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Biogeochemical processes controlling nutrients at the turbidity maximum and the plume water fronts in the Changjiang Estuary

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Abstract. In order to study geochemical and biogeochemical processes in estuaries, particularly in the turbidity maximum and at the plume water fronts, two cruises were carried out in the summer and winter of 1988 in the Changjiang Estuary region. The study permitted to identify two major sources of nutrients: firstly the Changjiang River carried abundant nutrients with 90–110 μmol/l of $Si(OH)_4$, 70–95 μmol/l of NO_3^- and 0.5–0.8 μmol/l of PO_4^{3-}. The annual average nutrient fluxes of the studied year were estimated as about 2.5 $\times$ 10^{12}, 1.0 $\times$ 10^{12} and 1.9 $\times$ 10^{10} g/yr for Si, N and P, respectively. However, NO_2^- and NH_4^+ did not principally originate from the freshwater discharge. Their distribution was more affected by geochemical and biogeochemical processes. Secondly nutrient release in the turbidity maximum and from sediments outside the plume water fronts was observed. In the regions where vertical convection was strengthened due to the complex hydrographic features of the studied region, nutrients released from sediments dispersed upward to the surface waters providing a basis for an increase of primary productivity.

In addition to seawater dilution, biological activities were another important factor for nutrient consumption, particularly outside the plume water fronts where biological consumption led to a noticeable removal of nutrients from surface waters.

Introduction

Estuaries are usually important ecological environments for fishing and aquaculture because rivers carry large amounts of nutrients, thus providing substantial basis for primary productivity (Bennekom et al. 1978; Cadée 1978; Edmond et al. 1981; Gu 1982; Sauders & Lewis 1988). However, when excessive amounts of nutrients are carried to estuarine systems, due to anthropogenic inputs for example, catastrophic eutrophication or events such as 'red-tides' might occur, resulting in disequilibrium of the ecosystem (Huang et al. 1986; Yang et al. 1987; Meybeck et al. 1988). Nutrients are therefore a major subject in estuarine studies.

The Changjiang River is the largest river system in China and ranks in the world the third in length (6300 km), the fifth in freshwater discharge (9.24×10^{11} m^3/yr) and the fourth in solid discharge (4.86×10^8 tons/yr). It branches three times in the estuarine region (Fig. 1): first into North Branch (NB) and South Branch (SB), then the SB into North Passage (NP) and South Passage (SP) and finally the SP into North Channel (NC) and South Channel (SC). The NP carries about two thirds of the total discharge, the SP the rest of which the NC carries another two thirds, whereas practically no net freshwater discharge passes through the NB. The hydrographic structure is very complex in the Changjiang estuarine region. In addition to the river discharge, the Taiwan Warm Current (TWC) flowing northwestward from the South and the Yellow Sea Coastal Current (YSCC) flowing southeastward from the North, influence the region. For a detailed description, readers are referred to Limeburner et al. 1983; Beardsley et al. 1985; Hu et al. 1988; Yun et al. 1988; Wang et al. 1990. Although some investigations have been carried out in this region (Gu 1982; Huang et al. 1983; Edmond et al. 1985; Gu 1987; Tang et al. 1990), biogeochemical processes controlling nutrients are far from well known in the Changjiang Estuary. Moreover, few of them dealt with the turbidity maximum and the plume water fronts. In this context, two cruises were carried out in the summer (August) and winter (December) of 1988 in the river mouth area, during which nutrients ($Si(OH)_4$, PO_4^{3-}, NO_3^-, NO_2^-, NH_4^+) and other related chemical parameters were measured. We present here the data obtained during this study, with emphasis on elucidation of the origin and the biogeochemical processes controlling nutrient behaviour in the turbidity maximum and at the plume water fronts zones.

Sampling and methods

Thirty eight sites were occupied during both 1988 summer and winter cruises (Fig. 1). Stations 1—22 were located in the South Branch and its offshore area in order to study the mixing processes between freshwater and seawater. The North Branch was not sampled because of the very low freshwater discharge passing through. The northern profiles were chosen in order to investigate the influence of the Yellow Sea Coastal Current on the estuarine system.

Salinity was measured aboard with the Endco CTD probe system and water samples were collected with a clean plastic pump. In addition to surface and bottom waters, samples were collected every 5 m above 15 m

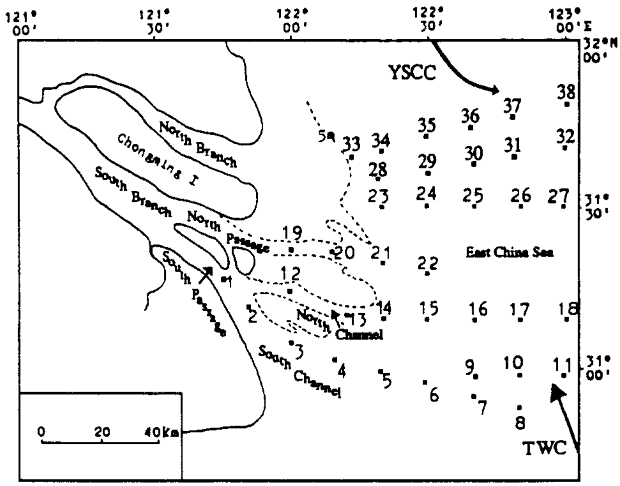

Fig. 1. Changjiang Estuary: location of sampling sites occupied during the 1988 summer and winter cruises (YSCC: Yellow Sea Coastal Current; TWC: Taiwan Warm Current).

