



Isotope variability of particulate organic matter at the PN section in the East China Sea

Y. WU^{1,*}, J. ZHANG^{1,2}, D.J. LI¹, H. WEI³ and R.X. LU⁴

¹State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai, 200062, P.R. China; ²College of Chemistry and Chemical Engineering, Ocean University of Qingdao, Qingdao, 266003, P.R. China; ³Physical Oceanography Lab, Ocean University of Qingdao, Qingdao, 266003, P.R. China; ⁴First Institute of Oceanography, SOA, Qingdao, 266071, P.R. China; *Author for correspondence (e-mail: wuying@sklec.ecnu.edu.cn; phone: +86-21-62232887; fax: +86-21-62546441)

Received 2 April 2002; accepted in revised form 26 February 2003

Key words: Carbon stable isotope, Nitrogen stable isotope, Particulate organic matter, East China Sea, PN section

Abstract. The source of particulate organic matter at the PN section in the East China Sea has been evaluated using stable carbon and nitrogen isotopes. The results showed that the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ compositions varied from -19 to -31‰ and 0.7 – 9.5‰ respectively, and the isotope compositions were statistically distinct, enabling, by use of a simple components mixing equations, assessment of the ability of each tracer to estimate the terrestrial, Kuroshio Water, marine and remineralized sources' contributions. The dominance of terrestrial inputs of the Changjiang could be observed 250 km far from the river mouth in the East China Sea. In the shelf water column, the remineralization of biogenic organic matter becomes an important source except for the terrigenous and marine sources. The estimation of sources recorded by $\delta^{13}\text{C}$ data was partly confirmed by equivalent $\delta^{15}\text{N}$ and C/N compositions that reflected greater control by organic matter diagenesis and biological processing. However, the lighter contribution of $\delta^{13}\text{C}$ data of the Kuroshio samples also indicates the alteration of the isotope values by microbial or other processes. The net export flux of POC in the PN section is estimated to be 4.1 kmol C/s and the annual export is 129 Gmol C/yr , which is account for 20% of the East China Sea.

Introduction

The continental margins of the ocean are characterized by very active biogeochemical processes – primary productivity generation, organic matter and nutrient sinks for example (Wollast 1993; Hall et al. 1996). Scientific interest has been focused recently on the marginal seas with special emphasis on the exchange of carbon between compartments, e.g., shelves and the open ocean, in order to better constrain the continental margin carbon fluxes on a global scale (Walsh et al. 1988; SCOR 1994; Chen and Wang 1999a; Liu et al. 1999). Many regional studies indicate that active cross-shelf transport and biogeochemical processes in the margins influence the carbon cycle of the ocean as a whole (Tsunogai et al. 1999; Liu 2000; Liu et al. 2000).

The East China Sea (ECS) is known for its broad continental shelf, rich natural resources and tremendous river runoff from China (e.g., Changjiang (the Yangtze

River)). The riverine carbon fluxes comprise 12 Tg C yr^{-1} in organic form and 20 Tg C yr^{-1} in dissolved inorganic form. The estimated organic carbon burial rate in the ECS shelf sediments is no more than 10 Mt C yr^{-1} (Chen and Wang 1999a). On the east of ECS, the Kuroshio Current, a strong western boundary current, flowing along the Pacific Margin of northeastern Asia, borders the shelf slope of the East China Sea. When passing through the ECS, it brings forth great effects on the ocean environment of the continental shelf area of the ECS. Such characteristics make the ECS as the key studying area for several decades (DeMaster et al. 1985; Kim 1992; Ichikawa and Beardsley 1993; Liu et al. 1995; Chen et al. 1999b).

Although it has been well recognized that the Changjiang dilution and the Kuroshio upwelling are two principal sources of materials of the ECS, few studies addressed the processes of the transport of organic substance (e.g., carbon) and exchange of materials, either dissolved or particulate, between various sources (such as terrestrial and marine source) across the ECS shelf (Chen et al. 1995; Hung et al. 2000; Chen et al. 2001). For instance, the improved knowledge of the fates of organic carbon is critical in understanding quantitatively the significance of terrestrial inputs and marine production in continental margins relative to global carbon cycles (Liu et al. 1995; Chen and Wang 1999a; Chen et al. 1999b).

Hence, we examined isotopic compositions of carbon and nitrogen of the PN section across the ECS shelf. The PN section starts off the Changjiang Estuary and ends southeasterly at Ryukyu Islands (Figure 1). It crosses the Changjiang plume front and shelf waters until Okinawa Through at the depth of 50–100 m of the Kuroshio upwells along the margin until inner shelf. It is a typical area for the physical, chemical and biological oceanographic interactions between Changjiang plume front, shelf water and Kuroshio. Studies were undertaken along the PN section with regards to volume, heat transport of the Kuroshio and interaction with the shelf water etc (Yuan et al. 1993; Sun and Kaneko 1993; Liu 2001).

In this study, the emphasis is given to the utilization of organic carbon and nitrogen stable isotope ratios to identify provenance materials and organic mass flow and material flows in aquatic ecosystems and coastal ocean environment as previously described in other world regions (Goering et al. 1990; Lucotte et al. 1991; Fry and Quinones 1994; Thornton and McManus 1994; Wu et al. 1999). Use of stable isotopes relies on the implicit assumption that they are more conservative relative to chemical composition, and hence distributions reflect mixing of materials from compositionally distinct end-member sources (Cifuentes et al. 1988). The uncertainty of provenance discrimination is greatly reduced by simultaneous application of two or more isotope tracers (Cifuentes et al. 1988; Tan et al. 1991), though the primary isotopic signatures can be obscured in heterotrophic event (e.g., catabolism) in early diagenesis (Benner et al. 1991; Montoya 1994).

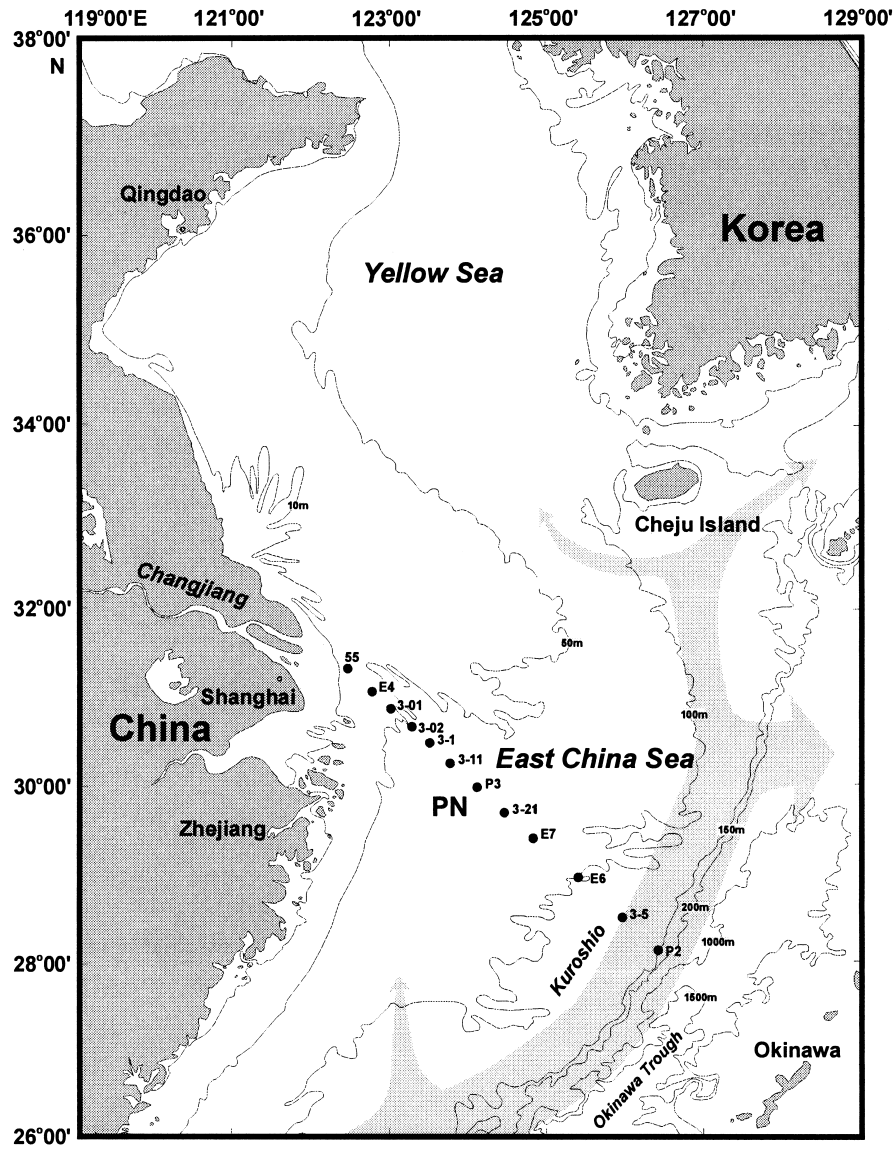


Figure 1. Stations of survey reported in this study.

