-shelf transects in the southern East China Sea during summer 2013.

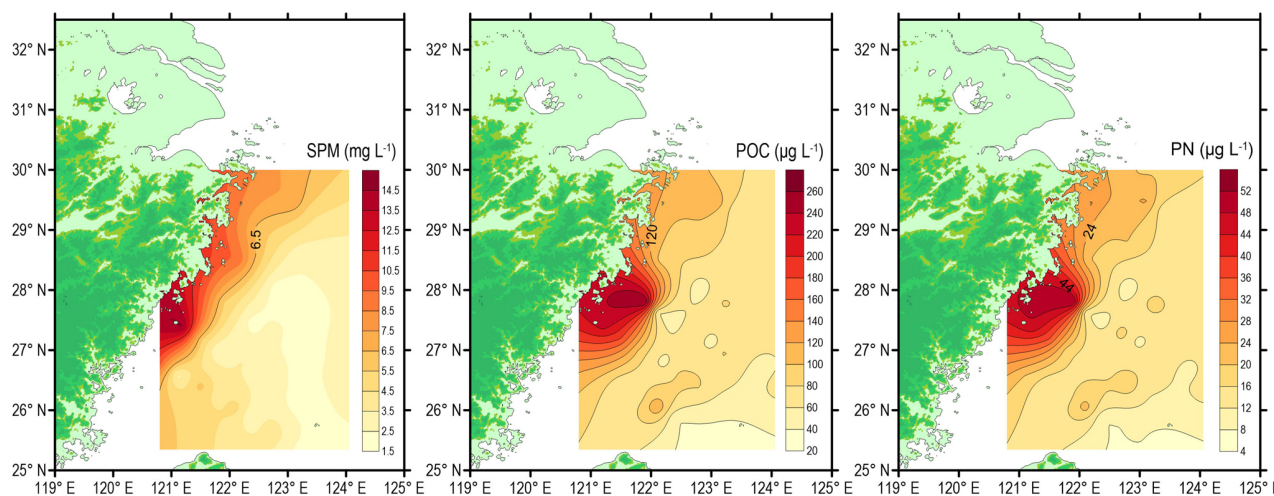


Figure 4. Spatial distributions of suspended particulate matter (SPM, mg L^{-1}), particulate organic carbon (POC, $\mu\text{g L}^{-1}$) and particulate nitrogen (PN, $\mu\text{g L}^{-1}$) around the deep chlorophyll maximum layer in the southern East China Sea during summer 2013.

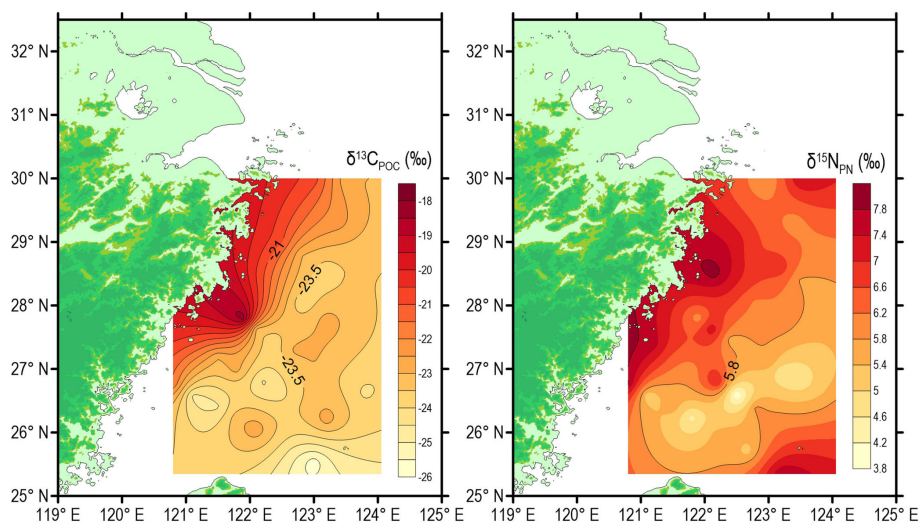


Figure 5. Spatial distributions of stable isotopic values of particulate organic carbon and nitrogen ($\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$) around the deep chlorophyll maximum layer in the southern East China Sea during summer 2013.

value of $17.7 \mu\text{g L}^{-1}$ ($n = 36$). The spatial distributions of POC and PN resemble each other (Fig. 4). The highest concentrations of POC ($263 \mu\text{g L}^{-1}$) and PN ($52.8 \mu\text{g L}^{-1}$) were associated with station DH5-1 (Fig. 4 and Table S1). POC and PN concentrations were higher near the coast on the inner shelf (> 90 and $> 21 \mu\text{g L}^{-1}$, respectively) and decreased gradually with distance offshore (Fig. 4). Lower concentrations of POC and PN are observed in the easternmost stations, near north-eastern Taiwan Island (Fig. 4). Although the concentrations of both POC and PN varied by more than an order of magnitude (Fig. 4), the molar C/N ratios are fairly uniform at DCM layers throughout sampling, ranging from 4.1 to 6.3 with a mean ratio of 5.6 ± 0.5 ($n = 36$) (Table 1).