and every 10 m below. Surface waters imply a collection depth at 0.6 m below the sea surface and bottom waters 1 m above the sediment surface. Once collected, water samples were filtered on 0.45 μm Millipore filters and analyzed aboard by spectrophotometry for nutrient concentrations: $Si(OH)_4$ using silicomolybdenum yellow method; PO_4^{3-} by the so-called 'single-reagent' method (ascorbic acid reduction and phospho-molybdenum blue method); NO_2^- with the diazotization colorimetric method. NO_3^- was first reduced by zinc-cadmium chloride and NH_4^+ was oxidized by chlorite under alkaline condition to NO_2^- respectively and then measured according to the diazotization method used for NO_2^- analysis. All these methods are described in detail by Strickland & Parsons (1968), Grasshoff (1976) and Aminot & Chaussepied (1983). Some samples were measured up to 5 times in order to control the measurement accuracy. The detection limits and precisions were estimated respectively as below: $Si(OH)_4$: 2 μmol/l, <6%; PO_4^{3-}: 0.02 μmol/l, <10%; NO_3^-: 0.2 μmol/l, <6%; NO_2^-: 0.02 μmol/l, <15%; NH_4^+: 0.05 μmol/l, <15%.

Results and discussion

1. *Salinity*

At the land/ocean interface where mixing between freshwater and seawater occur, estuarine systems are characterized by drastic changes of physical and chemical conditions, which are primarily related to the salinity gradient. The salinity data obtained during the cruises are presented in Fig. 2 and discussed below.

Summer flood season

At the most upstream station 1 in summer, salinity was 0.27 and 0.28‰ in surface and bottom waters, respectively, whereas the highest salinity encountered downstream was 32‰ at station 38 in surface waters. Thus the studied area covered most of the mixing region. The salinity gradient was much higher upstream from the 26‰ isohaline nearby stations 9, 15, 22 and 23 than downstream. Such a salinity distribution has been found in previous studies (Mao et al. 1963; Mao & Guan 1982; Limeburner et al. 1983; Wang et al. 1983; Beardsley et al. 1985; Pan et al. 1988). Although the plume water fronts are a zone rather than a single line, the 26‰ isohaline is suggested here as its demarcating line.

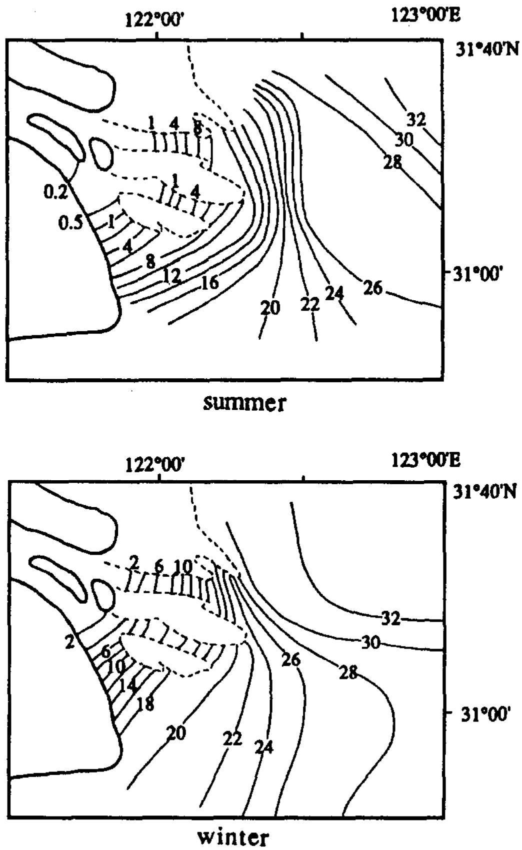

Fig. 2. Distribution of salinity in surface waters in summer and winter 1988.

The salinity distribution also shows that, leaving the river mouth, the freshwater discharge dispersed initially southeastward and then turned east. Assuming that the 26‰ isohaline demarcates the plume water fronts, it ran north-south outside the North Passage, turned southeast further downstream outside the South Passage and extended practically eastward outside the studied region. According to previous studies, the Changjiang River water flows initially southeastward during the flood season in summer. Under the influence of the Taiwan Warm Current, it turns east and northeast further offshore. Our results are in good agreement with this generalization of the Changjiang freshwater dispersion.

Winter dry season

The seawater intrusion was more pronounced upstream in winter than in summer due to lower freshwater discharge (Fig. 2). The 10‰ isohaline in winter corresponded to that of about 1‰ in summer. The salinity distribution in winter also evidenced that the plume water fronts were not as obvious as in summer. The salinity gradient inside the 26‰ isohaline remarkably differed from that outside in summer, whereas no noticeable variation was observed in winter. The cold weather in winter leads to an increase of the surface freshwater density, which allows vertical convection so that the plume water fronts can not well develop. According to Pingree & Giffiths (1978), Simpson et al. (1978) and Bowman (1988), seawater fronts in temperate latitudes vanish in winter due to the increase of the surface water density resulting from cold weather conditions. Moreover the Changjiang River discharge in winter is about 2.5 times lower than in summer, which is unfavorable to the stability and formation of the plume water fronts since the tide action becomes dominating over river current and thus enhances vertical mixing processes.

