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Zhiliang Shen *Editor*

Studies of the Biogeochemistry of Typical Estuaries and Bays in China

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Editor

Studies of the Biogeochemistry of Typical Estuaries and Bays in China

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Foreword

Estuaries and Gulf regions are among the most heavily populated areas on earth with the most intensive human activities. It is roughly estimated that the riverine inputs lead to an annual freshwater discharge of 4.7×10^{13} m^3 into the ocean, with the transportation of $\sim 1.83 \times 10^{10}$ tons of particulate matter and $\sim 0.42 \times 10^{10}$ tons of dissolved material. Influenced by the complex hydrodynamics such as tide, wind, diluted water, and ocean currents, the estuaries and bay areas experience a series of significant physical and chemical changes, making the estuarine ecosystems unique from other marine waters. Due to the considerable nutrient input, estuaries, bays, and coastal waters represent one of the most productive areas in the world, where also harbor more than 90% of the marine fish and other economic biological resources. Therefore, the coastal zone including estuaries and bays plays an essential role in the survival and evolution of human society. However, rapid economic development and increasing human activities also cause the degradation of the estuarine and coastal systems, and the resultant eutrophication has become a global problem. Thus, studies on estuary and bay have received much attention from the oceanographers, among which estuarine biogeochemistry is one of the major focuses.

Marine biogeochemistry is an interdisciplinary research that mainly focuses on the source, distribution, transport, sink, and cycling of the compounds related to the marine biota and biological processes. In particular, the biogeochemical cycling of biogenic elements including carbon, nitrogen, phosphorus, silicon is among one of the most important and fundamental studies. As one of the key topics in the research of global change, marine biogeochemistry involves many subjects including oceanography, chemistry, biology, geology, ecology, and environmental sciences.

This book is devoted to the studies of the biogeochemistry of typical estuaries and bays in China, with the focus on biogeochemical cycling of the biogenic elements. The study areas include the Changjiang River, the largest river in China; the estuaries of the two largest rivers, the Changjiang estuary and the Yellow River estuary; and a semi-enclosed bay that is significantly impacted by human activities, the Jiaozhou Bay. These areas involve an important inland economic belt and two

coastal integrated economic belts in China, the Changjiang basin, the Changjiang River delta, and the Shandong Peninsula. To some extent, they are representative of typical rivers, estuaries, and bays environments and also have extensive research interests for oceanographers.

This study investigated Changjiang and its estuarine area as an integrated ecosystem, from the Changjiang upper reaches (Jinshajiang River) to the downstream estuary and the marine waters and from the atmosphere, land, to the ocean. The authors systematically studied the concentration distributions, variations, and removals as well as the molar ratios of various forms of nitrogen, phosphorus, and silicate in the Changjiang mainstream and tributaries in the dry and flood seasons. They provided a new perspective for the nutrient budget in the large watershed and quantitatively constrained the budget and control mechanisms of nitrogen and phosphorus in the Changjiang basin for the first time. They also investigated the behaviors and removals of various forms of phosphorus and silicon during estuarine mixing. Furthermore, they made the first measurements for the sedimentation fluxes of suspended particulate matter, phosphorus, and silicon and calculations for the mass balances of phosphorus and silicon in the turbidity maximum zone of the Changjiang estuary. A novel method was also established to estimate the ratio of resuspension of sediment. They are among the first to study nutrient structure, nutrient balance, and the ecological responses of phytoplankton in Jiaozhou Bay. They monitored the long-term changes in nutrients and their structure, documented the influences on phytoplankton community in the Changjiang estuary and Jiaozhou Bay, and explored the mechanism that triggers the occurrence of red tide. In this study, carbon, nitrogen, phosphorus, and silicon composition and their mole ratios of various size fractions of phytoplankton were reported; the silicon limitation on the growth of phytoplankton was illustrated in Jiaozhou Bay; a new concept was proposed for the nutrient structures in seawater and phytoplankton, and the balance between them. For the first time, they successfully isolated a large diatom of *Coscinodiscus asteromphalus* from natural seawater, determined its carbon, nitrogen, phosphorus, silicon, and chlorophyll *a* contents, and further estimated its contribution to the phytoplankton biomass in Jiaozhou Bay. Collectively, those studies are among the research frontier of the marine sciences, the findings of which will open a window and provide references to further studies.

Data of this book come directly from Prof. Shen's substantial research surveys and seagoing cruises. This book summarizes findings and discoveries in his long-term studies on biogeochemistry of the estuaries and bays and presents a number of innovations and creativity in this field. Some of the research outcomes mark pioneering discoveries in estuary/bay studies, which have aroused international influence and been frequently cited by researchers of home and abroad. This recounting of these research findings represents China's research excellence in estuarine biogeochemistry and is of essential theoretical significance and academic values, so as to provide scientific support for coastal management and ecological–environmental protection.

The publishing of this book is dedicated to the 50th anniversary of Prof. Zhiliang Shen's research in marine sciences. It is with great pleasure I am writing this forward and I would like to express congratulations on this publication, which contributes to the development of China's marine research and greatly advances biogeochemical studies on estuaries and bays.

Qingdao, China
August 2018

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Preface

The special natural geographical environments and the processes of mixing of freshwater–saltwater, tide, terrigenous matter input, etc., of estuaries and bays make them to be unique ecological systems with complex structure different from other waters of the ocean. On the other hand, the important function of estuaries and bays in the global economy and social development also makes them strongly affected by human activities, and thus their ecological structure and function are sometimes vulnerable and unstable. There are three major problems for human at present: population, resources, and environment, all which become more serious in the areas of estuary and bay. In the long term, the impact of human activities on the marine ecosystem is consistent, and human impact on the biogenic elements is fundamental and significant. Nitrogen, phosphorus, and silicon are essential nutrients for marine phytoplankton, which run through every link of the food chain and marine biological processes, and directly affect the primary productivity of the ocean. However, excessive nutrient is a kind of pollutant, harmful for water area and endangering marine ecological environment. For nearly half of a century, a global eutrophication has been caused by the input of excessive nutrients into estuaries, bays, and coastal waters. In China's Changjiang estuary, Bohai Bay, and Jiaozhou Bay waters, nitrogen and phosphorus have increased several times, and as a result the original nutrient structure was changed, which led to abnormal reproduction of phytoplankton, destroyed the ecological balance, and did harm to biological resources. The pollution caused by the increase of nitrogen and phosphorus in coastal waters is the most common problem in the world. Red tide is an inevitable result of eutrophication in waters. Before the 1970s, the red tide occurred only in a few coastal countries, but now more than 30 countries in the world were threatened by the red tide. These problems have restricted the development of human beings and brought us to a hot topic: How to protect the marine ecological environment? How to maintain the sustainable use of marine biological resources?

Marine biogeochemistry was developed after the 1980s with the implementation of major international cooperation programs such as International Global Change Study. The biogeochemical study on marine biogenic elements has been incorporated into many major international cooperative research projects and has become

one of the hot spots in the frontier of international marine research. For example, the plan of Land Ocean Interaction in Coastal Zone (LOICZ) organized by the International Geosphere-Biosphere Programme (IGBP) has taken the biogenic element transport in rivers and estuaries as a fundamental goal of its first action. The Joint Global Ocean Flux Study (JGOFS), Global Ocean Ecosystem Dynamics (GLOBEC) research, and Global Ocean Euphotic Zone Study (GOEZS) include the biogeochemical study of biogenic elements as its important research contents. In China, the biogeochemical study of biogenic elements in estuaries and bays can be dated back to the 1960s. Professor Li faxi et al. studied the geochemistry of silicon in Jiulongjiang estuary, and Prof. Gu Hongkan et al. carried out researches on "geochemistry of nitrogen in Jiaozhou Bay" and "geochemistry of nitrogen in the Changjiang estuary." After the 1980s, the related studies were more popular in China, such as "the study of fishery resources, ecological environment, and its proliferation potential in the Bohai Sea waters," "the investigation of marine environment and resources in Jiaozhou Bay," and "the investigation and study of impacts of the three gorge projects on ecology and environment of the Changjiang estuary." Some international cooperative studies had also been carried out, such as "study on sedimentary dynamics of the Changjiang estuary and its adjacent waters of China and the USA," "studies on the biochemical processes of pollutants and nutrients in the Changjiang estuary and its adjacent waters of China and France," and "study on biogeochemistry in the Yellow River estuary of China and France." In these projects, the biogeochemical studies of biogenic elements were important topics. Since the 1990s, in order to follow the development of the frontier field of international marine science, National Natural Science Foundation of China organized and implemented part of national key funds on the biogeochemical studies of biogenic elements in estuaries and bays, such as "study on key processes of ocean flux in the East China Sea," "study on fluxes of the Changjiang River estuary," "study on biogeochemical cycle of biogenic elements in Taiwan Strait," "study on carbon flux in the north China Sea," "study on dynamic process and sustainable development of typical bay ecosystem," and the national fund of "study on the controlling mechanism of inorganic nitrogen content in the Changjiang mouth." During the "Ninth Five-Year Plan" of the Chinese Academy of Sciences, a major project was set up to "study on the optimization model and productivity sustainability of typical bay ecosystems." And a key project "study on the budget dynamics of inorganic nitrogen in the Changjiang mouth" and the knowledge innovation projects "study on degradation mechanism of ecosystem in the eutrophication process of typical bays" and "study on the dynamic change of typical bay ecosystems in China under the influence of human activities" were carried out as well. In addition, the Chinese National Basic Research Priority Program (973) funded the project of "Ecology and Oceanography of Harmful Algal Blooms in China," and National Natural Science Foundation of China funded the key project of "study of eutrophication characteristics and countermeasures in the Changjiang estuary waters" and the national fund "stoichiometric nutrient balance and its ecological responses in Jiaozhou Bay," etc. The implementation of these projects has promoted our country to a new level in the biogeochemical study of

biogenic elements in the estuaries and bays. The publication of this book is based on the implementation of some of above projects.

This book focuses on the Changjiang estuary and Jiaozhou Bay as the main research areas, including nutrients, suspended particulate matter, phytoplankton, and heavy metals, involving biogeochemistry, marine chemistry, ecology, environmental science, oceanography, and biology.

This book consists of four parts. Part I systematically studies the distributions, variations, and removals of concentrations and molar ratios of various forms of nitrogen, phosphorus, and silicate in the Changjiang mainstream and tributaries in the dry and flood seasons, estimates the nutrient fluxes transported from tributaries to mainstream and the nutrients output fluxes of the Changjiang mouth, and illuminates the relationships of seasonal distributions and variations of nutrients in the estuary and the Changjiang runoff. For the first time, it quantitatively reveals the budgets and controlling mechanisms of nitrogen and phosphorus in the Changjiang catchment, suggests nitrogen coming mainly from precipitation, fertilizer nitrogen losses from gaseousness and agricultural nonpoint sources, the key factor in controlling high-content inorganic N in the Changjiang mouth, and suggests that the phosphorus in the Changjiang catchment comes mainly from agricultural nonpoint source fertilizer and soil phosphorus losses, and most of them are transferred to freshwater wetlands during transportation. Part II studies the behaviors and transfers of various forms of phosphorus and silicon during the Changjiang estuarine mixing, for the first time, measures the sedimentation fluxes of suspended particulate matter, phosphorus, and silicon, estimates the mass balances of phosphorus and silicon in the turbidity maximum zone, and establishes a new method for estimating the ratio of resuspension of estuary sediment. In this part, the distributions and variations of nutrient concentrations and structure and their effect on chlorophyll *a* in the upwelling area of the Changjiang estuary were studied, and the sources and transport fluxes of nutrients were estimated. In addition, this part also studies the removals and changes of heavy metals in the Changjiang estuary and studies the distributions and removals of nutrients in seawater and interstitial water of surface sediments in the Huanghe River estuary, nutrient transports in the Yellow River mouth, and phosphorus cycle in the estuary. Part III studies the long-term changes of nutrient concentrations and structure and its influences on phytoplankton community in the Changjiang estuary and Jiaozhou Bay, and discusses the succession of phytoplankton community and the occurrence mechanism of large-scale red tide in the Changjiang estuary. It is the first time to study nutrient structure, nutrient balance, and the ecological responses of phytoplankton in Jiaozhou Bay, measures the contents of carbon, nitrogen, phosphorus, silicon, and chlorophyll *a* in different-sized suspended particulates, studies the compositions of carbon, nitrogen, phosphorus, silicon, and molar ratios of different-sized fractions of phytoplankton and their ecological response to the nutrient structure of seawater, and reveals silica limitation of phytoplankton growth. A new concept of nutrient structure including the nutrient structures in seawater and in particulate, and the nutrient balance in between is proposed. This part also discusses the primary cause of the increased algal blooms in recent years in Jiaozhou Bay. Part IV studies the spatial and

temporal distributions and composition of particulate organic carbon in Jiaozhou Bay. It also studies the nutrient structure of laboratory-cultured dominant phytoplankton species, explores the differences of nutrient structures of cultured different-sized fractions of dominant phytoplankton species in different sea areas and seasons, and studies their relationship with the nutrient structure of seawater. In this part, in addition, the large diatom *Coscinodiscus asteromphalus* was separated from natural seawater for the first time, its chemical composition of carbon, nitrogen, phosphorus, and silicon combined with chlorophyll *a* was measured, and its contribution to phytoplankton biomass was estimated in Jiaozhou Bay. These studies are the hot spots in the forefront of international marine science.

Based on a large number of field investigations, this book summarizes the partial results of the author's long-term study on the biogeochemistry of the estuaries and bays, and it reflects the research level and progress in this field in China. These achievements have been innovated and developed in academic thinking, and some achievements and discoveries are the first time. These results have been widely influenced and cited at home and abroad. The research achievements showed by this book not only have important theoretical and practical significances for further studying the biogeochemistry of estuaries and bays, but also will provide a scientific basis for ecological–environmental management and protection in China.

Should point out that the results showed by this book only involve the part of the subject, some results are still preliminary and also need to be verified and perfected, and the related research may also need to be further strengthened. Since the study involving multiple subjects, the unique natural geographical environment of estuaries and bays, and the strong influences of human activities, the ecological environment is fragile and changeable, and new problems emerge in endlessly. We should further strengthen the study of the long-term changes of the biogenic elements in estuaries and bays, and strengthen the study on the balance of nutrient structure between seawater and phytoplankton and their ecological responses. It is necessary to further explore the mechanism of the transfer and interfacial exchange of the biogenic elements, and the dynamics process model of each link in the biogeochemical cycle of the biogenic elements is still to be established. It is suggested to strengthen the long-term regular and fixed-point observation of the main river estuaries and bays in China, and conduct multi-disciplinary joint research. At present, a contradiction between the worsening environmental pollution in the coastal waters and the rapid development of national economy in the coastal areas is faced in China, which provides a new opportunity for the development of this subject. Looking to the future, the study of biogeochemistry of estuaries and bays will benefit mankind.

The achievements of this book is dependent on the long-term funding of the Chinese Academy of Sciences and the National Natural Science Fund Committee, and also cannot leave the support and help of the leaders and colleagues of Institute of Oceanology, Chinese Academy of Sciences. We are very grateful to Yaping Ao, M. Dagg, Minhan Dai, Yuanchao Gai, Shangwu Gao, Hongkan Gu, Yujie Guo, P. Harisorn, Minghou Ji, Chaolun Li, Pengcheng Li, Yan Li, Xinian Ma, Hui Miao, Shaofeng Pei, Guangfa Ren, Huijuan Tang, Xuchen Wang, Yunfeng Wang, Yulin

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Qingdao, China Zhiliang Shen
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1. Shen Z. L., Zhou S. Q., Pei S. F., 2008. Transfer and transport of phosphorus and silica in the turbidity maximum zone of the Changjiang estuary. ***Estuarine, Coastal and Shelf Science*** 78 (3), 481–492. (Reproduced with permission from Elsevier)
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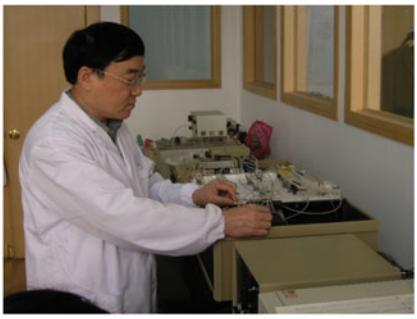

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1—In the office; 2—in the laboratory; 3—at the gate of Institute of Oceanology, Chinese Academy of Sciences; and 4—report at the fifth international symposium on the marine sciences of the Yellow Sea (Incheon, South Korea)

Zhiliang Shen an expert in marine chemistry and marine ecology environment in China is a Research Professor and Ph.D. supervisor at Institute of Oceanology, Chinese Academy of Sciences. Before 2007, he was a responsible researcher of Marine Biogeochemistry in Institute of Oceanology, Chinese Academy of Sciences, led a team, hosted or participated in more than 30 national, provincial, ministerial, and municipal research projects, including the national key projects of the sixth and seventh five-year programs and National Natural Science Foundation of China, and published about 100 peer-reviewed journal articles and coauthor 11 books and atlases. The representative articles in recent years include "Zhiliang Shen et al. 2017, Chemical composition and biomass of *Coscinodiscus asteromphalus* in Jiaozhou Bay, China. Environ Monit Assess, 189: 94," "Zhiliang Shen et al. 2012, An estimation on budget and control of phosphorus in the Changjiang River catchment. Environ Monit Assess, 184, 6491–6505," "Zhiliang Shen, 2012, A new method for the estimation of fine-sediment resuspension ratios in estuaries—taking the turbidity maximum zone of the Changjiang (Yangtze) estuary as an example. Chin J Oceanol Limnol, 30(5), 791–795," "Zhiliang Shen et al. 2009, Nutrients in the Changjiang River. Environ Monit Assess, 153 (1), 27–44," "Zhiliang Shen et al. 2008, Transfer and transport of phosphorus and silica in the turbidity maximum zone of the Changjiang estuary. Estuar Coast Shelf Sci, 78 (3), 481–492," and the representative books are "Yu Zhiming and Zhiliang Shen et al. 2011, Eutrophication in the Changjiang River Estuary and Adjacent Waters, Beijing: Science Press" (in Chinese).

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Part I
Source, Control and Transport of Nutrients in the Changjiang River and Its Estuary

Nutrients and Their Transport in the Changjiang River

Zhiliang Shen and Qun Liu

Abstract Nitrogen (N), phosphorus (P), and silicate (SiO_3–Si) in the Changjiang mainstream and its major tributaries and lakes were investigated. An even distribution of SiO_3–Si was found along the Changjiang River. However, the concentrations of total nitrogen (TN), total dissolved nitrogen, dissolved inorganic nitrogen (DIN), nitrate (NO_3–N) and total phosphorus (TP), and total particulate phosphorus increased notably in the upper reaches, which reflected an increasing impact from human activities. Those concentrations in the middle and lower reaches of the river were relatively constant. Dissolved N was the major form of N and the particulate P was the major form of P in the Changjiang River. The molar ratio of dissolved N to dissolved P was extremely high (192.5–317.5), while that of the particulate form was low (5.6–37.7). High N/P ratio reflected a significant input of anthropogenic N such as N from precipitation and N lost from water and soil. Dissolved N and P were in a quasi-equilibrium state in the process from precipitate to the river. In the turbid river water, light limitation, rather than P limitation, seemed more likely to be a controlling factor for the growth of phytoplankton. A positive linear correlationship between the concentration of dissolved N and the river's runoff was found, mainly in the upper reaches, which was related to the non-point sources of N. Over the past decades, N concentration has greatly increased, but the change of P concentration was not as significant as N. The nutrient fluxes of the Changjiang mainstream and tributaries were mainly controlled by the runoff, of which more than a half came from the tributaries.

Keywords Nutrients · Distributions · Molar ratios · Historical changes · Transport Changjiang River

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Due to influences of human activities, within only a few decades, numerous previously pristine, oligotrophic estuarine, and coastal waters have undergone a transformation to more mesotrophic and eutrophic conditions; at present, eutrophication in estuaries and coasts is one of the extrusive problems (Nixon 1995; Paerl 1997). The change of molar ratios among the key limiting nutrients breaks the balance of nutrients and deteriorates the ecosystem (Turner and Rabalais 1994; Justic et al. 1995; Shen 2001b). Therefore, nutrients transported from rivers to oceans received much attention from oceanographers (Meybeck 1982; Hopkins and Kinder 1993; Aiexander et al. 1996; Leeks et al. 1997; Humborg et al. 2003). Human activities have obviously increased N concentrations in some rivers (Duce et al. 1991; Galloway et al. 1995; Howart et al. 1996), and the fluxes to oceans of mineral nutrients, such as N and P, have increased worldwide by a factor of more than two (Meybeck 1998).

The Changjiang estuary is strongly influenced by human activities. Over the past 40 years, nutrient (especially N) concentrations changed dramatically, and eutrophication has become more and more serious. Harmful algal blooms frequently break out in sea areas adjacent to the estuary of Changjiang River due likely to the large amounts of nutrients transported to the sea (Shen et al. 1992; Duan et al. 2000). This has drawn much attention from public (Gu et al. 1981; Edmond et al. 1985; Wong et al. 1998), especially after the construction of the Three Gorges Dam. Arguments on the influences of the Three Gorges Dam on the ecosystem of the Changjiang River and its estuary have arisen. To estimate the potential impact, sixteen surveys at the Changjiang estuary and its adjacent waters were carried out by the authors from 1985 to 1988, before the construction of Three Gorges Dam, in order to obtain background data of nutrients in the Changjiang estuary (Shen 1991, 1993; Shen et al. 1992). However, most of the studies were located in the estuary area and only a few studies were carried out in the Changjiang River from the viewpoint of the whole catchment (Shen 1997; Zhang et al. 1999; Liu et al. 2003; Shen et al. 2003). Based on the more systematic investigations of the Changjiang catchment including the mainstream of the Jinshajiang River in the Changjiang upper reaches to its mouth, and the major tributaries and lakes along the river, this section focuses on the discussions of the distributions and variations of N, P, SiO_3–Si, and their molar ratios in the dry and flood seasons, as well as the relations of N, P, and SiO_3–Si to suspended materials and river runoff. The long-term changes of nutrients and the main influencing factors, and the nutrients transported to estuary, are also considered. Before this study, the Three Gorges Dam had completed the first stage of construction, and the main river course was closed on November 8, 1997. Then, in June 2003, the sluice gates of the dam were closed for water storage and the water level had reached 135 m. At present, the water level has reached 156 m. After the completion of the dam, the water level of the reservoir will be 175 m in 2009. This study aims to summarize the background data of the nutrients in the Changjiang catchment prior to the water storage of the Three Gorges reservoir in order to provide the scientific base for assessing the impact of the Three Gorges Dam on the ecosystem of the Changjiang River and its estuary and to assess the previous estimation (Shen et al. 1992) after the construction of the dam.

1 Study Areas and Methods

The Changjiang River, which originates in the Qinghai–Tibet Plateau, is the largest river in China and the third largest in the world. After converging point of the Jinshajiang River and the Minjiang River in the upper reaches, it is called the Changjiang River. It is 6300 km long, with a catchment area of more than 1.8×10^6 km^2. The river's upper reaches, starting from the headstream to Yichang City in Hubei Province, add up to more than 4500 km, with a catchment area over 1.0×10^6 km^2. The middle reaches, stretching across an alluvial plain from Yichang to Hukou in Jiangxi Province, add up to more than 900 km, with a catchment area of 0.68×10^6 km^2. The lower reaches stretch over low plain terrain, located below Hukou, are more than 800 km long, with a catchment area of 0.13×10^6 km^2. From the headstream to the mouth, the Changjiang River has a fall about 5400 m, mainly in the upper reaches. The average runoff of the Changjiang River into the East China Sea is about 29,000 m^3 s^{-1} or 9282 $\times$ 10^8 m^3 a^{-1}, most of which comes from precipitation. The annual average and annual total of precipitation are 1057 mm and 19,120 $\times$ 10^8 m^3, respectively, of which 70–90% fall during May–October. The proportions of precipitation in the upper, middle, and lower reaches to the total precipitation are 44.7, 47.2, and 8.1%, respectively. The annual mean runoff coefficient in the Changjiang catchment is 0.49, indicating that about half of the precipitation form the runoff. The average concentration and the annual flux of the suspended material in the Changjiang River are 0.5–1.7 kg m^{-3} and 5×10^8 t, respectively. The characteristic parameters of main tributaries of the Changjiang River are listed in Table 1.

Investigations were carried out from November 25 to December 25, 1997 (dry season), from August 1 to 22 in the river's upper reaches (investigation has to stop due to the especially heavy flood), and from October 5 to 15 in the middle and lower reaches in 1998 (flood season). Twenty transects with three stations each (located at the left, middle, and right side of the transect, the stations at the left and right sides of the transect were set one-third of the river width from the bank) were set up along the river's mainstream, including Panzhihua, Yibin, Chongqing, Fuling, Wanxian, Yichang, Yueyang, Hankou, Jiujiang, Datong, Nanjing and the mouth, and at the mouths of the major tributaries of the Yalongjiang River, Minjiang River, Jialingjiang River, Wujiang River, Dongtinghu Lake, Hanshui River, Poyanghu Lake, and Huangpujiang River (Fig. 1). The stations were set up in the upper reaches of the city center to avoid the direct effect of sewage from the city and far from the pollution band along the bank. Water samples were collected from a water depth of 0.5 m, using a stainless steel sampler. The water samples at the Changjiang mouth were collected during ebb tide to avoid the interference of seawater. Rainwater was also collected in Panzhihua and Chengdu (the upper reaches), Jiujiang (the middle reaches), and Datong and Shanghai (the lower reaches) in the flood season and were taken monthly in the Donghu Lake (the middle reaches) and Taihu Lake region (the lower reaches). Water samples for analysis of dissolved form of nitrogen, phosphorus, and silica were filtered in situ with pre-ignited (450 °C, for 6 h) Whatman GF/C filters, and filtered membranes were used for analysis of suspended materials (observed only for

Table 1 Characteristics of the Changjiang water system

Water systems	Catchment areas (km^2)	Ratios (%)	Length (km)	Annual average Runoff ($m^3 s^{-1}$)	Ratios (%)	Sediment load (10^6 t a^{-1})
Changjiang	1,808,500	100.00	6300	29,000	100.00	500
Yalongjiang	128,444	7.10	1571	1810	6.24	27.50
Minjiang	133,000	7.35	735	2850	9.83	50.20
Jialingjiang	160,000	8.85	1120	2120	7.31	145
Wujiang	87,920	4.86	1037	1650	5.69	32.80
Dongtinghu[a]	262,823	14.53		5873[a]	20.25	35.84[a]
Hanshui	159,000	8.79	1577	1710	5.90	124
Poyanghu[b]	162,200	8.97		4068[b]	14.03	17.40[b]
Huangpujiang			113			
Total	1,093,387	60.5		20,081	69.25	432.74

[a]The runoff and sediment load of main tributaries of the Xiangjiang River, Zishui River, Yuanjiang River, and Lishui River

[b]The runoff and sediment load of main tributaries of the Ganjiang River, Fuhe River, Xinjiang River, Raohe River, and Xiushui River

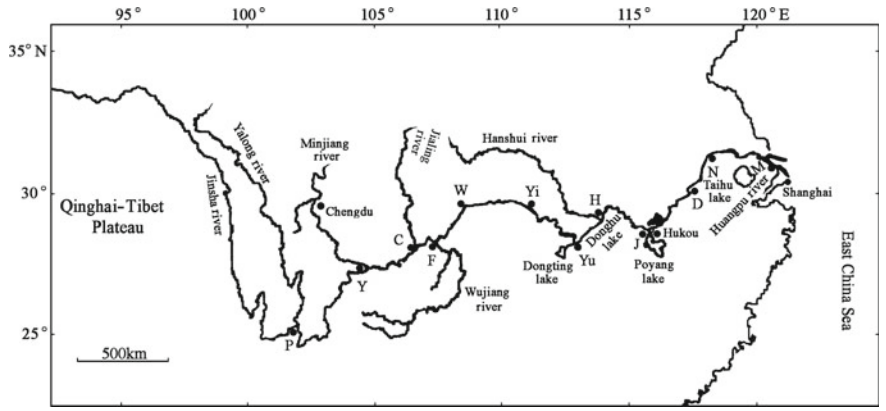

Fig. 1 Investigation stations: *P*, Panzhihua; *Y*, Yibin; *C*, Chongqing; *F*, Fuling; *W*, Wanxian; *Yi*, Yichang; *Yu*, Yueyang; *H*, Hankou; *J*, Jiujiang; *D*, Datong; *N*, Nanjing; *M*, River mouth

river water in the flood season, water volumes recorded). Water samples for analysis of total nitrogen and total phosphorus were not filtered. All water samples were preserved in polyethene bottles (marinate for 24 h in 1:10 hydrochloric acid solution beforehand) and immediately frozen together with particulate samples in a portable freezer for periodic analysis later in the laboratory.