4.3 $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$

Spatial distributions of $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ around DCM layers are presented in Fig. 5. The $\delta^{13}\text{C}_{\text{POC}}$ decreased from the inner shelf to offshore region, varying widely from -25.8 to -18.2 ‰ (Table 1). Consistent with the POC concentration, the highest $\delta^{13}\text{C}_{\text{POC}}$ value (-18.2 ‰) is also associated with the coastal station DH5-1. The range of $\delta^{15}\text{N}_{\text{PN}}$ is 4.2‰, varying between 3.8 and 8.0‰ (Table 1). The lowest $\delta^{13}\text{C}_{\text{POC}}$ values (-25.8 and -25.2 ‰) were observed north-east of Taiwan Island in the Okinawa Trough, whereas $\delta^{15}\text{N}_{\text{PN}}$ values (6.73 and 7.78‰) in this region were higher than those of the surrounding area (Fig. 5). The spatial distribution of $\delta^{13}\text{C}_{\text{POC}}$ was quite similar to the spatial distribution

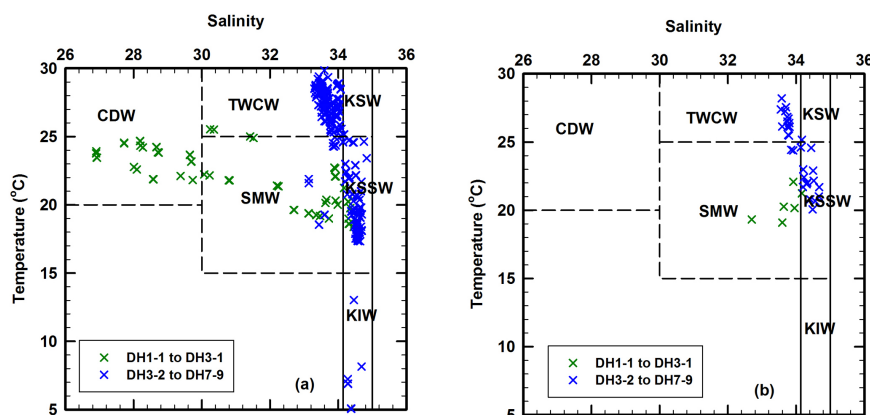


Figure 6. Temperature–salinity (T – S) diagrams for (a) the entire water column in the East China Sea and (b) the deep chlorophyll maximum layer where the suspended particulate matter were collected for the present investigation. T – S ranges of six water masses are taken from Umezawa et al. (2014). CDW – Changjiang Diluted Water; TWCW – Taiwan Warm Current Water; SMW – Shelf Mixed Water; KSW – Kuroshio Surface Water; KSSW – Kuroshio Subsurface Water; KIW – Kuroshio Intermediate Water.

of POC (Fig. 4), and the correlation coefficient (R^2) between $\delta^{13}\text{C}_{\text{POC}}$ and POC was 0.55 ($p < 0.0001$; Fig. 10).

5 Discussion

5.1 Influence of different water masses in the southern ECS

In order to identify the different water sources in the study area, temperature–salinity (T – S) diagrams were drawn for the entire water column (Fig. 6a) as well as for the SPM sampling depth around DCM layers (Fig. 6b). The T – S diagram for all the water depths shows a convergence at around 17°C , 34.6 (Fig. 6a), representing the upwelling of KSSW (Umezawa et al., 2014). There are two trends in the T – S diagram, indicating a mixing of three water masses: one is less saline and much colder water, mainly CDW, another is more saline and warmer, mainly Taiwan Warm Current Water (TWCW), and the third one is KSSW (Fig. 6a). The low salinity observed at five coastal sites (DH1-1, DH2-1, DH2-2, DH3-1 and CON02; Fig. 2) indicates the influence of CDW mostly in surface water, but also some of the DCM depths where water was sampled for SPM. This is also evident from Fig. 6b where five stations fall within the area of shelf mixed water (SMW), which is a water body composed of a mixing between CDW and KSSW. However, apart from at these five coastal stations, most DCM depths where water was sampled for SPM seem to be weakly influenced by the CDW (Fig. 6b). Based on the T – S range of different water masses (Fig. 6), we further delineated the area and water depths influenced by three important water masses: CDW, TWCW and KSSW (Fig. 7). Interestingly, the influence of CDW was constrained to the upper 10 m in five coastal stations, whereas TWCW influenced the upper 30 m and covered three quarters of the study region, with KSSW largely

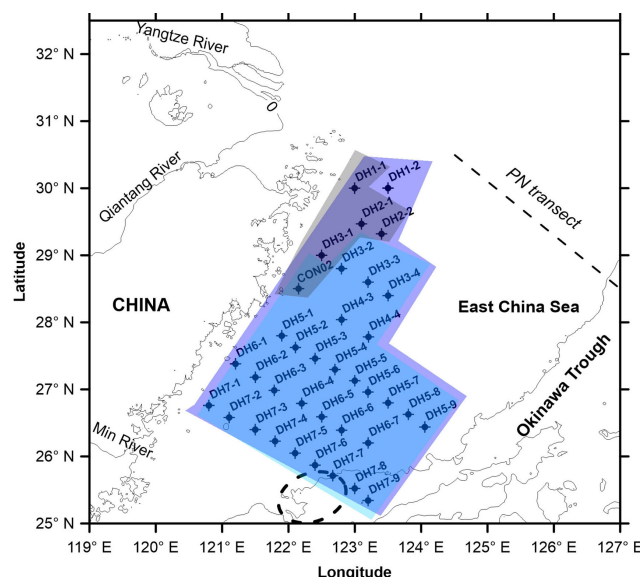


Figure 7. A diagram delineating the regions influenced by three main water masses based on the T – S relationship (Figs. 2 and 6) in the study area. Area with grey polygon represents the influence of CDW, which is limited only in the upper 10 m. The sky-blue area represents the dominance of TWCW, which is limited to ~ 30 m below the surface. The polygon coloured by deep blue represents the area influenced by the KSSW, indicating that the bottom water of the entire study area was dominated by KSSW.

influencing the bottom water across the entire study region (Figs. 2, 6a and 7).