2. *Nutrients in summer*

The nutrient distribution in summer shows the following major features:

(1) The nutrient distribution in surface waters was characterized by a general tendency to decrease from the inner estuary to the outer estuary due to water mixing between freshwater of high nutrient and seawater of low nutrient contents. The maximum contents of $Si(OH)_4$, NO_3^- and PO_4^{3-} in the inner estuary were 110, 70—110 and 0.8 μmol/l, respectively, which indicated that the Changjiang River carried large amounts of nutrients (Fig. 3). These results are comparable to that found 8 years ago: 105, 65 and 0.8 μmol/l respectively for $Si(OH)_4$, NO_3^- and PO_4^{3-} (Edmond et al. 1985). If the $Si(OH)_4$ and PO_4^{3-} concentrations are comparable with those of other world major rivers, the NO_3^- one is much

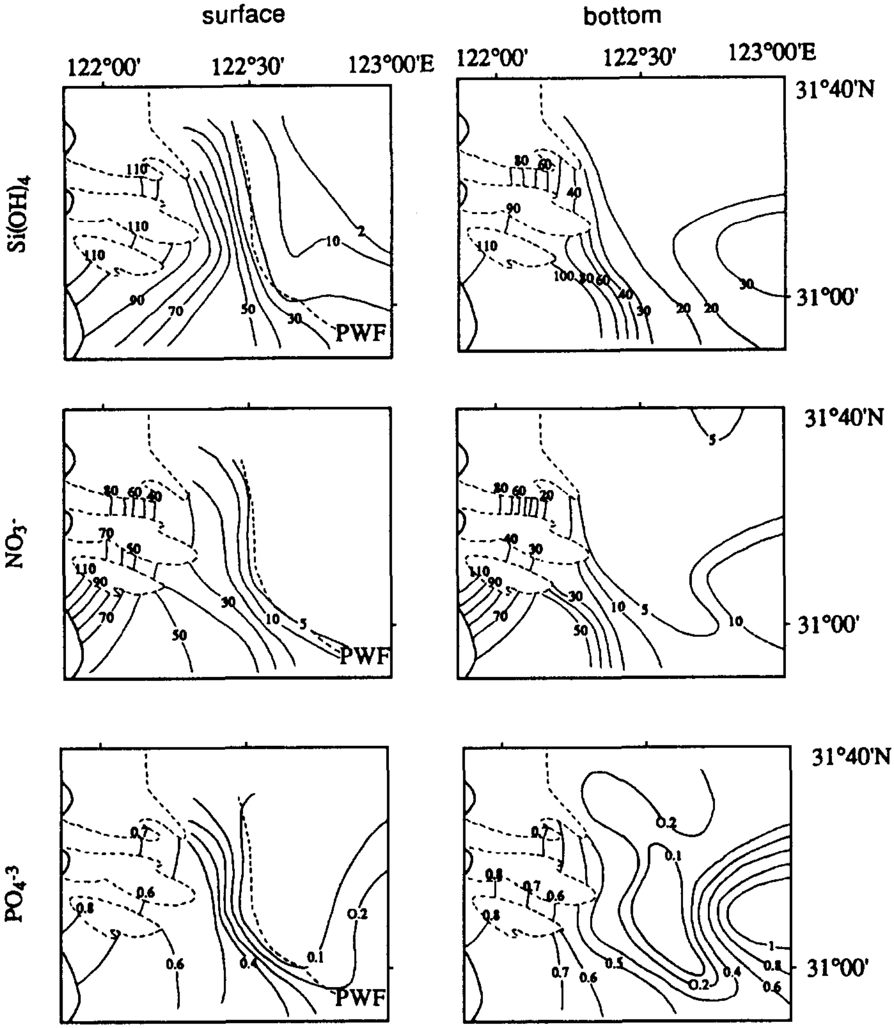

Fig. 3. Distribution of nutrients (μmol/l) in surface and bottom waters in summer 1988 (PWF: plume water fronts).

higher in the Changjiang Estuary, confirming the earlier observations by Edmond et al. (1985). NO_3^- concentration ranges from 10 to 20 μmol/l in other rivers (Bennekom et al. 1978; Edmond et al. 1981), whereas it reaches 110 μmol/l in the South Channel. In fact, the lower reaches of the Changjiang River are the most populated and developed regions in China, both in agriculture and industry. Thus chemical fertilizers and industrial sewage may be important sources of nitrogen. Only in the suburban district of Shanghai for example, 1.34 × 10^6 tons of nitrogen fertilizers were used in 1983 (Yang 1988). It should be pointed out that the NO_3^- content in the South Channel (110 μmol/l) is higher than that in the North Channel (70 μmol/l). Part of this nitrogen might be issued from the Huangpu River, the last tributary with 1×10^{10} m^3/yr discharge, which goes through the Shanghai city, with 1.46×10^9 m^3/yr of raw sewage drained into the river (Zhang 1988; Yang 1988). The discharges of the Huangpu River and other sewers (with 2.9×10^8 m^3/yr of total drainage) empty into the Changjiang River at the South Bank and disperse mainly through the South Channel (Hu 1986).