Nitrate (NO_3–N) was measured using the cadmium-copper reduction method; nitrite (NO_2–N) using the Griess–Ilosvay method; ammonia (NH_4–N) using

Table 2 Average concentrations[a] (μmol L^{-1}) of N in the Changjiang mainstream

Seasons	NO_3–N	DIN	TDN	TN
Dry	53.2 ± 16.9	66.7 ± 19.9	114.9 ± 27.7	147.7 ± 30.9
Flood	53.5 ± 14.9	59.1 ± 15.2	83.0 ± 20.3	107.9 ± 22.5

[a]Average concentrations from Panzhihua to the mouth

the indophenol blue method; phosphate (PO_4–P) using the molybdenum–antimony–ascorbic method; silicate (SiO_3–Si) using the silicon–molybdenum blue method; total nitrogen (TN), total phosphorus (TP) and total dissolved nitrogen (TDN), and total dissolved phosphorus (TDP) using the potassium peroxodisulphate oxidation-colorimetry method (Valderrama 1981). The suspended matter (TSM) was analyzed using the weighing method (State Oceanic Administration, China 1991). All water samples for analysis of nutrients were determined using a Skalar Flow Analyzer produced in the Netherlands. Dissolved inorganic nitrogen (DIN) is equal to the sum of NO_3–N, NO_2–N, and NH_4–N; TN minus DIN is total organic nitrogen (TON); TDN minus DIN is dissolved organic nitrogen (DON); and TN minus TDN is total particulate nitrogen (TPN). TP minus TDP is total particulate phosphorus (TPP), and TDP minus PO_4–P is dissolved organic phosphorus (DOP).

2 Distributions and Removals of Nutrients in the Changjiang River

2.1 Nitrogen

The distributions and variations of N in the Changjiang mainstream in the dry and flood seasons are indicated in Fig. 2a, c, where every point is a transect-averaged concentration. The lowest concentrations of NO_3–N, DIN, TDN, TN in the dry and flood seasons were found in Panzhihua, being 16.5, 23.2, 66.5, 74.1 μmol L^{-1} and 18.9, 23.1, 39.2, 58.4 μmol L^{-1}, respectively. NO_3–N concentration was very close to the level of 14.3 μmol L^{-1} previously reported by Wang and Zuo (1986). The variations in DIN and NO_3–N concentrations were almost the same from the upper reaches to the lower reaches. The variations of various N concentrations were also similar, obvious increasing in the upper reaches and keeping relatively constant in the middle and lower reaches. The highest concentrations of NO_3–N, DIN, TDN, and TN in the mainstream were found in the upper and middle reaches, being 75.1 (Yueyang), 88.2 (Hankou), 150.3 (Wanxian), and 178.9 μmol L^{-1} (Wanxian), respectively, in the dry season, and 67.3 (Yichang), 72.7(Yichang), 110.6 (Hankou), and 128.7 μmol L^{-1} (Jiujiang), respectively, in the flood season. Except for NO_3–N, the average concentrations of other N in the Changjiang mainstream were all lower in the flood season than in the dry season (Table 2).

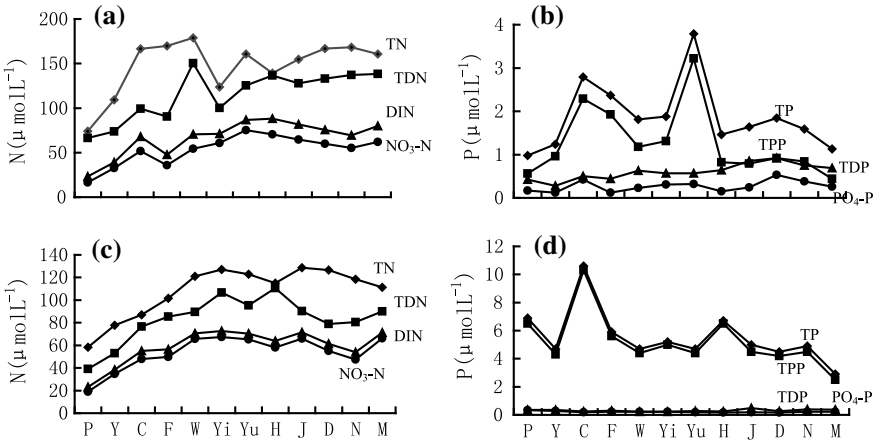

Fig. 2 Distributions and variations of N and P in the Changjiang mainstream in the dry and flood seasons: **a**, **b** dry seasons; **c**, **d** flood seasons. *F, Y, Q, F, W, Yi, Yu, H, J, D, N, M* have the same meaning as Fig. 1

The distributions and variations of N in the Changjiang water were not only related to the N input to the mainstream, but also that to the tributaries. High concentrations of N were found in the dry and flood seasons in the tributaries, such as the Jialingjiang River, Hanshui River, and Huangpujiang River (Table 3), which flow across three major cities of Chongqing, Hankou, and Shanghai with populations of 3090×10^4, 831×10^4, and 1674×10^4, respectively. Relatively lower N concentration was found in the Yalongjiang River. In the upper reaches, the N concentrations in the tributaries were obviously higher than that in the mainstream, which caused a continuous increase of N concentration in the mainstream. In the middle and lower reaches, however, relatively constant or even decreasing N concentrations were found, despite the high concentration of N flowing from the Hanshui River. It was probably caused by the input of water with low concentrations of N from the Dongtinghu and Poyanghu water systems, which comprised one-third of the total Changjiang River runoff (Table 1). Most of the data on N concentrations in the tributaries in the flood or dry season were in accordance with those reported previously by Zhang et al. (1999) and Liu et al. (2003) (Table 3); some discrepancy in data was probably caused by the difference in sampling time, location, or sample preservation and analytical method used.

2.2 Phosphorus

Figure 2b, d shows the distributions and variations of P in the Changjiang mainstream in the dry and flood seasons. PO_4–P concentration was relatively constant in the mainstream, ranging from 0.12 to 0.53 μmol L^{-1} in the dry season and 0.17–0.45 μmol L^{-1} in the flood season. TDP concentrations increased gradu-

Table 3 Average concentrations ($\mu mol\ L^{-1}$) of N in the mouths of the major tributaries and lakes of the Changjiang River

Tributaries	NO_3–N			DIN			TDN			TN		
	Dry	Level[a]	Flood	Dry	Level[a]	Flood	Dry	Level[a]	Flood	Dry	Level[a]	Flood
Yalongjiang	14.8	13.0	22.4	22.2	13.7	28.7	59.2	18.5	38.3	76.8	20.1	62.6
Minjiang	60.0	75.7	40.2	74.7	80.3	45.0	126.9	104.5	74.4	132.5	105.2	112.8
Jialingjiang	81.6	48.7	72.9	110.3	59.2	78.9	161.1	76.2	109.4	231.4	76.9	151.3
Wujiang	52.5	91.9	97.5	60.2	92.7	103.5	116.5	127.1	144.7	187.4	132.6	166.8
Dongtinghu	53.4	49.8	39.1	69.3	58.3	47.5	112.6	74.7	71.5	126.2	82.3	84.3
Hanshui	79.1	74.0	60.9	142.6	80.6	75.9	216.4	103.1	107.7	266.9	104.7	146.7
Poyanghu	39.3	39.9	17.3	51.6	43.3	24.6	87.5	56.5	46.3	103.4	64.3	55.3
Huangpujiang	78.4		73.8	151.7		207.7			209.2	309.6		237.1
Average[b]	54.4 ± 23.0	56.1 ± 26.5	50.0 ± 28.7	75.8 ± 39.6	61.2 ± 26.8	57.7 ± 29.1	125.8 ± 51.1	80.1 ± 35.9	84.6 ± 38.0	160.7 ± 69.9	83.7 ± 36.0	111.4 ± 60.9

[a]N concentrations in April–May 1997 among N concentrations in the Dongtinghu Lake for the average of its three tributaries of the Xiangjiang River, Zishui River, and Yuanjiang River and those in the Poyanghu Lake for its tributary of the Ganjiang River (Zhang et al. 1999; Liu et al. 2003)
[b]Not including the Huangpujiang River

ally from 0.28 to 0.92 μmol L^{-1} from the upper reaches to the lower reaches in the dry season and varied less from 0.22 to 0.49 μmol L^{-1} in the flood season. The variations of TP and TPP concentrations were almost synchronous along the river. In the dry season, the lowest concentrations of TP (0.98 μmol L^{-1}) and TPP (0.56 μmol L^{-1}) were found in Panzhihua, while high those were in Chongqing (2.79 and 2.29 μmol L^{-1}, respectively) and Yueyong (3.79 and 3.22 μmol L^{-1}, respectively). From Hankou to the mouth, the concentrations of TP and TPP were relatively constant (1.13–1.84 μmol L^{-1} for TP and 0.44–0.92 μmol L^{-1} for TPP). In the flood season, the concentrations of TP and TPP were from 2.9 to 10.6 μmol L^{-1} and 2.5 to 10.3 μmol L^{-1}, respectively, with the highest concentration found in Chongqing. The concentrations of TP and TPP were relatively constant between Wanxian and the mouth. Compared to the report of Zhang et al. (1999), the PO_4–P and TDP concentrations in the tributaries in this study were obviously lower and the TPP concentrations were much higher, while TP concentrations in the flood season were much higher, and in the dry season, the data were fairly close (Table 4). The variation trend, however, was similar. It was found that TP concentration increased mainly in the upper reaches, while decreased in the middle and lower reaches. The distribution patterns of various P concentrations along the mainstream were significantly different between flood season and dry season (Fig. 2b, d). Dramatic differences were also found in average concentrations of various P in the mainstream (Table 5). Dissolved P concentration in the dry season was evidently higher than that in the flood season, while the concentrations of TP and TPP were on the contrary.

The variations of P concentrations in the Changjiang mainstream were also affected by the tributaries. A gradual increase in TDP concentration was seen from the upper reaches to the lower reaches, due to high P input from the Jialingjiang River, Hanshui River, and Poyanghu Lake in the dry season (Table 4). High concentration of PO_4–P in the Hanshui River and Poyanghu Lake continues to contribute for the increasing concentration of PO_4–P in the mainstream till reaching the maximum in Datong. TPP and TP concentrations in the tributaries were close to those in the mainstream in the dry season (Tables 4 and 5). The average concentration of TDP in the tributaries in the flood season was only 38% of that in the dry season. TDP was mainly composed of PO_4–P, and PO_4–P concentrations in the tributaries were close to that in the mainstream (73 ± 19% and 85 ± 18% of TDP in the mainstream and tributaries, respectively), resulting in relatively lower TDP concentrations in the mainstream in the flood season. The distributions of TPP and TP concentrations in the tributaries in the flood season were opposite to those of the dissolved form of P. Firstly, the concentrations of TPP and TP in the tributaries were very high, which is an important factor for the high concentration of P in the mainstream. Another characteristic of TPP and TP in the tributaries was that their concentrations in the upper reaches were significantly higher than those in the middle and lower reaches except for the Huangpujiang River (Table 4).

Table 4 Average concentrations (μmol L^{-1}) of P and SiO_3–Si at the mouths of the major tributaries and lakes of the Changjiang River

Tributaries	PO_4–P			TDP			TPP			TP			SiO_3–Si		
	Dry	Level[a]	Flood	Dry	Level[a]	Flood	Dry	Level[a]	Flood	Dry	Level[a]	Flood	Dry	Level[a]	Flood
Yalongjiang	0.19	0.12	0.38	0.32	0.33	0.38	0.69	0.11	6.54	1.01	0.43	6.92	208.8	114.0	146.0
Minjiang	0.27	1.06	0.30	0.36	1.21	0.30	1.66	0.29	4.96	2.02	1.50	5.26	176.0	91.9	96.4
Jialingjiang	0.30	0.94	0.24	1.66	1.26	0.27	0.90	0.21	4.81	2.56	1.47	5.08	87.6	48.4	140.4
Wujiang	0.30	6.06	0.26	0.43	6.90	0.26	1.99	0.52	5.49	2.42	7.42	5.75	126.4	68.3	107.2
Dongtinghu	0.24	0.20	0.14	0.55	0.79	0.21	0.95	0.31	1.22	1.50	1.11	1.43	188.8	106.2	140.8
Hanshui	0.69	0.20	0.39	1.44	0.95	0.48	1.22	0.36	1.82	2.66	1.31	2.33	177.6	99.1	134.8
Poyanghu	0.52	0.15	0.15	1.01	0.54	0.29	0.39	0.48	0.34	1.40	1.02	0.63	208.0	150.0	121.2
Huangpujiang	0.57		2.39	2.71		2.77	0.96		4.50	3.67		7.27	201.2		166.0
Average[b]	0.36 ± 0.18	1.25 ± 2.16	0.27 ± 0.10	0.82 ± 0.55	1.71 ± 2.31	0.31 ± 0.09	1.11 ± 0.56	0.33 ± 0.14	3.63 ± 2.44	1.94 ± 0.64	2.03 ± 2.40	3.91 ± 2.42	167.6 ± 44.8	96.8 ± 32.7	126.7 ± 18.9

[a]P and SiO_3–Si concentrations in April–May 1997 among their concentrations in the Dongtinghu Lake for the average of its three tributaries of the Xiangjiang River, Zishui River, and Yuanjiang River and those in the Poyanghu Lake for its tributary of the Ganjiang River (Zhang et al. 1999; Liu et al. 2003)
[b]Not including the Huangpujiang River

Table 5 Average concentrations [a] (μmol L^{-1}) of P and SiO_3–Si in the Changjiang mainstream

Seasons	PO_4–P	TDP	TPP	TP	SiO_3–Si
Dry	0.27 ± 0.13	0.61 ± 0.18	1.27 ± 0.82	1.88 ± 0.79	187.6 ± 9.2
Flood	0.25 ± 0.09	0.31 ± 0.08	5.22 ± 1.93	5.56 ± 1.90	143.6 ± 10.8

[a]Average concentrations from Panzhihua to the mouth

2.3 Silicate

The variations of SiO_3–Si concentrations in the mainstream in the dry and flood seasons were not significant, ranging from 175.6 to 201.2 μmol L^{-1} and from 128.4 to 162.0 μmol L^{-1}, respectively. SiO_3–Si concentrations in the flood season were obviously lower than those in the dry season, and the concentrations in the tributaries are a little lower than that in the mainstream (Tables 4 and 5). Since SiO_3–Si concentration is not significantly affected by environmental pollution, it would be expected that the SiO_3–Si concentration has a even distribution along the river, not like N and P. SiO_3–Si concentrations in precipitation in Panzhihua and Chengdu were below the detection limit in the flood season in this study. SiO_3–Si concentration in the Changjiang water, with a average value of 150 μmol L^{-1}, is a little higher than that in other rivers around the world (Treguer et al. 1995).

3 Distribution and Composition Characteristics of N and P in the Changjiang River

The distribution patterns of various N along the mainstream were similar. The concentrations increased in the upper reaches and kept relatively constant in the middle and lower reaches. This distribution pattern of N in the Changjiang River in the dry and flood seasons was mainly due to the differences in human activities. There is limited anthropogenic disturbance above Panzhihua in the upper reaches due to the low population density (1–10 people per square kilometer). In the lower reaches of Panzhihua, population density increases to 10–200 people per square kilometer, which results in intensive anthropogenic disturbance, through industrial and agricultural production, stockbreeding, municipal sewage, etc. Therefore, N concentrations increased dramatically in the upper reaches. In the middle and lower reaches, N concentrations remained somewhat stable due to less differences in anthropogenic disturbance (population density 200–300 people per square kilometer). According to the estimation, only 5.7% of the inorganic N imported to the Changjiang River from precipitation came from the Jinshajiang catchment in the upper reaches (the area accounting for 27% of the total Changjiang catchment), and the inorganic N imported to the Changjiang River from fertilizer N loss and point sources sewage also mainly come from the lower reaches of Panzhihua (Shen et al. 2003).

Among the three forms of inorganic N, NO_3–N was the major form in the Changjiang water. The average NO_3–N/DIN ratio in the mainstream (0.79 ± 0.05 and 0.90 ± 0.04 in the dry and flood seasons, respectively) was higher than that in the tributaries (0.74 ± 0.10 and 0.84 ± 0.09 in the dry and flood seasons, respectively). The ratio was also higher in the flood season than in the dry season, which was related to the large runoff in the mainstream and the high water temperature in the flood season, favoring the transformation from NH_4–N and NO_2–N to NO_3–N. This result is consistent with literature reports in Changjiang River and its estuary. For example, Fu and Shen (2002) found that the average NO_3–N/DIN ratios were 74 and 95% in the dry and flood seasons, respectively, inside the river mouth. Higher NO_3–N/DIN ratio (95.5% in average in the flood season) and relatively lower that (93.2% in average in the dry season) were also found in inside and outside the river mouth by Zhou et al. (2006). This result is also consistent with the previous studies done by authors (Shen et al. 1992; Shen 1997). The study also showed that the ratio of NH_4–N in DIN from the external sources was much higher than that in the Changjiang water. For example, NH_4–N accounted for 87.7% of DIN in the precipitation in the Changjiang catchment (Shen et al. 2003). Besides, the NH_4–N concentrations in the tributaries were generally clearly higher than those in the mainstream water, and the ratios of NH_4–N in DIN in average were 30.9 and 29.5% in the dry and flood seasons, respectively. It showed that in the removal process of inorganic N in the Changjiang catchment, the above three forms of inorganic N were continuously transformed, with the transformations possibly occurring mainly in the catchment. DIN was the main form of total dissolved N, and DIN/TDN ratio in the mainstream was higher than that in the tributaries and that higher in the flood season than in the dry season. It was suggested that DON could be transformed into inorganic N more easily in the mainstream and in the flood season. Whether in the dry or flood season, the mainstream or tributaries, the average DIN/TN ratio was about 50%, and the average TDN/TN ratio was between 75 and 80% in the Changjiang River.

The distribution and composition of P were different from N, and TPP was major form of P in the Changjiang water. The average ratio of TPP to TP was higher in the flood season (94 ± 3 and 86 ± 16% in the mainstream and tributaries, respectively) than that in the dry season (64 ± 15 and 54 ± 23% in the mainstream and tributaries, respectively) and higher in the mainstream than that in the tributaries. The difference in concentrations of dissolved and particulate P in the mainstream and tributaries in the dry and flood seasons was mainly related to suspended matter content. The suspended matter transported in the flood season was about 82–87% of the annual amount transported (Institute of Geography, Chinese Academy of Sciences et al. 1985). Dissolved P including inorganic and organic P is easily adsorbed by suspended matter. In natural waters, P exists almost exclusively in the form of phosphate ion, which has strong particle affinity. Therefore, P is almost always in the particulate phase (Berge et al. 1997). TP and TPP concentrations in the Changjiang River in the flood season were much higher than those in the dry season, which was related to the large amounts of soil washed into the river by heavy rain, catching high concentration of P in the form of particulate. TP concentration (0.66 $\mu mol\ L^{-1}$ in average) was very low in precipitation, so the high concentrations of TP and TPP in the flood season were

not a result of precipitation. Particularly in the upper reaches, water and soil losses were the most serious, accounting for 60.5% of total losses in the whole catchment (Shen et al. 2003). During this investigation, especially heavy flood occurred and it took a lot of P from the ground into the river. The content of the suspended matter in the mainstream was 1.9 times of that in the tributaries found this investigation; it is also higher in the upper reaches than in the middle and lower reaches. In the tributaries, the content of suspended matter in the upper reaches could reach 16 times of those in the middle and lower reaches. The suspended matter in the Changjiang River mainly came from the upper reaches; the average annual transport of the suspended matter in Yichang was about $52{,}100 \times 10^4$ t a^{-1} (Institute of Geography, Chinese Academy of Sciences et al. 1985). P transport in the Changjiang River mainly depended on the suspended matter. Particulate P became dominant is a characteristic in turbid river, which could be seen in many rivers in the world (Baturin 1978).

4 The Molar Ratios of N, P, Si in the Changjiang River

The TN/TP ratio was from 42.4 (in Yueyang) to 142.1 (at the mouth) in the Changjiang mainstream in the dry season. In the flood season, the ratio increased from the upper reaches to the lower reaches, with the maximum value at the mouth (38.4) and lower value in Chongqing (8.2) and Panzhihua (8.5). The variations of TDN/TDP and DIN/PO_4–P ratios along the mainstream were significant. At the mouth, the ratios were 200.4 and 306.9, respectively, in the dry season and 237.1 and 310.0, respectively, in the flood season. The TPN/TPP ratios in the mainstream and tributaries in the dry and flood seasons were low (Table 6). Among the molar ratios of N/P in the Changjiang water, the highest ratio was found in dissolved form and the lowest was in particulate form (Table 6). The variations of SiO_3–Si/DIN ratios were similar in the dry and flood seasons along the mainstream; high value could be observed in the upper reaches of Chongqing and low value in the lower reaches of Chongqing. Similar variations also occurred in the tributaries. The variations of SiO_3–Si/PO_4–P ratios in the mainstream and tributaries were very large and the ratios were extremely high (Table 6).

The molar ratios of N/P, Si/N and Si/P in the Changjiang water were much higher than the Redfield value of N/Si/P = 16/16/1 (Brzezinski 1985), suggesting that phytoplankton was probably limited by P. The content of chlorophyll-*a* was only 0.5 mg m^{-3} inside the mouth. However, in this turbid river (transparence was 0.2–0.3 m inside the mouth), light limitation, rather than P limitation, seemed more likely to be a limiting factor for algal growth. The very high N/P ratio mainly reflected the effects of human activity, especially large inputs of anthropogenic N from precipitation and fertilizer lost, etc. (Shen et al. 2003). The authors found that the average molar ratios of TN/TP, TDN/TDP, and DIN/PO_4–P in precipitation were 191.1, 283.7, and 248.5, respectively, in the Changjiang catchment in the flood season, and the latter two were very close to those in the Changjiang mainstream and tributaries (Table 6). The Changjiang water comes mainly from precipitation, which suggests

Table 6 Average molar ratios of N, P, Si in the Changjiang River

Seasons		TN/TP	TDN/TDP	DIN/PO_4–P	TPN/TPP	SiO_3–Si/DIN	SiO_3–Si/PO_4–P
Dry	Mainstream[a]	85.9 ± 25.6	196.0 ± 35.8	282.1 ± 128.5	28.0 ± 14.1	3.3 ± 1.8	859.1 ± 432.4
	Tributaries[b]	81.1 ± 11.5	192.5 ± 94.9	222.4 ± 96.2	37.7 ± 32.1	3.3 ± 2.9	558.3 ± 305.1
Flood	Mainstream[a]	21.7 ± 8.6	287.1 ± 34.0	265.9 ± 107.8	5.6 ± 3.3	2.7 ± 1.1	641.2 ± 208.5
	Tributaries[b]	43.0 ± 28.1	317.5 ± 62.9	235.8 ± 119.4	11.8 ± 8.8	2.8 ± 1.6	551.7 ± 263.3

[a]Average ratios from Panzhihua to the mouth
[b]Not including the Huangpujiang River in the tributaries

during the process from precipitation to river water, dissolved forms of N and P were in a quasi-equilibrium state. The ratio of DIN/PO_4–P in precipitation in the Changjiang catchment was close to that of precipitation in Chesapeake Bay (300) (Fisher et al. 1992). The ratio of TN/TP in precipitation was much higher than that in the river water. It is due to the low concentration of TP in precipitation, where the P existed mainly in dissolved form (accounting for 65.2%). The higher concentration of TP in river water was mainly in particulate form (Tables 4 and 5). The very high concentration of TN (126.1 μmol L^{-1} in average) in precipitation was close to that in river water (Tables 2 and 3). The lower content of P in precipitation showed that precipitation was not the major source of P in the Changjiang water, which was different from N (Shen et al. 2003). As Si is not affected by environmental pollution, the molar ratios of Si/N and Si/P might be used to evaluate the level of pollution. The high ratios of N/P, Si/N, and Si/P in the Changjiang River were the major reason for the elevated ratios of these nutrients in sea areas adjacent to the Changjiang estuary (Shen et al. 1992).

5 The Relationships of Nutrient Concentrations, Suspended Matter, and Runoff in the Changjiang River

Of the various N in the Changjiang mainstream and tributaries in the flood season, only TN, TON, and TSM showed clearer negative linear correlationships (Fig. 3), suggesting that organic N could be more easily adsorbed by suspended matter. There was no correlationship between NO_3–N and TSM, because nitrate ions have almost no particle affinity and thus do not settle out of the water column (Berge et al. 1997). Strong positive correlationships were found between TP, TPP, and TSM, and negative correlationship was found between DOP and TSM (Fig. 3), suggesting that suspended particulate matter was important in sorption of P. The P adsorbed on suspended particulate matter (including some clay minerals and organic colloids) included inorganic and organic P imported from land by the heavy flood, as well as the organic P originated from the decomposition of organisms. The adsorption quantity is related to the physical and chemical properties of suspended matter. There was no correlation between SiO_3–Si and TSM. These results are consistent with previous results from the hydrological station of Hankou in the 1980s, which showed that there was no correlation between various forms of inorganic N and TSM, while there was close correlation between TSM and TP (Duan and Zhang 1999).

Correlative statistics between N, P concentrations, and daily-averaged runoff at each station in the Changjiang mainstream in the dry season showed that there were clearer positive linear correlationships between NO_3–N, NH_4–N, DIN, TDN, DOP, TDP concentrations, and the river runoff (Fig. 4). With the increasing runoff in the Changjiang River from the upper reaches to lower reaches, the concentrations of dissolved forms of N and P also increased. This pattern in the upper reaches, however, was more obvious than that in the middle and lower reaches (Fig. 2). The positive

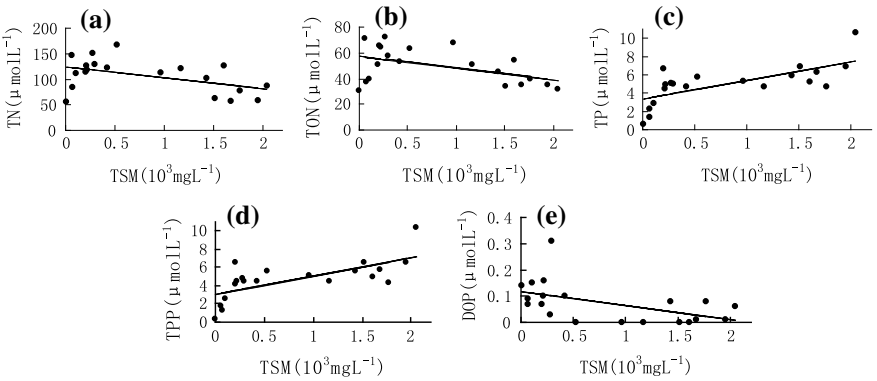

Fig. 3 Relationships between N, P concentrations, and suspended matter, respectively, in the Changjiang mainstream and tributaries in the flood season: **a** TN = 124.28–21.363 TSM, r^2 = 0.231, $p < 0.05$; **b** TON = 57.29–9.032 TSM, $r^2 = 0.222$, $p < 0.05$; **c** TP = 3.35 + 2.020 TSM, r^2 = 0.471, $p < 0.01$; **d** TPP = 3.03 + 2.007 TSM, $r^2 = 0.463$, $p < 0.01$; **e** DOP = 0.12–0.054 TSM, r^2 = 0.263, $p < 0.05$

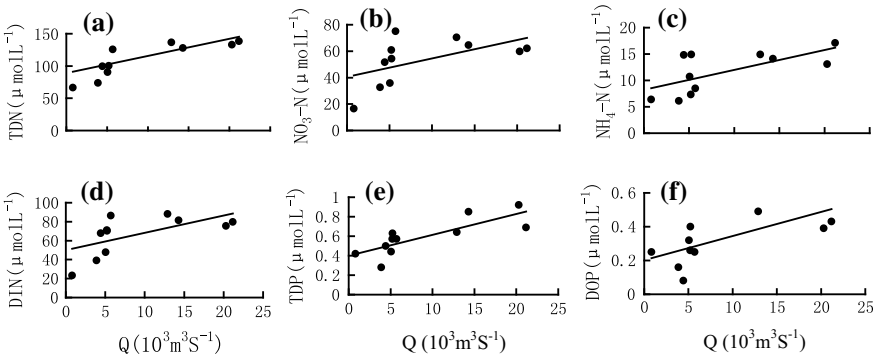

Fig. 4 Relationships between N, P concentrations, and the Changjiang runoffs Q, respectively, in the Changjiang mainstream in the dry reason: **a** TDN = 88.86 + 2.670 Q, $r^2 = 0.439$, $p < 0.05$; **b** NO_3–N = 40.46 + 1.402 Q, $r^2 = 0.304$, $p < 0.10$; **c** NH_4–N = 8.24 + 0.377 Q, $r^2 = 0.441$, $p < 0.05$; **d** DIN = 49.96 + 1.829 Q, $r^2 = 0.374$, $p < 0.05$; **e** TDP = 0.40 + 0.021 Q, $r^2 = 0.650$, $p < 0.01$; **f** DOP = 0.20 + 0.014 Q, $r^2 = 0.430$, $p < 0.05$

correlations between dissolved forms of N, P, and runoff reflected the continuous import of N and P from the precipitation and surface water to the river, mainly from agricultural non-point sources (Jarvie et al. 1998). SiO_3–Si in the Changjiang River mainly came from natural weathering and erosion of silicate minerals, and there was no correlation between SiO_3–Si concentration and runoff.