In summary, although the river run-off was huge, the influence of CDW plume in the southern part of the ECS was weak during summer 2013 mainly because most of the CDW plume was transported north-eastward of the Yangtze estuary to the Korean coast (Isobe et al., 2004; Bai et al., 2014;

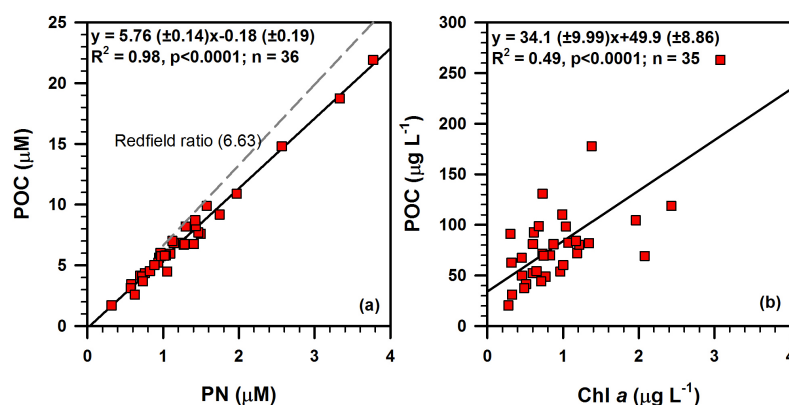


Figure 8. Bi-plots showing the relationships of (a) POC vs. PN and (b) POC vs. Chl *a* in suspended particulate matter investigated in this study. Redfield ratio (dashed line in panel a) is taken from Redfield (1958).

Gao et al., 2014). This contrasts with summer 2003 when the plume front moved southward (Bai et al., 2014). Meanwhile, the intrusion of TWCW and KSSW was strong in the continental shelf of the East China Sea during summer 2013.

5.2 Characterization of POM in DCM layers

5.2.1 Molar C / N ratio

A necessary first step in the source analysis of POM using bulk carbon and nitrogen isotopes as well as the molar carbon to nitrogen ratio is to identify the form of total nitrogen in the measured SPM, so that inorganic nitrogen is not mis-assigned as nitrogenous organic end-member (Hedges et al., 1986). The linear relationship between POC and PN ($R^2 = 0.98$, $p < 0.0001$; Fig. 8a) suggests that nitrogen is strongly associated with organic carbon. The slope of linear regression of POC against PN corresponds to a molar C / N ratio of 5.76 (Fig. 8a). The positive intercept on the PN axis when POC is zero represents the amount of inorganic nitrogen ($\sim 0.03 \mu\text{M}$), indicating that essentially all nitrogen is in organic form. The molar C / N ratios of all SPM samples (4.1–6.3) from the DCM layers are lower than the canonical Redfield ratio (6.63) (Fig. 8a), but are similar to the average molar C / N ratios of 5.6 for marine POM (Copin-Montegut and Copin-Montegut, 1983) and 6 for POM in cold, nutrient-rich waters at high latitudes (Martiny et al., 2013). The range also falls within the range of 3.8 to 17 reported for marine POM (Geider and La Roche, 2002), but it is higher than an unprecedented low C / N ratio (2.65 ± 0.19) of POM in the Canada Basin that was attributed to a dominant contribution of smaller-sized ($< 8 \mu\text{m}$) phytoplankton to POC (Crawford et al., 2015). Wu et al. (2003) investigated the C / N ratio of POM (4.3–29.2) at all depths along the PN transect, a standard cross-shelf section extending from the Yangtze estuary south-east to the Ryukyu Islands, cross-cutting the Okinawa Trough and perpendicular to the principle axis of Kuroshio Current in the ECS (Fig. 1). Liu et al. (1998) measured the

C / N ratio of POM in the surface water of the ECS and found a wider C / N ratio from 4.0 to 26.9 with a mean ratio of 7.6 in spring and from 4.7 to 34.3 with a mean ratio of 15.2 in autumn 1994. The authors attributed the lower C / N in spring to more intense biological activity than in autumn, and the spatial distribution of C / N was thought to be related to that of phytoplankton abundance.

Characteristically, a narrow range of low C / N ratios in our SPM samples and less influence of CDW in the study region (Fig. 7) confirm the lack of terrestrial signals transported mainly by the Yangtze River. We therefore suggest that the POM in the DCM layers of the southern East China Sea is dominated by marine-sourced OM with an unrecognized contribution of terrestrial OM. Low C / N ratios further restrict the assumption of degradation of nitrogen-rich OM, a process that normally increases the C / N ratio to more than that of the Redfield ratio. Therefore, the molar C / N ratio can be better explained as a source signal of OM rather than OM degradation in the SPM investigated in this study.

5.2.2 POC / Chl *a* ratio

The linear correlation between POC and Chl *a* ($R^2 = 0.49$, $p < 0.0001$; Fig. 8b) further indicates that the phytoplankton productivity is largely responsible for the POC production in the SPM samples. Moreover, the POC / Chl *a* ratio of 34.1 g g^{-1} derived from the slope of a regression line ($y = 34.1(\pm 9.99)x + 49.9(\pm 8.86)$) (Fig. 8b) is consistent with the reported POC / Chl *a* ratios in the ECS (36.1 g g^{-1} ; Chang et al., 2003) and the north-western Pacific (48 g g^{-1} ; Furuya, 1990). However, the POC / Chl *a* ratio obtained in this study is lower than that estimated (64 g g^{-1}) for the sinking particles in the ECS and the Kuroshio region, off north-eastern Taiwan Island (Hung et al., 2013). The range is well within the range ($13\text{--}93 \text{ g g}^{-1}$) reported for POM in the ECS by Chang et al. (2003) and is also consistent with the range ($18\text{--}94 \text{ g g}^{-1}$) estimated from phytoplankton cell volumes by the same authors. Although the Chl *a* concentration in our study

was converted based on the linear relationship between measured Chl *a* and in situ fluorescence values (see Sect. 3.2 and Fig. S1 in the Supplement for more details), it is more or less similar to Chl *a* concentrations obtained in the above-mentioned studies, which were mostly extracted from filtered particles (Chang et al., 2003; Hung et al., 2013).