(2) There was a remarkable decrease of the nutrient content across the plume water fronts. PO_4^{3-} content decreased from 0.5 μmol/l inside the plume water fronts to about 0.1 μmol/l outside, NO_3^- from 40 to below 5 μmol/l and $Si(OH)_4$ from 50 to about 10 μmol/l. Plots of nutrient concentrations versus salinity for the South Branch data showed that nutrient concentrations were conservative in the salinity range <26‰ and a noticeable removal in the higher salinity range (Fig. 4). The measurements corresponding to high salinity range (>26‰) were always below the regression line, particularly for $Si(OH)_4$ and NO_3^-. Therefore the nutrient distributions in surface waters were not only controlled by water mixing, but also by other processes.

It has been often found that the plume water fronts sustain a high primary productivity (Conomos et al. 1972; Cadée 1978; Edmond et al. 1981). Ning et al. (1988) and Tian (1989) reported a highest primary production region just outside the plume water fronts in the Changjiang Estuary. According to the turbidity measurements performed during the cruise, the content of suspended matter was below 10 mg/l outside the plume water fronts in surface waters whereas it was above 100 mg/l inside, with some values higher than 500 mg/l at the turbidity maximum. Because of the high water turbidity inside the plume water fronts, restriction of light penetration probably limited photosynthesis and phytoplankton development. Outside the plume water fronts light penetration was no longer a limiting factor and phytoplankton blooms occurred, which resulted in the removal of nutrients in surface waters. Table 1 shows the result of multi-element regression analysis carried out on the South Passage data (18 stations). Nutrients are negatively correlated with salinity and chlorophyll *a* content. The regression calculated with the accumulated chlorophyll content is better than that with the content itself; accumulated chlorophyll content implies the integration of chlorophyll content from the inner estuary to the outer estuary:

$$\sum \mathrm{chl}(j) = \sum_{i=1}^{j} \mathrm{chl}(i)$$

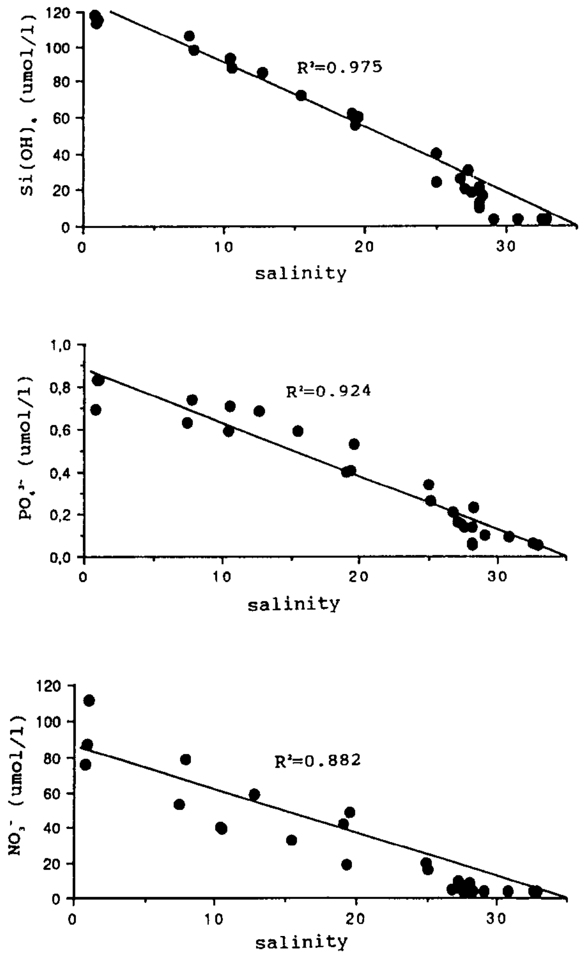

Fig. 4. Plots of nutrient concentrations versus salinity for surface waters of the South Branch in summer (straight lines are the linear regression ones).

$j = 1, 2, 3, \ldots, 18$ (station number); chl(i): chlorophyll *a* content at each station. This is not surprising since the accumulated chlorophyll content would better reflect the total biomass than the punctual pigment measurements.

(3) At the river mouth in the South Channel, the gradient of nutrient concentration in bottom waters was lower compared to that of salinity. For example, the two $Si(OH)_4$ isolines of 110 and 100 μmol/l cross four stations (from station 2 to 5), whereas the salinity increased from 2 to 24‰. If nutrient content was only controlled by water mixing, a linear relation with salinity should exist:

Table 1. Multi-element regression of nutrients as a function of salinity and chlorophyll *a* content.

function of regression	coefficient
$Si(OH)_4 = 92—3.1\ chl—1.44S$	$r = 0.66$
$Si(OH)_4 = 111.9—2.2\Sigma chl—1.15S$	$r = 1.00$
$PO_4^{3-} = 0.69—0.19chl—0.04S$	$r = 0.66$
$PO_4^{3-} = 0.85—0.18\Sigma chl—0.01S$	$r = 0.99$
$NO_3^- = 88—1.9chl—2.93S$	$r = 0.75$
$NO_3^- = 104—1.9\Sigma chl—1.8S$	$r = 0.97$