Materials and methods

The field observation was carried out along the PN section of R/V "Dong Fang Hong 2" cruise on October 20 – November 8, 2000 (Figure 1). A CTD-Rosette assembly with Niskin bottles was used to measure the profiles of temperature, salin-

ity and total suspended matter continuously along the depth in all stations. Water is sampled for chlorophyll and POC/N, stable isotope ratios in most sample station at certain depths (Figures 2d and 3). After collection, the water samples were filtered through Whatman 47 mm GF/F glass fiber filters with controlled pressure to avoid the broken of cells. The filters were pre-heated at 450 °C to reduce background carbon level. After filtration, filters plus trapped particles were frozen and stored in a freezer. In the laboratory, the samples were dried in a freeze-dryer.

The contents of organic carbon and nitrogen were determined using a CHN elemental analyzer (Carlo Erba 1108) after removing the carbonate fraction by leaching with 0.1 N HCl (Zhang et al. 1997). The detection limit is 1×10^{-5} with precision of < 5–10%, estimated by repeated analysis. The carbon and nitrogen isotopic compositions of POM were determined using attached to a DELTA^{plus}/XL isotopic ratio mass spectrometer (Finnigan MAT Com. USA) and a Carlo Erba 2500 elemental analyzer in combination. Duplicate determinations were made for each of the samples. The isotopic compositions of carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) are expressed by:

$$\delta^{13}\text{C} \quad \text{or} \quad \delta^{15}\text{N} = (R_{\text{sample}}/R_{\text{standard}} - 1.0) \times 1000 \quad (1)$$

where R_{sample} and R_{standard} are the heavy (^{13}C and ^{15}N) to light (^{12}C and ^{14}N) isotope ratios of sample and standard, respectively. The standards for isotopic measure are PDB for carbon and air for nitrogen (Fritz and Fontes 1980). The precision of the analysis is $\pm 0.2\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.3\text{‰}$ for $\delta^{15}\text{N}$, respectively.

Results

Hydrographic properties

Vertical profiles of temperature, salinity, total suspended matter and chlorophyll *a* were obtained at the PN section of the ECS shelf. Temperature of surface waters (0–30 m) shows a vertically well mixed profile, increasing from 20 °C off Changjiang Estuary to 24 °C at the edge of the shelf (Figure 2a). At P2 station, the depth of well-mixed profile of surface water temperature could reach around 80 m. Temperature decreased across the thermocline, which is normally at depth of 35 m in this season. The near-bottom waters over the shelf at the depth (< 60 m) have a narrow range of temperature, i.e., 20–22 °C, typically at P3 and E7 stations. However, the bottom water of Kuroshio has, however, much lower temperature, for example 15–17 °C at P2 station.

The salinity distribution along the PN section is shown in Figure 2b. In the distance of 250 km off the Changjiang Estuary, there was a typical cross-section distribution of salinity along the transect (increased from 26 to 33‰), which is quite different from the distribution in summer. In the summer, the Changjiang effluent plume spread over the surface water of the continental shelf with stratified distribution (Liu 2001). In this study, it indicated the well mixing of fresh Changjiang

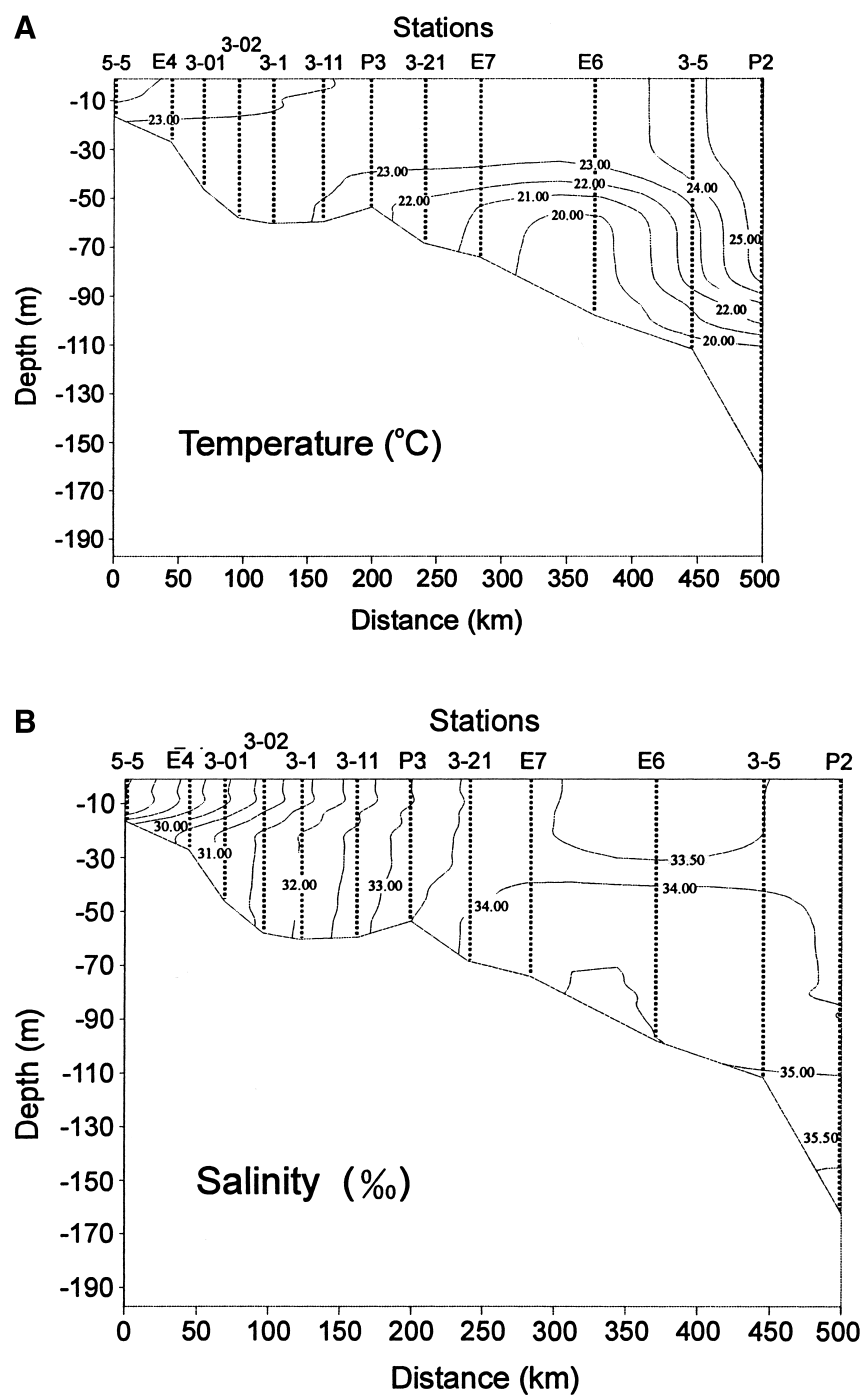


Figure 2. Vertical sections of the distributions of temperature (a) and salinity (b) and total suspended matter (TSM) (c) and chlorophyll (d) for the PN section on the autumn cruise.