The POC / Chl *a* ratio has been used for the discrimination of POM sources in coastal ocean waters (Cifuentes et al., 1988). The POC / Chl *a* ratio in living phytoplankton varies with temperature, growth rate, day length, phytoplankton species and irradiance (Savoye et al., 2003 and references therein). The POC / Chl *a* ratio of living phytoplankton was reported to be between 40 and 140 g g⁻¹ (Geider, 1987; Thompson et al., 1992; Montagnes et al., 1994; Head et al., 1996). Furthermore, a POC / Chl *a* ratio of less than 200 g g⁻¹ is an indication of a predominance of newly produced phytoplankton (or autotrophic-dominated) in POM, and that a value higher than 200 g g⁻¹ is an indication of detrital or degraded organic matter (or heterotrophic/mixture-dominated) (Cifuentes et al., 1988; Savoye et al., 2003; Liénart et al., 2016). The POC / Chl *a* ratio in the DCM layer of the ECS is almost < 200 g g⁻¹ (33–200 g g⁻¹), with one exception (CON02: 303 g g⁻¹; Fig. 9), indicating that POM in the DCM layers of ECS was dominated by phytoplankton, as also indicated by the low C / N ratios (4.1–6.3). The relatively high POC / Chl *a* ratio in only one station, CON02 (Fig. 9), suggests that the POM in this sample was likely sourced from degraded phytoplankton OM, terrestrial OM or heterotrophic-dominated OM. However, the molar C / N ratio of CON02 (5.3) is lower than the canonical Redfield ratio (6.63), eliminating the probability of degraded and terrestrial OM sources. In addition, the insignificant linear correlation between the C / N ratio and POC / Chl *a* ratio (Fig. 9) supports the non-degraded POM, a process resulting in a simultaneous increase in C / N and POC / Chl *a* ratios, mainly because of the preferential decomposition of N-rich OM, as well as a fast degradation of Chl *a* than the bulk POC pool (e.g. Savoye et al., 2003). Thus, the POM in CON02 seems to be dominated by heterotrophic biota, though the exact reason for the dominance of heterotrophic biota at only one location in our study area is unknown and needs further investigation.

Briefly, several clues indicate the predominance of newly produced, phytoplankton-synthesized OM around DCM layers of the southern East China Sea: (1) low influence of fresh water, (2) low molar C / N ratios, (3) a linear correlation between POC and chlorophyll *a*, and (4) low POC / Chl *a* ratios, mostly < 200 g g⁻¹.

5.3 Dynamics of $\delta^{13}\text{C}_{\text{POC}}$ in POM in DCM

Although a narrow range of molar C / N ratio in the SPM indicated an aquatic origin for the POM at DCM layers, the wide variability of $\delta^{13}\text{C}_{\text{POC}}$ (−25.8 to −18.2‰) suggests that the POM around DCM layers would be a mixture of terrestrial C3 plants with a typical $\delta^{13}\text{C}$ value of ca. −27‰

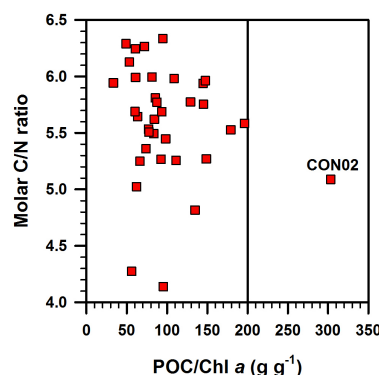


Figure 9. Molar C / N ratio vs. POC / Chl *a* ratio in suspended particulates investigated in this study. The vertical line represents POC / Chl *a* ratio of 200 g g⁻¹, the upper limit for phytoplankton-dominated particulate organic matter (Savoye et al., 2003). See text for more details. CON02 is the station where red tide was observed during the sampling time and the colour of the surface water was brown and dissolved oxygen in the bottom water was 1.6 mg L⁻¹.

(e.g. Peters et al., 1978; Wada et al., 1987) and marine phytoplankton with a typical $\delta^{13}\text{C}$ range of −18 to −20‰ (e.g. Goericke and Fry, 1994). However, Fig. 5 illustrates a distinct decreasing trend in $\delta^{13}\text{C}_{\text{POC}}$ towards the outer shelf; a pattern opposite to an increasing trend in $\delta^{13}\text{C}$ evident in suspended particles and surface sediments, i.e. seaward decrease in terrestrial OC in surface sediments of many river-dominated margins (Emerson and Hedges, 1988; Meyers, 1994; Hedges et al., 1997; Kao et al., 2003; Wu et al., 2003). Such a spatial distribution with less negative $\delta^{13}\text{C}_{\text{POC}}$ values in the coastal region, but more negative $\delta^{13}\text{C}_{\text{POC}}$ values in the middle-outer shelf is inconsistent with the idea of terrestrial OC influence. The elevated $\delta^{13}\text{C}_{\text{POC}}$ values (average of −20.7‰) in the coastal region, concomitant with high POC concentrations (Fig. 4), are consistent with the higher marine primary productivity (11 g C m⁻² yr⁻¹) reported in the western than that in the eastern parts of the East China Sea (Gong et al., 2003). The lower $\delta^{13}\text{C}_{\text{POC}}$ occurred in the middle-outer shelf region where oligotrophic Taiwan Warm Current Water and Kuroshio Water spread (Fig. 5). The lowest $\delta^{13}\text{C}_{\text{POC}}$ (−25.8‰) was observed at a water depth of 85 m, off north-eastern Taiwan, likely due to the intrusion of Kuroshio Sub-surface Water with low $\delta^{13}\text{C}$ from −31 to −27‰ (Wu et al., 2003), is also in agreement with the hydrographic parameters of this location (Figs. 2 and 7).