S: salinity; chl: chlorophyll *a* content;
Σchl: accumulated chlorophyll *a* content.

$$[Si(OH)_4] = a \times S + b$$

The $Si(OH)_4$ content and salinity in bottom waters were 110 μmol/l and 2.3‰ at station 2 and 26 μmol/l and 27.6‰ at station 6, respectively, implying that the theoretical dilution line of $Si(OH)_4$ should be:

$$[Si(OH)_4] = -3.3 \times S + 117$$

The salinity of bottom waters at station 4 is 13‰. According to the preceding equation, the $Si(OH)_4$ content should be 74 μmol/l, while the observed *in-situ* content was 105 μmol/l, much higher than the theoretical dilution content. Moreover, the $Si(OH)_4$ content in bottom waters (105 μmol/l) was higher than that in surface waters (81 μmol/l), in disagreement with water mixing process, for which freshwater of high nutrient content was located above the low nutrient salt water. Therefore this distribution feature could not be explained by water mixing processes. Because this anomalous area coincides well with the turbidity maximum (Shen et al. 1982; Tian 1989), release of nutrients at the turbidity maximum probably explains it. During a previous study in the same region, Huang et al. (1986) found a release of nutrients occurring in the salinity range 5—15‰ in summer, a salinity range within which is situated the turbidity maximum in the Changjiang Estuary (Shen et al. 1982). The intense resuspension at the turbidity maximum has been shown to be favourable for the decomposition of organic matter and nutrient release from sediments (Fanning et al. 1982; Watanabe & Tsunogai 1984; Owens 1986; Simon 1988).

(4) Except at the turbidity maximum discussed above, nutrient con-

centrations were higher in surface waters than in bottom waters upstream from the plume water fronts because of the inputs from freshwater. In contrast, they were higher in bottom waters than in surface waters outside the plume water fronts (Figs. 3, 5). Near stations 17, 18 and 11 for example, the concentrations of $Si(OH)_4$, NO_3^- and PO_4^{3-} were 30, 10 and 1 μmol/l in bottom waters respectively, whereas they were only <10, <1 and <0.1 μmol/l in surface waters. This may be explained by nutrient

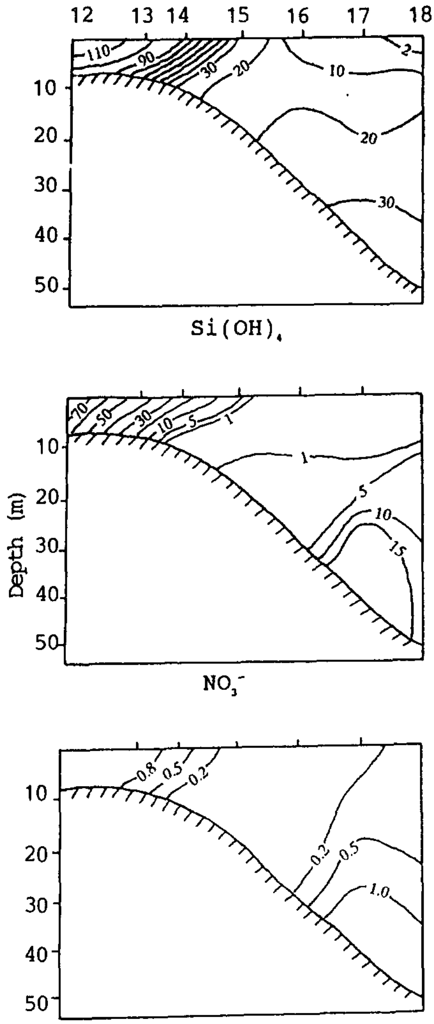

Fig. 5. Transect distribution of nutrients (μmol/l) along the profile stations 12—18 in summer.

release from sediments. It has been observed that this area located just outside the plume water fronts is very productive. Biological production can lead to sedimentation of organic matter which, when decomposing, can increase the release of nutrients. During a study of the Potomac River, Callender & Hammond (1982) found a release flux of Si from sediments from 2 to 19 mmol m^{-2} day^{-1} and a flux of P from 0.1 to 2.0 mmol m^{-2} day^{-1}. Fanning et al. (1982) also observed the release of $Si(OH)_4$ and