In the flood season, only correlations between NO_3–N, DIN, and runoff could be found in the Changjiang mainstream (Fig. 5). If we, however, consider the correlation in the upper reaches, we could find that there were clear positive linear correlationships between the concentrations of NO_3–N, DIN, TDN, TN, and river

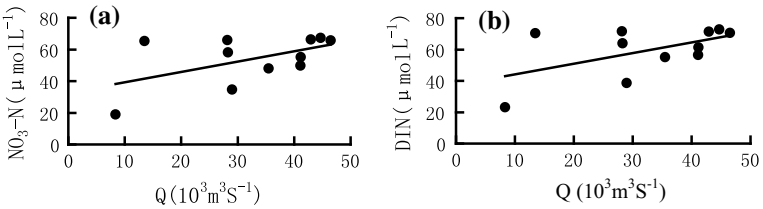

Fig. 5 Relationships between inorganic N concentrations and the Changjiang runoffs Q in the Changjiang mainstream in the flood reason: **a** NO_3–N = 32.84 + 0.650 Q, $r^2 = 0.281$, $p < 0.10$; **b** DIN = 37.34 + 0.679 Q, $r^2 = 0.294$, $p < 0.10$

runoff, respectively ($r^2 = 0.913$, 0.922, 0.848, 0.860, respectively, $p < 0.01$). The difference in the correlations between N concentration and runoff in the upper, middle, and lower reaches was related to the N sources of the Changjiang River. Inorganic N and TN in the Changjiang water mainly came from non-point sources, such as precipitation, N lost from agricultural fertilizer, and soil erosion (Shen et al. 2003). There are significant differences in scale and nature of human activities along the upper reaches, which lead to the dramatic difference in non-point sources N imported into the Changjiang River. Therefore, the N concentration increased significantly along the river (Fig. 2). In the middle and lower reaches, however, the scale and nature of human activities have little difference, the N concentration in the river keeps relatively constant (Fig. 2). The difference in the upper, middle, and lower reaches in the flood season was more significant than that in dry season, because precipitation occurred mainly in the flood season. The N in precipitation mainly comes from the gaseous loss of fertilizer N, fossil fuels combustion, and released matters from metabolisms of organisms (people, plants, and animals, etc.) (Shen 2003). Further, the import of N from point sources is also one of the factors affecting the positive correlation between N and runoff, which is a process diluted by river water (Jarvie et al. 1998). According to the statistical results, the inorganic N imported from point sources into the middle and lower reaches of the Changjiang River (186,123 t a^{-1}) was much higher than that into the upper reaches (65,828 t a^{-1}) in 1998 (Shen et al. 2003). This corresponded with the differences in correlations between N concentration and the river's runoff in the middle, lower, and upper reaches, respectively. There were no correlations between various P concentrations and runoff in the Changjiang mainstream in the flood season; this was notably different from the relationship of P and TSM, which further showed that P concentration was mainly controlled by suspended matter rather than runoff. There was no correlationship between SiO_3–Si concentration and runoff. The reports on the correlations of nutrient concentrations and runoff in the Changjiang River were very limited. It was reported that there was no correlation between inorganic N and runoff, but a clear positive correlationship between TP and runoff presented at the Hankou hydrological station in the 1980s (Duan and Zhang 1999). And there were no correlationships between either NO_3–N from the 1960s to the 1990s, or NH_4–N, NO_3–N, PO_4–P, SiO_3–Si from the 1960s to 1980s, and the river's runoff at the Datong hydrological station (Shen 2001a). These

investigations reflected the relationships between seasonal and annual variations of nutrient concentrations and the runoff, but the coverage of time and space in these studies were different from that in the current study. Relations between nutrient concentrations and runoff are complex, and different rivers have different characteristics (Brooker and Johnson 1984; van der Weijden and Middelburg 1989; Bhangu and Whitfield 1997).

6 Historical Changes in Nutrient Concentrations in the Changjiang River

Over the past decades, nutrient concentrations (especially of N) increased notably in the Changjiang water. Figure 6 compares the changes in average concentration of NO_3–N in the Changjiang mainstream during 1980–1982 (sum of 692 water samples per annum; the runoffs in annual average were 31,483, 27,942, and 30,692 $m^3\ s^{-1}$, respectively, at the Datong hydrological station), with the data from the dry and flood seasons in this study (average annual runoff was 39,325 $m^3\ s^{-1}$ at the Datong station). Data shows that from the early 1980s to the late 1990s, the average concentration of NO_3–N in the mainstream increased by 0.7 times (from 31.1 to 53.4 $\mu mol\ L^{-1}$) and that in the main tributaries, such as the Minjiang River, Jialingjiang River, Wujiang River, Dongtinghu Lake, Hanshui River, and Poyanghu Lake (sum 278 water samples per annum), increased 0.6 times (from 36.1 to 57.8 $\mu mol\ L^{-1}$). In Fig. 6, it could be seen that the increase of NO_3–N concentration becomes more evident from the upper reaches to the mouth (about 2.7 $\mu mol\ L^{-1}$ in Panzhihua, but 40.3 $\mu mol\ L^{-1}$ at the mouth) from the early 1980s to the late 1990s. NO_3–N concentration increased by a factor of 1.9 and 1.7 in Datong and the mouth, respectively. This is consistent with the impacts of human activities in the catchment. According to the monthly data at the Datong hydrological station, average inorganic N concentration has increased

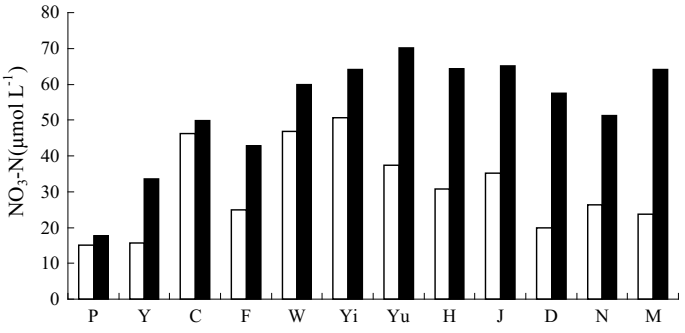

Fig. 6 Changes in NO_3–N concentrations in the Changjiang mainstream: 1997–1998 (*black bars*); 1980–1982(*white bars*). *F, Y, Q, F, W, Yi, Yu, H, J, D, N, M* have the same meaning as Fig. 1. The data (1980–1982) supplied by Changjiang Water Resource Protection Bureau

significantly since the 1960s, especially after the 1980s (Duan et al. 2000; Liu et al. 2002). These figures are in correspondence with the economic development in China. For example, from 1962 to 1980, the gross value of industrial output in China only increased 4.6-fold, while from 1980 to 1997, there was an increase of 21-fold. Statistics show that there were clear positive relationships between the increases in total discharged amounts of the wastes and sewage from county and above county-level enterprises, and the increase in population and gross value of industrial output (r^2 = 0.783, 0.936, respectively, $p < 0.01$) (Shen 2003). The data on P was limited and not so systematically collated as the data of N. It is, therefore, difficult to estimate accurately the trend of P concentration. PO_4–P concentration showed an increasing trend at Datong station from 1967 to 1984 (Duan et al. 2000; Liu et al. 2002), with the average concentration of 0.22 μmol L^{-1} (Liu et al. 2002). According to the weighted mean observational data from the Global Environment Measurement System (GEMS), TP concentration was 5.2 μmol L^{-1} at the Hankou station during 1985–1989 (Duan and Zhang 1999). In the dry and flood seasons in this study, the average concentrations were 0.35 μmol L^{-1} for PO_4–P and 4.1 μmol L^{-1} for TP in Datong and Hankou, respectively. Table 7 displays the concentrations of N, P, and SiO_3–Si in other rivers, showing that the N concentrations in the Changjiang River and some other Chinese rivers were much higher than those in the rivers of less-developed areas and closer to those in the developed areas. Research showed that the N in the Changjiang River came mainly from precipitation, agricultural non–point sources, and point sources of industrial waste and residential sewage discharge, among which the TN and DIN from precipitation were 56.2 and 62.3%, respectively, of the N outflow in the Changjiang mouth (Shen et al. 2003). Over the last 40 years, N concentration in precipitation in the Changjiang catchment has significantly increased. The average DIN concentration in precipitation in the Donghu Lake region in Hankou was 31.9 μmol L^{-1} during 1962–1963 (Liu et al. 1983), 41.8 μmol L^{-1} during 1979–1981 (Zhang et al. 1984), and 64.8 μmol L^{-1} during 1997–1998 (Tong Huijuan, personal communication). The concentration of inorganic N in precipitation in the Donghu Lake region has increased about twice from the 1960s to the 1990s. The increase in concentration of N in precipitation occurred mainly from the 1980s, which was in accordance with the historical changes of N in the Changjiang River. The N concentration in precipitation in the Changjiang catchment was much higher than averaged level in the world and close to that found in the polluted areas in developed countries (Meybeck 1982). In the Changjiang catchment during the flood season in 1998, the average concentrations of DIN and TN in precipitation in seven areas were 90.7 and 115.7 μmol L^{-1}, respectively. Modern agricultural activities using N fertilizers have a major impact on global atmospheric pollution. About 85% of NH_3, 81% of N_2O, and 35% of NO + NO_2 were from agricultural activities (Krapfenbauer and Wriessning 1995). China is a large agricultural country where agricultural activities comprise the primary economic activity. Fertilizer N has increased nearly 15 times in the Changjiang catchment from 1968 to 1997. The increase was most notably from the late 1970s (Duan et al. 2000), which was consistent with the increase of N in the Changjiang water and precipitation. Clear positive correlationships between N concentration in the river water and the consumption of fertilizer N have been found in a number of

reports (Berankova and Ungerman 1996; Chen et al. 1998). The fertilizer N losses include gaseous loss and N loss from farmland, but especially the former through denitrification and NH_3 volatilization, and N in the atmosphere transported to the ground by precipitation and dry deposition. It was estimated that about 3.44×10^6 t of fertilizer N was released into the atmosphere annually; this was twice of the inorganic N outflow from the Changjiang mouth in 1998 and was the major reason for N increase in the Changjiang River (Shen 2003).

Increase of N concentration in the Changjiang River has led to the increase of N concentration in the sea areas adjacent to the Changjiang estuarine. This has resulted in abnormal nutrient ratios and great changes in the ecological environment. The imports of exogenous new N will change the molar ratios such as N: P, Si: N, and Si: P of the key limiting nutrients (Justic et al. 1995; Shen 2001b). The maximum molar ratio of NO_3–N/PO_4–P in the early 1960s was 30–40 at the Changjiang mouth (Gu et al. 1981). During the annual investigations at the Changjiang mouth from August 1985 to July 1986, the molar ratios of NO_3–N/PO_4–P and DIN/PO_4–P were 103 and 158, respectively. In this investigation, the values were 268 and 308, respectively. Great increases in N concentration caused increases in DIN/PO_4–P ratio and decreases in SiO_3–Si/DIN ratio. Excess nitrate appeared in the East China Sea (Wong et al. 1998). The imbalance in nutrient ratios led to change in the phytoplankton community accompanied by the appearance and persistence of harmful algal blooms (Conley and Malone 1992; Paerl 1997). Waters eutrophication is becoming more and more serious, and red tide is tending to increase in the sea areas adjacent to the estuary of Changjiang River, which has become popular site for harmful red tide in China. According to the report from the Chinese Ocean Yearbook, harmful red tides occurred twice in the 1970s and 27 times in the 1980s, and 132 times from 1993 to 1997 in the East China Sea (Sun 1999). The scope of red tide was becoming larger and larger. In recent years, the area of large-scale red tide of *Prorocentrum* could reach thousands of square kilometers (Wang and Huang 2003). This is possibly related to the nutrients transported by the Changjiang River into the sea. The well-known Three Gorges Project of the Changjiang River started in 1994. It was forecasted by authors that after the completion of the Three Gorges Dam, it would considerably reduce the sediment load into the estuary and improve the transparence of seawater, due to settlement of suspended matter up to 60–70% in the reservoir. The high-density area of phytoplankton would move toward the river's mouth with very high concentration of nutrients and possibly arouse abnormal proliferation of phytoplankton (Shen et al. 1992). Zhang et al. (1999) thought that the Three Gorges Dam may reduce considerably the sediment load to the estuary, which in turn affects the region where photosynthesis is in radiation limitation and facilitates the primary production sustained by riverine nutrient supply (Ning et al. 1988). Chen (2000) suggested that whether the East China Sea will become eutrophicated actually depends on the amount of phosphorus supply supported by onshore advection. This supply will very likely be reduced after the completion of the Three Gorges Dam, and this will lead to a diminished productivity in the East China Sea. These forecasts are

Table 7 Nutrients concentrations (μmol L^{-1}) in some large world rivers

Rivers	Periods	NO_3–N	NO_2–N	NH_4–N	DIN	PO_4–P	TP	SiO_3–Si	References
Changjiang (Datong)	1997.12 1998.8,10	57.5	1.3	9.7	68.5	0.35	3.2	163.8	This study
Huanghe (Lijin)	2002.5–2003.2	101.4	2.7	46.0	150.1	0.38		104.0	Unpublished
Zhujiang (Gaonu)	1985–1989	47.0	0.64	1.2	48.8	0.12	2.2	150[a]	Duan and Zhang (1999), [a] Chen et al. (1990)
Mississippi (Venice etc.)	1981–1987	114					7.7	108	Turner and Rabalais (1991)
Rhine (Lobith)	1975–1984	273.6		59.3		11.5		92.5	van der Weijden and Middelburg (1989)
Seine (Poses)	1990–1992	314.3		172.1		21.9		105.0	Cossa et al. (1994)
Amazon (Morth)		16		0.4		0.7		144	Demaster and Pope (1996)
Zaire (Malela-Boma)	1976.111978.5	6.5	0.2	0.4	7.1	0.8		165	van Bennekom et al. (1978)

[a]data from Chen et al. (1990)

awaiting for validation. However, it could be expected that, with the construction of the Three Gorges Dam, population increase, and rapid economic development in the Changjiang catchment, more ecological and environmental issues might arise in the estuary.

7 Nutrient Transport in the Changjiang River

The average annual fluxes of N, P, and Si from each tributary entering the Changjiang River were calculated as follows:

$$F = \Sigma \bar{C} \cdot Q \cdot f$$

where F is average annual transport fluxes (kg s^{-1}) of N, P, and Si, Σ C is the average concentrations (μmol L^{-1}) of N, P, and Si in the dry and flood seasons, Q is the average annual runoff of the Changjiang tributaries, and f is conversion coefficients of units. Annual fluxes of nutrients (t a^{-1}) were calculated using the above average annual fluxes, and areal yields (kg a^{-1} km^{-2}) of the tributaries and the Changjiang River were defined as the annual fluxes divided by the drainage areas of each tributary or the Changjiang River.

The average annual fluxes of N, P, and SiO_3–Si from each tributary entering the Changjiang River and their ratios in export fluxes of the Changjiang mouth are listed in Table 8. Except for PO_4–P (for the Poyanghu Lake), the Dongtinghu Lake followed by the Poyanghu Lake contributed most of the fluxes of various N, P, and SiO_3–Si entering the Changjiang River. Statistics indicate that there were clear positive linear correlationships between the transport fluxes of various N, P, and SiO_3–Si and the runoffs of each tributary, suggesting that the fluxes in the tributaries were mainly controlled by the runoffs. The ratios of the fluxes of various N, P, and SiO_3–Si in the tributaries to the export fluxes of the Changjiang mouth were from 37.0 to 73.6%, with the highest for SiO_3–Si and the lowest for PO_4–P. Among exported N and P from the Changjiang mouth, approximately 50% plus were contributed by the tributaries. The average annual total runoff of the tributaries was 30,990 m^3 s^{-1} in 1998 and accounted for 75.4% of exported runoff of the Changjiang mouth, which was very close to the ratio of SiO_3–S flux from the tributaries to the mainstream in the export fluxes of the Changjiang mouth, suggesting that SiO_3–Si was nearly free from environmental pollution. The annual fluxes and areal yields of nutrients of the tributaries are listed in Table 9. The areal yields of nutrients of the tributaries increased from the west of the tributaries to the east of the tributaries, except for the Hanshui River. And the yields of nutrients in the south of the tributaries were higher than those in the north of the tributaries. This pattern of differences accorded with the extent of impact by human activities. It was relatively developed in the east and the south of the Changjiang River and less developed in the west and the north. The

magnitude of the areal yield reflects the nutrient load and the level of pollution in the catchment. High SiO_3–Si yield in the south of the tributaries were related to the chemical weathering, which is much stronger in the hot and wet south than in the cool and dry north of the watersheds (Qu et al. 1993). The areal yields of NO_3–N, PO_4–P, and SiO_3–Si in the Changjiang tributaries were commonly higher than those in the rivers in northern part of China, such as the Yellow River. The areal yields in the tributaries in the south of the Changjiang River were closer to those of other southern Chinese rivers (Zhang 1996).

Previous study showed that there were clear positive linear relationships between the export fluxes of NO_3–N, NO_2–N, NH_4–N, DIN, TON, and TN in the Changjiang mouth and the river's runoff (Shen et al. 2003). The current study found that, using above same method, there were also clear positive linear relationships between the export fluxes of PO_4–P and TP and runoff, respectively (r^2 are 0.926 and 0.944 respectively, $p < 0.01$). This showed that the export fluxes of the above forms of N and P were controlled by the river's runoff. The export fluxes and areal yields of N and P of the Changjiang River were obtained from their correlative equations listed in Table 10. There were very limited reports on nutrients fluxes in the Changjiang River mouth. Compared to results in 1985–1986 (Shen et al. 1992), the export fluxes of NO_3–N, DIN and PO_4–P increased 1.3, 1.0, and 0.6 times, respectively, mainly due to 0.7-fold increase in the Changjiang River runoff (because of the especially heavy floods in the current study). This possibly showed that inorganic N concentration had increased and PO_4–P seems no change at the Changjiang mouth from the 1980s to the 1990s. The estimate for export flux of NO_3–N in this study was consistent with the result (149.9×10^4 t a^{-1}) derived from the data of monthly investigations at the Datong hydrological station in 1998 (Liu et al. 2002). The areal yield of NO_3–N in this study, however, was much higher than the previous studies, such as 420 kg a^{-1} km^{-2} estimated by Edmond et al. (1985) (based on two cruises during 1980–1981), 236.6 kg a^{-1} km^{-2} estimated by Zhang (1996) (based on three cruises during 1986–1988), and 581.0 kg a^{-1} km^{-2} estimated by Liu et al. (2003) (based on one cruise in 1997). The areal yield of PO_4–P in this study was also higher than the value 9.4 kg a^{-1} km^{-2} estimated by Zhang (1996), and 9.9 kg a^{-1} km^{-2} estimated by Liu et al. (2003), but was lower than 21.8 kg a^{-1} km^{-2} (possibly including particulate actively P) estimated by Edmond et al. (1985). The differences in the areal yields of NO_3–N were possibly related to the especially heavy floods during our investigation, the increase in N concentration in recent years, and the estimating methods, etc. The Changjiang River export flux of NO_3–N was much higher than that of the Amazon River, but the export flux of PO_4–P (from the Changjiang River) was much lower than that of the Amazon River (Edmond et al. 1985).

Table 8 Average annual transport fluxes (kg s^{-1}) of N, P, and Si from the tributaries into the mainstream and their ratios (%) in export fluxes of the Changjiang mouth

Tributaries		Yalongjiang	Minjiang	Jialingjiang	Wujiang	Dongtinghu	Hanshui	Poyanghu	Total	Mouth
NO_3–N	Fluxes	0.47	1.85	2.43	1.91	8.22	1.37	3.32	19.58	45.59
	Ratios	1.0	4.0	5.3	4.2	18.0	3.0	7.3	42.8	100.0
NO_2–N	Fluxes	0.010	0.037	0.051	0.009	0.178	0.039	0.056	0.380	0.601
	Ratios	1.7	6.2	8.4	1.5	29.6	6.5	9.3	63.2	100.0
NH_4–N	Fluxes	0.16	0.32	0.50	0.17	1.97	0.73	1.09	4.94	9.21
	Ratios	1.8	3.5	5.4	1.8	21.4	7.9	11.8	53.6	100.0
DIN	Fluxes	0.64	2.20	2.98	2.09	10.38	2.14	4.48	24.91	55.38
	Ratios	1.2	4.0	5.4	3.8	18.7	3.9	8.1	45.1	100.0
TON	Fluxes	1.12	2.31	3.05	2.43	8.33	1.91	4.85	23.99	34.98
	Ratios	3.2	6.6	8.7	6.9	23.8	5.5	13.9	68.6	100.0
TN	Fluxes	1.76	4.52	6.03	4.51	18.71	4.05	9.32	48.90	90.35
	Ratios	1.9	5.0	6.7	5.0	20.7	4.5	10.3	54.1	100.0
PO_4–P	Fluxes	0.016	0.024	0.019	0.016	0.077	0.024	0.090	0.266	0.718
	Ratios	2.3	3.3	2.7	2.3	10.8	3.3	12.5	37.0	100.0
TP	Fluxes	0.23	0.31	0.28	0.24	0.60	0.11	0.27	2.03	4.01
	Ratios	5.7	7.6	6.9	5.9	14.8	2.8	6.8	50.5	100.0
SiO_3–Si	Fluxes	8.94	10.03	7.18	5.95	58.60	6.12	38.67	135.50	184.06
	Ratios	4.9	5.4	3.9	3.2	31.8	3.3	21.0	73.6	100.0

Table 9 Annual fluxes and areal yields of nutrients of the tributaries

Tributaries	Fluxes	NO_3–N	NO_2–N	NH_4–N	DIN	TON	TN	PO_4–P	TP	SiO_3–Si
Yalongjiang	10^4 t a^{-1}	1.48	0.032	0.51	2.02	3.52	5.54	0.050	0.72	28.20
	kg a^{-1} km^{-2}	115.1	2.49	40.0	157.3	273.7	431.2	3.89	55.98	2195.2
Minjiang	10^4 t a^{-1}	5.82	0.117	1.02	6.95	7.29	14.24	0.076	0.97	31.63
	kg a^{-1} km^{-2}	437.4	8.80	76.3	522.6	548.2	1070.8	5.71	72.56	2378.3
Jialingjiang	10^4 t a^{-1}	7.67	0.161	1.56	9.40	9.61	19.01	0.060	0.87	22.65
	kg a^{-1} km^{-2}	479.6	10.06	97.6	587.4	600.8	1188.1	3.75	54.19	1415.6
Wujiang	10^4 t a^{-1}	6.03	0.028	0.52	6.58	7.65	14.23	0.050	0.75	18.77
	kg a^{-1} km^{-2}	685.5	3.18	59.5	748.2	870.6	1618.7	5.69	85.42	2134.9
Dongtinghu	10^4 t a^{-1}	25.93	0.561	6.23	32.75	26.27	59.01	0.243	1.88	184.81
	kg a^{-1} km^{-2}	986.7	21.35	236.9	1246.0	999.5	2245.4	9.25	71.38	7031.7
Hanshui	10^4 t a^{-1}	4.33	0.123	2.30	6.75	6.03	12.78	0.076	0.35	19.31
	kg a^{-1} km^{-2}	272.1	7.74	144.8	424.7	379.2	803.9	4.78	22.20	1214.4
Poyanghu	10^4 t a^{-1}	10.48	0.177	3.43	14.11	15.28	29.39	0.284	0.86	121.94
	kg a^{-1} km^{-2}	646.3	10.91	211.3	870.0	942.0	1812.1	17.51	53.08	7518.1
Total	10^4 t a^{-1}	61.74	1.199	15.57	78.56	75.65	154.21	0.839	6.39	427.31
Averages	kg a^{-1} km^{-2}	564.7	10.97	142.4	718.5	691.9	1410.4	7.673	58.46	3908.1

Table 10 Export fluxes and areal yields of nutrients of the Changjiang River

Fluxes	NO_3–N	NO_2–N	NH_4–N	DIN	TON	TN	PO_4–P	TP
kg s^{-1}	45.59	0.60	9.21	55.38	34.98	90.35	0.72	4.01
10^4 t a^{-1}	143.8	1.9	29.1	174.6	110.3	284.9	2.3	12.7
kg $a^{-1}km^{-2}$	795.1	10.5	160.9	963.4	610.0	1575.0	12.6	70.3
1985–1986[a] (10^4 t a^{-1})	63.6	0.38	24.9	88.8			1.4	

[a]Estimating based on the correlative equations between nutrients fluxes and runoff in the Changjiang mouth in annual investigations in 1985–1986 (Shen et al. 1992)

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The Relationships of the Nutrients in the Changjiang River Estuary and the Flow of the Changjiang River Water

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Abstract In the Changjiang estuary, the high concentration area of phosphate (PO_4–P), SiO_3–Si and NO_3–N gradually reduced with the reduction of the area of the Changjiang diluted water from summer, autumn to winter. The seasonal distributions of the nutrients were mainly controlled by the river flow and were also related to the growth and decline of phytoplankton. The conservation of SiO_3–Si and NO_3–N in the estuary in the flood season was poorer than that in the dry season. The behaviour of PO_4–P shows that in addition to biological removal, the buffering of PO_4–P is possible in the estuary. The Changjiang's annual nutrient transports to the sea were estimated. The investigation shows that the seasonal variations of the nutrient transport closely correlate with that of the flow of the Changjiang River and is confirmed by the investigations in 1997–1998 (Shen et al. in Ambio 32:65–69, 2003; Shen in Acta Geogr Sinica 61:741–751, 2006) and 2004 (Shen et al. in Environ Monitor Assess 184:6491–6505, 2012).

Keywords Nutrients · Seasonal variations · Transport · Flow · Changjiang River Estuary

It is well known that the 6300-km-long Changjiang River is the largest river in China and the third largest in the world. The average Changjiang River runoff into the East China Sea is 9282 × 10^8 m^3 a^{-1} or 29,000 m^3 s^{-1}. Flood season (May to October) runoff is 71.7% of annual runoff. After entering the sea, the Changjiang River diluted water is mixed continuously with Taiwan Warm Current Water from the south and Yellow Sea water from the north. The convergence of various water masses in the area near the Changjiang River estuary and the great quantity of nutrient material transported annually by river water to the estuary makes the area a most important fishing ground in China and known as one of the best in the world. This study is mainly based on the results of eleven investigations in the Changjiang River estuary from August 1985 to July 1986 (station locations in Fig. 1). The seasonal variations of the

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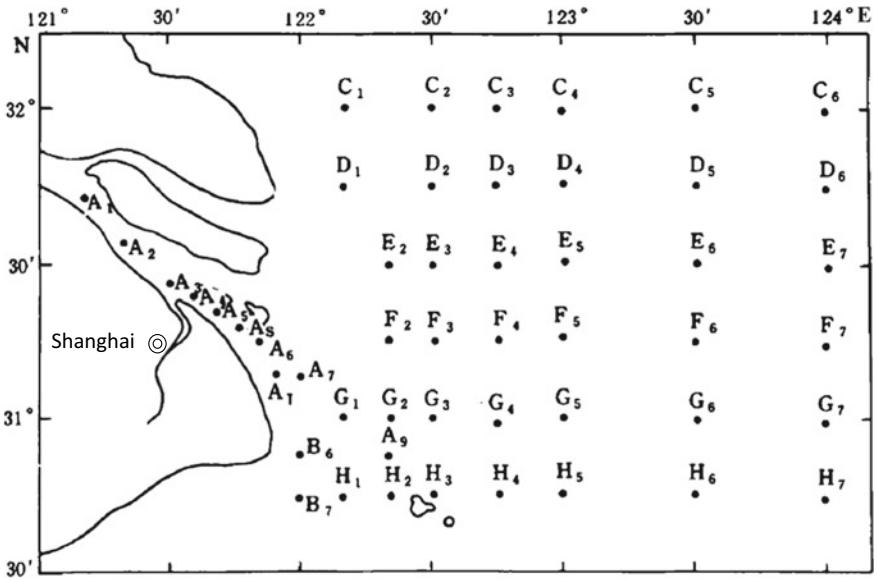

Fig. 1 Sampling stations

phosphate (PO_4–P), silicate (SiO_3–Si) and nitrate (NO_3–N), and their relation to the Changjiang River flow, and effects on the transportation, distributions, variations and the behaviour of the nutrients in the estuary, nutrients transport, etc., are discussed.

1 The Seasonal Variations of the Nutrients in the Changjiang River Mouth

The seasonal variations of the average nutrient concentrations in the Changjiang River mouth freshwater and the average flow of the Changjiang River at Datong hydrological station are indicated in Fig. 2. The concentrations of PO_4–P and NO_3–N were high (average 0.62 and 63.7 μmol L^{-1}, respectively) in the flood season and low (average 0.48 and 51.1 μmol L^{-1}, respectively) in the dry season. The highest concentrations were in August for PO_4–P (average 0.88 μmol L^{-1}) and in May for NO_3–N (average 81.6 μmol L^{-1}), and the lowest were in March (average 0.34 and 43.7 μmol L^{-1}, respectively). The relationship between the seasonal variation of SiO_3–Si concentration and the flow of the Changjiang River water was not regular. The highest concentration of SiO_3–Si was 191.5 μmol L^{-1} in November, and the lowest was 58.5 μmol L^{-1} in April.

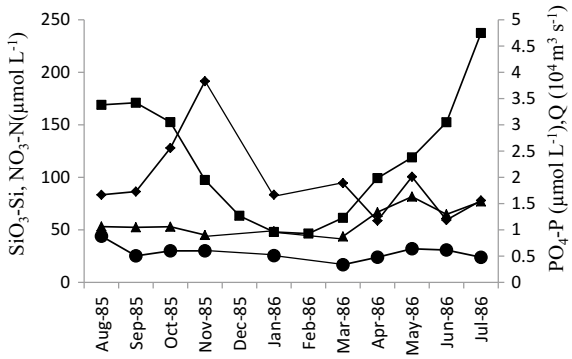

Fig. 2 Seasonal variations of the nutrients and flow in the Changjiang River water: filled diamond—SiO_3–Si; filled triangle—NO_3–N; filled circle—PO_4–P; filled square—Q

2 The Relationships Between the Seasonal Variations of the Nutrient Concentrations in the Changjiang River Estuary Sea Water and the Flow of the River Water

The relationships among the seasonal variations of the average concentrations of the nutrients in the surface sea water (the area west of 123°30′ E), the flow of the river water and phytoplankton are indicated in Fig. 3, which shows that during the annual phytoplankton peak in the flood season (August to September) PO_4–P, SiO_3–Si and NO_3–N concentrations all decreased. After September, although the flow was higher, there was a rapid decrease of phytoplankton and marked increase in the concentrations of SiO_3–Si and NO_3–N to the annual maximum of 30.9 μmol L^{-1} for SiO_3–Si and 13.3 μmol L^{-1} for NO_3–N in November. The concentration of PO_4–P rose only after October and reached a peak in November. In late autumn and winter (dry season), phytoplankton was at low ebb; the concentrations decreased a little for PO_4–P and markedly for SiO_3–Si and NO_3–N. The annual lowest values of SiO_3–Si and NO_3–N appeared in April. Then, all nutrient concentrations increased with the increase of the river water flow. In May to June, due to phytoplankton bloom, all of them decreased. The seasonal variations of PO_4–P, SiO_3–Si and NO_3–N show that in addition to control by the Changjiang River water flow, their concentrations were also related to the growth and decline of phytoplankton.