A positive linear correlation between $\delta^{13}\text{C}_{\text{POC}}$ and POC ($R^2 = 0.55$, $p < 0.0001$; Fig. 10a), a characteristic feature of productive oceanic regions (Savoye et al., 2003), suggesting the effect of growing primary productivity (and or increasing cell growth rate) on a decrease in carbon fractionation during photosynthesis (Miller et al., 2013). This is likely because of a limitation of dissolved CO₂, which cannot be compensated for in time by the surrounding water in a relatively closed system because of stratification (Kopczyńska et al.,

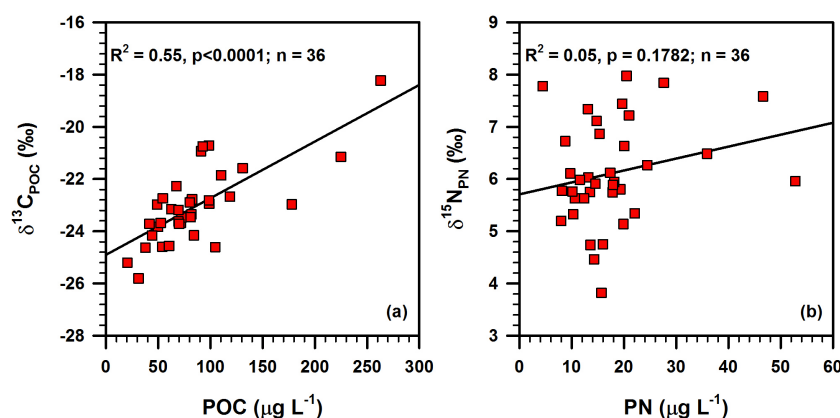


Figure 10. Bi-plots showing the relationships of (a) $\delta^{13}\text{C}_{\text{POC}}$ vs. POC and (b) $\delta^{15}\text{N}_{\text{PN}}$ vs. PN in suspended particulate matter around the deep chlorophyll maximum layer in the southern East China Sea.

1995). Further, high productivity makes ^{13}C -enriched OM in phytoplankton (Fry and Wainwright, 1991; Nakatsuka et al., 1992; Miller et al., 2013). Lowe et al. (2014) observed increased $\delta^{13}\text{C}$ and fatty acid concentration in the POM while increasing phytoplankton abundance in the nearshore waters of San Juan Archipelago, WA. Although primary productivity has a significant correlation with $\delta^{13}\text{C}_{\text{POC}}$, only 55 % of $\delta^{13}\text{C}_{\text{POC}}$ variation can be explained by primary productivity (Fig. 10a), implying that other factors, such as species and sizes of phytoplankton, must have influenced $\delta^{13}\text{C}$ values of phytoplankton living in the DCM layers (Falkowski, 1991; Hinga et al., 1994).

The distribution of the phytoplankton community in the East China Sea is affected by physico-chemical properties (temperature, salinity and nutrients) of different water masses and surface currents (Umezawa et al., 2014; Jiang et al., 2015, 2017). Diatoms and dinoflagellates are the main phytoplankton communities in summer, with 136 taxa of diatoms from 55 genera and 67 taxa of dinoflagellates from 11 genera having been reported, along with minor communities of chrysophyta, chlorophyta and cyanophyta (Guo et al., 2014b). There is a clear decreasing trend in phytoplankton abundances in the East China Sea from the surface to the bottom, as well as from the coastal to offshore region that is widely believed to be due to nutrient availability (Zheng et al., 2015). The phytoplankton species have distinct spatial characteristics, but no significant differences in species between surface waters and the DCM layers (Zheng et al., 2015). Diatoms with large cell sizes were the dominant species in the coastal region, while phytoplankton with small sizes was dominant in the oligotrophic offshore shelf and Kuroshio waters (Furuya et al., 2003; Zhou et al., 2012). According to Jiang et al. (2015), the contribution of micro- ($> 20 \mu\text{m}$), nano- ($3\text{--}20 \mu\text{m}$) and pico-phytoplankton ($< 3 \mu\text{m}$) to Chl *a* was 40, 46 and 14 %, respectively, in nutrient-rich inshore waters, and 14, 34 and 52 % in offshore regions in summer 2009. The outer shelf region was

composed of small-sized phytoplankton, mainly cyanobacteria and cryptophytes transported by Taiwan Warm Current and Kuroshio Current. It has been reported that diatoms have higher $\delta^{13}\text{C}$ values (-19 to -15 ‰) than dinoflagellates (-22 to -20 ‰; Fry and Wainwright, 1991; Lowe et al., 2014). Likewise, large phytoplankton have higher $\delta^{13}\text{C}$ values than small phytoplankton and heterotrophic dinoflagellates have higher $\delta^{13}\text{C}$ values than autotrophic dinoflagellates (Kopczyńska et al., 1995). Similarly, wide variations of $\delta^{13}\text{C}_{\text{POC}}$ (-22.05 to -27.62 ‰) at DCM layers in the northern East China Sea were documented by Gao et al. (2014). Significant variations of $\delta^{13}\text{C}$ in suspended OM that was dominated by phytoplankton were reported from the Delaware estuary (-25 to -20 ‰; Cifuentes et al., 1988), the Bay of Seine (-24.3 to -19.7 ‰; Savoye et al., 2003), the Santa Barbara Channel (Miller et al., 2013) and the nearshore waters of San Juan Archipelago, WA (-24.1 to -18.9 ‰; Lowe et al., 2014). These variations were influenced largely by the isotopic fractionation during phytoplankton photosynthesis and degradation than by changes in the relative contributions of terrestrial and aquatic OM (Fogel and Cifuentes, 1993; Savoye et al., 2003).