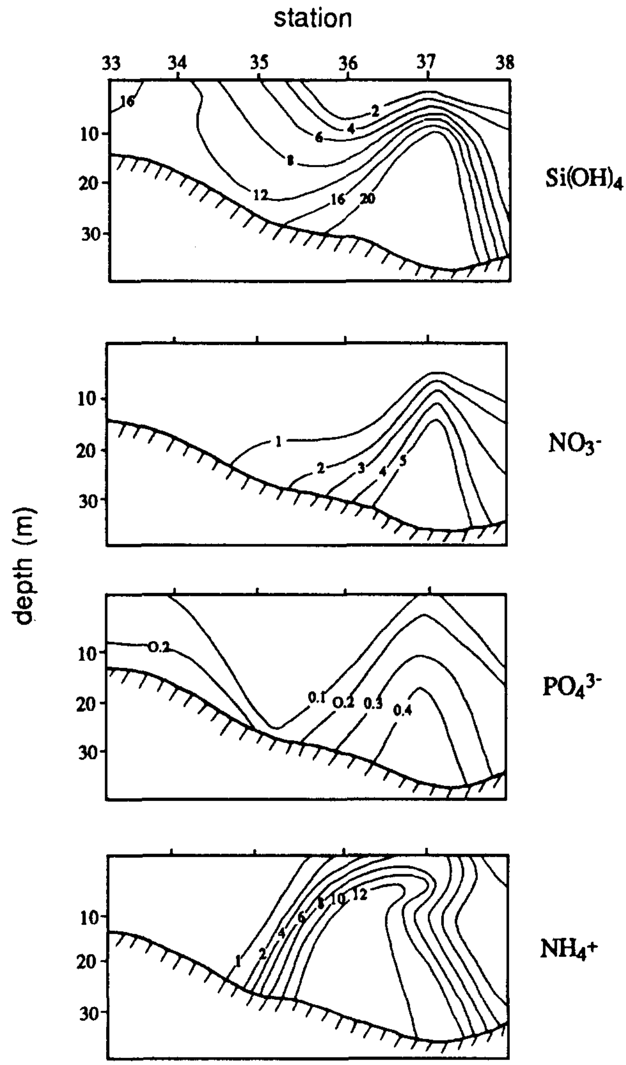

Fig. 6. Transect distribution of nutrients (μmol/l) along the profile stations 33—38 in summer.

NO_3^- in the eastern part of the Mississippi River delta. Fisher et al. (1982) have reported that 28—38% of nutrients needed for the primary productivity were provided by sediment release in several estuaries of North Carolina.

(5) The transect from station 33 to 38 in the northern part of the studied area was characterized by depth profiles of nutrients having a convex form around station 37 (Fig. 6). The nutrient content was higher in bottom waters than in surface waters, which indicated noticeable release of nutrients from sediments. Moreover, the released nutrients dispersed upward to the surface, particularly for NH_4^+ which reached the surface and formed a NH_4^+-rich area (Fig. 7). This kind of distribution is specific to upwelling areas or, at least, indicates intense vertical convection carrying nutrients released from sediments up to the surface, providing a basis for primary production. Ning et al. (1988) and Tian (1989) have reported high primary production in this area. Additionally, activities of nekton and zooplankton, which produce NH_4^+ (Gu 1982; Shi 1986), can contribute to the formation of this high NH_4^+ region. The hydrographic features of this area are very complex. The Changjiang River water, the Yellow Sea Coastal Current and the Taiwan Warm Current can all influence here (Yu 1986). According to Wang et al. (1990), the Taiwan Warm Current flows northwestward along the bottom due to its heavier density and encounters the Yellow Sea Coastal Current in this region in summer. Such a convergency can result in vertical convection. The salinity and temperature distributions were in agreement with this suggestion with convex depth profiles comparable to that of nutrients (Fig. 8). The Taiwan Warm Current is characterized by salinity ⩾33‰ and temperature ⩾20 °C in

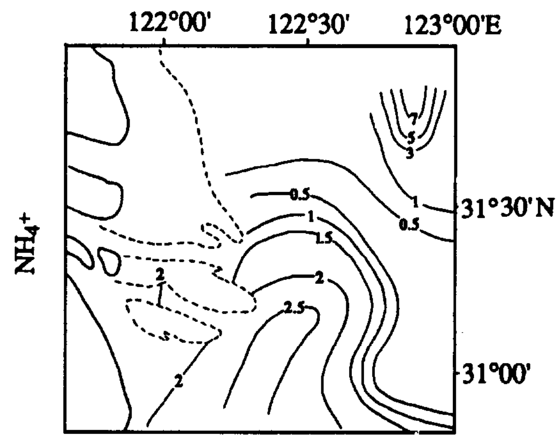

Fig. 7. Distribution of NH_4^+ in surface waters in summer (μmol/l).

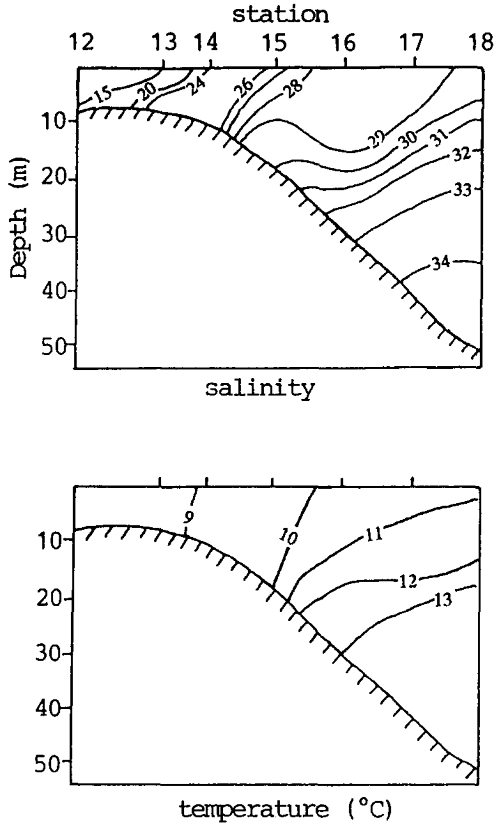

Fig. 8. Transect distribution of salinity and temperature (°C) along the profile stations 12—18 in summer.

summer (Beardsley et al. 1985; Hu et al. 1988; Wang et al. 1990). It is evident that the Taiwan Warm Current cannot be identified in this region since only its edge part and mixed waters are concerned.