The seasonal variations of the nutrient concentrations in the sea area were similar in many ways to those in the Changjiang River mouth. The maximum concentrations of PO_4–P all appeared in August, and the seasonal variations were small. The monthly average concentrations of PO_4–P at the seaward side of the river mouth were between 0.29 and 0.68 μmol L^{-1} and a little higher in winter than in summer, which may be related to oxidation and decomposition of organisms. The change of SiO_3–Si concentration here was very similar to that in the river freshwater, the maximum in November, second in October, and the minimum in April. The relationship between them was as follows:

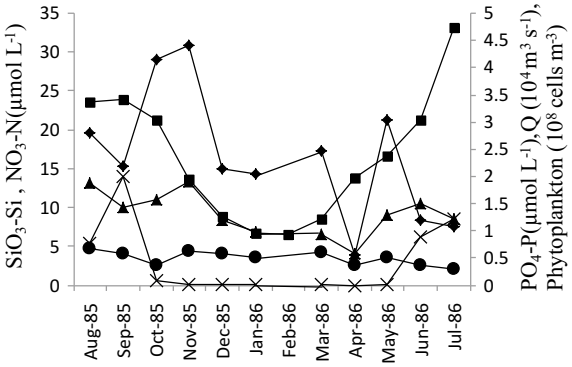

Fig. 3 Relationships among the seasonal variations of the nutrients in the Changjiang River estuary sea water and the flow of the Changjiang River water and phytoplankton: filled diamond—SiO_3–Si; filled triangle—NO_3-N; filled circle—PO_4–P; filled square—Q; multiplication sign—phytoplankton

$$\mathrm{SiO_3{-}Si\ (in\ seawater)} = 0.200\ \mathrm{SiO_3{-}Si\ (in\ river\ water)} - 2.454\ (r = 0.877, n = 10)$$

The concentration of NO_3–N in the sea area was also higher in the flood season (average 10.4 μmol L^{-1}) than in the dry season (average 7.6 μmol L^{-1}), and there was a delay in the seasonal variation as compared with that in the river water area. The concentration of NO_3–N in the river water area decreased to minimum from October to next March, rapidly rose again until May and then decreased again. NO_3–N concentration in the sea area decreased from November to next April (minimum in April), rapidly rose again until June and then decreased again.

3 The Effects of the Changjiang River Water Flow on the Distributions and Changes of the Nutrients in the Sea Area

From August, November to January (from the flood to dry season), the average Changjiang River runoffs into the sea were 3.38×10^4, 1.95×10^4 and 0.96×10^4 m^3 a^{-1}, respectively. The Changjiang River diluted water area gradually reduced from August to January, and the 30 isohalines contracted towards the river mouth. The research shows positive linear correlationships between the Changjiang River diluted water area and the Changjiang River runoff into the sea (Zhang et al. 1987). With the reduction of the area of the diluted water, the higher concentration areas of the nutrients were reduced and all the isograms gradually moved towards the river mouth. For SiO_3–Si and NO_3–N (Figs. 4 and 5), the areas covered by the 20 μmol L^{-1}

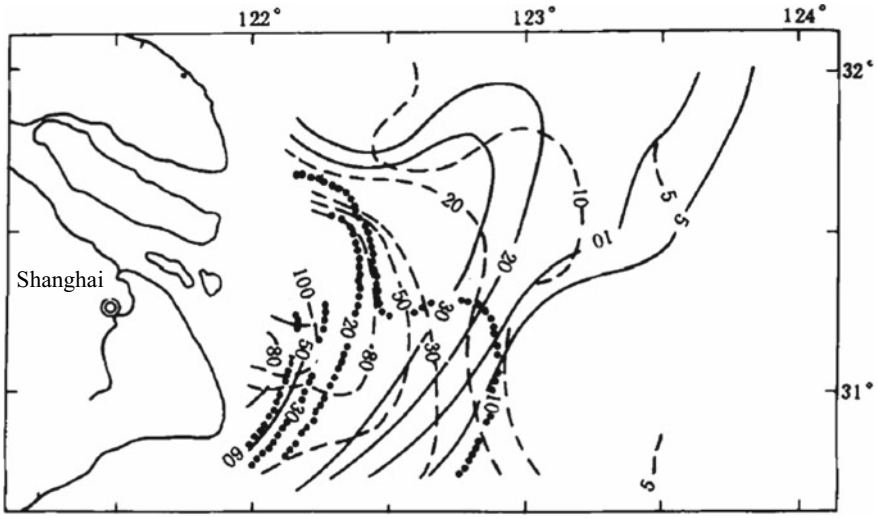

Fig. 4 Distribution of SiO_3–Si (μmol L^{-1}) in surface sea water: solid line—August; dashed line—November; dotted line—January

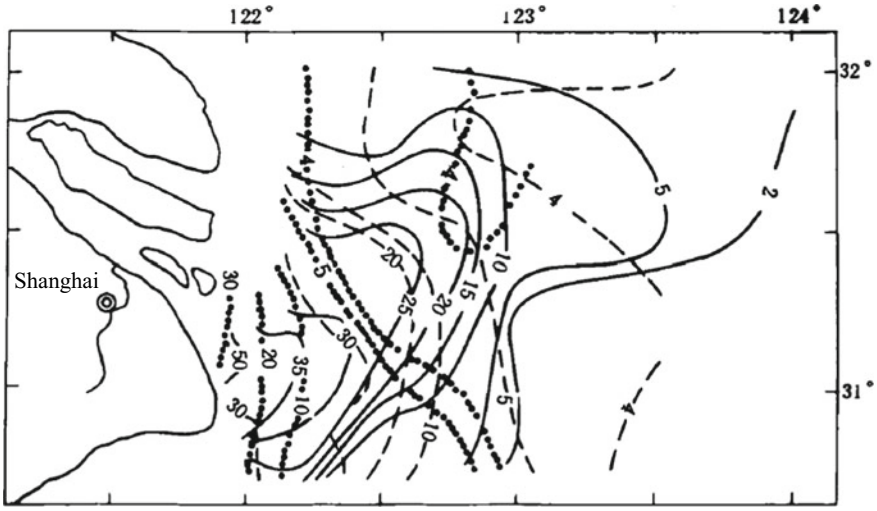

Fig. 5 Distribution of NO_3–N (μmol L^{-1}) in surface sea water: solid line—August; dashed line—November; dotted line—January

isogram were smaller and smaller from summer to winter, and in winter the waters of 20 μmol L^{-1} concentration for SiO_3–Si were limited to west of 122º30′ E and for NO_3–N near the river mouth. This shows that the seasonal distributions and changes of the nutrients are mainly controlled by the flow of the Changjiang River.

4 The Effects of the Changjiang River Flow on the Behaviours of the Nutrients in the Estuary

Correlation statistics show that there were monthly negative linear correlationships between SiO_3–Si or NO_3–N and salinity and that the correlationship between PO_4–P and salinity was not close. The correlation coefficients and statistical ranges are listed in Table 1, showing that the correlationships between SiO_3–Si or NO_3–N and salinity, respectively, in the flood season were poorer than that in the dry season. This was due to the phytoplankton bloom (average 7648×10^4 cells m^{-3} in August). In the Changjiang River flood season, nutrients were largely taken up by phytoplankton in surface seawater and the decomposition of organisms released nutrients in the lower seawater (mainly in the waters of salinity higher than 30). It is evident that the change of SiO_3–Si with salinity was similar to that of NO_3–N with salinity and that there was positive linear correlationship between SiO_3–Si and NO_3–N (in August) indicated as:

$$NO_3\text{–N} = 0.582\,SiO_3\text{–Si} + 0.913 \ (r = 0.936,\ n = 51)$$

It clearly shows that part of them were removed through biological processes.

The correlationship between PO_4–P and salinity was poor in the flood or dry season. The investigations show that the concentration of PO_4–P in surface water

Table 1 Correlationships of the nutrients and salinity

Months	Water layers	Salinity ranges	PO_4–P		SiO_3–Si		NO_3–N	
			r	*n*	*r*	*n*	*r*	*n*
August	All layers	0–34.5	−0.177	153	−0.815	153	−0.889	153
September	Surface	0–31.7	−0.086	39	−0.819	39	−0.816	39
October	All layers	0–33.6	−0.625	149	−0.871	150	−0.921	150
November	All layers	0–33.8	−0.249	114	−0.918	114	−0.933	114
December	Surface	15–33.2	−0.630	36	−0.914	35	−0.910	36
January	All layers	0–33.7	−0.145	109	−0.925	109	−0.964	109
March	Surface	0–34.0	0.063	43	−0.898	43	−0.920	43
April	Surface	0–33.7	−0.834	36	−0.936	36	-0.940	36
May	All layers	0–33.6	−0.183	122	-0.888	123	−0.905	123
June	Surface	0–31.1	−0.864	37	−0.781	37	−0.860	37
July	Surface	0–31.1	−0.645	39	−0.761	39	−0.796	39

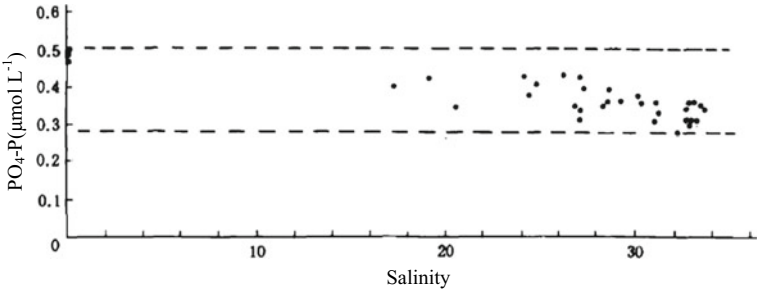

Fig. 6 Relationship between PO_4–P and salinity (April)

outside the river mouth was higher than that within the river mouth in many months, and that its distribution was even in some months. In April (Fig. 6), the concentration of PO_4–P was 0.38 ± 0.058 μmol L^{-1} all over the surveyed area where salinity was between 0 and 33.7. The behaviour of PO_4–P in the estuary shows that in addition to biological removal, PO_4–P removal can also possibly be caused by the buffering action of suspensions and sediments of the estuary. The author thinks this is the main reason that in the long term PO_4–P content is at the same level in the sea area of the Changjiang River estuary.

5 Nutrient Transport to the Sea from the Changjiang River

The monthly average concentrations of the nutrients in the river water area of the Changjiang River mouth can be used to calculate the nutrient transport from the Changjiang River. Their seasonal variations and the relationships between them and the Changjiang River runoff to the sea are indicated in Fig. 7. Related statistics show that the seasonal variations of the nutrient transports F (kg s^{-1}) of PO_4–P, SiO_3–Si, NO_3–N, NO_2–N, NH_4–N and DIN (dissolved total inorganic nitrogen) and the water flow Q (m^3 s^{-1}) of the Changjiang River were very closely correlated as indicated in the equations:

$$\begin{aligned}
\mathrm{F(PO_4{-}P)} &= 0.110\exp\,(0.0000497Q)\ (r = 0.880, n = 10)\\
\mathrm{F(SiO_3{-}Si)} &= 23.070\exp\,(0.0000366Q)\ (r = 0.735, n = 10)\\
\mathrm{F(NO_3{-}N)} &= 4.899\exp\,(0.0000518Q)\ (r = 0.929, n = 10)\\
\mathrm{F(NO_2{-}N)} &= 0.0342\exp\,(0.0000446Q)\ (r = 0.850, n = 10)\\
\mathrm{E(NH_4{-}N)} &= 29.212\exp\,(-0.0000759Q)\ (r = -0.692, n = 10)\\
\mathrm{F(DIN)} &= 16.270\exp\,(0.0000208Q)\ (r = 0.754, n = 10)
\end{aligned}$$

That clearly shows that the nutrient transports are mainly controlled by the Changjiang River flow. Monthly calculations summing up the Changjiang's annual

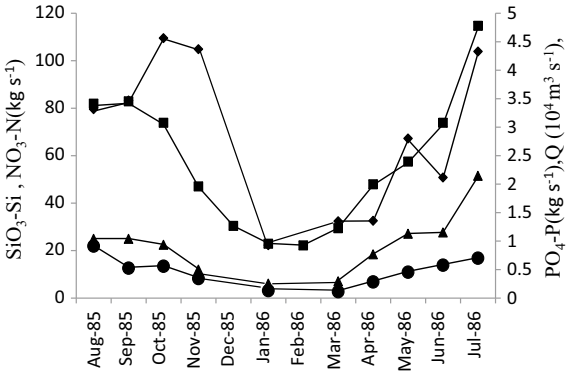

Fig. 7 Relationships between the nutrient transports and the flow Q of the Changjiang River: filled diamond—SiO_3–Si; filled triangle—NO_3–N; filled circle—PO_4–P; filled square—Q

Table 2 Nutrient transports

Nutrient transport	PO_4–P	SiO_3–Si	NO_3-N	NO_2–N	NH_4–N	DIN
Kg s^{-1}	0.43	63.3	20.0	0.12	7.79	27.9
10^4 t a^{-1}	1.4	204.4	63.6	0.38	24.9	88.9

nutrient transports to the sea listed in Table 2 show them to be 1.4×10^4 tons for PO_4–P, 204.4×10^4 tons for SiO_3–Si, 63.6×10^4 tons for NO_3–N, 0.38×10^4 tons for NO_2-N, 24.90×10^4 tons for NH_4–N and 88.9×10^4 tons for DIN, which are about 10 times that from the Huanghe River (Shen et al. 1988).

The above results of close correlations between nutrient transport from the Changjiang River mouth and the Changjiang River runoff have already been confirmed by the investigations in 1997–1998 (Shen et al. 2003; Shen 2006) and 2004 (Shen et al. 2012).

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Budget and Control of Nitrogen in the Changjiang River Catchment and Its Mouth

Zhiliang Shen, Qun Liu, Shumei Zhang, Hui Miao and Ping Zhang

Abstract The various sources of total nitrogen (TN) and dissolved inorganic nitrogen (DIN) in the Changjiang catchment and N transport in the Changjiang mouth were estimated. The export fluxes of various form of N were mainly controlled by the river runoff, and the export fluxes of NO_3–N, DIN, and TN in 1998 (an especially heavy flood year) were 1438 $\times$ 10^3 t a^{-1} or 795.1 kg km^{-2} a^{-1}, 1746 $\times$ 10^3 t a^{-1} or 965.4 kg km^{-2} a^{-1}, and 2849 $\times$ 10^3 t a^{-1} or 1575.3 kg km^{-2} a^{-1}, respectively. The TN and DIN in the Changjiang River came mainly from precipitation, agricultural nonpoint sources, N lost from fertilizer and soil, and point sources of industrial waste and residential sewage discharge, which were about 56.2 and 62.3%, 15.4 and 18.5%, 17.1 and 14.4%, respectively, of the N outflow at the Changjiang mouth, maximum transport being in the middle reaches. The inorganic N in precipitation in the Changjiang catchment mainly comes from gaseous loss of fertilizer N, N resulting from the increases of population and livestock and from high-temperature combustions of fossil fuels. N from precipitation is the first N source in the Changjiang water and the only direct cause of high content of inorganic N in the Changjiang River and its mouth. The lost N in gaseous form and from agriculture nonpoint sources fertilizer comprised about 60% of annual consumption of fertilizer N in the Changjiang catchment and were key factors controlling the high content of inorganic N in the Changjiang mouth. The fate of the N in precipitation and other N sources in the Changjiang River catchment are also discussed in this section.

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Keywords Nitrogen · Budget · Source · Control · Precipitation
Agricultural nonpoint source · Fertilizer · Point source
Changjiang River catchment · Mouth

This study on the nitrogen budget of the Changjiang River and its mouth relates to river, ocean, atmosphere, and land, as important research areas for global nitrogen cycling. Human activities have increased nitrogen concentrations in some rivers, with those in most larger European rivers having increased 2–20 times (Howart et al. 1996). The 1974–1981 statistics show that at more than 300 locations on major US rivers, increasing trends in nitrate concentrations were both frequent and widespread. Among the 383 stations tested, nitrogen increased at 116 stations and decreased at 27 (Smith et al. 1987). Duce et al. (1991) and Galloway et al. (1995) estimated that about 14–35 $\times$ 10^6 t a^{-1} total dissolved nitrogen is naturally transported from the world's rivers to coastal areas and that the net increase of total dissolved nitrogen caused by pollution was about 7–35 $\times$ 10^6 t a^{-1}, which was probably due to fertilizer nitrogen losses, combustion of fossil fuels, sewage from the growing human population, and the nitrogen output from plants and animal processes. During the last 50 years, the world consumption of fertilizer nitrogen has increased rapidly. World fertilizer nitrogen production was 2.4 $\times$ 10^6, 7.3 $\times$ 10^6, 21.5 $\times$ 10^6, 45.9 $\times$ 10^6, 75.6 $\times$ 10^6 t in 1946, 1956, 1966, 1976, 1986, respectively, and approximately a quarter of the import to global terrestrial total nitrogen in 1986 (Jenkinson 1990). Many researchers have revealed positive correlations between the consumption of fertilizer nitrogen and nitrogen concentrations in river water (Smith et al. 1987; Berankova and Ungerman 1996; Chen et al. 1998). Fertilizer nitrogen losses include gaseous losses and runoff losses from agricultural fields. Modern agriculture activities using nitrogen fertilizers have a large impact on global atmospheric environment pollution. About 85% of ammonia (NH_3), 81% of N_2O, and 35% of NO + NO_2 originate from agricultural activities (Krapfenbauer and Wriessning 1995).

Atmospheric pollution resulted in increasing nitrogen deposition; nitrogen content in precipitation has increased by several folds (Meybeck 1982; Wang and Ding 1997). Part of the nitrogen from atmospheric precipitation is deposited directly into the ocean, and part is transported to the ocean by terrestrial runoff. Within only a few decades, numerous previously pristine, oligotrophic estuarine and coastal waters have undergone a transformation to more mesotrophic and eutrophic conditions (Nixon 1995; Paerl 1997). Examples are the Baltic Sea and the North Sea (van Bennekom and Wetsteijn 1990), the Mississippi River estuary (Turner and Rabalais 1994), Jiaozhou Bay (Shen 2001), and Bohai Sea (Shen 1999). The import of exogenous nitrogen will change the molar ratios among key limiting nutrients such as N:P, Si:N, and Si:P (Shen 2001; Graneli et al. 1990; Justic et al. 1995) and cause phytoplankton community change accompanied by the appearance and persistence of harmful algal blooms (Smayda 1990; Conley and Malone 1992).

The Changjiang River catchment is a prime economic area in China. Following economic development, destruction of the environment has become increasingly obvious, e.g., reduced forest cover, water and soil losses, increased siltation in rivers,

large decreases in the area of lakes, growing water pollution. Thus, environmental protection in the Changjiang River catchment is very urgent. Sino-American cooperative investigations in the Changjiang River estuary revealed strikingly high nitrate (0.910 mg L^{-1}) concentrations, which were thought to be due to large-scale fixation of nitrogen by a rice field symbiotic cyanobacterium (Edmond et al. 1983) and derived from agricultural sources (Edmond et al. 1985). Gu et al. (1981) pointed out that the high value (about 4 times higher than that in 1963) was probably due to the rapid increase in small fertilizer plants in the Changjiang River basin. High concentrations of nitrate reflect the influence of the dense population and intensive rice culture (Meybeck 1982) and indicate the extensive use of chemical fertilizers and domestic waste (Zhang 1996). So far, the study of the sources of inorganic N in the Changjiang River mouth has been limited to qualitative analyses only. Over the past 30 years and more, eutrophication has become increasingly serious, and red tides have tended to increase in the Changjiang River estuary area. Inorganic nitrogen of 888×10^3 t a^{-1} is transported to the Changjiang River estuary area (Shen et al. 1992). This high nitrogen content is of major concern to oceanographers both in China and abroad. In this study, the authors estimated the nitrogen budget of the Changjiang River catchment and revealed the major sources of the high nitrogen concentration.

One to three sections with three stations each were set up at the Changjiang River mouth (salinity ≈ 0) in December 1997, May, and August, and October 1998. Five stations were set up in November 1998. The stations were all at a distance from the pollution band along the bank. River water samples were collected from the surface and deep water layers. Rain samples were collected in Panzhihua and Chengdu (the upper reaches), Jiujiang (the middle reaches), Datong and Shanghai (the lower reaches). Rain samples were taken monthly in the Donghu Lake (the middle reaches) and Taihu Lake region (the lower reaches) (Fig. 1). In this section, dissolved inorganic nitrogen (DIN) is equal to the sum of nitrate (NO_3–N), nitrite (NO_2–N), and ammonia (NH_4–N), and total nitrogen (TN) minus DIN is total organic nitrogen (TON).

1 The Export Fluxes of N in the Changjiang River Mouth

The regressive relation between the export fluxes of various forms of N in the Changjiang River mouth (which are equal to the average concentrations of N (mg L^{-1}) at the river mouth (salinity ≈ 0) times the runoff (m^3 s^{-1})) in December, 1997, May, August, October, and November 1998, and the monthly average runoff Q were:

$$\mathrm{NO_3{-}N\ (kg\ s^{-1})} = -8.519 + 0.001294\mathrm{Q\ (m^3 s^{-1})}\ (r^2 = 0.976,\ p < 0.01)$$

$$\mathrm{NO_2{-}N(kg\ s^{-1})} = -0.570 + 0.000028\mathrm{Q\ (m^3 s^{-1})}\ (r^2 = 0.883,\ p < 0.05)$$

$$\mathrm{NH_4{-}N\ (kg\ s^{-1})} = -4.710 + 0.000333\mathrm{Q\ (m^3 s^{-1})}\ (r^2 = 0.850,\ p < 0.05)$$

$$\mathrm{DIN\ (kg\ s^{-1})} = -13.781 + 0.001654\mathrm{Q\ (m^3 s^{-1})}\ (r^2 = 0.962,\ p < 0.01)$$

$$\mathrm{TON\ (kg\ s^{-1})} = -11.857 + 0.001120\mathrm{Q\ (m^3 s^{-1})}\ (r^2 = 0.908,\ p < 0.05)$$

$$\mathrm{TN\ (kg\ s^{-1})} = -25.638 + 0.002774\mathrm{Q\ (m^3 s^{-1})}\ (r^2 = 0.960,\ p < 0.01)$$

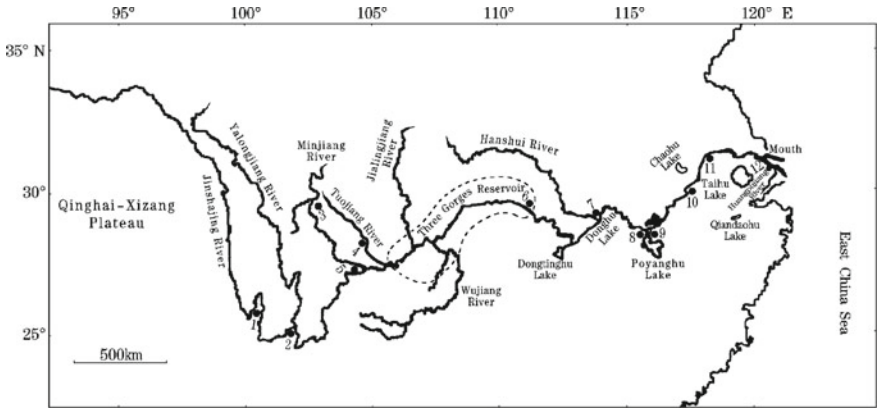

Fig. 1 Investigation situation: 1—Lijiang; 2—Panzhihua; 3—Chengdu; 4—Neijiang; 5—Pingshan; 6—Yichang; 7—Wuhan; 8—Jiujiang; 9—Hukou; 10—Datong; 11—Meishan; 12—Shanghai

The export flux of N from the Changjiang River to its estuary was mainly controlled by the Changjiang River runoff. The export flux of NO_3–N was 1438 $\times$ 10^3 t a^{-1} or 795.1 kg km^{-2} a^{-1} in the Changjiang River mouth in 1998 (which was an exceptionally large flood year) as calculated by the above equations being 82.4% of DIN and 50.8% of TN, that of NO_2–N 19 $\times$ 10^3 t a^{-1} or 10.5 kg km^{-2} a^{-1} being 1.1% of DIN, and that of NH_4–N being 291 $\times$ 10^3 t a^{-1} or 160.9 kg km^{-2} a^{-1} being 16.7% of DIN, that of DIN was 1746 $\times$ 10^3 t a^{-1} or 965.4 kg km^{-2} a^{-1} being 61.3% of TN, which was 2849 $\times$ 10^3 t a^{-1} or 1575.3 kg km^{-2} a^{-1}. The ratio of DIN and TON was 1.6, and DIN flux was obviously higher than TON. The export flux of NO_3–N in the Changjiang River mouth in 1998 was higher than the Changjiang (Caraco, 495 kg km^{-2} a^{-1}) and other major world rivers and lower than in the River Rhine (1520 kg km^{-2} a^{-1}) and the River Thames (1120 kg km^{-2} a^{-1}) (Caraco and Cole 1999).

2 The Primary Sources of N in the Changjiang Catchment

2.1 Precipitation Imports of N in the Changjiang River Catchment

The influence of human activities divides the Changjiang River catchment into four subcatchments, the subcatchment above the Jinshajiang River (with low N content of 0.325 mg $L^{-1}$for DIN and 1.037 mg $L^{-1}$for TN because of less pollution), that from Pingshan to Yichang in the upper reaches of Changjiang River, and the middle and lower reaches, respectively. The inorganic N concentrations in precipitation in the Jinshajiang River catchment were taken from the data on snow in the Qinghai-

Xizang Plateau (as a background value) (Qin et al. 1999), data from the precipitation station in the global inland region in Lijiang, China (Liu et al. 1993), and data from Panzhihua in the Jinshajiang River's lower reaches. Data on the Pingshan-Yichang catchment were taken from Panzhihua and Chengdu. Data on the middle reaches were taken from Jiujiang, the Donghu Lake region, and Hubei Province, and those from below Datong and the Taihu Lake region. In order to increase the credibility of these estimations, the above data were compared with those for 1985–1986 (Shen 1996) and 1992–1993 (Wang and Ding 1997) listed in Table 1, showing that the weighted mean concentrations of inorganic N in the whole catchment were a little higher than those in 1985–1986. The lower N content in precipitation in the Jinshajiang River catchment was consistent with that in the river water.

The Changjiang River catchment is situated in the southeast subtropical monsoon area. In spring and summer, the prevailing southwest monsoon wind from the Indian Ocean and the southeast monsoon wind from the western Pacific Ocean subtropics often produce heavy rains and storms which, when they converge with the cold air from the north, comprise major sources of water in the catchment. Except for the supplies of water from high-mountain ice and snow, Changjiang River runoff mainly originates from rain, comprising 70–80% of annual runoff. The precipitation supply is taken as 75% here. In this study, the precipitation supply in every subcatchment was calculated on the basis of the Changjiang River mouth runoff and the average share of every subcatchment in the whole catchment over the years. Each subcatchment's inorganic N fluxes from precipitation into the Changjiang River were calculated based on the precipitation supply and its inorganic N concentrations. The results are listed in Table 2 showing that NH_4–N comprised 87.7% and NO_3–N 12.3%, of DIN fluxes. Obtained data showed that NO_2–N concentration in precipitation was similar to that in river water and was about 1% of DIN. So DIN flux in precipitation was 1.09×10^6 t a^{-1} being 62.3% of DIN export flux in the Changjiang River mouth and came mainly from the Bingshen-Yichang subcatchment and the middle reaches supplying 33.1% and 54.7% of DIN in the whole catchment, respectively. A late 1970s estimation showed that the DIN and DON contents were 64.3% and 35.7%, respectively, of dissolved N in continental precipitation throughout the world (Meybeck 1982). The average content of DIN and DON in precipitation in Europe, America, the Pacific, and the Atlantic Ocean were 69.3 and 30.7% of dissolved N, respectively (Cornell et al. 1995). The average TN content in precipitation in Panzhihua, Chengdu, Jiujiang, the Donghu Lake, Datong, the Taihu Lake, and Shanghai in 1998 was 1.620 mg L^{-1}. Estimations showed that TN transport from precipitation in the Changjiang River catchment in 1998 was 1,601,950 t, and TON annual import flux was 514,371 t (minus DIN flux). DIN comprised 67.9% of TN, and close to their ratio (61.3%) in river water in this investigation showing that in the precipitation into river water, inorganic and organic forms of N were in a quasi-equilibrium state.