5.4 Temperature effect on the $\delta^{13}\text{C}_{\text{POC}}$ around the DCM layer

Apart from primary production and the growth rate and species composition, temperature and biomass degradation may influence the carbon isotopic composition of phytoplankton (Savoye et al., 2003). Temperature has an indirect effect on isotopic fractionation between phytoplankton carbon and dissolved CO_2 , and therefore on phytoplankton $\delta^{13}\text{C}$ (e.g. Rau et al., 1992; Savoye et al., 2003). The C/N ratio, POC/Chl *a* ratio and $\delta^{13}\text{C}_{\text{POC}}$ all indicated that the POM around the DCM layer is dominated by newly produced phytoplankton OM (see Sect. 5.1–5.3). Therefore, to understand the temperature effect on $\delta^{13}\text{C}$ of phytoplankton, we plotted our $\delta^{13}\text{C}_{\text{POC}}$ data against temperature after separat-

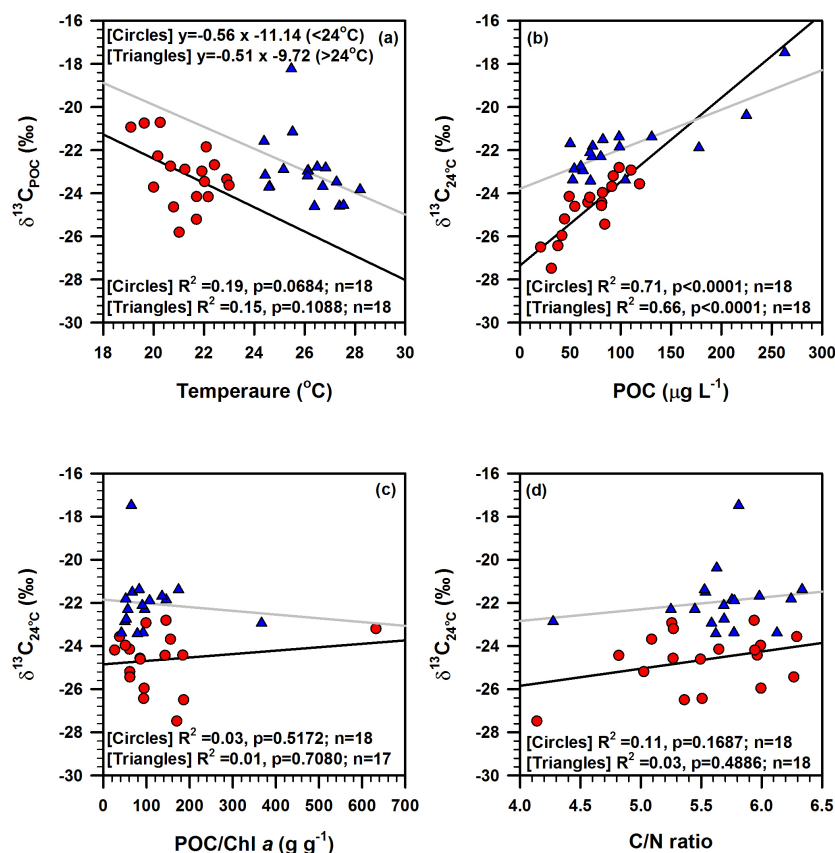


Figure 11. Bi-plots showing the relationships of (a) $\delta^{13}\text{C}_{\text{POC}}$ vs. temperature for samples separated into two groups based on temperature: $< 24^\circ\text{C}$ and $> 24^\circ\text{C}$, (b) temperature-normalized $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{24^\circ\text{C}}$) vs. POC concentration, (c) $\delta^{13}\text{C}_{24^\circ\text{C}}$ vs. POC / Chl *a* ratio, and (d) $\delta^{13}\text{C}_{24^\circ\text{C}}$ vs. molar C / N ratio in suspended particulate matter around deep chlorophyll maximum layers in the southern East China Sea.

ing samples into two groups based on temperature: $< 24^\circ\text{C}$ and $> 24^\circ\text{C}$ (Fig. 11a). Data points of both groups show a decreasing $\delta^{13}\text{C}$ of phytoplankton biomass with increasing temperature around the water depths of DCM in the southern ECS (Fig. 11a). Such a relationship is in contrast to the positive relationship between these two variables observed for the surface ocean POM around the world (Sackett et al., 1965; Fontugne, 1983; Fontugne and Duplessy, 1981).

The negative relationship between $\delta^{13}\text{C}_{\text{POC}}$ and temperature is likely related to biological activity and carbonate dissolution equilibrium; both may control the concentration of dissolved inorganic carbon in the DCM layers, which are closer to euphotic depths (see Sect. 4.1). The weak correlation between $\delta^{13}\text{C}_{\text{POC}}$ and temperature supports a weak influence of temperature on $\delta^{13}\text{C}_{\text{POC}}$ around DCM layers in the study area (Fig. 11a). A decrease in fractionation of approximately $-0.56\text{‰}^\circ\text{C}^{-1}$ is estimated for POM collected at $< 24^\circ\text{C}$, whereas a decrease in fractionation of roughly $-0.51\text{‰}^\circ\text{C}^{-1}$ is estimated for POM collected at $> 24^\circ\text{C}$ (Fig. 11a). In order to distinguish the influence of biological parameters from temperature on $\delta^{13}\text{C}_{\text{POC}}$, the $\delta^{13}\text{C}_{\text{POC}}$ data

were corrected for the “temperature effect” by normalizing the data using the following equation: $\delta^{13}\text{C}_{\text{POC}} = f(T)$.

In the present study, since most $\delta^{13}\text{C}_{\text{POC}}$ values come from the DCM layer and the $\delta^{13}\text{C}_{\text{POC}}$ is negatively correlated with temperature (Fig. 11a), we applied our own temperature coefficients (-0.56 and $-0.51\text{‰}^\circ\text{C}^{-1}$) and $\delta^{13}\text{C}_{\text{POC}}$ was normalized at 24°C (i.e. the mean temperature at sampled water depths) using the following formula (Savoye et al., 2003): $\delta^{13}\text{C}_{24^\circ\text{C}} = \delta^{13}\text{C}_{\text{POC}} - s(T - 24)$, where $\delta^{13}\text{C}_{24^\circ\text{C}}$ is the temperature-normalized $\delta^{13}\text{C}_{\text{POC}}$, T is the seawater temperature in $^\circ\text{C}$ from water depths where SPM sampled, and s is the slope of the linear regression $\delta^{13}\text{C}_{\text{POC}} = f(T)$ in $\text{‰}^\circ\text{C}^{-1}$ obtained from Fig. 11a. There are significant correlations between $\delta^{13}\text{C}_{24^\circ\text{C}}$ of biomass and POC concentration (circles: $R^2 = 0.71$, $p < 0.0001$, $n = 18$; triangles: $R^2 = 0.66$, $p < 0.0001$, $n = 18$; Fig. 11b), indicating that primary production drives $\sim 70\%$ of the variation of phytoplankton $\delta^{13}\text{C}$ around DCM layers in the southern ECS. A similar positive relationship between temperature-normalized $\delta^{13}\text{C}$ and POC concentration was observed by Savoye et al. (2003) during spring phytoplankton blooms in the Bay of Seine, France. However, $\delta^{13}\text{C}_{24^\circ\text{C}}$ correlated insignificantly with