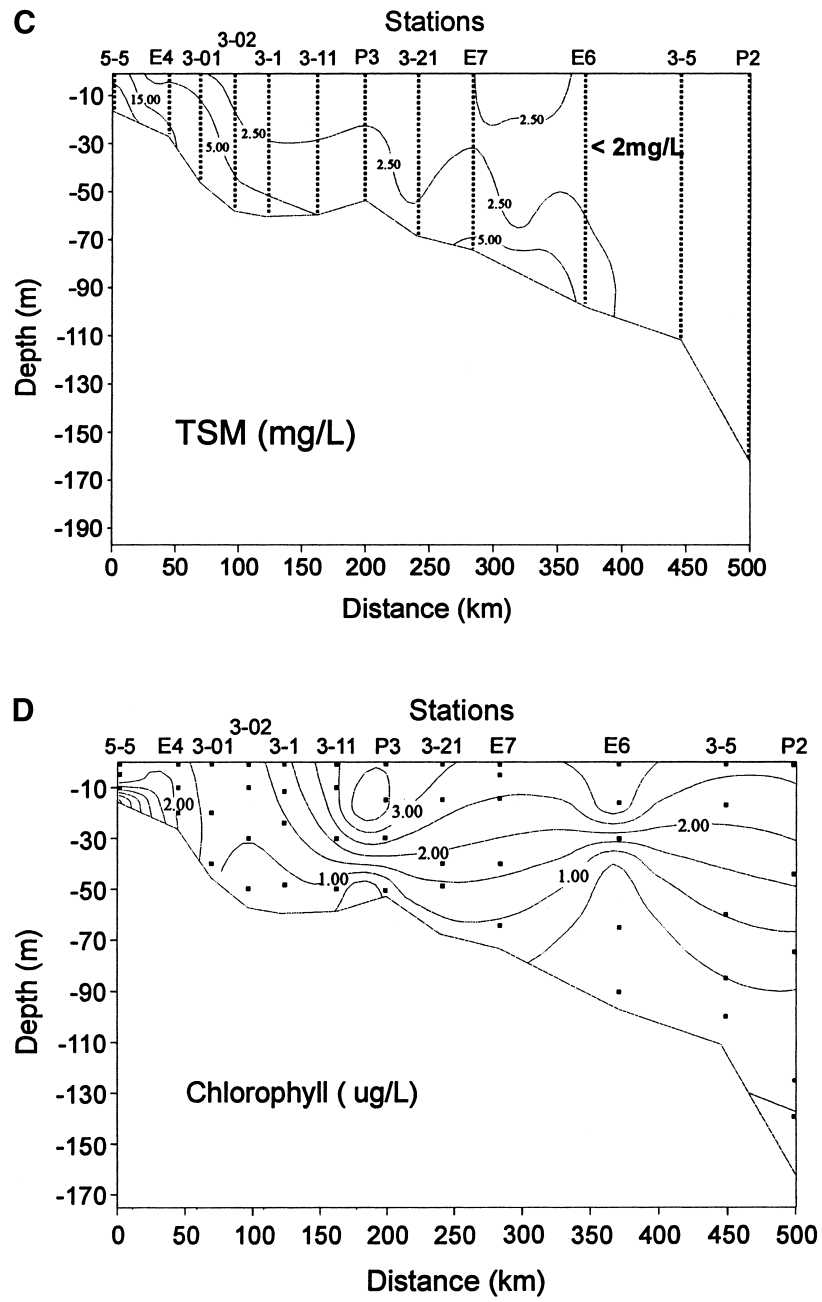


Figure 2. Continued.

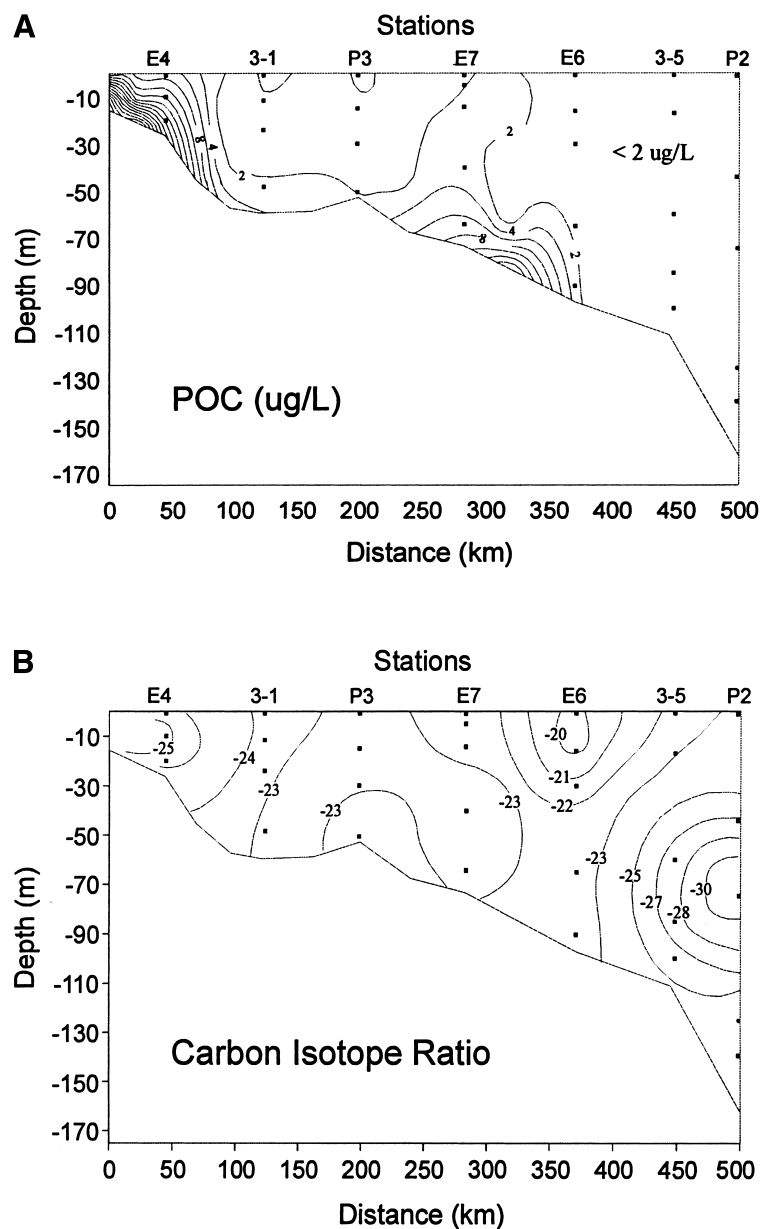


Figure 3. Vertical sections of the distributions of POC (a) and $\delta^{13}\text{C}$ (b) and $\delta^{15}\text{N}$ (c) for the PN section on the autumn cruise.