If all DIN in the precipitation supply enters the river water, the relation between the DIN content in the precipitation supply and that in the river water may be expressed as follows:

$$c(\mathrm{N})_1 \cdot \mathrm{Q}_1 = c(\mathrm{N})_2 \cdot \mathrm{Q}_2$$

Table 1 Inorganic N concentrations (mg L^{-1}) in precipitation in the Changjiang River catchment

Catchments	1998			1992–1993			1985–1986		
	NH_4–N	NO_3–N	NH_4–N + NO_3–N	NH_4–N	NO_3–N	NH_4–N + NO_3–N	NH_4–N	NO_3–N	NH_4–N + NO_3–N
Jinshajiang River	0.321	0.084	0.405				0.102	0.119	0.221
Pingshan to Yichang	1.068	0.056	1.124				1.329	0.210	1.539
Middle	1.091	0.188	1.279	1.089	0.280	1.369	0.795	0.077	0.872
Lower	0.913	0.253	1.166	0.874	0.281	1.155	1.005	0.189	1.194
Whole catchment weighted mean	0.955	0.134	1.089				0.874	0.133	1.007

Table 2 Inorganic N fluxes from precipitation into the Changjiang River

Catchments	Runoff (10^9 m^3)	Precipitation supply ($10^9 m^3$)	Inorganic N fluxes (t a^{-1})		
			NH_4–N	NO_3–N	NH_4–N + NO_3–N
Jinshajiang River	201.07	150.80	48,347	12,667	61,014
Pingshan to Yichang	422.36	316.77	338,374	17,739	356,113
Middle	614.48	460.86	502,614	86,457	589,071
Lower	80.73	60.55	55,270	15,343	70,613
Whole catchment	1318.64	988.98	944,604	132,207	1,076,811

where $c(N)_1$ and $c(N)_2$ are DIN contents in the river water and precipitation, respectively, Q_1 and Q_2 are runoffs of the river water and precipitation supply, respectively. Thus, the DIN contents in every subcatchments formed by the precipitation supply can be calculated using the above equation. The results were compared with the average DIN contents actual measured in the dry and flood in the Changjiang River water listed in Table 3. It shows that NH_4–N + NO_3–N contents in the river water formed by the precipitation supply from every subcatchments comprise mostly those actual measured in the river water, respectively, further showing that the DIN from precipitation was the major source of DIN in the Changjiang River water.

Table 3 Comparing DIN contents in the precipitation supply and river water actual measured

	Precipitation supply	River water actual measured	Precipitation/river water (%)
	NH_4–N + NO_3–N (μmol L^{-1})	NH_4–N + NO_3–N (μmol L^{-1})	
Jinshajiang River	21.7	38.8	55.9
Pingshan to Yichang	60.2	71.9	83.7
Middle	68.5	76.6	89.4
Lower	62.5	75.6	82.7
Whole catchment weighted mean	58.4	69.3	84.3

2.2 N Import from Agricultural Nonpoint Sources in the Changjiang River Catchment

Agricultural nonpoint sources of N were the actual N loss from fertilizer and soil, without precipitation N. The 1998 China Statistics Yearbook and the 1993 and 1997 Changjiang River yearbooks were used as references for the arable land areas, applied fertilizer N, and water and soil losses in the Changjiang River catchment listed in Table 4. These show that the most arable land areas and the greatest consumption of fertilizer N were in the middle reaches and were 47.1 and 49.1%, respectively, of those of the whole catchment; water and soil losses were most serious in the upper reaches, accounting for 60.5% of those of the whole catchment; and the largest N-fertilizer administered area was in the middle reaches.

The calculated 65% of DIN in TN was based on the average ratio in the Taihu Lake region (Zhu and Wen 1990) and Chaohu Lake region (Yan and Wang 1998). Table 4 lists water and soil losses for areas including arable land and nonarable land. Due to the scarcity of data, all the water and soil losses were calculated for nonarable land (the losses in arable land were calculated repeatedly). Fertilizer and soil N losses in the lower reaches were based on the pollution of agricultural nonpoint sources in the Taihu Lake catchment in Jiangsu Province (Ma et al. 1997). TN input fluxes in precipitation and irrigation water were reduced by surface runoff levels in irrigated fields, were equal to the actual losses of fertilizer and soil N through surface runoff in irrigated fields, and were calculated as the average TN loss flux of 1.4 t km^{-2} a^{-1}. Based on TN concentration in precipitation and the surface runoff amount in dry fields, precipitation TN transport in dry fields was calculated as 0.934 kg ha^{-1} a^{-1}, which was reduced by TN transport in surface runoff in dry fields, and equaled the actual losses of fertilizer and soil N through surface runoff in dry fields, calculated as TN loss flux of 1.087 t km^{-2} a^{-1}. The fertilizer and soil N losses in the arable lands in the lower reaches could be estimated from the above-calculated values. In the lower reaches, irrigated and dry fields were 80% and 20% of arable lands, respectively. So the losses of TN and DIN from fertilizer and soil in the lower reaches arable lands were 48,908 t a^{-1} and 31,790 t a^{-1}, respectively. Fluxes of N lost in water and soil were based on data on N losses in nonarable lands (including forest, grassland, beach, wasteland) of the Poyanghu Lake region (Zhu and Zhang 1997).

Table 4 Statistics on the Changjiang River catchment

Catchments	Arable lands areas (10^3 km^2)	Consumptions of fertilizer N (10^3 t)	Water and soil losses areas (10^3 km^2)	Administered areas (10^3 km^2)	Administered ratio (%)
Upper	86.57	1964.32	346.01	54.26	15.7
Middle	109.63	3070.53	205.88	88.03	42.8
Lower	36.57	1223.17	20.40	14.61	71.6
Whole catchment	232.77	6258.02	572.29	156.90	27.4

Our estimation showed that TN input through surface runoff and precipitation was 0.989 t km^{-2} a^{-1} and 0.912 t km^{-2} a^{-1}, respectively, so the actual TN input was 0.077 t km^{-2} a^{-1} in nonarable lands. Based on water and soil losses (Table 4), TN and DIN losses were calculated as 1571 t a^{-1} and 1021 t a^{-1}, respectively. From the above calculations, the TN and DIN losses from fertilizer and soil into the lower leaches of the Changjiang River were 50,479 t a^{-1} and 32,811 t a^{-1}, respectively.

The fertilizer and soil N losses in the middle reaches were based on those of the Poyanghu Lake region. Calculations based on TN input data on surface runoff in six small area tests of arable land units, including irrigated and dry fields (Zhu and Zhang 1997), showed that TN input in surface runoff and precipitation were 3.281 and 1.225 t km^{-2} a^{-1}, respectively, so fertilizer and soil TN input from arable lands into Poyanghu Lake were 2.056 t km^{-2} a^{-1}. From the above calculations, the fertilizer and soil losses were estimated as 225,399 t a^{-1} for TN and 146,509 t a^{-1} for DIN in the middle reaches. Based on the region with TN input of 0.077 t km^{-2} a^{-1}, in nonarable lands and in water and soil loss areas in the middle reaches (Table 4), the water and soil losses were calculated to be 15,853 t a^{-1} for TN and 10,304 t a^{-1} for DIN. Thus, TN and DIN losses from fertilizer and soil in the middle reaches were 241,252 and 156,813 t a^{-1}, respectively.

The estimation of N loss in the upper reaches was based on the Three Gorges Reservoir Region. According to the 1998 Monitor Communiqué on Ecology and Environment in the Changjiang River Three Gorges, the fertilizer N loss in the reservoir region was 11.9×10^3 t a^{-1}, arable land areas were 9777 km^2, so fertilizer DIN loss from arable land was 1.217 t km^{-2} a^{-1}. Based on arable land areas in the upper reaches (Table 4), the fertilizer DIN loss from the upper reaches arable lands was calculated to be 105,356 t a^{-1}. Soil losses there were estimated to be 42,559 t a^{-1} for TN and 27,663 t a^{-1} for DIN, based on soil TN losses of 0.123 t km^{-2} a^{-1} (Huang et al. 1994) and water and soil loss areas (Table 4). So, TN and DIN losses from fertilizer and soil in the upper reaches were 147,915 t a^{-1} and 133,019 t a^{-1}, respectively.

These estimated results show that DIN and TN loss occurred mainly in the middle reaches, where they were 48.6 and 54.9%, respectively, of that of the whole catchment and were mainly due to the large area of arable lands in the region, and high fertilizer consumption (Table 4). DIN losses in the upper and lower reaches accounted for 41.2 and 10.2% of that of the whole catchment, respectively, and TN losses accounted for 33.6 and 11.5%, respectively. The fertilizer and soil DIN and TN losses from surface runoff in the whole catchment were 322,643 and 439,646 t a^{-1} and 18.5 and 15.4% of export fluxes in the Changjiang River mouth, respectively.

2.3 N Import from Point Source Sewage Wastes in the Changjiang River Catchment

We used data from the 1998 China Environment Yearbook to calculate total industrial waste and total residential sewage discharged from every province and district into the Changjiang River catchment (Table 5). Data on N concentrations in industrial waste and residential sewage in the Changjiang River catchment are scarce, but the authors have data from the Neijiang region in the Tuojiang River catchment (Wang and Xue 1989) and from the Three Gorges Reservoir Region (Monitor Communiqué on Ecology and Environment in the Changjiang River Three Gorges in 1998 and 2000) in the upper reaches; data from the Wuhan Iron and Steel Company in 1988 and from monthly investigations in the Donghu Lake region in 1998 in the middle reaches; data from the Chaohu Lake catchment (Zhang et al. 1999), from the Meishan section in the Changjiang River (Lu 1992), from the Taihu Lake region (Jin et al. 1999), from the Qiandao Lake region (Han et al. 1997), and from the Huangpu River region (Zhang et al. 1987) in the lower reaches. According to the ratios for some forms, N content in the residential sewage and industrial wastes in the Donghu Lake region and the Wuhan Iron and Steel Company, NH_4–N/DIN and DIN/TN were taken as 0.8 and 0.5, respectively, and used to calculate the average concentrations of DIN and TN as 16.716 and 30.609 mg L^{-1} for residential sewage and 17.405 and 34.810 mg L^{-1} for industrial waste in the Changjiang River catchment.

Based on discharged amounts and N contents in residential sewage and industrial waste in the Changjiang River catchment, the input amounts of N from point sources may be estimated. Most of the residential sewage N and industrial waste N were inputs into the middle reaches, and of total input into the whole catchment, N inputs from the point sources in the upper, middle, and lower reaches were 26.1, 46.0, and 27.9%, respectively. The DIN and TN input from the point sources in the whole catchment accounted for 14.4 and 17.1% of their export flux at the Changjiang River mouth.

2.4 N Import from Town Runoff in the Changjiang River Catchment

There is a scarcity of data on the N transport from urban runoff. The N inputs of the urban runoff into the Changjiang River catchment were estimated on the basis of the Poyanghu Lake region for small towns (Zhu and Zhang 1997), the Donghu Lake region in Wuhan City for larger cities, and Three Gorges Reservoir Region for mountain towns (Huang et al. 1994). The average TN transport through town runoff above the three regions was 0.379 t km^{-2} a^{-1}. The DIN:TN ratios of 0.623 for the surface pollutants in Chengdu City streets (Shi 1991) and of 0.417 for the Donghu Lake region (Zhang et al. 1984a, b) were taken as averaging 0.5, so the actual DIN transport through town runoff was 0.190 t km^{-2} a^{-1}. According to the estimates

Table 5 N input from point sources in the Changjiang River catchment

Catchments	Living sewages			Industrial wastes			Total input amounts	
	Sewages amounts (10^6 t a^{-1})	DIN (t a^{-1})	TN (t a^{-1})	Wastes amounts (10^6 t a^{-1})	DIN (t a^{-1})	TN (t a^{-1})	DIN (t a^{-1})	TN (t a^{-1})
Upper	1703.26	28,472	52,135	2146.30	37,365	74,713	65,828	126,848
Middle	2882.03	48,176	88,216	3888.09	67,672	135,344	115,848	223,560
Lower	1793.75	29,984	54,905	2314.93	40,291	80,583	70,275	135,488
Whole catchment	6379.04	106,632	195,256	8349.32	145,320	290,640	251,952	485,896

for urban areas in the Changjiang River catchment (statistical data from the latest national resources and environment spatial information system), the DIN and TN input into the Changjiang River from urban runoff was 1292 and 2578 t a^{-1} and accounted for 0.07 and 0.09% of their export flux of the Changjiang River mouth, respectively.

2.5 *N Import from Flow Sources Sewage in the Changjiang River Catchment*

The source of sewage is mainly from the daily waste discharged from ships into the Changjiang River waterway. The passenger capacity in the Changjiang River mainstream was 40×10^6 persons, and the number of passengers was less than 15×10^6 persons in 1999. If the yearly passenger number was 30×10^6 persons, 20×10^6 in the mainstream, and 10×10^6 in the tributaries and if the passenger number of cargo ships on the waterway was also 30×10^6 persons, this adds up to 60×10^6 persons with a personal average of 3-day voyage and daily water use of 0.123 t per person per day (including toilet, kitchen, and washroom) (Huang et al. 1994). Based on the calculation method of Huang et al. (1994), and 0.5 as the DIN:TN ratio in daily sewage, the TN and DIN input fluxes were 48.74 and 24.37 t a^{-1} and accounted for only 0.0017 and 0.0014% of the export flux in the Changjiang River mouth, respectively.

According to the above estimations, the N budget of the Changjiang River catchment shown in Table 6 indicates that the N in the Changjiang River and its mouth came mainly from precipitation, agricultural nonpoint source N losses from fertilizer and soil, point source industrial waste, residential sewage, etc., and that the N from precipitation was the primary source of high N content in the Changjiang River and its mouth, which were 62.3% for DIN and 56.2% for TN, of N export fluxes in the Changjiang River mouth, a percentage close to that of the Bjerkreim River catchment (70%) in Norway (Kaste et al. 1997). China has a large agricultural production, so the greater part of the sources of N including the N from precipitation are related to agricultural activities. Gaseous losses from chemical fertilizer were possibly due to the large quantity of chemical fertilizer used; N imported from precipitation was only a direct cause of high content of N in the Changjiang River and its mouth. Although our estimations were rather rough, it is significant that this is the first attempt to quantitatively analyze the sources of N in such a large river catchment.

Table 6 N budget of the Changjiang River catchment

N import, export	DIN (10^3 a^{-1})	Import/export ratio (%)	TN (10^3 a^{-1})	Import/export ratio (%)
N export	1746.00		2849.00	
N import				
Precipitation	1087.58	62.3	1601.95	56.2
Point sources	251.95	14.4	485.90	17.1
Nonpoint sources	322.64	18.5	439.65	15.4
Town runoff	1.29	0.07	2.58	0.09
Flow sources	0.02	0.0014	0.05	0.0017
Total	1663.48	95.3	2530.13	88.8

3 The Dominant Control Factors of High Content Inorganic N in the Changjiang River and Its Mouth

3.1 N Contents in Precipitation in the Changjiang River Catchment

Over the past 40 years, N contents in precipitation have largely increased in the Changjiang River catchment. There were no studies in China on precipitation N until the mid-1980s when there were a few reports on the historical changes of N contents in precipitation, and some occasional studies on the Changjiang River catchment. The average DIN contents in precipitation in the Donghu Lake region were determined to be 31.9 μmol L^{-1} during 1962–1963 (Liu et al. 1983), 41.8 μmol L^{-1} during 1979–1981 (Zhang et al. 1984b), and 64.8 μmol L^{-1} during 1997–1998 (Tong Huijuan, personal communication). The inorganic N contents in precipitation in the Donghu Lake region have increased to about twice from the 1960s to the 1990s. The average contents of NO_3–N and NH_4–N in precipitation were 26.0 and 89.2 μmol/L, respectively, in eight cities in south China (including five cities in the Changjiang River catchment) during 1985–1986, and reached 45.0 and 185.1 μmol/L, respectively, during 1992–1993 (Ding et al. 1996).

3.2 The Main Sources of N in Precipitation in the Changjiang River Catchment

3.2.1 The Gaseous Loss of Fertilizer N

Figure 2 shows the increases of fertilizer N applied to agriculture since 1980 in China. The consumption of fertilizer N was only 0.06×10^6 t in 1952 (Zhang et al.

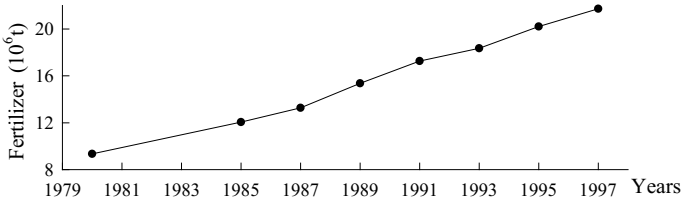

Fig. 2 Historical changes in the consumption of fertilizer N in China

1984a) and 0.45×10^6 t in 1962. Based on the 1998 China Statistics Yearbook, the consumption of fertilizer N reached 9.34×10^6 t in 1980. Fertilizer N increased about 20 times during 1962–1980 and that in 1997 was 2.3 times that in 1980. Fertilizer production in China occupied first place in the world and accounted for about 20% of world total production in 1996. Based on the 1998 China Statistics Yearbook and the 1993 and 1997 The Changjiang Yearbook revealed that the consumption of fertilizer N in the Changjiang River catchment was 6.26×10^6 t and accounted for about 29.2% of China's total consumption. Many researches revealed obvious positive correlationships between the consumption of fertilizer N and N concentrations in river water (Brooker and Johnson 1984; Smith et al. 1987; Berankova and Ungerman 1996). The rapid increase in the consumption of fertilizer N led to the aggravation of environmental pollution day by day. The fertilizer N losses are mainly through denitrification and NH_3 volatilization. Zhu and Wen (1990) estimated the ratio of fertilizer N losses in irrigated fields to be about 60% in China (35% for denitrification and 25% for NH_3 volatilization) and that in dry fields was about 50%. The NO_3–N in fertilizer and soil discharge N_2 and N_2O toward the atmosphere through denitrification are mainly in the form of N_2 in general. A little of the N_2O from denitrification into the atmosphere can return to the earth's surface, where much of the N_2O is destroyed by light chemistry in the isothermal layer to produce O_2 and N_2, and about 5–10% is changed into NO (Jenkinson 1990). NO and NO_2 in atmosphere can be changed into NO_3^- and fall to the ground with precipitation. NH_3 can only stay 6 days in the atmospheric troposphere, and the major part can come down to near the ground from where it was produced (Jenkinson 1990). If fertilizer N loss of 55% occurs in the Changjiang River catchment, and about as high as 3.44×10^6 t of fertilizer N is released into the atmosphere annually, the amount would be twice that of the Changjiang River mouth's inorganic N outflow in 1998 (Shen et al. 2003).

3.2.2 Sewage from the Growing Human Population and the N Output from Animal Processes

The increased human and livestock population is one of three major sources of the increased fluxes of reactive N to the biosphere (Hessen et al. 1997). The Chinese population increased from 574.82×10^6 to 1236.26×10^6 during the period 1952–1997(net growth of 1.15 times) and in the Changjiang River catchment was

33.6% of that of China. The population increase led directly to the increase of NH_3 in the atmosphere. Another important source of NH_3 in the atmosphere is that released from animal excreta. Based on the 1981 and 1986 China Agriculture Yearbook, 1982 China Economy Yearbook, and 1998 China Statistics Yearbook, the average production of meat in the world was only 106.63×10^6 t during 1969 to 1971, but reached to 215.17×10^6 t in 1997. The production of pork, beef, and mutton in China was only 0.034×10^6 t in 1952 and 5.51×10^6 t in 1965. Meat production reached 59.15×10^6 t in 1997 and accounted for 27.5% of total production in the world. Based on Jenkinson's (1990) estimation, the amount of NH_3 released from animal excreta was more than that from soil, plants, and fertilizers. NH_4–N being 87.7% of DIN in precipitation in the Changjiang River catchment (Shen et al. 2003) also proved the importance of the above two kinds of N sources.

3.2.3 The N from High-Temperature Combustions

Nitrogen oxides (NO_x), mainly NO and NO_2, are also important sources of N in precipitation. A large part of NO_x comes from the fossil fuels combustion, especially high-temperature combustions. N_2 and O_2 in the atmosphere directly react and transform NO_x into NO_3^-. Of the about 48×10^6 t $a^{-1}$of NO_x emitted into the atmosphere from the earth's surface, 32×10^6 t N come from combustion, 8×10^6 t N from the soil–plant system, and 8×10^6 t N from inherent in the atmosphere, but can stay only 5 days in the troposphere (Jenkinson 1990). A major part of the NO_x in the atmosphere return to the earth's surface by precipitation and partly by dry deposition. The sum of combustion and fixation by the fertilizer industry at present equals to natural biological fixation (Vitousek 1994; Galloway et al. 1995). Based on the 1998 China Statistics Yearbook, the production of raw coal and raw petroleum in China from 1965 to 1997 increased 5.9 and 14.2 times, respectively (Fig. 3). In 1996, China's raw coal production ranked first and raw petroleum ranked fifth in the world.

From the above discussions, the increase in N content in precipitation resulted mainly from human activities (fertilizer N consumption, discharge of sewage from the growing human population, partly from domesticated animal processes

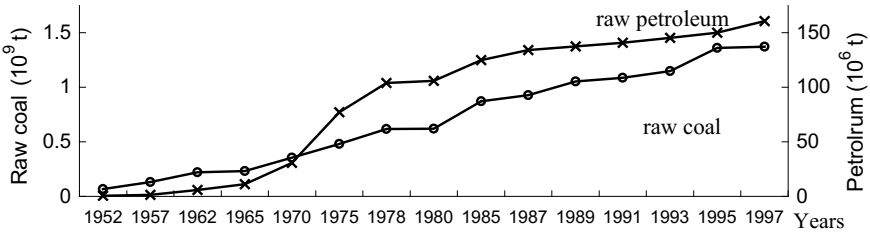

Fig. 3 Historical changes in the production of raw coal and raw petroleum in China

and high-temperature combustion of fossil fuels, etc.). Precipitation N is the first N source and only direct cause of high content of inorganic N in the Changjiang River mouth.

3.3 The Fate of the N in Precipitation in the Changjiang River Catchment

Atmospheric N inputted to the terrestrial ecosystem includes precipitation and dry deposition. About one-third of NH_4–N and less than one half of NO_3–N are inputted to the earth's surface through dry deposition from the atmosphere (Jenkinson 1990). Only a small part of the N reaching the earth's surface through dry deposition enters directly a waterbody; a major part is brought into it by precipitation runoff via agriculture nonpoint source losses, etc. Not all N from precipitation can enter the Changjiang River and reach coastal waters, because N retention can occur in the catchment and also in river (Gildea et al. 1986; Vorosmarty et al. 1995). N retention is due to biological processes, not to sedimentation processes (Berge et al. 1997). It is possible that N retention occurs mainly in the catchment and not in the Changjiang River, because of the very large flow (average of 29 000 $m^3\ s^{-1}$ at the Datong Station, about 700 km from the river mouth), turbid waterbody (average sand content 0.533 kg m^{-3} at the station Datong), high atomic ratio of DIN: PO_4-P (196.0 $\pm$ 35.8 for dry season and 287.1 $\pm$ 34.0 for flood season), and low phytoplankton density (about 0.5 mg m^{-3}chlorophyll-*a* inside the mouth) in the Changjiang River mainstream and major tributaries, all of which are unfavorable for N retention. Of the total precipitation amount in the Changjiang River catchment, about 49% forms runoff supplying 70–80% of surface water flowing into the Changjiang River. In this section, 75% is taken as the precipitation supply of runoff; i.e., only 36.8% of total precipitation amount forms surface runoff entering the Changjiang River. The above discussion shows that as high as 63.2% of total precipitation amount and N are retained in the Changjiang River catchment, where the surface types easiest for N retention are forests (which account for 20.3% of the whole catchment area) mainly concentrating in the upper reaches, prairie and meadow (which account for 41.0%) mainly in the Qinghai-Xizang Plateau and spreading in hill and mountainous region in the middle and east section regions, and arable lands (which account for 13.7%) mainly distributing in plain, hill, basin, and the river's coastal region. These three surface types comprise 74.1% of the whole catchment area, where N retention is mainly via assimilation by plants and storage in soils. An examination of 65 forested plots and catchments throughout Europe indicated that below a deposition threshold of about 1000 kg N $km^{-2}\ a^{-1}$, no significant N leaching occurred from the forests; that intermediate levels of 1000–2500 kg N $km^{-2}\ a^{-1}$, leaching occurred at some sites; and that above 2500 kg N $km^{-2}\ a^{-1}$, significant N leaching occurred at all sites (Dise and Wright 1995). In North America, the threshold deposition for N leaching was 500–600 kg N $km^{-2}\ a^{-1}$ (Stoddard 1994). The average wet deposition (precipitation)

of DIN in the Changjiang River catchment was 1628 kg km^{-2} a^{-1}, so N leaching is certain to occur. The mountains and plateaus comprising 65.6% of the whole catchment are also favorable for N leaching. Particularly during the flood season when precipitation exceeds 70% of annual total precipitation amount, N leaching occurs easily during heavy rains and storms. If all precipitation DIN formed runoff enters the Changjiang River, only 36.8% of total precipitation DIN enters the Changjiang River to account for 62.3% of N export flux in the Changjiang River mouth, a percentage similar to that of the Bjerkreim River catchment (70%) in Norway (Kaste et al. 1997). It is difficult to estimate accurately N retention and leaching due to the very large area and complex topography and surface type in the Changjiang River catchment.

3.4 Analyses on Other Sources of High Content of Inorganic N in the Changjiang River Mouth

3.4.1 Fertilizer N and Soil N Losses from Agriculture Nonpoint Sources

The increase of fertilizer N and soil N losses from agriculture nonpoint sources is another important reason for the high content of inorganic N in the Changjiang River mouth (Shen et al. 2003). It is obvious that the increase in consumption of agriculture fertilizer N and the aggravation of water and soil losses are the main reasons for the increase in fertilizer N and soil N losses. A notable relation between the consumption of fertilizer N and the N concentration in the Changjiang River had been reported. For example, during 1971–1983, there were obvious positive relationships between the mean annual TN concentrations in the dry and flood seasons at the Cuntan Station in Chongqing City and in the dry season the next year at Lijiawan Station in the Tuo River (tributary) and the consumption of fertilizer N in Sichuan Province, respectively, with the coefficients of correlation being 0.70, 0.86, and 0.97, respectively (Chen et al. 1998). The consumption of fertilizer N in China increased 47 times during the period 1962–1997. The estimation showed that fertilizer and soil DIN losses through surface runoff from the Changjiang River catchment's arable lands were 0.28×10^6 t a^{-1} or about 4.5% of annual total consumption of fertilizer N of the whole catchment or 16.2% of DIN export flux of the Changjiang River mouth (Shen et al. 2003). The Changjiang River's upper reaches once formed the second largest forest region (next to the Dongbei region in China) in China, but because of reckless exploitation over the years, the cover rate of the region's forests has greatly decreased. According to the 1987 demonstration report on the impacts of the Changjiang River Three Gorges Project on the ecology and environment, the ratio of felled trees to replaced trees was about 10:1 in Sichuan Province, and the cover rate of forests had dropped from 20% in the 1950s to 13% in the 1980s. Because forests vegetation was destroyed, the extent and intensity of soil erosion and water and soil loss have also increased and led to the increased fertilizer N and soil N losses, which

are particularly serious in the upper reaches, where the total amount of soil erosion reached 18×10^8 t a^{-1}. The lost areas of water and soil in Sichuan Province were only 16.1% of the province's total area in 1957 but have increased by a wide scale now. For example, the lost areas of water and soil were 57.9×10^3 km^2, being 58.2% of the total area of the Chuanzhong hills region, where the lost areas of water and soil were the largest in Sichuan Province (Hou 1997). The lost areas of water and soil in the Changjiang River catchment have reached 572.3×10^3 km^2, being 31.6% of total catchment area. The above estimations show that lost DIN from fertilizer and soil of arable lands account for 4.5% of annual consumption of fertilizer N in the whole catchment. If all lost DIN from fertilizer and soil of arable lands is discharged into the Changjiang River runoff, the DIN concentration in the river water can increase by 15.4 μmol/L. As may be inferred from this, the lost fertilizer N from volatilization and agriculture nonpoint sources comprised about 60% of annual consumption of fertilizer N in the Changjiang River catchment and played a decisive role in the high content of inorganic N in the Changjiang River and its mouth.