the POC / Chl *a* ratio and C / N ratio (Fig. 11c and d), implying that degradation has a minor effect on the carbon isotopic composition of POM in this study.

5.5 Dynamics of $\delta^{15}\text{N}_{\text{PN}}$ in POM in DCM layers

In contrast to the POC and $\delta^{13}\text{C}_{\text{POC}}$ relationship (Fig. 10a), there is no significant relationship between PN and the isotopic composition ($\delta^{15}\text{N}_{\text{PN}}$) of the POM investigated in the present study (Fig. 10b), implying that primary productivity has no significant control on the variability of $\delta^{15}\text{N}_{\text{PN}}$. As the POM around the water depths of DCM was dominantly from the newly produced, phytoplankton-synthesized source, $\delta^{15}\text{N}_{\text{PN}}$ should be similar to $\delta^{15}\text{N}$ in phytoplankton. Considering the prevalence of low N / P ratios in the DCM layer of the East China Sea (Lee et al., 2017), the degree of nitrate utilization by phytoplankton should be high and that would result in the composition of $\delta^{15}\text{N}_{\text{PN}}$ being similar to $\delta^{15}\text{N}$ of nitrate ($\delta^{15}\text{N}_{\text{NO}_3^-}$) (Altabet and Francois, 1994; Minagawa et al., 2001). Therefore, the spatial distribution of $\delta^{15}\text{N}_{\text{NO}_3^-}$ is probably crucial to decipher the distribution of $\delta^{15}\text{N}_{\text{PN}}$ in DCM layers. Importantly, the spatial distribution of $\delta^{15}\text{N}_{\text{PN}}$ (Fig. 5) resembles the surface current pattern (Fig. 1), as well as the distribution of different water masses (Fig. 7), suggesting that nitrate and the $\delta^{15}\text{N}_{\text{NO}_3^-}$ of CDW, TWCW and Kuroshio Water are largely governing the distribution of $\delta^{15}\text{N}_{\text{PN}}$ in the study area.

According to Li et al. (2010), the range of $\delta^{15}\text{N}_{\text{NO}_3^-}$ in the Yangtze River was 7.3–12.9‰, with a mean value of 8.3‰. In the north-east of Taiwan Island, $\delta^{15}\text{N}_{\text{NO}_3^-}$ was 5.5–6.1‰ at depths of 500 to 780 m (Liu et al., 1996). However, TWCW is nutrient-depleted, enabling incorporation of N-fixer-derived nitrogen in the suspended POM. This general spatial pattern of $\delta^{15}\text{N}_{\text{NO}_3^-}$ (i.e. higher $\delta^{15}\text{N}_{\text{NO}_3^-}$ (> 6‰) in the north-east coastal region and off north-east Taiwan, but lower $\delta^{15}\text{N}_{\text{PN}}$ in between these two regions) exactly resembles the distribution of $\delta^{15}\text{N}_{\text{PN}}$ in the DCM layers of this study (Fig. 5). Therefore, the $\delta^{15}\text{N}_{\text{PN}}$ variation in the DCM layer of the East China Sea was primarily governed by the nutrient status and $\delta^{15}\text{N}_{\text{NO}_3^-}$, though we do not have nutrient data generated during the same cruise to validate our interpretations.

There is another possibility that high $\delta^{15}\text{N}_{\text{PN}}$ (DH7-8: 6.7‰, DH7-9: 7.8‰) in the DCM layer, off north-east Taiwan (Fig. 5), may not result from the high degree of nitrate utilization, but instead from the incorporation of inorganic nitrogen (mainly NH_4^+) in the POM. According to Chen et al. (1996) and Liu et al. (1996), NO_3^- and NH_4^+ concentrations in KSSW were high due to the decomposition of OM in sinking particles. However, the concentrations of chlorophyll fluorescence as well as POC and PN are low (Figs. 3 and 4). The low chlorophyll fluorescence might be limited by the low temperature in this high-nutrient–low-chlorophyll region (Umezawa et al., 2014). Because of the low temperature, the

prevailing high CO_2 pressure is expected to decrease $\delta^{13}\text{C}$ in DIC and may drive a great carbon isotopic fractionation during carbon assimilation by phytoplankton (Rau et al., 1992), the potential reason why $\delta^{13}\text{C}_{\text{POC}}$ values in these two stations were low (−25.8 and −25.2‰) compared to values of other locations in the study area. Consistently, the low concentration of POC restricts the idea that the high $\delta^{15}\text{N}_{\text{PN}}$ could not be from the denitrification effect. The high $\delta^{15}\text{N}_{\text{PN}}$ (6.7, 7.8‰) values are probably due to the incorporation of inorganic nitrogen (mainly NH_4^+); the process normally drives the $\delta^{15}\text{N}_{\text{PN}}$ as high as that of inorganic nitrogen $\delta^{15}\text{N}$ (Coffin and Cifuentes, 1999). Although $\delta^{15}\text{N}$ of NH_4^+ in Kuroshio Water is not available for comparison, it seems that $\delta^{15}\text{N}$ of remineralized NH_4^+ was relatively greater than $\delta^{15}\text{N}$ of NO_3^- (York et al., 2010). This possibility is also supported by the high concentrations of NO_3^- and NH_4^+ in Kuroshio Subsurface Water (Liu et al., 1996) as well as the low contents of POC (< 1; 0.96, 0.98 %) and low molar C / N ratios (4.1, 5.4) of these two SPM samples (DH7-8 and DH7-9).