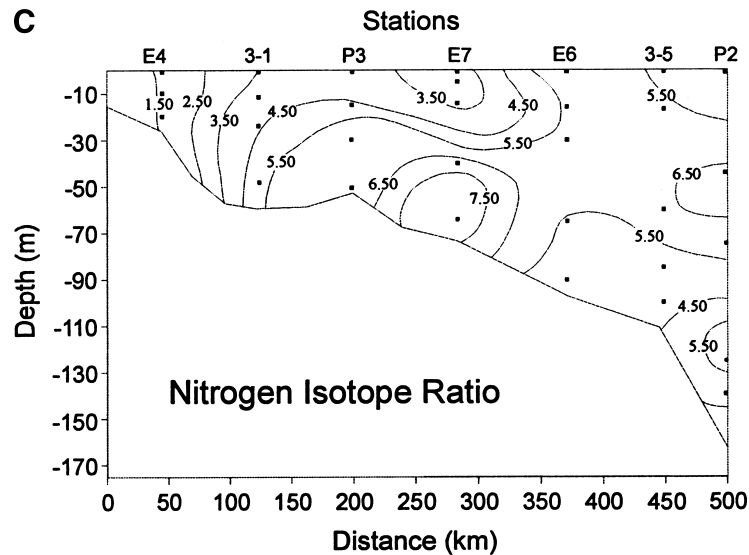


Figure 3. Continued.

water with high saline shelf water off the Changjiang Estuary. The salinity distributions of surface water of the shelf showed less saline than the intruding Kuroshio Surface Water ($S = 34.4\text{--}34.6\text{‰}$) at P2 station. The stratification structure of salinity distribution was observed in the outer shelf. There was a halocline at the depth of 40 m. At the bottom layer, there existed rather a uniform salinity ($35\text{--}36\text{‰}$), but a fairly strong vertical gradient ($15\text{--}22\text{ °C}$), which are characteristics of the Kuroshio Subsurface Water (KSSW). The cool and saline bottom water in the outer shelf indicated intrusion of KSSW.

As expected, total suspended matter (TSM) distributions resemble the salinity distributions off the Changjiang Estuary (Figure 2c). The concentration of TSM rapidly decreased along the transect of the shelf. The distribution of TSM of shelf water was quite uniform in whole water column and just in a narrow range of $2\text{--}4\text{ mg/l}$. At the bottom of shelf edge, a relatively high TSM was observed, which could be attributed to resuspension due to sharp topography. In P2 station, TSM concentrations in the whole water column were less than 2 mg/l .

The distribution of chlorophyll *a* showed strong stratified characteristics over the whole shelf and Kuroshio water (Figure 2d). Out of the Changjiang estuary, chlorophyll *a* distributed as cross-section variation. Two chlorophyll *a* maximum existed, one in Changjiang Estuary ($\sim 2\text{ mg m}^{-3}$) and the other on shelf surface layer ($\sim 4\text{ mg m}^{-3}$). In the upper 50 m shelf water (around euphotic zone), the chlorophyll *a* concentration varied in the narrow range of $1\text{--}3\text{ mg m}^{-3}$. Bottom chlorophyll *a* concentrations decreased to less than 1 mg m^{-3} .

Obviously, several types of water mass can be identified along the PN section according to distributions of temperature, salinity, TSM and chlorophyll *a*. The Changjiang plume front is characterized by low salinity as well as by high TSM,

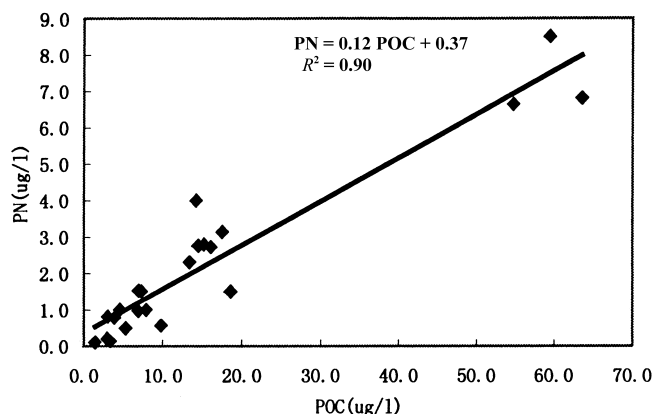


Figure 4. Particulate organic carbon content ($\mu\text{g/l}$) vs particulate nitrogen content ($\mu\text{g/l}$).

which occupied mainly at Station E4 and P3. The shelf water is largely found in the zone between Station P3 and E6. The water usually has a relative uniform temperature and salinity but low TSM. The Kuroshio surface water could be identified at P2 station surface layer because of high temperature and salinity. The intrusion of KSSW is also observed at the depth of 100–150 m of Station E6 and P2.

Organic carbon and nitrogen

Figure 3a is the POC profile in the PN section. The POC maximum occurred near to the Changjiang Estuary with the high turbidity (50–60 $\mu\text{g/l}$). In the inner shelf, the concentration was homogenous at the surface layer. POC abundance generally decreased seaward from the Changjiang Estuary to Kuroshio water (P2 station). The minimum concentrations of POC ($< 2 \mu\text{g/l}$) were observed around P2 station. A relatively high concentration of POC (15 $\mu\text{g/l}$) in the bottom water at the shelf edge obviously resulted from sediment resuspension.

The distribution of particulate nitrogen (PN) resembled that of POC as shown above. The correlation between POC and PN was very good (Figure 4). The correlation coefficient (R^2) was 0.90. The slopes of the linear regression of PN against POC was 0.12, corresponding to C/N atomic ratios of 9.72.

POM $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$

Figure 3b–c presents vertical profiles of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of POM at the PN section. The value of $\delta^{13}\text{C}$ was the greatest in the mid shelf ($-21 \sim -19\text{‰}$) and decreased at the surface layer in both eastwards and westwards. Out of the Changjiang Estuary, $\delta^{13}\text{C}$ values ($-25 \sim -23\text{‰}$) were observed homogenous in the whole water column. A much lighter $\delta^{13}\text{C}$ values ($-31 \sim -27\text{‰}$) intruded to the shelf water from the shelf slope at the mid layer. The downward decreasing trends were found

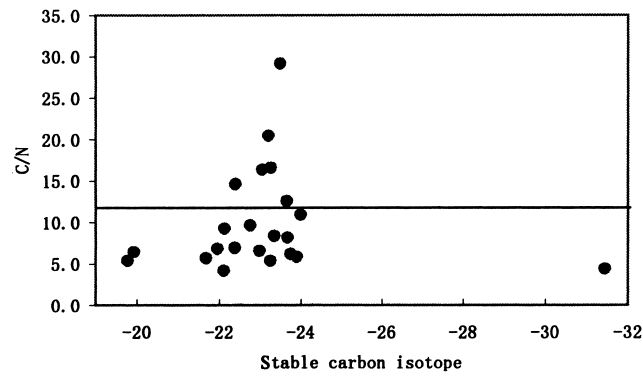


Figure 5. Stable carbon isotope ratio of TSM vs Atomic carbon: nitrogen ratio (C/N).

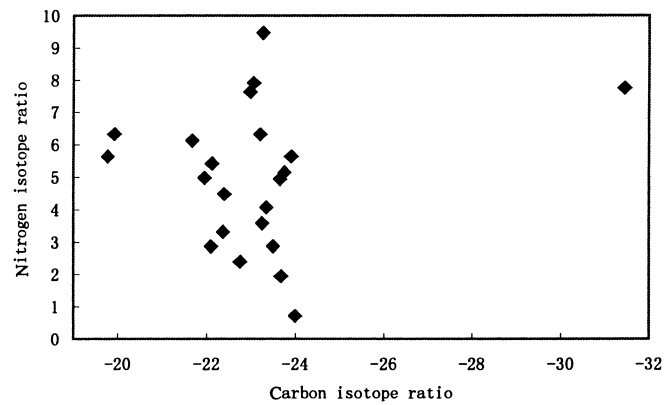


Figure 6. Stable carbon isotope ratio vs stable nitrogen isotope ratio of TSM at the PN section.

in the $\delta^{13}\text{C}$ values at the mid and inner shelf except for the bottom water of Kuroshio.

In contrast to $\delta^{13}\text{C}$ distribution, $\delta^{15}\text{N}$ profile is more complicated. Out of the Changjiang Estuary, minimum $\delta^{15}\text{N}$ value was observed and a cross-section variation stopped at the distance of 100 km. The vertical distribution of $\delta^{15}\text{N}$ showed an increase with the depth at P3 and E7 station, but more fine structure was observed in E7 station with maximum values observed at the bottom layer. At E6 station, $\delta^{15}\text{N}$ values were homogenous at the upper layer and increased downward. A higher $\delta^{15}\text{N}$ observed at intermediate depth (50–75 m) for the whole water column at Kuroshio Water.