3.4.2 The N Discharged from Point Sources Industrial Wastes and Residential Sewages

The high content of inorganic N in the Changjiang River mouth is also closely related to the N input from point sources (Shen et al. 2003) which are directly related to the discharged amounts of industrial wastes and residential sewages. Figure 4 based on data from the 1992 China Statistics Yearbook and from the 1990, 1997, and 1998 China Environment Yearbook presents the changes in the total discharged amounts of the wastes and sewages from county and above county level enterprises from 1980 to 1997. The population and gross industrial output value in China since 1980 nearly increased synchronously, and there are obvious positive relationships between population and gross industrial output value and the total discharged amounts of wastes and sewages, respectively ($r^2 = 0.783, 0.936, p < 0.01$). From 1980 to 1997, the population and gross industrial output value increased 0.25 and 21 times, respectively; the total discharged amounts of the wastes and sewages increased annually from 31.5×10^9 t to 37.7×10^9 t (1.2% average annual increase). The total discharged amount of industrial wastes and residential sewages in the Changjiang River catchment in 1997 was about 14.7×10^9 t, an increase of 1.95×10^9 t over that in 1985 (average annual increase was 1.3% over that of the whole country). Due to shortage of the pre-1980s relevant data, it is difficult to analyze quantitatively the changes of the discharged amounts of wastes and sewages during the 1960s to the 1980s. From the 1960s to the 1980s, the gross industrial output value increased 4.6 times in China. Due to shortage of environmental protection consciousness, the discharged amount of wastes and sewages increased fast and N discharge from wastes and sewages controlled rarely. In 21 main cities along the bank of the Changjiang River mainstream, the treated and treated to national standard residential sewages discharged into the Changjiang River in 1982 were only 17 and 36%, respectively, of total discharged into the river and those for industrial wastes 22 and 48%, respectively. Moreover,

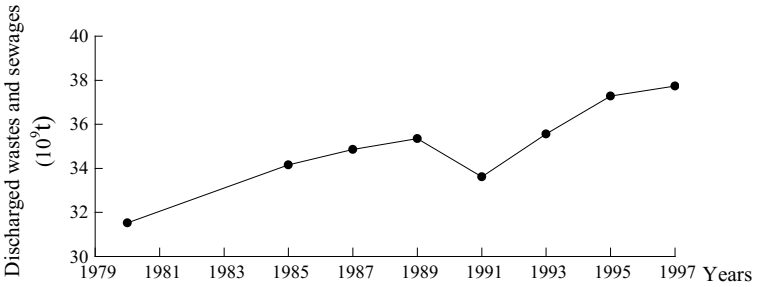

Fig. 4 Historical changes in total discharged amounts of wastes and sewages in China

the population increased rapidly from the 1960s to the 1980s in China (increased in number by 314×10^6 individuals) which led to increases in the discharge amount of residential sewages and the N inputted to the Changjiang River.

Over the past 40 years, N contents in precipitation have largely increased in the Changjiang River catchment. The N in precipitation mainly came from gaseous loss of fertilizer N, the N produced by the growing human population, the N output from animal processes, and from high-temperature combustions of fossil fuels, etc. N imported from precipitation was the first source in the Changjiang River water and the only direct cause of high content of inorganic N in the Changjiang River and its mouth. The lost N in gaseous form and from agriculture nonpoint sources fertilizer comprised about 60% of annual consumption of fertilizer N in the Changjiang River catchment. Therefore, how to control the loss of fertilizer N and soil N and improve the efficiency in the use of fertilizer N is the key for preventing N's continuous increase in the Changjiang River and its mouth. It is possible that regarding the N retention in the Changjiang River catchment, a great part of N is stored in soils and biotic substances there. The estimated DIN retention could exceed 63.2% of total precipitation DIN. In other words, the DIN that entered the Changjiang River from precipitation could possibly be less than 36.8% of total precipitation DIN. The surface types most favorable for N retention are forests, prairie, and arable lands. It is very difficult to estimate accurately N retention and leaching due to the very large catchment area and complex topography and surface type in the Changjiang River catchment.

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Budget and Control of Phosphorus in the Changjiang River Catchment and Its Mouth

Zhiliang Shen, Zheng Li and Hui Miao

Abstract The budget and major control factors of total phosphorus (TP) and dissolved inorganic phosphorus (DIP) in the Changjiang catchment were estimated and discussed from the catchment scale. Results show that the export fluxes of TP and DIP were mainly controlled by the river runoff. The TP and DIP in the Changjiang River came mainly from agricultural nonpoint source P losses from fertilizer and soil and point sources of industrial waste and residential sewage discharges. The export fluxes of TP and DIP in the river mouth were only 27.0 and 28.3% of the imports from the river catchment, respectively, suggesting that most of P were removed in transportation. A mass of freshwater marshes in the river catchment was the main areas to remove P. Significant increasing in utilization of fertilizer P and incessant increasing in water and soil loss areas were the primary reasons of agricultural nonpoint source P losses. How to decrease the agricultural nonpoint source P loss from the catchment scale is a key controlling P concentration in the Changjiang River and its mouth. The point source industrial waste P discharge has been primarily treated in the river catchment, but the residential sewage P discharge needs further control.

Keywords Phosphorus · Budget · Source · Control · Agricultural nonpoint source Point source · Changjiang River catchment · Mouth

Phosphorus is often the key nutrient found to be limiting in both estuarine and freshwater ecosystems (Reddy et al. 1999; Mainstone and Parr 2002). The accelerated eutrophication of most freshwaters is limited by P inputs (Sharpley et al. 1994; Lagreid et al. 1999). Water-soluble P that comes from runoff is the prime cause of eutrophication of the aquatic environment, which is a growing environmental problem worldwide (Sharpley et al. 2001; Jordan et al. 2005). Human activities have obviously increased nutrient concentrations in some rivers, and the fluxes to oceans

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of mineral nutrients, such as N and P, have increased worldwide by a factor of more than two (Meybeck 1998). There were many studies about the source and transport mechanism of P (Sharpley et al. 2001; Cao and Zhang 2004; McDowell and Wilcock 2007), which showed that the primary factor of influencing water body eutrophication was agricultural nonpoint source pollution. Therefore, minimizing eutrophication of a water body from agricultural nonpoint source pollution often requires controlling P inputs. P budget and transport from rivers and estuaries to oceans have received much attention from scientists (Mortazavi et al. 2000; Cooper et al. 2002; Shen 2006). Especially, the study in P transport and control from the whole catchment scale is a hot topic (Wit and Behreendt 1999; Behrendt and Opitz 2000; Steegen et al. 2001).

The Changjiang River catchment is a prime economic area in China. In the last 20 years, with the development of economy, destruction of the environment has become increasingly obvious. In some lakes in the catchment, such as Taihu Lake (Jin et al. 1999; Zhang et al. 2007), Chaohu Lake (Yin et al. 1993; Yan et al. 1999), Dianchi (Duan et al. 2005), and Three Gorges Reservoir (Li and Huang 2005), eutrophications are serious. In addition, eutrophication has become increasingly serious, and occurrence of red tides tended to increase in the Changjiang estuary (Wang and Huang 2003; Zhou et al. 2008), which may be related to P transportation in the Changjiang River. At present, most of the studies in P in the river catchment were located in the distribution and variation of P in the Changjiang River water (Shen 1997; Liu et al. 2003; Shen 2006; Shen and Liu 2009) and the source, budget, and control of P in interior small watersheds (Yan et al.1999; Li and Huang 2005; Zhang et al. 2007). However, the study in source and budget of P has not been carried out in the river catchment from the whole catchment scale. The major sources and budget of P in the river catchment are estimated quantitatively for the first time, and the control of P is discussed in this paper, in order to provide a scientific base for effective controlling P concentration in the Changjiang River and its mouth.

Nutrient budgets are generally based on either dissolved inorganic input (Nixon and Pilson 1983) or total nitrogen or total phosphorus input (Boynton et al. 1995). In this paper, we estimate the budgets of dissolved inorganic phosphorus (DIP) and total phosphorus (TP), consisting of P import from nonpoint and point sources to the river catchment and P export from the river mouth and the balance in between. Data used in this paper are from our field observations and other published literatures mainly from 1990s late and 2000s, which can reflect basically the status of the Changjiang River catchment.

1 The Export Fluxes of P in the Changjiang River Mouth

P export flux at the river mouth is calculated based on field investigations, which were carried out at the river mouth in February (winter), May (spring), August (summer), and November (autumn), 2004. Five stations (Fig. 1) were set up (salinity ≈ 0), and river water samples were collected from the surface and bottom layers water.

The month export flux of P at the river mouth is calculated as follows:

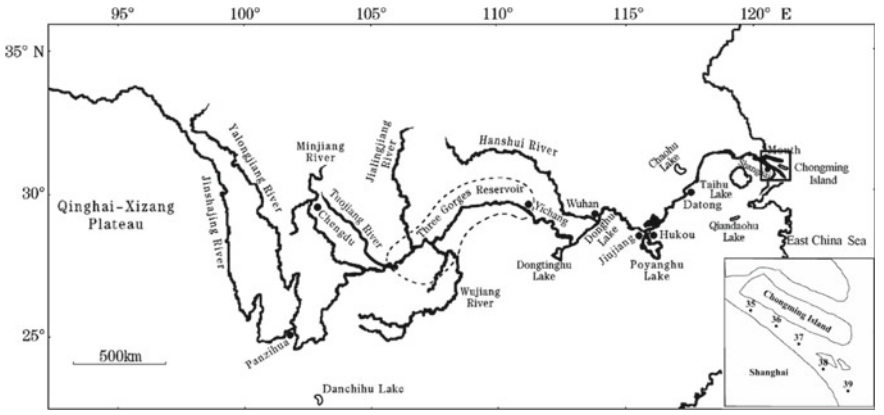

Fig. 1 Study area

$$F = CQf \tag{1}$$

where F is export fluxes (kg s^{-1}) of DIP and TP in investigation months, C is average concentrations (μmol L^{-1}) of DIP and TP in five stations, Q is average monthly runoff (m^3 s^{-1}) of the river mouth, and f is conversion coefficient of units.

The export fluxes of DIP and TP in the river mouth in February, May, August, and November 2004 can be calculated using formula (1). The seasonal variations in export fluxes of DIP and TP were large (Fig. 2) and depend mainly on the river runoff. The regressive relations between the export fluxes of DIP and TP in every month and the monthly average runoff Q at the river mouth were:

$$\mathrm{DIP}\left(\mathrm{kg\,s^{-1}}\right) = 0.104 + 0.216\,Q\left(10^4\,\mathrm{m^3\,s^{-1}}\right) \quad \left(r^2 = 0.916, p = 0.043, n = 4\right)$$

$$\mathrm{TP}\left(\mathrm{kg\,s^{-1}}\right) = -0.263 + 0.840\,Q\left(10^4\,\mathrm{m^3\,s^{-1}}\right) \quad \left(r^2 = 0.913, p = 0.044, n = 4\right)$$

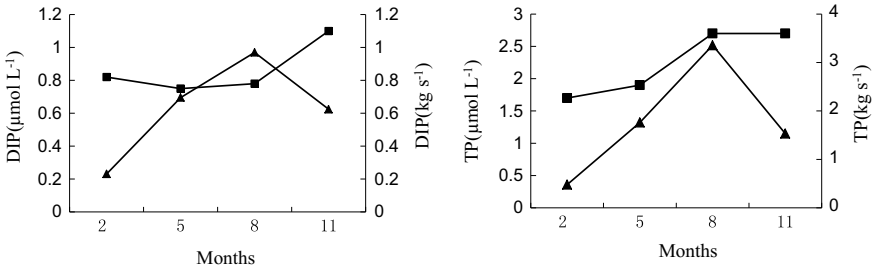

Fig. 2 Seasonal variations in average concentrations and export fluxes of DIP and TP in the Changjiang mouth: filled square—concentrations; filled triangle—fluxes

The above equations show that the exports of DIP and TP in the river mouth were mainly controlled by the river runoff. The export fluxes of DIP and TP were 0.65 kg s^{-1} (or 2.04×10^4 t a^{-1}, 11.34 kg km^{-2} a^{-1}) and 1.85 kg s^{-1} (or 5.83×10^4 t a^{-1}, 32.39 kg km^{-2} a^{-1}), respectively, in the river mouth in 2004 as calculated by the above equations. In case of calculation using the average in different seasons, the export fluxes of DIP and TP were 0.63 and 1.78 kg s^{-1}, respectively, showing little difference in two calculation methods. The export of DIP was 35.0% of TP. Compared with 1985–1986 investigation (Shen 1993), the export flux of DIP in 2004 increased 0.5 times. The average runoff in the river mouth in 2004 (25,148 m^3 s^{-1}) was higher than that in 1985–1986 (23,620 m^3 s^{-1}). But the export flux of DIP in 2004 was a little less than that in 1997–1998 (0.74 kg s^{-1}) (Shen 2006), while the export flux of TP was much less than that in 1997–1998 (4.11 kg s^{-1}). It was possibly related to runoff; the average runoff in the river mouth in 2004 was only 64% of that in 1997–1998 (especially heavy flood). The export flux of DIP in this study was higher than the data of Zhang (1996) (9.08 kg km^{-2} a^{-1}). The export flux of P in this study was much lower than that in the Amazon River (DIP, 49.60 kg km^{-2} a^{-1}) (Edmond et al. 1985) and the Mississippi River (TP, 10.7×10^4 t a^{-1}) (Turner and Rabalais 1991), and close to the Orinoco River (TP, 7.13×10^4 t a^{-1}) (Lewis and Saunders 1989).

2 P Imports in the Changjiang River Catchment

2.1 Precipitation Imports of P

The Changjiang River runoff mainly originates from rain, comprising 70–80% of annual runoff. The precipitation supply is taken as 75% here. The river catchment is divided into three subcatchments of the upper, middle, and lower reaches in this paper. The precipitation supply in every subcatchment was calculated on the basis of the river mouth runoff and the average share of every subcatchment in the whole catchment over the years. Precipitation import of P in every subcatchment can be calculated using formula (1), where F is annual import fluxes (t a^{-1}) of DIP and TP from precipitation, C is average concentrations (μg L^{-1}) of DIP and TP, and Q is annual precipitation amount (m^3) into the river (precipitation supply). The data in concentrations of DIP and TP come from field observations and relative literatures. Rain samples were collected in Panzhihua and Chengdu (the upper reaches), Jiujiang (the middle reaches), and Datong and Shanghai (the lower reaches) during the flood season in 1998. In addition, rain samples were taken monthly in the Donghu Lake region (the middle reaches) in 1997–1998, Taihu Lake region (the lower reaches) in 1998–1999, and Chongming Island (the lower reaches) in 2004–2005 (Fig. 1).

The report about P concentration in precipitation is very limited. Based on the data determined by us and relative references, the P concentrations in precipitation in the upper reaches were taken from Panzhihua and Chengdu; data in the middle reaches

Table 1 P fluxes from precipitation into the Changjiang River

Catchments	Runoff	Precipitation supply	DIP	TP	P fluxes (t a^{-1})	
	($\times 10^9$ m^3)	($\times 10^9$ m^3)	(μg L^{-1})	(μg L^{-1})	DIP (t a^{-1})	TP (t a^{-1})
Upper	383.07	287.30	12.4	20.9	3562.5	6004.6
Middle	390.50	292.88	10.1	19.2	2958.1	5623.3
Lower	52.01	39.01	15.8	28.4	616.4	1107.9
Whole catchment	825.58	619.19	11.6[a]	20.7[a]	7136.9	12,735.8

[a]Weighted mean

were from Jiujiang, the Donghu Lake region (Cai 1995; Tong Huijuan, personal communication), and the Poyanghu Lake region (Zhu and Zhang 1997); data in the lower reaches were from Datong, Shanghai, the Taihu Lake region (Zhang et al. 1993, Huang et al. 2000b; Yang Longyuan, personal communication), and Chongming Island. The above data are listed in Table 1, suggesting that the highest concentrations of DIP and TP in precipitation were found in the lower reaches, which was related to the highly developed economy and high-density population there. The weighted mean concentration of DIP was 56% of TP in the whole catchment, showing that DIP was the major form of P in precipitation.

The P fluxes from precipitation in the upper, middle, and lower reaches were calculated with formula (1) (Table 1), suggesting that DIP and TP fluxes from precipitation to the river catchment in the upper, middle, and lower reaches were 49.9, 41.4, 8.6% and 47.1, 44.2, 8.7%, respectively, of those of the whole catchment and came mainly from the upper and middle reaches.

2.2 P Import from Agricultural Nonpoint Sources

Agricultural nonpoint source P losses in this report are the actual P losses from fertilizer and soil, without precipitation P. Data in the arable land areas, applied fertilizer P, and water and soil losses in the river catchment are from the 2003 Changjiang River Yearbook and the 2003 China Statistics Yearbook. Due to wide area, complex terrain, and physiognomy in the river catchment, estimating P losses from agricultural nonpoint sources in the upper, middle, and lower reaches is based on those of the representative agriculture regions with main terrain feature of every subcatchment in present paper. Hill and plain are main surface type in the middle and lower reaches, where most of agriculture regions distribute and have the densest water web systems in China. Therefore, the calculations of P losses from agricultural nonpoint sources in the middle and lower reaches are based on those of Poyanghu Lake and Taihu Lake regions, respectively (accounting for 24 and 28% of the middle and lower reaches areas, respectively). In the upper reaches with mountains and plateaus, the estimation

of P losses is based on those of the Three Gorges Reservoir Region (accounting for 5.6% of the upper reaches area).

Table 2 shows that the most arable land areas and the greatest consumption of fertilizer P were in the middle reaches and were 44.2 and 51.0%, respectively, of those of the whole catchment; water and soil losses were most serious in the upper reaches, accounting for 71.4% of those of the whole catchment; and the largest ratio of administered area was in the lower reaches and the least was in the upper reaches.

The calculations of fertilizer and soil P losses in the lower reaches were based on the pollution of agricultural nonpoint sources in the Taihu Lake catchment (Guo et al. 2004; Wang et al. 2004b). The rice–wheat (cole) is a rotation cropping in irrigated fields. The import fluxes of TP and DIP in precipitation and irrigation water (0.056 and 0.009 t km^{-2}, respectively) were reduced by the exports of TP and DIP through surface runoff (0.171 and 0.034 t km^{-2}, respectively), were equal to the actual losses of fertilizer and soil P through surface runoff in the rice season in irrigated fields, and were calculated as the TP and DIP loss fluxes of 0.115 and 0.025 t km^{-2}, respectively. The export fluxes of TP and DIP in the wheat growing season were 41.4 and 38.4% of those in the rice season in irrigated fields (Wang et al. 2004b). Therefore, the actual TP and DIP losses from fertilizer and soil in irrigated fields were 0.163 and 0.035 t km^{-2} a^{-1}, respectively. Precipitation TP transport was reduced by TP transport through surface runoff in dry fields and equaled the actual losses of fertilizer and soil TP in dry fields, calculated as 0.056 t km^{-2} a^{-1} (Guo et al. 2004). According to DIP/TP ratio of 0.184 (Wang et al. 2004b), the actual DIP loss in dry fields was 0.010 t km^{-2} a^{-1}. In the lower reaches, irrigated and dry fields were 78.6 and 21.4% of arable lands, respectively. So, from the above calculated values, the TP and DIP losses from fertilizer and soil in the lower reaches arable lands were 5026.8 and 1063.8 t a^{-1}, respectively (Table 3). Fluxes of P lost in water and soil were based on data on P losses in nonarable lands of the Taihu Lake region, which were 9.0% of those in dry field (Chen et al. 1999). The TP and DIP losses from water and soil in nonarable lands were 0.005 and 0.001 t km^{-2} a^{-1}, respectively. Based on water and soil loss areas (Table 2), TP and DIP losses from water and soil were calculated as 105.4 and 21.1 t a^{-1}, respectively (Table 3). From the above calculations, the TP and DIP losses from fertilizer and soil into the lower reaches of the Changjiang River were 5132.2 and 1084.9 t a^{-1}, respectively (Table 3).

Table 2 Statistics on the Changjiang River catchment

Catchments	Arable land areas	Consumption of fertilizer P	Water and soil losses areas	Administered areas	Administered ratios
	($\times 10^4$ km^2)	($\times 10^4$ t)	($\times 10^4$ km^2)	($\times 10^4$ km^2)	(%)
Upper	9.192	69.598	50.772	13.456	26.5
Middle	10.113	107.155	18.206	9.909	54.4
Lower	3.588	33.304	2.107	1.687	80.1
Whole catchment	22.893	210.057	71.085	25.051	35.2

Table 3 Agricultural nonpoint source P losses in the Changjiang River catchment

Catchments	P loss fluxes in arable lands (t a^{-1})		P loss fluxes in nonarable lands (t a^{-1})		P loss fluxes (t a^{-1})	
	DIP	TP	DIP	TP	DIP	TP
Upper	6250.6	19,027.4	10,662.1	66,511.3	16,912.7	85,538.7
Middle	4403.5	21,576.2	910.3	27,855.2	5313.8	49,431.4
Lower	1063.8	5026.8	21.1	105.4	1084.9	5132.2
Whole catchment	11,717.9	45,630.4	11,593.5	94,471.9	23,311.4	140,102.3

The fertilizer and soil P losses in the middle reaches were based on those of the Poyanghu Lake region. Calculations based on TP output data on surface runoff in six small area tests of arable land units (Zhu and Zhang 1997), TP export in surface runoff in irrigated fields minus TP input in precipitation and irrigation water was equal to the actual fertilizer and soil TP losses of 0.213 t km^{-2} a^{-1} from surface runoff into the Poyanghu Lake in irrigated fields. Based on the ratio of DIP and TP losses of 0.215 in irrigated fields in the lower reaches, the actual fertilizer and soil DIP losses in irrigated fields in the middle reaches were 0.046 t km^{-2} a^{-1}. TP loss in dry fields in the middle reaches was based on that of various soil type of dry fields (yellow mud soil, horse liver soil, moisture soil, etc.) in the Poyanghu River region. Precipitation TP transport was reduced by TP transport in surface runoff levels of 0.250 t km^{-2} a^{-1}; the actual loss of TP in dry fields was equal to 0.214 t km^{-2} a^{-1}. The DIP/TP ratio was taken as 0.184 (Wang et al. 2004b); the actual DIP loss was 0.039 t km^{-2} a^{-1} in dry fields. The irrigated and dry fields were 64.9 and 35.1% of arable lands in the middle reaches, respectively. Therefore, TP and DIP losses from fertilizer and soil in arable lands in the middle reaches were 21,576.2 and 4403.5 t a^{-1}, respectively (Table 3). Estimation showed that TP loss from water and soil in nonarable lands (including different edaphic forests, grasslands, and beach, marsh, wasteland) of the Poyanghu Lake region was 0.189 t km^{-2} a^{-1}, and after minus the TP flux in precipitation, the actual loss of TP in nonarable lands was 0.153 t km^{-2} a^{-1}. DIP/TP ratio was 0.031 based on the data of Liu et al. (2001) and Shi et al. (2002) in the nonarable lands; the actual DIP loss in the nonarable lands was 0.005 t km^{-2} a^{-1}. Based on water and soil losses areas (Table 2), the water and soil losses in the middle reaches were calculated as 27,855.2 t a^{-1} for TP and 910.3 t a^{-1} for DIP (Table 3). Thus, TP and DIP losses from fertilizer and soil into the middle reaches of the Changjiang River were 49,431.4 and 5313.8 t a^{-1}, respectively (Table 3).

The estimation of P loss in the upper reaches was based on those of the Three Gorges Reservoir Region. The irrigated fields accounted for about 40% of arable lands in the Three Gorges Reservoir Region, which was close to the ratio in the upper reaches. The TP export flux through surface runoff in arable lands (including irrigated and dry fields) in 21 counties and cities of the Three Gorges Reservoir Region was 0.232 t km^{-2} a^{-1} (Li and Huang 2005). Based on TP import flux (0.024 t km^{-2} a^{-1}) measured by authors in precipitation in the upper reaches, the actual

TP loss from arable lands was 0.207 t km^{-2} a^{-1}. The DIP/TP ratio through surface runoff in arable lands was taken as the mean of irrigated and dry fields in the middle reaches as 0.329, so the DIP export flux in arable lands was 0.068 t km^{-2} a^{-1}. Based on the arable land areas in the upper reaches (Table 2), the TP and DIP losses from the upper reaches arable lands were calculated as 19,027.4 and 6250.6 t a^{-1}, respectively (Table 3). The calculation of water and soil losses in the upper reaches nonarable lands was based on the soil loss flux of TP of 0.155 t km^{-2} a^{-1} in the Three Gorges Reservoir Region (Huang et al. 1994), and after minus TP import in precipitation, the actual TP loss from water and soil in nonarable lands was 0.131 t km^{-2} a^{-1}. According to the DIP/TP ratio of 0.224 in dry slope nonarable lands (Yuan et al. 2003), the water and soil DIP loss was 0.035 t km^{-2} a^{-1}. Based on DIP content in precipitation measured by authors, the precipitation DIP import flux was calculated as 0.014 t km^{-2} a^{-1}. So, the actual DIP loss in nonarable lands was 0.021 t km^{-2} a^{-1}. According to the water and soil loss areas in the upper reaches (Table 2), TP and DIP losses from water and soil were calculated as 66,511.3 and 10,662.1 t a^{-1}, respectively (Table 3). Thus, TP and DIP losses from fertilizer and soil into the upper reaches of the Changjiang River were 85,538.7 and 16,912.7 t a^{-1}, respectively (Table 3).

The above-estimated results (Table 3) show that the agriculture nonpoint sources TP and DIP losses occurred mainly in the upper reaches, where they were 61.1 and 72.6%, respectively, of those of the whole catchment and were mainly due to the large area of water and soil losses in the upper reaches, which was 2.5 times of the plus in the middle and lower reaches. TP losses in the middle and lower reaches accounted for 35.3 and 3.7% of that of the whole catchment, respectively, and DIP losses accounted for 22.8 and 4.7%, respectively.

2.3 P Import from Point Source Sewage Wastes

Point source pollution is involved with residential sewage and industrial waste. P import from point sources can be calculated using formula (1), where F is import fluxes (t a^{-1}) of DIP and TP from point sources, C is average concentrations (mg L^{-1}) of DIP and TP in sewage (waste), and Q is annual discharged amount (t) of sewage (waste) into the Changjiang River. The data of P contents in residential sewage and industrial waste in the river catchment are from published literatures in recent years, which were the average concentrations of P treated and untreated discharged into the river web. We used data from the 2003 China Statistics Yearbook and the 2003 Changjiang River Yearbook to calculate total residential sewage and industrial waste discharged from every province and district into the river catchment.

The residential sewage and industrial waste discharged from the upper, middle, and lower reaches into the river catchment were listed in Table 4. Data on P concentrations in industrial waste and residential sewage in the river catchment are scarce. But the authors have data of residential sewage from the Three Gorges Reservoir Region (Li and Huang 2005) in the upper reaches; data from the Zhuzhou City

Table 4 P input from point sources in the Changjiang River catchment

Catchments	Living sewage			Industrial waste			Total input amount	
	Sewage amount	DIP	TP	Waste amount	DIP	TP	DIP	TP
	($\times 10^4$ t a^{-1})	(t a^{-1})	(t a^{-1})	($\times 10^4$ t a^{-1})	(t a^{-1})	(t a^{-1})	(t a^{-1})	(t a^{-1})
Upper	191,445.8	5990.3	9009.4	220,441.2	4466.1	8793.4	10,456.5	17,802.8
Middle	321,978.0	10,074.7	15,152.3	285,282.6	5779.8	11,379.9	15,854.5	26,532.2
Lower	247,624.6	7748.2	11,653.2	216,708.5	4390.5	8644.5	12,138.7	20,297.7
Whole catchment	761,048.4	23,813.2	35,814.9	722,432.3	14,636.5	28,817.8	38,449.7	64,632.7

(Li et al. 2001) and from the Donghu Lake region (He 1996) in the middle reaches; and data from the Taihu Lake region (Jin et al. 1999; Huang et al. 2001), from the Qiandaohu Lake region (Han et al. 1997), and from the Shanghai City (Hu et al. 2002) in the lower reaches. Data of industrial waste are from the Three Gorges Reservoir Region (Li and Huang 2005), from the Taihu Lake region (Jin et al. 1999; Huang et al. 2001; Yang et al. 2003), from the Qiandaohu Lake region (Han et al. 1997), and from the Shanghai City (Hu et al. 2002) and from chemical industry, dye printing, leather making, foodstuff, and coking industries. (Wang and Li 1999). Thus, the TP concentrations in residential sewage and industrial waste were calculated as 4.706 and 3.989 mg L^{-1}, respectively. Based on the concentration ratios of DIP/TP of 0.665 and 0.508 in residential sewage (He 1996; Li et al. 2001) and industrial waste (Tong Huijuan, personal communication), the DIP concentrations in residential sewage and industrial waste were calculated as 3.129 and 2.026 mg L^{-1}, respectively.

P input from point sources in the upper, middle, and lower reaches may be calculated using formula (1) (Table 4). The inputs of DIP and TP from the point sources in the upper, middle, and lower reaches were 27.2, 41.2, 31.6% and 27.5, 41.1, 31.4%, respectively, of those of the whole catchment, suggesting that most of the sewage (waste) P were from the middle reaches.

2.4 P Import from Town Runoff

Urban runoff P is from urban surface runoff, without precipitation P. Estimating P imports from urban runoff into the river catchment is based on those of different terrain and size towns in the upper, middle, and lower reaches in this paper.

There is a scarcity of data on the P transport from urban runoff. The P imports from urban runoff into the river catchment were estimated on the basis of the 12 boroughs and counties in Three Gorges Reservoir Region for mountain towns in the upper reaches (Li and Huang 2005), the Donghu Lake region in Wuhan for larger city (Cai 1995) and the Poyanghu Lake region for small towns (Zhu and Zhang 1997) in the middle reaches, and the Shanghai City for larger city (Gu et al. 2002) and the Taihu Lake region for plain towns (Xia et al. 2003) in the lower reaches. The

TP flux in precipitation was reduced by that in surface runoff and was equal to the actual import flux of TP from town runoff as 0.440 t km^{-2} a^{-1}. The DIP/TP ratio was taken as 0.606 (Gu et al. 2002), so the actual DIP transport through town runoff was 0.267 t km^{-2} a^{-1}. According to the estimates for urban areas (6800.8 km^2) in the Changjiang River catchment (statistical data from the National Resources and Environment Special Information System), the DIP and TP input into the river catchment from urban runoff were 1815.8 and 2992.4 t a^{-1}, respectively.