(6) The content of NO_2^- was always below 1.5 μmol/l in the whole studied area and without any clear distribution tendency. One noticeable feature of NO_2^- distribution is that its content in bottom waters (average 0.79 μmol/l) was higher than that in surface waters (average 0.42 μmol/l). At upstream stations 12, 2 and 3, NO_2^- content varied between 0.3 and 0.4 μmol/l in both surface and bottom waters, a range lower than the average (particularly for bottom waters). Therefore freshwater is not the main source for NO_2^- in the studied region. Its distribution is mainly controlled by other geochemical and biogeochemical processes such as reduction of NO_3^-, oxidation of NH_4^+, release from sediments and biological assimilation and excretion.

3. *Nutrients in winter*

$Si(OH)_4$ content in the inner estuary was about 100 μmol/l, nearly the same as that in summer. Contents of NO_3^-, NO_2^-, NH_4^+ and PO_4^{3-} were 58, 0.05, 2 and 0.5 μmol/l respectively, which were lower than those observed in summer (Table 2). This seasonal variation might be attributed to differences of chemical weathering, fertilization and biogeochemical processes which are different in summer and in winter.

Table 2. Nutrient concentrations in river waters (μmol/l)*.

	$Si(OH)_4$	NO_3^-	NO_2^-	NH_4^+	PO_4^{3-}
summer	110	95	0.38	6.1	0.8
winter	94	51	0.05	3.0	0.5

* indicates the average in surface waters for stations 1, 2, 12 and 19.

According to the data offered by the Shanghai Waterway Bureau, the average discharge rate during the flood season (from May to October) was 37600 m^3/s and that of dry season 16380 m^3/s in 1988 (year of study). Thus the total runoff in summer could be estimated at 5.93×10^{11} m^3 and that in winter at 2.58×10^{11} m^3. Based on the data listed in Table 2 and the atomic weight concerned, it is possible to calculate the nutrient flux of the studied year which are estimated as follows: Si: 2.5×10^{12} g/yr; N: 1.0×10^{12} g/yr; P: 1.9×10^{10} g/yr, where the nitrogen flux includes that of NO_3^-, NO_2^- and NH_4^+.

The distributions of $Si(OH)_4$ and NO_3^- in surface waters showed a general content decrease from the inner estuary to the outer estuary due to water mixing (Fig. 9). No evident plume water fronts were encountered as in summer identified by a drastic gradient change of nutrient concentration.

The situation was quite different for PO_4^{3-}. Its contents was higher in the outer estuary than in the inner estuary with maximum contents above 1.5 μmol/l near stations 15 and 16 (Fig. 9). Its vertical distribution was quasi-homogeneous there (Fig. 10). Such a distribution suggests important vertical convection carrying nutrients released from sediments upward to the surface, which can explain the high PO_4^{3-} content in surface waters. Although no very high contents of $Si(OH)_4$ and NO_3^- have been observed, this is not contradictory because surface waters have primarily high $Si(OH)_4$ contents originating from the river discharge, which probably overwhelm the influence of vertical convection. This phenomenon can be

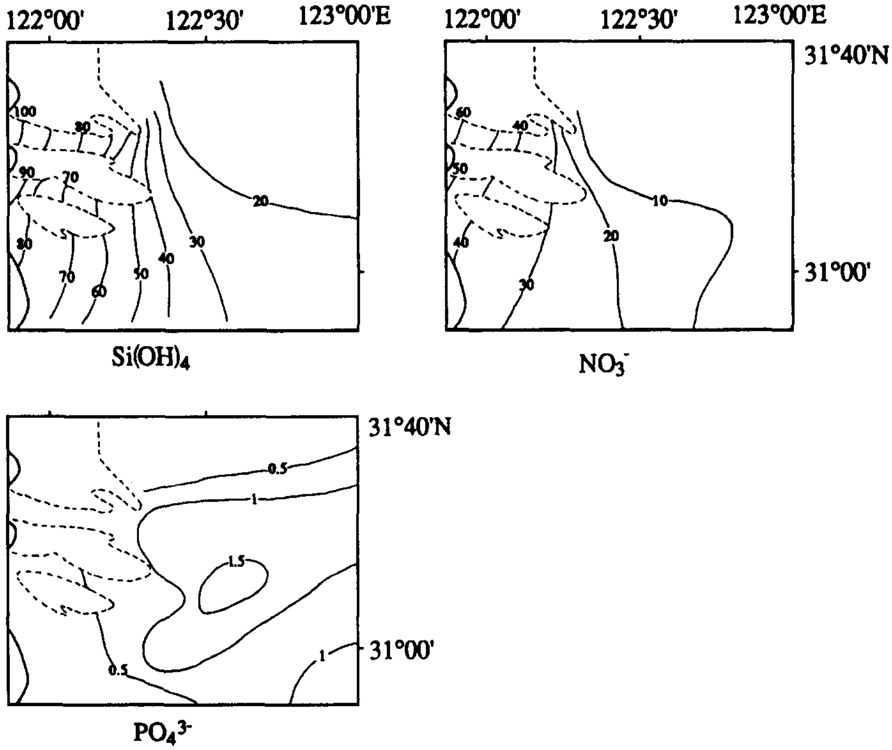

Fig. 9. Distribution of nutrients (μmol/l) in surface waters in winter 1988.