Discussions

Provenance of organic matter in the PN section

Particulate organic matter

Several sources of organic carbon may contribute to the POM in the ECS shelf: (1) terrestrial organic carbon from the Changjiang Estuary; (2) alive or dead organic matter of planktonic origin related to primary production; (3) the contribution from the Kuroshio water; (4) Resuspension of organic matter from the bottom sediments. The relative importance of (1) and (3) can be traced from the original data of POC (Figure 3a). The primary production in the East China Sea showed strong seasonal as well as spatial variation (Guo 1991). Its higher values were observed in summer and in the Changjiang Estuary (Wen 1995). In this study, higher Chl *a* values, which were in low concentrations (2.7–4.0 µg/l), were only observed in surface water over the continental shelf. The average C/N ratio was just 9.72, which is quite different from the Redfield ratio of 6.63 (Redfield et al. 1963). All the above, the contribution of organic matter from *in situ* primary production is quite limited in autumn. Many studies noticed high particulate fluxes and sedimentation rates observed on the shelf edge (Chung and Chang 1994; Chung and Hung 2000; Gao et al. 2000). The resuspension mechanism is still not clearly identified but the significant flux from the bottom boundary layer could not be overlooked (Hung et al. 2000).

The C/N ratio is often indicative as the predominant source of organic matter in a system. Phytoplankton C/N ranges from 6–9 (Holligan et al. 1984). Bacterioplankton are nitrogen-rich and have C/N from 2.6–4.3 (Lee and Fuhrman 1987). The terrestrial organic matter can have significantly higher (C/N) (> 12; Hedges & Mann, 1979). The C/N ratios of POM along the PN section varied from 4.2 to 29.2 (Figure 5), which were similar to the previous study in the ECS shelf (Liu et al. 1998). Higher C/N values were detected from the bottom samples and samples collected at the outer shelf. Figure 5 indicates the relationship between stable carbon isotope ratios and C/N ratios. Normally, high C/N ratio can be indicative as terrestrial origin with much light $\delta^{13}\text{C}$ value. However, some POM of bottom water have high C/N ratios with heavy $\delta^{13}\text{C}$ values and the POM of subsurface sample of P2 station have low C/N ratios with much light $\delta^{13}\text{C}$ values. The decomposition processes (e.g., autolysis, leaching and microbial mineralization) should be the explanation of such variations (Roman 1980; Meyers et al. 1984). In general, the C/N ratio of POM might be expected to decrease or increase during decomposition with various sources. Such variation could make the C/N ratio superimposed upon the estimation of different sources of organic matter (Rice and Tenore 1981; Thornton and McManus 1994).

Carbon isotope compositions

The range of carbon isotope ratios of organic matter is broad in aquatic ecosystems, ranging from $-30 \sim -26\text{‰}$ in runoff from terrestrial carbon sources to $-22 \sim -18\text{‰}$ for carbon from phytoplankton production (Cifuentes et al. 1996). In the Changjiang Estuary, organic matter comes from river runoff, *in situ* production and

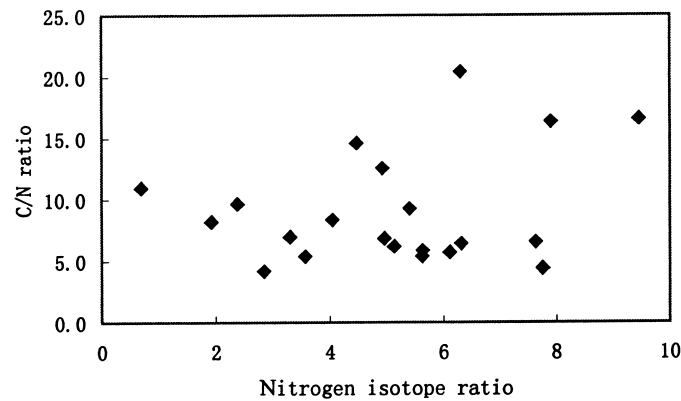


Figure 7. Stable nitrogen isotope ratio of TSM vs Atomic carbon: nitrogen ratio (C/N).

sewage. The $\delta^{13}\text{C}$ values were more positive ($-22 \sim -24\text{‰}$) than expected for terrestrial organic matter (-27‰) because of the modification of sewage and *in situ* production (Tan et al. 1991). In the shelf water, the variation of $\delta^{13}\text{C}$ values was quite narrow from -19.8 to -23.7‰ , which indicated the predominance of *in situ* production. From the distribution of $\delta^{13}\text{C}$ values of POM of surface waters except P2 station, an increase of $\delta^{13}\text{C}$ values was observed from the Changjiang Estuary to the shelf region. Theoretical considerations and laboratory studies suggest minimal changes in the $\delta^{13}\text{C}$ composition of organic detritus following extensive and prolonged decomposition (Gearing et al. 1984). But the seaward ^{13}C enrichment of POM observed here appears unlikely to reflect selective bacterially mediated removal of ^{12}C from terrigenous carbon for the reason of the consistence of the known water circulation.

However, the more ^{13}C – depleted values was observed in the subsurface water of P2 station, which locates on the shelf slope, where the Kuroshio Subsurface Water intrudes into the shelf water. Such more negative values (indicating ^{13}C depletion) were also observed in polar seas and have been attributed to an increase in the dissolved CO_2 pool due to lower temperatures, which results in a greater isotopic fractionation during carbon assimilation (Rau et al. 1992). More depleted bacterial $\delta^{13}\text{C}$ values were detected from Gulf of Mexico, which suggests that carbon from sources other than phytoplankton production or terrestrial organic matter support production of the bacterial assemblage. Possible sources include light hydrocarbons from seep areas (e.g., methane, ethane, propane and butane) and the chemoautotrophic processes of methane oxidation and nitrification (Kelley and Coffin 1998). The ^{13}C -depleted samples in P2 station could not have originated from vascular plant material because the low C/N ratios (Figure 5). Possibly they result from greater degradation of proteinaceous and carbohydrate components compared with lipid and lignin fractions (Benner et al. 1990). Since lipid and lignin fractions have more negative $\delta^{13}\text{C}$ than proteins and carbohydrates, the selective loss of the latter fractions would result in lighter carbon isotope ratios (Cifuentes et al. 1996). The second mechanism is ^{13}C – depleted isotope ratios of POM resulted from phy-

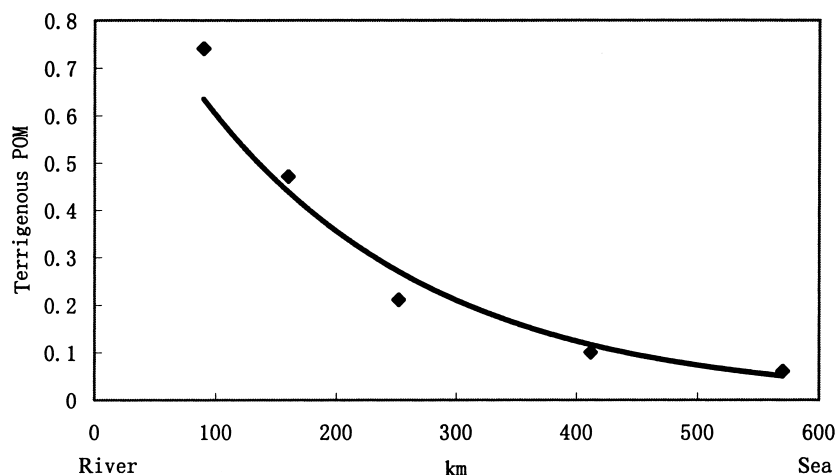


Figure 8. The estimated percentage of terrigenous POM distribution from the Changjiang to the shelf edge of ECS.

toplankton assimilated ^{13}C – depleted DIC, which is the product of active bacterial contribution of the organic matter within the study area (Coffin and Cifuentes 1999). Future research that applies to survey carbon cycling in the shelf slope needs to account for factors that cause variation in the isotopic signature of the DIC pool.