2.5 P Import from Flow Sources Sewage

Flow source sewage is mainly from the daily waste discharged from ships into the Changjiang River waterway. According to the data from the 2003 Changjiang River Yearbook, the passenger capacity in the Changjiang River mainstream was 15×10^6 persons in 2002. If the passenger number was 10×10^6 persons in the tributaries, the annual passenger number was 25×10^6 persons, and if the passenger number of cargo ships on the waterway was 10×10^6 persons, this adds up to 35×10^6 persons with a personal average of 3-day voyages (Shen et al. 2003) and daily water use of 0.123 t per person (including toilet, kitchen, and washroom) (Huang et al. 1994). Based on the calculation method of Huang et al. (1994) and 0.665 (He 1996; Li et al. 2001) as the ratio of DIP/TP in sewage, the TP and DIP import fluxes from flow sources sewage in the river catchment were 5.553 and 3.693 t a^{-1}, respectively

3 P Budget of the Changjiang River Catchment

The estimated results (Table 5) show that P in the Changjiang River water came mainly from agricultural nonpoint source P losses and point source industrial waste and residential sewage, etc., with agricultural nonpoint source being the primary source. The discharge of P from residential sewage was higher than that from industrial waste in the point source P. The DIP and TP fluxes from precipitation into the river catchment were less, suggesting that precipitation was not the main source of P in the Changjiang River and its mouth, which is different from N (Shen et al. 2003). Table 5 also shows that the imports of DIP and TP from the river catchment were largely higher than their exports in the Changjiang River mouth. The exports of DIP and TP in the river mouth were only 28.3 and 27.0% of the imports from the river catchment, respectively, suggesting that 71.7% DIP and 73.0% TP were removed in the transports from the catchment to the Changjiang River water and from the upper reaches to the lower reaches.

Behrendt and Opitz (2000) summarized 89 rivers with catchment areas greater than 100 km^2 in the middle Europe, where the ratios of export and import fluxes of TP were between 8.5 and 140% with an average of $57.9 \pm 29.3\%$. Almost half of TP was retained in the river catchments. In the Mississippi River, about 47% of

Table 5 P budget of the Changjiang River catchment

P imports/exports	DIP ($\times 10^4$ t a^{-1})	Ratios (%)	TP ($\times 10^4$ t a^{-1})	Ratios (%)
P import				
Precipitation	0.71	10.3	1.27	5.8
Living sewage	2.38	34.5	3.58	16.4
Industrial waste	1.46	21.2	2.88	13.2
Nonpoint sources	2.33	33.7	14.01	64.3
Town runoff	0.018	0.26	0.030	0.14
Flow sources	0.00037	0.005	0.00056	0.003
Total	6.91	100.0	21.77	100.0
P export	2.04		5.83	
P import/export		28.3		27.0

TP was retained in the catchment, and the rest of TP was transported to the Mexico Bay (Alexander et al. 2004). The P retained ratios in these Euramerican rivers were much lower than that in the Changjiang River catchment. Different from N, P transfer, except for biological, is mostly related to the adsorption and sedimentation processes. Therefore, P is almost always in the particulate phase (Berge et al. 1997). Many researches showed that particle P was the primary form of P export in various land type of farmlands (Sharpley et al. 1994; Carpenter et al. 1998; Hart et al. 2004). DIP only accounted for 16.6% of TP in agricultural nonpoint source P input in the river catchment (Table 5). The estimations of P source in the Changjiang River catchment showed that 33.7% of DIP and 64.3% of TP came from the agricultural nonpoint source P losses, which were mainly transported by runoff. The mountains and plateaus in the river catchment accounted for 65.6% of the whole catchment area and distributed mostly in the upper reaches. Such terrains are unfavorable for P retention, due to short settling time for runoff formed. The most serious P loss in the upper reaches (Table 3) was apparently related to above factors. In the middle and lower reaches, mainly in plain and hills regions, such as the Taihu Lake, Chaohu Lake, Poyanghu Lake, and Dongtinghu Lake regions, rivers and ditches systems in these regions were crisscrossed vertically and horizontally and formed complex river web ecosystems. On the one hand, these ecosystems offered passages for agricultural nonpoint source N and P losses into the Changjiang River; on the other hand, they became the buffer areas of nutritive material retention. P retention mechanisms reviewed include uptake and release by vegetation, periphyton, and microorganisms; sorption and exchange reactions with soils and sediments; chemical precipitation in the water column; and sedimentation and entrainment. These mechanisms exemplify the combined biological, physical, and chemical nature of P retention in wetlands and streams (Reddy et al. 1999). The ability of these systems to retain P is key to determining downstream water quality (Johnston 1991; Reddy et al. 1999). The research in the Chaohu Lake catchment found that this multi-pond system can effectively reduce the nonpoint source load of nutrients, such as phosphorus and nitrogen from

runoff water, and filter out sediments before they reach the lake (Yin et al. 1993; Yan et al. 1999). The retention of nonpoint source pollution in freshwater marshes in the Changjiang River catchment improved effectively the quality of the Changjiang River water.

4 Analysis on Primary Control Factors of P in the Changjiang River and Its Mouth

4.1 The Primary Control Factors of P in the Changjiang River and Its Mouth

The P budget of the river catchment (Table 5) showed that P in the Changjiang River and its mouth was mainly controlled by the agricultural nonpoint source P losses and the discharges of point source industrial waste and residential sewage, etc., with agricultural nonpoint sources being the primary in which considerable P was from water and soil losses accounting for 67.4 and 49.7% of TP and DIP, respectively, in agricultural nonpoint sources (Table 3). This is perhaps logical since that global estimate is strongly dominated by the high erosional input of material to the oceans from Asia and Oceania (Howarth et al. 1995). The researches showed that the nonpoint source nutritive material has become the largest pollution source in aquatic environments (Parry 1998; Sharpley et al. 2001; Rozemeijer and Broers 2007). The ratios of N and P from farmland in the nonpoint source pollution were the largest (Boers 1996; Carpenter et al. 1998). It was estimated that the pollution load ratio of the agriculture discharge P was about 24–71% in the surface water of some Europe countries (Vighi and Chiaudani 1987). About 50% of the annual phosphorus load to UK waters is now derived from agriculture (Defra 2004). The agricultural nonpoint source pollution has brought significant influences to the receiving water bodies (Sharpley et al. 2001). The agricultural nonpoint source nutrient loads in most of lakes in China were more than 50% of the pollution loads in the receiving water bodies (Jin et al. 1990). Some lakes in agricultural high-yield areas in the Changjiang River catchment have presented serious eutrophication, such as the Taihu Lake (Zhang et al. 2007), Chaohu Lake (Yin et al. 1993), Dianchihu Lake (Duan et al. 2005), Three Gorges Reservoir Region (Li and Huang 2005).

4.2 The Agricultural Nonpoint Sources of P Losses in the Changjiang River Catchment

Based on the data of the China Statistics Yearbook, the utilization of fertilizer P in the farmland in China from 1980 to 2003 increased 440.6×10^4 t a^{-1} (about increased 1.6 times) (Fig. 3). The utilization of fertilizer P in the Changjiang River catchment about

accounted for 29.4% of that in China. According to the data of agricultural nonpoint source P losses (Table 5), as calculated on the basis of DIP loss, the P loss accounts for 1.3% of the annual use of fertilizer P in the whole catchment, while on the basis of TP loss, the loss of P accounts for 6.6% of that. The simulated experiments and the actually measured results in different soil conditions, farming systems, and managing levels have proved that there were obvious correlations between the level of fertilizer P with quick result in the soil (especially in the surface soil) and various form of P contents in runoff (Sharpley et al. 1994; Heckrath et al. 1995; Pote et al. 1999). The field experiment in the Taihu Lake catchment showed that the losses of dissolved P, particle P, and TP in runoff had very evidently positive linear correlations to the applied fertilizer amounts, with the correlation coefficients r^2 of 0.996, 0.990, and 0.995, respectively (Zhao et al. 2005). Apparently, significant increase in utilization of fertilizer P was one of the primary reasons of agricultural nonpoint source P losses.

Incessant increase in water and soil loss areas is also an important reason of P loss and leads to the receiving water polluted (Wit and Behreendt 1999; Bardgett et al. 2001). The Changjiang River's upper reaches once formed the second largest forest region in China, and the coverage rate of forest reached 30–40% in 1940s. However, because of reckless exploitation over the years, the coverage rate of forest has dramatically decreased from 22% in 1957 to only 10% in 1986 (Wang et al. 2004a). Because forest vegetation was destroyed, the extent and intensity of soil erosion and water and soil losses increased and led to the increasing of fertilizer and soil P losses, which were particularly serious in the upper reaches. Based on the data of the Changjiang River Yearbook, the water and soil loss areas from 1992 to 2002 increased 13.86×10^4 km^2 in the whole catchment. The water and soil loss areas reached 71.08×10^4 km^2 in 2002, being 39.5% of total catchment area, while the loss areas in the upper reaches were 71.4% of those in the whole catchment. According to the 2004 China Bulletin on Water and Soil Conservation, the total amount of soil erosion in average of many years in the Changjiang River catchment was 23.9×10^8 t, which nearly accounted for half of the total amount in China, and the total amount of soil erosion in the upper reaches accounted for 62.9% of the whole catchment (Wang et al. 2004a). Most of nonpoint source P in particulate form

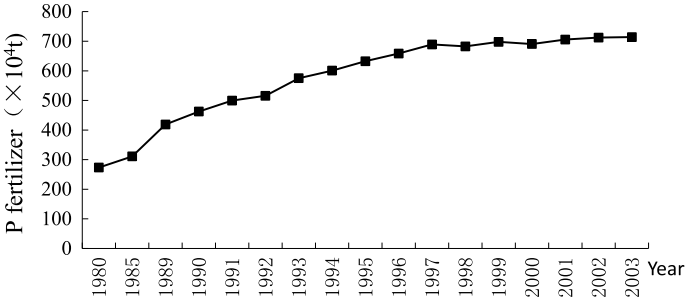

Fig. 3 Historical changes in fertilizer P consumption in China

in the Changjiang River catchment was likely a consequence of high rates of erosion and weathering. The direct results of water and soil loss areas increasing were lake bottom silting, riverbed elevation, channel shoaling, and marsh area decreasing. For example, the largest freshwater lake in China, the Poyanghu Lake, the area decreased from 5053 km^2 in 1954 to 3872 km^2 in 1999, and surface area of the lake decreased 23% and the capacity decreased 53×10^8 m^3. The decreasing in marsh area was closely related to the increasing in water and soil loss areas (Wang et al. 2004a). The decreasing in marsh area in the Changjiang River catchment not only weakened the ability of flood storage but also decreased greatly the buffer areas of agricultural nonpoint source N and P losses and increased the pollution load of the Changjiang River water.

4.3 The Discharge of Point Source P in the Changjiang River Catchment

4.3.1 The Discharge of Residential Sewage P

The discharge of P from residential sewage was more than that from industrial waste (Table 4). It is known that the discharge of P from residential sewage is directly related to the population, and the discharged amount of residential sewage increases with the population increasing. The research in the Hongzehu Lake (Yang 1997) in the river's lower reaches showed that there was obvious positive correlation between the discharged amount of residential sewage and the P content in receiving water body ($r = 0.521$, $p > 0.05$). Based on the data of the Changjiang River Yearbook, the population in the river catchment increased 28.55×10^6 from 1992 to 2002 (Fig. 4), in which the town population increased 32.72×10^6, while the country population decreased 4.17×10^6. According to the field investigation in the Taihu Lake catchment (Huang et al. 2000a), the annual P discharged amount per person (including urine and feces, residential washing wastewater) was 0.744 kg. If all the residential sewage P is discharged into the water body, the residential sewage P from town point source during 10 years can increase 24,342.6 t, which is about 68% of that of the whole catchment (Table 4). Because the above estimation did not think about the sewage treatment and the Taihu Lake catchment was the most rich area in the Changjiang River catchment, the estimated result may be higher than that of the actual result. However, it is obvious that the increasing year by year in point source residential sewage P discharge contributed more and more P to the Changjiang River and its mouth.

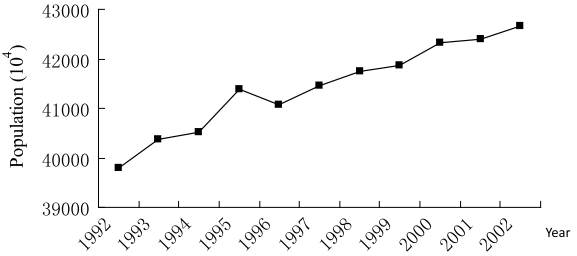

Fig. 4 Historical changes in population in the Changjiang River catchment

4.3.2 The Discharge of Industrial Waste P

The P discharged amount of industrial waste is directly related to the discharged amount of industrial waste. Different from the residential sewage, the discharged amount of industrial waste presented a decreasing tendency year by year in China (Fig. 5), with a decrease of 45.15×10^8 t from 1985 to 2003, accounting for 21.3% of total that in 2003. If the TP concentration in industrial waste was taken as the above-estimated value (3.989 mg L^{-1}), the TP discharged amount of industrial waste decreased 18,010.3 t from 1985 to 2003, accounting for about 62.5% of annual that in the Changjiang River catchment in 2003. The decreasing in the discharged amount of industrial waste was probably related to the adjustment of industrial structure and the developments of high and new technologies. In addition, people's environmental protection consciousness increased continually, and the work in environmental treatment was strengthened by government, which led to gradual decrease in the discharged amount of industrial waste.

The P discharged amount of industrial waste is also closely related to the P concentration in industrial waste. The ratio of up to P standard discharged amount of industrial waste to total discharged amount increased from 38.2% in 1985 to 89.2% in 2003, which reflected that the P concentration in the discharged industrial waste decreased significantly. It is shown that the P discharge from industrial waste has been efficiently controlled.

Since the late 1960s, the relative contribution of P to water bodies from point and nonpoint sources has changed dramatically in some developed countries in Europe and America. On the one hand, great strides have been made in the control of point source discharges of P, due, in part, to the ease in identifying point sources. On

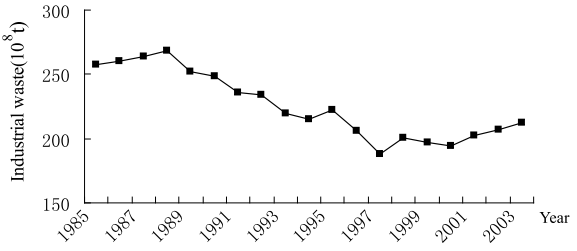

Fig. 5 Historical changes of the discharged amounts of industrial waste in China

the other hand, less attention has been directed to controlling nonpoint sources of P, due mainly to the difficulty in their identification and control (Sharpley and Rekolainen 1997). Thus, control of nonpoint sources of P is a major hurdle to protecting fresh surface waters from eutrophication (Sharpley and Tunney 2000; Withers et al. 2000). The point source industrial waste P discharge has been primarily treated in the Changjiang River catchment, but the residential sewage P discharge needs further control, especially how to decrease the agricultural nonpoint source P loss from catchment scale has become a key problem. It has significance to controlling the P concentration in the Changjiang River and its mouth and protecting estuary from eutrophication. However, our research is based on limited experiments and data. Overall and detail understanding the P budget of the Changjiang River catchment demands for more in-depth and systematic studies in the future.

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Part II
Removal and Transport of Matters in the Changjiang and Yellow River Estuaries

Removal and Mass Balance of Phosphorus and Silica in the Turbidity Maximum Zone of the Changjiang Estuary

Zhiliang Shen, Shuqing Zhou and Shaofeng Pei

Abstract The concentration of suspended particulate matter (SPM), sedimentation flux and various forms of phosphorus and silica in turbidity maximum zone (TMZ) in the Changjiang (Yangtze) estuary was studied. Based on the budget of P and Si, their mass balances in the TMZ were calculated. Research results show that the variation in concentration of dissolved inorganic silicon (DISi) was mainly controlled by sea water dilution in the Changjiang estuary, while that of dissolved inorganic phosphorus (DIP) was considerably affected by the buffering of suspended matter and sediment. The sedimentation fluxes of suspended particulate matter and particulate inorganic phosphorus (PIP), total particulate phosphorus (TPP), particulate inorganic silicon (PISi) and biological silicon (BSi) in the TMZ were 238.4 g m^{-2} d^{-1} and 28.3, 43.1, 79.0, 63.0 mg m^{-2} d^{-1}, respectively. In addition, a simple method to estimate the ratio of resuspension of sediment in the TMZ was established, indicating that the sediment resuspension in the TMZ influenced significantly the mass balances of P and Si. Particulate-adsorbed P (60.8%) and 35.5% of TPP discharged from the river were filtered and then deposited in the TMZ. The input flux of PIP from the river mouth was 55.9% of that of DIP, being important as biologically available P, while that of PISi was only 3.5% of DISi, showing that particulate-adsorbed Si was much less important than particulate-adsorbed P.

Keywords Phosphorus · Silica · Suspended particulate matter · Transport Turbidity maximum zone · Changjiang (Yangtze) estuary

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Turbidity maximum zone (TMZ) of a river estuary is a dynamic section of the estuary directly related to circulation, tide, deposition and scouring (Shen and Pan 2001); it is characterized by high concentration of suspended matter, higher than upstream or downstream of the estuary (Gebhardt et al. 2005). The TMZ plays many important roles during estuarine mixing processes, such as transport and accumulation of suspended particulate matter (SPM), deposition and resuspension of surface sediment, and the formation and development of the estuarine deltaic region. It could also affect the chemical behaviour, removal, and fate of nutrient, organic matter and many heavy metals in the estuary. In an estuarine area, the TMZ acts as a filter between the terrestrial and the marine realm (Gebhardt et al. 2005). The filtering effect reflects almost all the processes in physical, chemical, geological and biological manners in the estuary. Hence, study in biogeochemistry of the TMZ has become a hot topic of marine sciences. Many previous researches have been reported on the regions of the Gironde estuary (Allen et al. 1980), Chesapeake Bay (Fisher et al. 1988), Saint Lawrence estuary (Hamblin 1989), Tamar estuary (Uncles and Stephens 1993), Fly estuary (Wolanski et al. 1995) and Changjiang estuary (Jiufa and Chen 1998; Gebhardt et al. 2005).

The suspended particulate matter in the TMZ is derived mostly from riverine sources and accumulates there, in which it has a longer residence time than in the river upstream (Herman and Heip 1999). High SPM concentration in the TMZ provides an ideal site for physical, chemical and biological interactions between dissolved and particulate species, as well as interaction among particulate species (Gebhardt et al. 2005). Previous studies showed that in the TMZ, P and Si are more easily adsorbed to and released by SPM than other nutrients (Mackenzie and Garrels 1965; Siever and Woodford 1973; Mayer and Gloss 1980; Fox et al. 1986; Froelich 1988; Lebo 1991; Bowes and House 2001). Especially, the release of P from SPM is one of the most abundant sources in marine P cycling (Froelich 1988). Froelich (1988) estimated that on a global scale, fluvial particulates could transport from 1.4 to 14 $\times$ 10^{10} mol a^{-1} of reactive phosphate to the sea, some 2–5 times more than that in the dissolved load alone. Therefore, reactive phosphate in fluvial particulate is a potential biologically available source that cannot be ignored. It is known, however, excessive P entering estuary would cause eutrophication in coastal environments. Most SPM carried by rivers would deposit in the TMZ and part of dissolved components including P and Si would deposit later, which is significant for improving the estuarine and coastal environments. Lisitsyn (1995) calculated that in what he calls the "marginal filter", about 93–95% of the suspended and 20–40% of the dissolved riverine materials are deposited worldwide. Thus, it is very important to remove part of nutrient matters from riverine sources via deposition in the TMZ of an estuary.

The Changjiang River is the third largest in length and the fourth largest in sediment load in the world. The influence of the TMZ on transportation and deposition of sediment in Changjiang estuary has become a major issue in research (Milliman et al. 1985; He and Sun 1996; Jiufa and Chen 1998; Shen and Pan 2001; Chen et al. 2004). However, removal and delivery of P and Si in the TMZ in the estuary have not been fully understood. In the past 40 years, due to human activities including the construction of the Three Gorges Dam, eutrophication has become increasingly serious, and occurrence of red tides tended to increase in the Changjiang estuary. For

these reasons, this research was designed for studying the behaviour and removal of various forms of P and Si during estuarine mixing, and determining the sedimentation fluxes of SPM, P, and Si, estimating the mass balances of P and Si in the TMZ and seeking for scientific measures for remediation of eutrophication.

1 Study Area and Methods

The Changjiang estuary can be divided into three parts from the mouth seawards: upper, middle and lower estuaries. The upper estuarine is from Datong (the tidal stretch boundary) to Jiangyin (the tidal current boundary), 440 km long. The middle estuarine is from Jiangyin to the beach tip of river mouth, 210 km long, having river run-off and tidal current interacted and the river course branched. The lower estuarine is from the river mouth to the waters of 30–50 m isobath with a large submarine delta where tidal current dominated (Fig. 1). Near Xuliujing in the middle estuarine sector, the Changjiang River is divided into the South Branch and the North Branch, and the run-off and SPM are transported to the ocean mainly through the South Branch (Milliman et al. 1985). A special high SPM content zone stood out in the river mouth-bar area between the middle and lower estuaries, where the TMZ exists all year round. The TMZ was marked not only by high SPM concentration, but also by high wash-load content (Jiufa and Chen 1998). Tides in the estuary are regular semi-diurnal type. Turbidity maximum of the estuary is built in mechanisms of run-off–tidal current interaction and salt–freshwater mixing. The space–time distribution of turbidity maximum changes with the changes in run-off, tidal current and salt–freshwater mixing (Pan et al. 1999). The average run-off to the East China Sea was 29,000 $m^3\ s^{-1}$ or 928.2 $\times\ 10^9\ m^3\ a^{-1}$, of which most are formed in flood season from May to October. The average SPM content and annual total transport were 0.5–1.7 kg m^{-3} and 5×10^8 t, respectively.

Research cruises were carried out during 29 February–9 March, 24 May–31 May, 30 August–4 September and 3–8 November 2004. Water samples were collected in 23 stations at 0, 5, 10, 20, 30 m and bottom layer (Fig. 1). Salinity (S), SPM, dissolved inorganic phosphorus (DIP), total phosphorus (TP, the sum of dissolved and particulate phosphorus), dissolved inorganic silicon (DISi), chlorophyll-*a* (Chl-*a*) and transparence were measured. Besides, sampling along a transect passing stations 38, 39, 40, 22, 23, 24 and 25 was conducted in May 2004 across the TMZ for determining particulate inorganic phosphorus (PIP), total particulate phosphorus (TPP), particulate inorganic silicon (PISi) and biological silicon (BSi). Sedimentation fluxes of SPM, P and Si were determined using Bloesch multi-tube sediment traps at stations 22 and 23 (water depth ~10 m). Each trap had five columniform sampling tubes (92 cm high and 6.5 cm inner diameter). The sampling system had been fully tested previously (Bloesch and Burns 1980; Zhang et al. 2004). The sediment traps were placed 3–4 m above the bottom for 24 h. After the traps were lifted up, most clear liquid in tubes was carefully removed. The residual water samples and particulate matters were transferred into polyethene bottles and filtered in situ with pre-weighed 0.45 μm Millipore filters. All the filtered membranes were rinsed with deionized water for desalination and stored in an icebox for determining PIP,

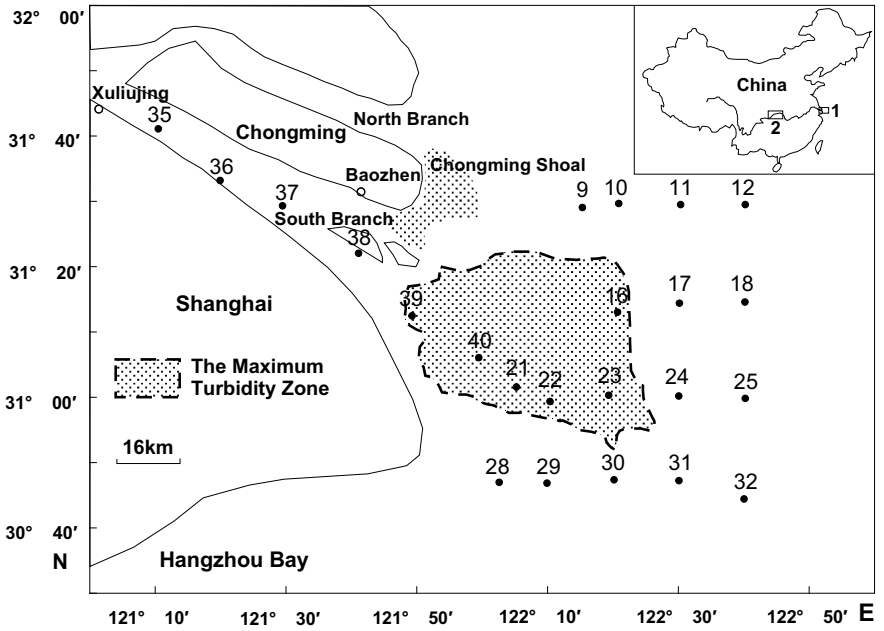

Fig. 1 Sampling stations in the Changjiang estuary. The shaded area is the TMZ (Shen and Pan 2001); 1: study area; 2: Three Gorges Dam

TPP, PISi and BSi. The filtered membrane for determining particulate matter was dried to a constant weight at 60 °C and stored in a desiccator for further analysis. PIP and PISi were extracted using HCl. The HCl-extracted P was from apatite; laboratory and field studies showed that the phosphorus was released from apatite in natural environment (Smith et al. 1977, 1978; Fox et al. 1985, 1987). The TPP was measured using the method of TP (Koroleff and Grasshoff 1976). The BSi samples were measured as per Treguer and Gueneley (1988). The total inorganic P (TIP) was defined as the sum of DIP and PIP; total inorganic Si (TISi) was the sum of DISi and PISi; and total particulate Si was the sum of PISi and BSi.

2 Horizontal Distributions of Salinity, SPM, DIP, TP and DISi

2.1 Salinity and SPM

Horizontal distributions of salinity and SPM in the study area in May are plotted in Fig. 2a and b. In May, the river experienced a season transition from dry to flood. The river-diluted water extended from the river mouth seawards, and salinity gradually increased (Fig. 2a). The salinity was higher in bottom than that in surface. Lower

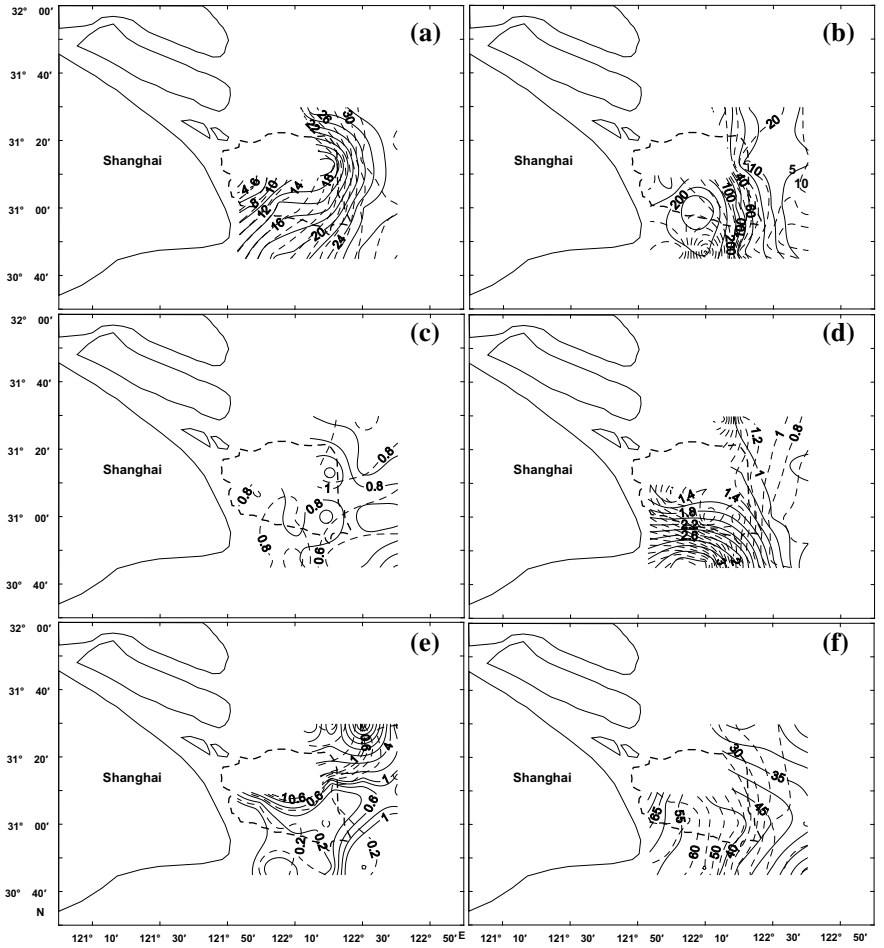

Fig. 2 Horizontal distributions of S, SPM, DIP, TP, Chl-*a* and DISi; **a** salinity; **b** SPM (mg L^{-1}); **c** DIP (μmol L^{-1}); **d** TP (μmol L^{-1}); **e** Chl-*a* (μg L^{-1}); **f** DISi (μmol L^{-1}); solid line—surface; dashed line—bottom

salinity was found in most areas of the TMZ, less than 16 and 20 in surface and bottom layer waters, respectively.