5.6 Impact of Yangtze River on POM in DCM of ECS

The range of POC / Chl *a* obtained in this study (33–200 g g^{-1}) is within the range (< 200 g g^{-1}) reported for the phytoplankton-dominated POM in the coastal and shelf waters (e.g. Chang et al., 2003; Savoye et al., 2003; Hung et al., 2013; Liénart et al., 2016). We also obtained a narrow range of C / N ratios (4.1–6.3), but a wide range of $\delta^{13}\text{C}_{\text{POC}}$ (−25.8 to −18.2‰) compared to previous studies in the ECS (4.0–34.3, Liu et al., 1998; −24.0 to −19.8‰, Wu et al., 2003). Our results indicate that POM at the DCM was largely produced in situ and derived from phytoplankton biomass, with little terrestrial influence. The lack of terrestrial OM signals seems to be related to reservoir- and dam-building along the river in recent years that has shifted the location of the Yangtze-derived POC deposition from the inner shelf of the ECS to terrestrial reservoirs (Li et al., 2015). The sediment delivered from the river to the estuary has been reduced by 40 % since 2003 when the Three Gorges Dam was completed (Yang et al., 2011, and references therein). Recently, Dai et al. (2014) reported that the particulate load discharged by the Yangtze has declined to 150 Mt yr^{-1} , less than ~ 70 % of its sediment delivery to the ECS during the 1950s. Although 87 % of the mean annual sediment of Yangtze River is discharged during the flood season from June to September (Wang et al., 2007; Zhu et al., 2011), approximately 60 out of 87 % of the fine-grained sediments are temporarily deposited near the estuary and then later resuspended and transported southward along the inner shelf, off mainland China (Chen et al., 2017, and references therein). The Yangtze-transported POM moves up toward the north-east across the shelf along the so-called Changjiang transport pathway in summer season (e.g. Gao et al., 2014), which is largely affected by the combined effects of high river discharge, south-west summer monsoon and the intensified TWC (Beardsley et al., 1985;

Ichikawa and Beardsley, 2002; Lee and Chao, 2003). The $T-S$ diagrams (Figs. 6 and 7) of this study also illustrate this view.

Accompanying the decreasing sediment input, dam-building in the Yangtze River basin since 2003 has buried around $4.9 \pm 1.9 \text{ Mt yr}^{-1}$ biospheric POC, approximately 10 % of the world riverine POC burial flux to the oceans (Li et al., 2015). The POC flux from the Yangtze to the ECS (range: $1.27\text{--}8.5 \times 10^{12} \text{ g C yr}^{-1}$; Wang et al., 1989; Qi et al., 2014) was significantly less than the estimated primary productivity ($72.5 \times 10^{12} \text{ g C yr}^{-1}$; Gong et al., 2003), implying the predominance of marine-sourced organic matter in the ECS. Moreover, the substantial quantity of organic substances that transported by the Yangtze River may be completely modified before being ultimately deposited on the inner shelf of the ECS and being transported further offshore (Katoh et al., 2000; Lie et al., 2003; Chen et al., 2008; Isobe and Matsuno, 2008). Wu et al. (2007b), for instance, observed an advanced stage of POM degradation in the entire Yangtze River with an average degradation index of -1.1 . Based on the investigation of lipid biomarkers in a sediment core collected from the ECS, Wang et al. (2016) suggested the dominant preservation of marine autochthonous organic matter ($\sim 90\%$) in the ECS.

6 Summary and conclusions

In this study, we comprehensively characterized the particulate organic matter collected from the deep chlorophyll maximum layer in the southern East China Sea using hydrographic data (temperature, salinity and turbidity) and fluorescence (chlorophyll a) as well as elemental (POC, PN) concentrations and isotopic ($\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$) compositions. All these parameters indicated that the POM around DCM layers was dominantly composed of newly produced OM by phytoplankton with a weak contribution from terrestrial input despite the study area being the best example of a river-dominated continental margin in the world. We also discussed the main factors controlling the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ variations in phytoplankton in the study area. As for the $\delta^{13}\text{C}_{\text{POC}}$, the variations in primary productivity, as indicated by the positive correlation between $\delta^{13}\text{C}_{\text{POC}}$ and POC, and phytoplankton species were the main factors; the former explained $\sim 70\%$ of the variability in $\delta^{13}\text{C}_{\text{POC}}$, after accounting for temperature effects. However, $\delta^{15}\text{N}_{\text{PN}}$ variation seems to be related to uptake of nitrate or locally regenerated ammonia, which needs to be substantiated by the nutrient data in future studies. Our results show that phytoplankton dynamics drive marine POM composition around DCM layers in the southern East China Sea.

Moreover, phytoplankton in the southern East China Sea contain relatively lower $\delta^{13}\text{C}_{\text{POC}}$ values than that of typical marine phytoplankton (-18 to -20‰). This emphasizes the need for sufficient investigation of end-member variability,

which is crucial for the estimation of relative contributions of terrestrial and marine OM by an end-member mixing model. Therefore, our results of highly variable $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ values in the autotrophic-dominated DCM layers can provide unique ranges for these two isotopes in the East China Sea, especially the region south of 29°N , and form a basis for the long-term evaluation of organic carbon burial along the inner shelf mud belt, which is largely accumulated in the East China Sea during the Holocene.

Data availability. All data are available within this paper (Table 1) and the Supplement (Table S1).

Supplement. The supplement related to this article is available online at: <https://doi.org/10.5194/bg-15-2091-2018-supplement>.

Competing interests. The authors declare that they have no conflict of interest.

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