Nitrogen isotope compositions

Two-dimensional stable isotope analysis ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) provides a possibility to survey relative contribution of multiple sources of organic matter to an interested region. Figure 6 shows that the bottom of shelf water could be the fourth potential source of organic matter in the ECS shelf area except for the three distinct organic material sources (the Changjiang contribution, *in situ* primary production in the shelf water and the Kuroshio intrusion). However, the relative contributions of the Changjiang Estuary and *in situ* primary production are dominant in most samples. The exchange of the shelf water and the Kuroshio Current is limited in autumn season.

Although nitrogen stable isotopes have been successfully employed as organic tracers in aquatic systems, dynamic cycling of nitrogen are subject to kinetic isotope fraction effects especially during the biogenic transformation and recycling of dissolved and particulate nitrogen compounds (Gearing et al. 1984; Cifuentes et al. 1988; Goering et al. 1990; Montoya 1994; Wu et al. 1999). It is expected that nitrogen cycling in the bottom of shelf water would create isotopically enriched nitrogen in the particulate organic matter through remineralization (such as $\delta^{15}\text{N}$ in E7 station). High $\delta^{15}\text{N}$ values correspond with high C/N ratios, which suggests the latter are produced principally as a result of organic matter diagenesis (Figure 7) (DeMaster et al. 1985; Thornton and McManus 1994; Cifuentes et al. 1996). As (i.e., microbial mineralization) proceeds and the total amount of nitrogen presented

is reduces, ^{14}N is preferentially lost from the organic substrate, which become progressively enriched in ^{15}N . Consequently higher decomposed organic matter will contain little nitrogen but with enriched in ^{15}N . Such alteration of POM $\delta^{15}\text{N}$ has been observed in other studies (Cifuentes et al. 1988; Goering et al. 1990; Montoya 1994), and is regarded as one of the sources of organic nitrogen in this system.

However, in the Kuroshio waters it is not expected that higher $\delta^{15}\text{N}$ values correspond with higher C/N ratios (Figure 7). The source of this nitrogen contained in POM was likely to be inorganic nitrogen that is assimilated into POM by microbial activity (Coffin and Cifuentes 1999). Such conclusion is support with the characteristics of the Kuroshio water, which is rich in nitrate and ammonium resulted in remineralization of sinking particles (Liu et al. 1996). The average of $\delta^{15}\text{N}$ values of POM in the Kuroshio water is 5.6–7.8‰. This was similar to the average of $\delta^{15}\text{N}$ values of nitrate of the Kuroshio water (5.5 to 6.1‰), and suggests microbial assimilation of the inorganic nitrogen in to POM (Liu et al. 1996).

Cross shelf export of POC

The exchange of water masses between the ECS and the KW is a highlight in recent year (Nitani 1977; Tang et al. 1994; Yuan et al. 1999). Advective export of POC was observed in association with a cyclonic eddy at the shelf edge northeast of Taiwan (Liu et al. 2000). Water exchange in the PN section also showed a cyclonic eddy: the KW inserts to the shelf area from the bottom and the subsurface layer and the SW extends to the Kuroshio area from surface and sub-surface. The total amount of exchange what in autumn is estimated to be $1.17 \times 10^6 \text{ m}^3 \cdot \text{s}^{-1}$, which is larger than the winter ($0.90 \times 10^6 \text{ m}^3 \cdot \text{s}^{-1}$) and less than the summer ($3.22 \times 10^6 \text{ m}^3 \cdot \text{s}^{-1}$), similar to the spring ($1.25 \times 10^6 \text{ m}^3 \cdot \text{s}^{-1}$) (Lin et al. 1999). The amount of KW intruding into the shelf is about $0.53 \times 10^6 \text{ m}^3 \cdot \text{s}^{-1}$, while the export of shelf water is $0.64 \times 10^6 \text{ m}^3 \cdot \text{s}^{-1}$ (Lin et al. 1999). The inflow concentration is taken as the POC concentrations at 160 m in depth in the KW; the outflow concentration is taken as the mean concentration in the top 50 m in the outer shelf. Thus the horizontal transport of POC across the shelf in the PN section can be derived from the mean POC concentration and exchange water volumes. The net export flux of POC in the PN section is 4.1 kmol C/s and the annual export is 129 Gmol C/yr. The POC export is more than the export of POC at the south ESC in summer (106 Gmol C/yr) but considerably smaller than the riverine inputs (750–875 Gmol C/yr, Cauwet and MacKenzie (1993)). The outflowing shelf water over the whole ECS are estimated to export $506 \pm 185 \text{ Gmol C/yr POC}$, which means the export of POC from the PN section could account to $\sim 20\%$ of the total (Chen and Wang 1999a).

Impact of changjiang over the shelf regions

To better understand the carbon cycles and biogeochemical processes in the East China Sea, which is one of the most broad and productive shelf area in the world, it is important to study the contribution of terrigenous organic matter from Changjiang over the shelf region. As mentioned before, the terrigenous inputs from the Changjiang, together with the contribution of KW and the marine POM by *in*

Table 1. The distinction of four end members in this study.

	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$	POC%
Terrestrial POM ^a	-27	0.7	0.5
Kuroshio POM ^b	-24	4	1.0
Marine POM	-19	6.5	1.5
Detritus POM	-22	9.5	0.06

^aThe data of Terrestrial POM is referred from Wu et al. (2002); ^bThe data of Kuroshio POM is referred from Sheu et al. (1999) and Nakatsuka et al. (1997).

situ primary production, the detritus from remineralization process, are the main sources of POM in the ECS shelf. Then the contribution of individual sources/pathways to the POM composition at marine station can be estimated by matrix arithmetic:

$$\begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1m} \\ a_{21} & \cdots & & \\ \vdots & & & \\ a_{n1} & a_{n2} & \cdots & a_{nm} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ \vdots \\ X_m \end{bmatrix} = \begin{bmatrix} Y_1 \\ Y_2 \\ \vdots \\ Y_n \end{bmatrix} \quad (2)$$

where (a_{ij}) represents the percentage concentration of the j th component in the i th source material (X_i), Y_i accounts for the i th element concentration in marine environment. The weight factor (a_{ij} in%) of various source contributions to the observed POM composition can be solved by statistics (e.g., least-squares method) when $m = n$ (Haswell 1992). In the case of $m = n$, a definite solution can be obtained. In this study we will use $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and POC(%) of particulate matter to characterize organic matter sources. The four end members of particulates are listed in Table 1.

Figure 8 indicates the percentage of terrigenous POM distribution from the Changjiang estimated by this study, which shows the contribution of continental materials upon the biogeochemical cycles of POM in the East China Sea. Within a distance of < 100 km off the river mouth, the terrigenous POM is dominated as 70–80% of total POM where the biogeochemical cycling of POM is controlled by water/sediment processes. The percentage of terrestrial POM decreases quickly at the distance around 150 km off the mouth and only half of POM could be traced from the continental inputs, where is also a productive fishing area and the fruitful terrigenous POM are the important nourishing contributor. Further off shore (> 250 km), the contribution of terrigenous POM is quite limited where the KW intrudes into from the shelf edge and brings the organic matter from marine pool. Such distribution is expected to be similar to the previous study of fluvial transport for particulate heavy metals from the Changjiang into the East China Sea and the terrestrial POM can be traced over a distance of ~ 250 km over the shelf region (Zhang 1999).

Conclusion

The PN section is an ideal site to observe the active physical and biogeochemical process that transport, transform, or exchange carbon. The vertical and geographical variation of carbon and nitrogen isotope of POM showed predominance features that reflect the contribution of the terrigenous POM from the Changjiang and the Kuroshio Water's intrusion at the shelf edge. The incorporation of resuspended sediment particles in the bottom layer was observed in this study too.