illustrated by the $Si(OH)_4$ section distribution with a minimum content at mid-depth in this area. The salinity distribution showed upward dispersion of bottom waters near station 15 and practically no vertical gradient of temperature can be identified (Fig. 11). This vertical convection may be linked to the Taiwan Warm Current as observed in summer in the northern part of the studied region. It is known that the reaches of the Taiwan Warm Current is located more South in winter than in summer, characterized by salinity $>33‰$ and temperature $>11.5\,°C$ in winter (Wang et al. 1983; Beardsley et al. 1985; Hu et al. 1988; Wang et al. 1990).

Conclusion

The analysis of nutrients performed in summer and winter in the Changjiang Estuary has shown the following points:

(1) The Changjiang River is the main source of nutrients for the

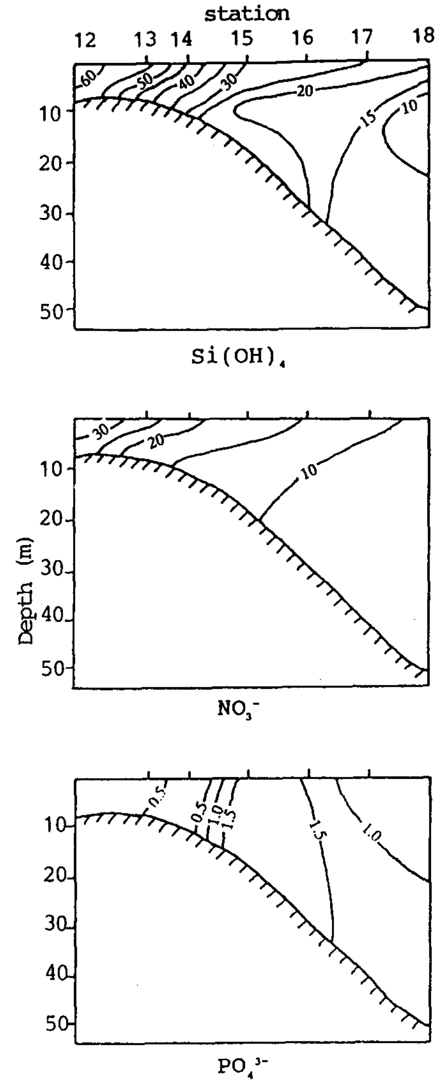

Fig. 10. Transect distribution of nutrients (μmol/l) along the profile stations 12—18 in winter.

studied region, with 90—110 μmol/l of $Si(OH)_4$, 70—95 μmol/l of NO_3^- and 0.5—0.8 μmol/l of PO_4^{3-}. The nutrient fluxes for the studied year (1988) could be estimated at 2.5×10^{12}, 1.0×10^{12} and 1.9×10^{10} g/yr for Si, N and P, respectively.

(2) Nutrients are also released at the turbidity maximum and from deposited sediments, particularly outside the plume water fronts where nutrient content is higher in bottom waters than in surface waters. Pro-

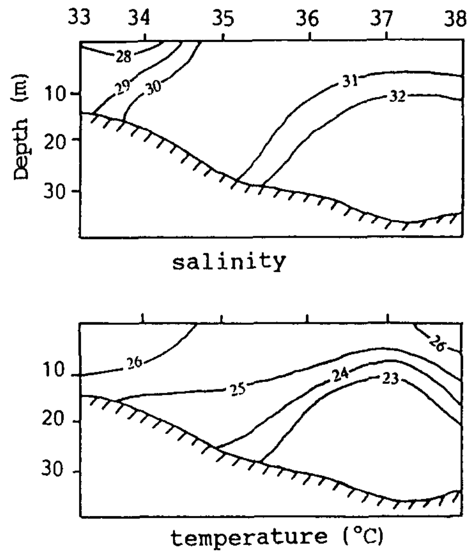

Fig. 11. Transect distribution of salinity and temperature (°C) along the profile stations 33—38 in winter.

nounced upward dispersion of nutrients released from sediments has been observed around station 37 at about 122°50′E and 31°48′N in summer, which coincides with a high primary production area reported in previous studies. Such intensified vertical convection of nutrients is linked to the complex hydrographic features of the area, particularly the influences of the Taiwan Warm Current and the Yellow Sea Coastal Current. Pronounced upward dispersion of the nutrients has also been observed in a more southern region outside the South Branch in winter.

(3) Water mixing, biological consumption and vertical convection are three major factors controlling the nutrient distribution: water mixing which explains the gradual decrease of nutrient content offshore, biological consumption which leads to noticeable removal of nutrients across the plume water fronts and vertical convection which carries nutrients released from deposited sediments upward to the surface waters.

(4) NO_2^- and NH_4^+ do not principally originate from the Changjiang River. Their distribution is influenced more by geochemical and biogeochemical processes such as nitrification, denitrification, release from sediments, biological assimilation and excretion.

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