The distribution of terrestrial inputs was estimated by matrix arithmetic based on the POM mass balance and the isotope values that only controlled by physical mixing. It is expected that the continental material could disperse over a distance of 250 km eastwards on the East China Sea shelf region.

The estimation of sources recorded by $\delta^{13}\text{C}$ data was partly confirmed by equivalent $\delta^{15}\text{N}$ and C/N compositions that reflected greater control by organic matter diagenesis and biological processing. However, the lighter contribution of $\delta^{13}\text{C}$ data of the Kuroshio samples also indicates the alteration of the isotope values by microbial or other processes.

The net export flux of POC in the PN section is 4.1 kmol C/s and the annual export is 129 Gmol C/yr and 23 Gmol C/yr more than the export of POC at the south ESC in summer, which could account to $\sim 20\%$ of the total (Chen and Wang 1999a).

Acknowledgements

This study is funded by the Special Funds from National Key Basic Research Program of P. R. China (G1999043705) and of Natural Science Foundation of China (No. 40006008). The authors thank Drs. S.M. Liu, Dr J.L. Ren and Q. Wang for their assistance in field and laboratory work. The anonymous reviewers and Dr Billen G. are thanked for constructive comments on the manuscript.

References

- Benner R., Hatcher P.G. and Hedges J.I. 1990. Early diagenesis of mangrove leaves in a tropical estuary bulk chemical characterization using solid-state ^{13}C NMR and elemental analysis. *Geochim. Cosmochim. Acta* 54: 2003–2014.
- Benner R., Fogel M.L. and Sprague E.K. 1991. Diagenesis of below ground biomass of *spartina alterniflora* in salt marsh sediments. *Limnol. Oceanogr.* 36: 1358–1374.
- Cauwet G. and MacKenzie F.T. 1993. Carbon inputs and distributions in estuaries of turbid rivers: the yangtze and yellow Rivers (china). *Mar. Chem.* 43: 235–246.
- Chen C.T.A., Ruo R., Pai S.C., Liu C.T. and Wong G.T.F. 1995. Exchange of water masses between the East China Sea and the Kuroshio off northeastern Taiwan. *Cont. Shelf Res.* 15: 19–39.
- Chen T.A.C. and Wang S.L. 1999a. Carbon, alkalinity and nutrient budgets on the East China Sea continental shelf. *J. Geophys. Res.* 104: 20675–20686.

- Chen Y.L.L., Lu H.B., Shiah F.K., Gong G.C., Liu K.K. and Kanda J. 1999b. New production and F-ratio on the continental shelf of the East China Sea: comparisons between nitrate inputs from the subsurface Kuroshio current and the Changjiang River. *Estuarine, Coastal and Shelf Sci.* 48: 59–75.
- Chen Y.L.L., Chen H.Y., Lee W.H., Hung C.C., Wong G.T.F. and Kanda J. 2001. New production in the East China Sea, comparison between well-mixed winter and stratified summer conditions. *Cont. Shelf Res.* 21: 751–764.
- Chung Y. and Chang W.C. 1994. Pb-210 fluxes and sedimentation rates on the lower continental slope between Taiwan and south Okinawa Trough. *Cont. Shelf Res.* 15: 149–164.
- Chung Y. and Hung G.W. 2000. Particulate fluxes and transport on the slope between the southern East China Sea and the South Okinawa Trough. *Cont. Shelf Res.* 20: 571–597.
- Cifuentes L.A., Sharp J.H. and Fogel M.L. 1988. Stable carbon and nitrogen isotope biogeochemistry in the Delaware Estuary. *Limnol. and Oceanogr.* 33: 1102–1115.
- Cifuentes L.A., Coffin R.B., Solorzano L., Cardenas W., Espinoza J. and Twilley R.R. 1996. Isotopic and elemental variations of carbon and nitrogen in a Mangrove Estuary. *Estuarine, Coastal and Shelf Sci.* 43: 781–800.
- Coffin R.B. and Cifuentes L.A. 1999. Stable isotope analysis of carbon cycling in the Perdido Estuary, Florida. *Estuaries* 22: 917–926.
- DeMaster D.J., McKee B.A., Nittrouer J., Qian J. and Cheng G. 1985. Rates of sediment accumulation and particle reworking based on radiochemical measurements from continental shelf deposits in the East China Sea. *Cont. Shelf Res.* 4: 143–158.
- Fritz P. and Fontes J.C. 1980. *Handbook of environmental isotope geochemistry*. Elsevier Scientific Publishing Co., Amsterdam.
- Fry B. and Quinones R.B. 1994. Biomass spectra and stable isotope indicators of trophic level in zooplankton of the northwest Atlantic. *Mar. Ecol. Prog. Ser.* 76: 149–157.
- Gao S., Cheng P., Wang Y.P. and Cao Q.Y. 2000. Characteristics of suspended sediment concentrations over the areas adjacent to Changjiang River Estuary, the Summer of 1998. *Mar. Sci. Bulletin* 2: 14–24.
- Gearing J.N., Gearing R.J., Rudrick D.T., Requejo A.G. and Hutchins M.J. 1984. Isotope variation of organic carbon in a phytoplankton based temperate estuary. *Geochim. Cosmochim. Acta* 48: 1089–1098.
- Goering J.N., Alexander V. and Haubensack N. 1990. Seasonal variability of stable carbon and nitrogen isotope ratios of organisms in a North Pacific Bay. *Estuar. Coast. and Shelf Sci.* 30: 239–260.
- Guo Y.J. 1991. The Kuroshio. Part II. Primary productivity and phytoplankton. *Oceanographic Mar. Biol. Ann. Rev.* 29: 155–189.
- Hall J., Smith S.V. and Boudreau P.R. 1996. Report on the international workshop on continental shelf fluxes of carbon, nitrogen and phosphorus. LOICZ Reports and Studies 96-9. Texel, The Netherlands.
- Haswell S.J. 1992. *Practical Guide to Chemometrics*. Marcel Dekker, Inc., New York, pp. 5–37.
- Hedges J.I. and Man D.C. 1979. The characterization of plant tissues by their lignin oxidation products. *Geochim. Cosmochim. Acta* 43: 1803–1807.
- Holligan S.G., Montoya J.P., Nevins J.L. and McCarthy J.J. 1984. Vertical distribution and partitioning of organic carbon in mixed, frontal and stratified waters of the English Channel. *Mar. Ecol. Prog. Ser.* 14: 111–127.
- Hung J.J., Lin P.L. and Liu K.K. 2000. Dissolved and particulate organic carbon in the southern East China Sea. *Cont. Shelf Res.* 20: 545–569.
- Ichikawa H. and Beardsley R.C. 1993. Temporal and spatial variability of the volume transport of the Kuroshio in the East China Sea. *Deep-sea Res.* 40: 583–605.
- Kelley C.A. and Coffin R.B. 1998. Stable isotope evidence for alternative bacterial carbon sources in the Gulf of Mexico. *Limnol. Oceanogr.* 43: 1962–1969.
- Kim Y.L. 1992. *Marine Geology of the East China Sea* (in Chinese). China Ocean Press, Beijing.
- Lee S.H. and Fuhrman J.A. 1987. Relationships between biovolume and biomass of naturally derived marine bacterioplankton. *Appl. and Environ. Microbiol.* 53: 1298–1303.

- Lin K., Chen Z.S., Guo B.H. and Tang Y.X. 1999. Seasonal transport and exchange between the Kuroshio water and shelf water. In: Hu D.X. and Tsunogai S. (eds), *Margin Flux in the East China Sea*. China Ocean Press, Beijing, pp. 21–34.
- Liu K.K., Lai Z.L., Gong G.C. and Shiah F.K. 1995. Distribution of particulate organic matter in the southern East China Sea: implications in production and transport. *Terre. Atmos. and Ocean. Sci.* 6: 27–45.
- Liu K.K., Su M.J., Hsueh C.R. and Gong G.C. 1996. The nitrogen isotopic composition of nitrate in the Kuroshio Water northeast of Taiwan: evidence for nitrogen fixation as a source of isotopically light nitrate. *Mar. Chem.* 54: 273–292.
- Liu K.K. and Chao S.Y. 1999. Continental margin carbon fluxes. In: Hanson R.B., Ducklow H. and Field J.G. (eds), *The Dynamic Ocean Carbon Cycle*. Cambridge University Press, Cambridge, pp. 187–239.
- Liu K.K. 2000. Exploring continental margin carbon fluxes on a global scale. *Eos*. 81: 641–644.
- Liu K.K., Iseki K. and Chao S.Y. 2000. Continental margin carbon fluxes. In: Hanson R.B., Ducklow H.W. and Field J.G. (eds), *The Changing Ocean Carbon Cycle: A Midterm Synthesis of the Joint Global Ocean Study*. International Geosphere-Biosphere Programme Book Series, Cambridge University Press, Cambridge, pp. 187–239.
- Liu X.Q. 2001. Distribution features of T-S and chemical constituents at the PN section in the East China Sea during summer. *Oceanologia et Limnologia Sinica* 32: 204–212, (in Chinese).
- Liu W.C., Wang R. and Li C.L. 1998. C/N ratios of particulate organic matter in the East China Sea. *Oceanologia et Limnologia Sinica* 29: 467–470, (in Chinese).
- Lucotte M., Hillaire-Marcel C. and Louchouart P. 1991. First order organic carbon budget in the St Lawrence Lower Estuary from ^{13}C data. *Estuar. Coast. and Shelf Sci.* 32: 297–312.
- Meyers P.A., Leenheer M.J., Eadie B.J. and Maule S.J. 1984. Organic geochemistry of suspended settling particulate matter in Lake Michigan. *Geochim. Cosmochim. Acta* 48: 443–452.
- Montoya J.P. 1994. Nitrogen isotope fraction in the modern ocean: implications for the sedimentary record. In: Zahn R., Kaminski M.A., Labeyrie L. and Pederson T.F. (eds), *Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change*. Springer-Verlag, pp. 259–279.
- Nakatsuka T., Handa N., Harada N., Sugimoto T. and Imaizumi S. 1997. Origin and decomposition of sinking particulate organic matter in the deep water column inferred from the vertical distributions of its $\delta^{15}\text{N}$, $\delta^{13}\text{C}$ and $\delta^{14}\text{C}$. *Deep-Sea Research I* 44: 1957–1979.
- Nitani H. 1977. Kuroshio—its physical aspects. In: *Beginning of the Kuroshio*. Tokyo Univ. Press, Tokyo, pp. 129–163.
- Rau G.H., Takahashi T., Des Marais D.J., Repeta D.J. and Martin J.H. 1992. The relationship between $\delta^{13}\text{C}$ of organic matter and $[\text{CO}_2(\text{aq})]$ in ocean surface water: Data from a JGOFS site in the northeast Atlantic Ocean and a model. *Geochim. Cosmochim. Acta* 56: 1413–1419.
- Redfield A.C., Ketchum B.H. and Richards F.A. 1963. The influence of organisms in the composition of seawater. In: Hill M.N. (ed.), *The Sea*. Vol. 2. Interscience, NY, USA, pp. 26–77.
- Rice D.L. and Tenore K.R. 1981. Dynamics of carbon and nitrogen during the decomposition of detritus derived from estuarine macrophytes. *Estuar. Coast. and Shelf Sci.* 13: 681–690.
- Roman M.R. 1980. Tidal resuspension in Buzzards Bay, Massachusetts. III. Seasonal cycles of nitrogen and carbon: nitrogen ratios in the seston and zooplankton. *Estuar. Coast. and Shelf Sci.* 11: 9–16.
- SCOR 1994. Report of the JGOFS/LOICZ Task Team on continental Margin Studies. JGOFS Report No. 16. Scientific Committee on Oceanic Research, Baltimore.
- Sheu D.D., Jou W.C., Chung Y.C., Tang T.Y. and Hung J.J. 1999. Geochemical and carbon isotopic characterization of particles collected in sediment traps from the East China Sea continental slope and the Okinawa Trough northeast of Taiwan. *Cont. Shelf Res.* 19: 183–203.
- Sun X.P. and Kaneko I. 1993. Variations of the Kuroshio during the period of 1989–1991. *Essays on the Investigation of Kuroshio Heichao Diaocha Yanjiu Luwenxuan* 5: 52–68.
- Tan F.C., Cai D.L. and Edmond J.M. 1991. Carbon isotope geochemistry of the Changjiang Estuary. *Estuar. Coast. and Shelf Sci.* 32: 395–404.
- Tang Y., Lin K. and Tomosi T. 1994. Analysis of some features of volume transport of the Kuroshio in the East China Sea. *Oceanologia et Limnologia Sinica* (in Chinese) 25: 643–651.

- Thornton S.F. and McManus J. 1994. Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: evidence from the Tay estuary, Scotland. *Estuar. Coast. and Shelf Sci.* 38: 219–233.
- Tian R.C., Hu F.X. and Martin J.M. 1993. Summer nutrient fronts in the Changjiang (Yangtze River) estuary. *Estuar. Coast. and Shelf Sci.* 37: 27–41.
- Tsunogai S., Watanabe S. and Sato T. 1999. Is there a "continental shelf pump" for the absorption of atmospheric CO₂? *Tellus* 51B: 701–712.
- Walsh J.J., Biscaye P.E. and Csanady G.T. 1988. The 1983–1984 Shelf Edge Exchange Processes (SEEP)-I experiment: hypotheses and highlights. *Cont. Shelf Res.* 8: 435–456.
- Wollast R. 1993. Interactions of carbon and nitrogen cycles in the coastal zone. In: Wollast R., Mackenzie F.T. and Chou L. (eds), *Interactions of C, N, P and S Biogeochemical Cycles and Global Change*. Springer, Berlin, pp. 195–210.
- Wen Y.H. 1995. A Preliminary Study of the Seasonal Variation of Primary Productivity and Light/Chlorophyll Model in the Sea Off Northern Taiwan. MS Thesis, National Taiwan Ocean University, Keelung, Taiwan, (in Chinese).
- Wu J.P., Calvert S.E. and Wong C.S. 1999. Carbon and nitrogen isotope ratios in sedimenting particulate organic matter at an upwelling site off Vancouver Island. *Estuarine, Coastal and Shelf Science* 48: 193–203.
- Wu Y., Zhang J., Zhang Z.F., Ren J.L. and Cao J.P. 2002. Seasonal variability of stable carbon and nitrogen isotopes of suspended particulate matter in the Changjiang River. *Oceanologia et Limnologia Sinica* 33: 546–552, (in Chinese).
- Yuan Y.C., Pan Z.Q., Ikuo K. and Masahiro E. 1993. Variability of the Kuroshio in the East China Sea and currents east of the Ryukyu Islands. *Essays on the Investigation of Kuroshio Heichao Diaocha Yanjiu Luwenxuan* 5: 279–297.
- Yuan Y.C., Pan Z.Q. and Wang H.Q. 1999. Volume and heat transport and material fluxes in the East China Sea during April of 1994. In: Hu D.X. and Tsunogai S. (eds), *Margin Flux in the East Chin Sea*. China Ocean Press, Beijing, pp. 11–20.
- Zhang J., Yu Z.G., Liu S.M., Xu H., Wen Q.B., Shao B. et al. 1997. Dominance of terrigenous particulate organic carbon in the high-turbidity Shuangtaizihe estuary. *Chem. Geol.* 138: 211–219.
- Zhang J. 1999. Heavy metal compositions of suspended sediments in the Changjiang (Yangtze River) estuary: significance of riverine transport to the ocean. *Cont. Shelf Res.* 19: 1521–1543.