SPM contents were 3.3–298.0 and 2.7–628.7 mg L^{-1} in surface and bottom layers with an average of 76.9 ± 95.8 and 122.1 ± 163.0 mg L^{-1}, respectively, in the investigation area, and higher in bottom and lower in surface. High SPM content distributed mainly along the river mouth to the south-eastern waters of the mouth and decreased quickly from outer mouth towards the east and north-east (Fig. 2b). The average SPM content in the TMZ was 147.1 ± 120.1 mg L^{-1} in surface layer and 214.8 ± 126.6 mg L^{-1} in bottom layer. High SPM content was found in the west and south of the TMZ, which is consistent with moving direction of the Changjiang diluted water. From stations 21–23 south of the TMZ to station 24 east of the TMZ,

SPM contents in surface and bottom layers decreased from 291.3 to 8.0 mg L^{-1} and from 284.3 to 13.3 mg L^{-1}, respectively. Rapid horizontal decrease in SPM content and very high SPM content in bottom layer (Fig. 2b) suggest that the SPM from the Changjiang River deposited mostly in the TMZ. The very high SPM content in bottom layer was probably due to sediment resuspension. A previous study showed that the turbidity maximum was formed by local resuspension of deposits and seabed erosion (Jiufa and Chen 1998). However, the highest SPM content in bottom layer was not inside the TMZ, but at station 29 to the south (Fig. 2b) at 628.7 mg L^{-1}, which was three times higher than that in surface layer, because of the proximity to the Hangzhou Bay (Qiantang River mouth, south of the Changjiang mouth) (Chen et al. 2004), in which tide movement was magnificent, such as famous Qiantang Tide there. Sedimentation in the bay mouth caused a large increase in SPM content in waters as flood and ebb tides moving back and forth. A part of SPM turned north-east and invaded the area beyond the Changjiang mouth and formed a locally high SPM concentration area (Yang et al. 1992).

2.2 DIP and TP

The maximum concentration of DIP (1.3 μmol L^{-1}) in surface layer occurred outside the mouth at station 16 in the north-eastern part of the TMZ (Fig. 2c). At the station, low transparence (0.6 m) and Chl-*a* content (0.722 μg L^{-1}) indicated low biological influence; therefore, the high concentration of DIP was probably related to the P released from suspended matter. In addition, higher DIP concentrations (>0.8 μmol L^{-1}) were found in middle part of the investigation area and decreased towards north-east and south-west. DIP concentration was higher in most waters of the TMZ where SPM content was high, transparence was low (0.5–0.8 m) and Chl-*a* content was also low (0.125–0.440 μg L^{-1}). It has been shown that transparence was probably a main limiting factor for phytoplankton growth in the TMZ (Shen 1993a; Herman and Heip 1999), shown similarly in the Elbe, Schelde and Gironde estuaries in the western Europe (Muylaert and Sabbe 1999).

The distribution of TP concentration in surface and bottom layers (Fig. 2d) showed similar patterns to those of SPM. High TP concentration was observed mainly in the south-eastern parts outside the mouth. The highest concentration in surface and bottom layers was 3.5 and 4.5 μmol L^{-1}, respectively, and decreased towards the east and north-east. In the TMZ, higher TP concentration distributed in the parts west and south of the region, in maximum of 2.0 in surface and 3.1 μmol L^{-1} in bottom layers; and both were >1 μmol L^{-1} seen in other waters of the region. The maximum TP concentration occurred not in the TMZ but in the south of the TMZ. Similar distributions of both TP and SPM in the TMZ suggest that P was likely being adsorbed by suspended particles. TP was mainly composed of particulate P, especially in high TP concentration waters. The average DIP/TP ratio for both surface and bottom layers was 0.30, which was much lower than that of the whole investigation area (0.46). SPM contents were <10 mg L^{-1} in the most areas to the

east of 122 30′ E where TP was mainly composed of DIP; and the average DIP/TP ratio was 0.82. In addition to the Changjiang River input, partial DIP came from dead and decomposed plankton, especially in the north-east part, where Chl-*a* content was very high (Fig. 2e).

2.3 DISi

The distribution of DISi concentration was very different from that of DIP. High concentrations of DISi were found in the river mouth with the maximum inside the mouth. DISi concentration decreased greatly towards the east from the river mouth to the open waters (Fig. 2f). The isoline pattern of DISi was similar to that of the salinity but in opposite magnitude. The average concentration of DISi in surface and bottom layers was 44.2 and 37.0 μmol L^{-1}, respectively. The TMZ featured high DISi concentrations with averages of 69.8 μmol L^{-1} in surface layer and 54.1 μmol L^{-1} in bottom layer.

3 Variations of P and Si Concentrations Across the TMZ

3.1 Variations in P Concentration

Across the TMZ from stations 38–25 along in May, salinity was from ~0 to 31.73, and concentrations of DIP, PIP, and TPP varied 0.48–1.2 μmol L^{-1}, 0.15–0.44, and 0.31–1.5 mg g^{-1}, respectively, in surface water, and 0.50–0.78 μmol L^{-1}, 0.13–0.35, and 0.24–0.81 mg g^{-1} in bottom. The concentration variation was much smaller in bottom water than in surface water. From station 38 inside the river mouth to station 23 in the TMZ, the DIP concentrations did not decrease with salinity increasing, and the variation showed an opposite pattern to the variations of PIP and TPP concentrations (Fig. 3a and b).

On the east side of the TMZ, SPM contents decreased clearly. Small variation in PIP concentration and increasing in TPP concentration were probably related to the increasing in biological particulate organic P (Fig. 2e), which is consistent with the variation in BSi content (Fig. 3c and d). From the TMZ to the places offshore, the transparence increased from 0.5 to 2.8, which was beneficial to phytoplankton growth. In addition, it could be also proved with positive linear relationship between TPP concentrations and Chl-*a* contents ($r = 0.830$, $p = 0.00044$). The concentration of particulate P increased with SPM decrease in the estuary that was also noticed by Edmond et al. (1985).

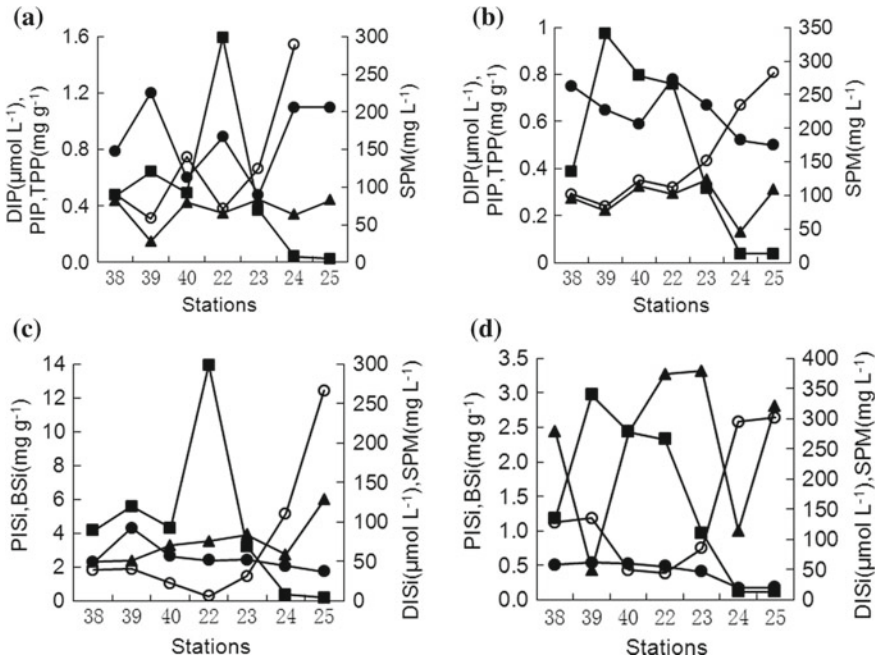

Fig. 3 Variations in P, Si and SPM contents along the transect: **a** and **c**—surface; **b** and **d**—bottom; **a** and **b**: filled circle—DIP, filled triangle—PIP, open circle—TPP, filled square—SPM; **c** and **d**: filled circle—DISi, filled triangle—PISi, open circle—BSi, filled square—SPM

3.2 Variations in Si Concentration

The variation along the transect in concentration of various forms of Si was much greater than that of P. The concentration ranges of DISi, PISi and BSi were 37.3–92.2 μmol L^{-1}, 2.3–6.0 and 0.28–12.4 mg g^{-1} in surface layer; and 19.3–61.4 μmol L^{-1}, 0.43–3.3 and 0.39–2.6 mg g^{-1}, in bottom layer, respectively. The variation in DISi concentration was generally opposite to that of PISi in the TMZ (Fig. 3c and d). In the area east of the TMZ, with salinity increase, the influence of biological activity increased (Fig. 2e), shown by the variation in BSi content that increased rapidly and reached 12.4 and 2.6 mg g^{-1} in surface and bottom waters, respectively, at station 25. The average concentrations of PISi were higher at 2.7 ± 0.99 mg g^{-1} than that of BSi at 1.0 ± 0.58 mg g^{-1} in the TMZ, whereas in the area east of the TMZ, the concentrations of the PISi were smaller at 3.0 ± 2.0 mg g^{-1} than that of BSi at 6.1 ± 3.4 mg g^{-1}. Correlation analyses on data of the stations on the transect show clearly positive linear relationships among Chl-*a* content, sea water transparence ($r = 0.979$, $p = 0.00068$) and BSi concentration ($r = 0.827$, $p = 0.00048$).

4 Removals of P and Si in the TMZ and Its Adjacent Waters

4.1 Removal of P in the TMZ and Its Adjacent Waters

4.1.1 Mixing Process of P in the Estuary

A negative linear relationship was found between DIP and salinity in all the investigation waters (Fig. 4a), showing that from river mouth to open sea, physical mixing controlled DIP concentration to a great extent. However, phytoplankton bloomed in May just before the sampling; it was likely that a part of DIP had been taken up by phytoplankton in upper layer sea water. The biological influence occurred mainly in the area of intermediate salinity north and east to the investigation area and far from the river mouth (Fig. 2e). At stations such as stations 9 and 11, Chl-*a* content in surface water reached as high as 11.659 and 19.515 $\mu g\ L^{-1}$. If we draw a theoretical dilution line in Fig. 4a connecting the average DIP concentrations in river water end-member and sea water end-member at average salinity above 33, one would find that above the data points fall below this line, suggesting that DIP was taken up by phytoplankton. In addition, DIP adsorbed by and released from suspended particles and resuspended sediment could also affect the distribution of DIP in the estuary. For example, at stations 28 and 29 in mild salinity region (Fig. 4a), their data points situate above the theoretical dilution line. Many field observations and laboratory experiments have demonstrated that aquatic particles can release DIP through a desorption reaction (Fox et al. 1986; Froelich 1988; Lebo 1991; Chambers et al. 1995; Suzumura et al. 2000, 2004). Since DIP concentration in the estuary was affected by several processes besides just the dilution mixing, correlation between DIP and salinity was low especially in the TMZ (Fig. 4a), where biological influence was low but suspended particles and sediment resuspension were high.

TP was more negatively correlated with salinity than DIP did (Fig. 4b), suggesting that the distribution of TP in estuarine waters depended mainly on physical mixing, as the distribution of TP (including all forms of P, organic and inorganic, and dissolved and particulate) is irrelevant to biological activity. However, TP distribution in the TMZ was largely affected by both sedimentation of suspended particulate P and constantly released P from resuspended sediment into sea water. If we draw a theoretical dilution line in Fig. 4b with above-mentioned method, it can be also found that some data points (stations 28, 29, etc.) of high concentrations of TP would be positioned above this line, which is consistent to the behaviours of DIP (Fig. 4a).

4.1.2 Buffering of Suspended Particulate

Many studies have demonstrated that the interaction of DIP with suspended particulate material was probably one of the most important mechanisms affecting geochemistry of P in estuarine area (Fox et al. 1986; Froelich 1988; Lebo 1991; Chambers

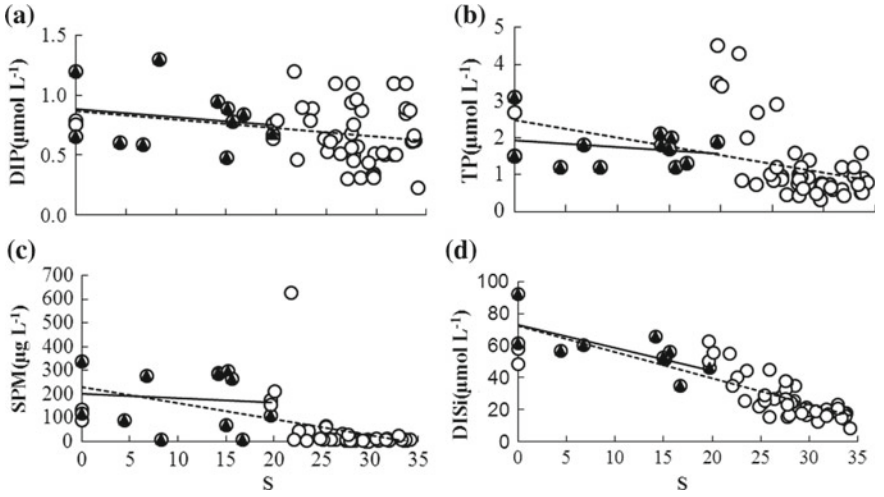

Fig. 4 Relationships of DIP, TP, DISi and SPM to S, in the Changjiang estuary: open circle—all data; filled triangle—data for the turbidity maximum zone; dashed line—correlative curves for all data; solid line—correlative curves for the turbidity maximum zone; **a**: open circle—DIP = 0.871 − 0.007 S ($r = -0.278$, $p = 0.033$, $n = 59$), filled triangle—DIP = 0.885 − 0.007 S ($r = -0.181$, $p = 0.595$, $n = 11$); **b**: open circle—TP = 2.483 − 0.048 S ($r = -0.473$, $p = 0.00016$, $n = 59$), filled triangle—TP = 1.930 − 0.018 S ($r = -0.225$, $p = 0.483$, $n = 12$); **c**: open circle—SPM = 229.807 − 6.794 S ($r = -0.542$, $p = 7.59 \times 10^{-6}$, $n = 60$), filled triangle—SPM = 201.281 − 1.875 S ($r = -0.752$, $p = 0.102$, $n = 12$); **d**: open circle—DISi = 72.260 − 1.638 S ($r = -0.854$, $p = 1.58 \times 10^{-17}$, $n = 58$), filled triangle—DISi = 73.208 − 1.437 S ($r = -0.702$, $p = 0.024$, $n = 10$)

et al. 1995; Conley et al. 1995; Fang 2000). The variation in DIP concentration was obviously opposite to those of PIP and TPP (Fig. 3a and b), indicating that DIP was adsorbed by or released from SPM. By the buffering of SPM in the TMZ, DIP and PIP concentrations were retained 0.48–1.2 μmol L^{-1} and 0.15–0.44 mg g^{-1} in surface sea water, and 0.59–0.78 μmol L^{-1} and 0.22–0.35 mg g^{-1} in bottom, respectively, which is similar to the result of our previous study (Shen et al. 1992). The general mechanism of DIP buffering involves the equilibration of the dissolved P pool with a reservoir of particle-bound P (Froelich 1988). When the ambient DIP concentration differs from the equilibrium concentration, DIP is either released or adsorbed until equilibrium is achieved (Lebo 1991). Strong disturbance by wind, tide and current would increase the contact between DIP and suspended particulate material; therefore, the DIP equilibrium was closely related to the disturbance.

4.1.3 Resuspension of Sediment and the Behaviour of P

In the TMZ, the SPM came mainly from the Changjiang River run-off and resuspension of sediment. The SPM content in the estuarine waters was higher than that of the river run-off, meaning additional SPM from downstream to outside the river

mouth resulted from sediment resuspension (Fig. 4c). The ranges of variation for DIP, PIP and TPP concentrations were notably less in bottom water than those in surface (Fig. 3a and b), reflecting greater buffering effect of suspended matter and sediment to P in bottom water because of near-bottom resuspension.

4.1.4 Compositions of P

The average ratio of PIP to TPP was 0.81 ± 0.17 inside the river mouth and the TMZ, and 0.22 ± 0.12 in the area east of the TMZ, suggesting that inorganic P adsorbed by suspended matter and sediment was a major form of particulate P in the TMZ, while that of DIP/TP was 0.44 ± 0.19 within the TMZ and 0.85 ± 0.18 beyond the TMZ to the east, indicating that DIP was a main form of P in open sea. The phenomenon that distribution of TPP decreased with change in the seaward direction was also found in other estuaries (Fang 2000).

4.1.5 Compared with Other Rivers

TPP concentrations within the salinity gradient ($S < 32$) of the Changjiang estuary ranged from 0.24 to 2.0 mg g^{-1} in average of 0.90 ± 0.78 mg g^{-1}, which were higher than the P content (0.44–1.10 mg g^{-1}) in surface sediment of the TMZ and its upstream (Hou et al. 2006). The average TPP we measured in the Changjiang estuary is close to the total P contents in the fluvial suspended particulate of 0.81 (Sholkovitz et al. 1978) and 1.05 mg g^{-1} (Edmond et al. 1981) in the Amazon River, and 0.99 mg g^{-1} in the Zaire River (van Bennekom et al. 1978), but below the global average of 1.15–1.20 mg g^{-1} (Martin and Meybeck 1979; Froelich 1988). When compared with other urbanized estuaries, the TPP concentration within the salinity gradient of the Changjiang estuary is much lower. For example, the TPP contents in the American Delaware estuary were 1.24–1.55 (Lebo 1991), and 2.70–8.99 mg g^{-1} in northern European Ems and Weser estuaries (Calmano 1981; Salomons and Gerritse 1981; Rehm 1985), possibly indicating locally high content of DIP. The TPP content within the salinity gradient is generally smaller than the total P content in fluvial suspended particulate, possibly due to the part of adsorbed P released from fluvial suspended particulate within the salinity gradient. Lebo (1991) found that the P content of particles within the salinity gradient of the Delaware estuary was much lower than particles from the river.

The PIP concentrations within the salinity gradient in the Changjiang estuary ranged 0.13–0.69 mg g^{-1} in average of 0.33 ± 0.15 mg g^{-1}, close to the particulate active P concentration of 0.34 mg g^{-1} in the Amazon estuary (Edmond et al. 1981) and 0.31 mg g^{-1} in the Ochlockonee estuary (Kaul and Froelich 1984). All these values are above the global average of 0.16 mg g^{-1} (Froelich 1988). The fraction of PIP in TPP concentration was 36.7% within the salinity gradient in the Changjiang estuary, well above the global one at 15% (Froelich 1988).

4.2 Removal of Si in the TMZ and Its Adjacent Waters

DISi concentration was mainly controlled by sea water dilution as shown by the negative linear relationship to the salinity (Fig. 4d). Compared with DIP (Fig. 4a), the relationship between DISi concentration and salinity is stronger (Fig. 4d). However, many data points of DISi distribute in two sides of the theoretical dilution line, suggesting that the behaviour of DISi in the estuary was somewhat non-conservative as it was affected by biological activity and suspended sediments. Biological activity influence on DISi occurred mainly in middle- and high-salinity zones.

Variation in DISi concentration is also opposite to that of PISi in the TMZ (Fig. 3c and d). From stations 39–23, with salinity increase from ~0 to 15.01 in surface layer and from ~0 to 19.71 in bottom layer, the DISi concentration decreased from 92.2 to 52.5 μmol L^{-1} and from 61.4 to 46.4 μmol L^{-1}, respectively, and PISi concentration increased from 2.4 to 3.9 mg g^{-1} and from 2.2 to 3.5 mg g^{-1}, respectively. Different from DIP, DISi concentrations continuously decreased with salinity due to dilution and adsorption onto particles. Studies have also shown that DISi could be adsorbed by suspended matter and desorbed from suspended matter during estuarine mixing (Mackenzie and Garrels 1965; Fanning and Pilson 1973; Mayer and Gloss 1980; Bowes and House 2001).

Removal of Si and that of P in the studied estuary was similar as both were controlled by sea water dilution. A positive linear relationship between DISi and DIP concentrations existed (through stations 38–25: $r = 0.492$, $p = 0.045$). Additionally, they were affected by the buffering of suspended matter and sediment; therefore, a positive linear relationship between PISi and PIP concentrations was also found (stations 38–25: $r = 0.750$, $p = 0.00052$). During the removal, however, impacting factors of physics, chemistry and biology were considerably different. Compared to the DIP, the DISi concentration was more sea water dilution affected, while DIP concentration was influenced more by suspended matter and sediment.

5 Sedimentation Fluxes of P and Si in the TMZ of the Changjiang Estuary

5.1 Sedimentation Fluxes of P and Si in the TMZ

Sedimentation flux of particulate matter was calculated by the following equations (Zhang et al. 2004):

$$F = M/HV \tag{1}$$

$$F_c = Mf_c/HV \tag{2}$$

where F is sedimentation flux of particulate matter (g m^{-2} d^{-1}); M is the dry weight (g) of particulate matter in the sampling tubes; V, the section area (m^2) of sampling

tubes; H, the sampling time (d); F_c is sedimentation flux of some components in particulate matter (mg m^{-2} d^{-1}); and f_c is the content of certain component of particulate matter (mg g^{-1}).

The dry weight of particulate matter and its components P and Si contents at stations 22 and 23 are summarized in Table 1. The P and Si contents in sinking particles were less than those in the SPM, indicating probably that part of the P and Si was released from sinking particles during sedimentation. With Formulas (1) and (2), the sedimentation fluxes were calculated and listed in Table 2. Taking the calculated results of stations 22 and 23 as the average value for the TMZ, we obtained the sedimentation fluxes of particulate matter and its components PIP, TPP, PISi, BSi and TPSi in the TMZ (Table 2). PIP flux accounted for 65.7% of TPP, showing that inorganic P dominated the sinking particle P and was consistent with that of SPM. The sedimentation flux of PISi was higher than that of BSi, suggesting that it was related to low phytoplankton quantity. The area of the TMZ was estimated about 20.579×10^8 m^2. Thus, the annual sedimentation fluxes of particulate matter, P and Si were calculated and listed in Table 2.

Table 1 Dry weight (g) of particulate matter and its components of P and Si contents (mg g^{-1})

Stations	SPM	PIP	TPP	PISi	BSi	TPSi
22	4.471	0.11	0.16	0.30	0.26	0.56
23	3.438	0.12		0.38	0.27	0.65

Table 2 Sedimentation fluxes of particulate matter (g m^{-2} d^{-1}) and its components of P and Si (mg m^{-2} d^{-1})

Stations	SPM	PIP	TPP	PISi	BSi	TPSi
22	269.5	30.9	43.1	79.6	70.1	149.7
23	207.2	25.7		78.4	55.9	134.3
Averages	238.4	28.3	43.1	79.0	63.0	142.0
Annual sedimentation (t)	1.79×10^8	2.126×10^4	3.237×10^4	5.934×10^4	4.732×10^4	10.666×10^4
Annual resuspension (t)	1.18×10^8	1.405×10^4	2.140×10^4	3.922×10^4	3.128×10^4	7.050×10^4
Annual net sedimentation (t)	0.61×10^8	0.721×10^4	1.097×10^4	2.012×10^4	1.604×10^4	3.616×10^4

5.2 Net Sedimentation Fluxes of P and Si in the TMZ

Most suspended particulate matter carried out by Changjiang River deposited in the TMZ. Flocculation and sedimentation are two important mechanisms (Krone 1962; Jiufa and Chen 1998; Shen and Pan 2001) affecting the character and fate of the dissolved and particulate matters from a river (Herman and Heip 1999; Gebhardt et al. 2005).

5.2.1 Estimation of the Resuspension Ratio

Due to the influences of wind, tide and current, suspended particulate matter in the TMZ of the Changjiang estuary was frequently disturbed in cycles of suspension, sedimentation, resuspension and resedimentation (Shen and Pan 2001). The suspended particulate matters in the TMZ include those from the river run-off and resuspended sediment. A simple method was used to estimate the ratio of resuspension from sediment of the TMZ. Taking SPM content at station 35 in downstream Xuliujing area as the background value of the river run-off (Chen et al. 2004), a theoretical dilution line between freshwater end-member and sea water end-member would be drawn (Fig. 4c). In case of resuspension or resedimentation, the SPM content would fall over or below this line. As the fraction of combustible particulate matter is very small, only 7.1% in May for our samples, among the total suspended particles in the Changjiang River, biological influence could be ignored. Therefore, the difference in SPM content between the measured in a station and its corresponding point at the salinity line would be equal to the resuspension amount. The resuspension ratio R can be calculated by:

$$R = ((\mathrm{SPM}_1 - \mathrm{SPM}_2)/\mathrm{SPM}_1) \times 100\% \quad (3)$$

where SPM_1 is the SPM content determined at a station in the TMZ, SPM_2 is the corresponding SPM value at the salinity line of theoretical dilution.

5.2.2 Net Sedimentation Fluxes of P and Si

Based on the investigation data of suspended matter in February, May, August and November 2004, using Formula (3), the resuspension ratio of particulate matter in bottom water of the TMZ was between 55.7 ± 28.7 and 80.5 ± 10.5% in annual average of 66.1%. Therefore, the annual resuspension amount and net sedimentation of particulate matter and its components of P and Si were calculated (Table 2). It shows that over half of the annual net sedimentation of particulate matter and its components of P and Si came from resuspension of sediment. With the same method, we calculated the resuspension ratio in surface water in the TMZ, which varied between 25.0 ± 40.6 and 73.0 ± 22.2% in annual average of 55.7%, and

smaller than that in bottom layer. Thus, annual resuspension amount of particulate matter and its P and Si components in surface water of the TMZ were calculated to be 1.00×10^8 t for SPM, 1.186×10^4, 1.806×10^4, 3.311×10^4, 2.641×10^4 and 5.952×10^4 t for PIP, TPP, PISI, BSi and TPSi, respectively. It also shows that the resuspension of sediment is one of the main mechanisms forming the TMZ (Jiufa and Chen 1998; Pan et al. 1999). Sedimentation and resuspension of huge amounts of P and Si are important to keep their concentrations at certain ecological levels in the estuarine water.

6 The Mass Balances of P and Si in the TMZ

The mass balances of P and Si in the TMZ of the Changjiang estuary can be calculated by:

$$F_{ai} + F_{ri} + F_{si} = F_d + F_{so} + F_{bo} + F_{eo} \tag{4}$$

where F_{ai} is the input flux (kg s^{-1}) of atmosphere sedimentation, F_{ri} is the input flux of river (kg s^{-1}), F_{si} is the input flux of sediment diffusion to sea water, F_d is the dilution and diffusion flux (kg s^{-1}) intercepted in the TMZ, F_{so} is sediment output flux (kg s^{-1}), F_{bo} is biological output flux and F_{eo} is the output flux (kg s^{-1}) to the East China Sea. The item of F_{si} is not considered due to relatively insignificant and data absence. The Chl-*a* contents in the TMZ were 0.287 mg L^{-1} in May and 0.776 mg L^{-1} in average of February, May, August and November, showing relatively less biological output, and is not considered here. Thus, the above formula becomes:

$$F_{ai} + F_{ri} = F_d + F_{so} + F_{eo} \tag{5}$$

6.1 Atmosphere Inputs of P and Si in the TMZ

The atmospheric sedimentation is considered only in the case of wet sedimentation. Based on observations of 32 times near Baozhen Town (121° 36.5′ E, 31° 30.3′ N) east part of Chongming Island from May 2004 to May 2005, the average contents of DIP and DISi in precipitation were 0.51 and 0.23 μmol L^{-1}. For TP content, we used the value of 0.66 μmol L^{-1} observed in the Changjiang River catchment in our previous study. Thus, the precipitation fluxes of P and Si can be computed as follows:

$$F_{ai} = C_a \cdot Q_a \cdot A \cdot f_a \tag{6}$$

where F_{ai} is the average annual precipitation input fluxes (kg s^{-1}) of P and Si, C_a is average contents (μmol L^{-1}) of P and Si in the precipitation, Q_a is the rainfall (mm) in Shanghai City in 2005, A is area (m^2) of the TMZ and f_a is the conversion coefficient

of units (from molar concentration to quality concentration). With Formula (6), the deposition fluxes of DIP, DISi and TP in the TMZ by precipitation were calculated (Table 3), which shows that DIP flux accounted for 77.3% of TP and was the main form of P.

6.2 River Inputs of P and Si in the TMZ

The input fluxes of P and Si from the Changjiang River can be calculated with:

$$F_{\mathrm{ri}} = C_{\mathrm{r}} Q_{\mathrm{r}} f_{\mathrm{r}} \tag{7}$$

where F_{ri} is the average annual input fluxes of P and Si (kg s^{-1}) from the river; C_{r} is the average concentrations of DIP, TP and DISi in five stations within the river mouth (stations 35–39, salinity ~ 0) in February, May, August and November 2004. The values were 0.86, 2.3 and 120.6 μmol L^{-1}, respectively. Q_{r} is the average annual run-off (m^3 s^{-1}) of the river mouth, and f_{r} is the conversion coefficient of units. With Formula (7), the fluxes of DIP, DISi and TP to the TMZ from the river were calculated (Table 3). The input fluxes of DIP and DISi in this study are higher than those (0.43 and 63.3 kg s^{-1}) annual investigation records during 1985–1986 (Shen 1993b). The input flux of DISi calculated in this study was below 106.5 kg s^{-1} than that reported by Edmond et al. (1985). The input flux of DIP of this study was well below that of the Amazon River in December 1982 (2.35 kg s^{-1}) and May 1983 (4.62 kg s^{-1}) with corresponding average annual run-offs of the river at 123,668 and 171,232 m^3 s^{-1}, respectively (Edmond et al. 1981, 1985; Fox et al. 1986; Froelich 1988), which is 4.9 and 6.8 times higher than that of the Changjiang River in this study.

The input fluxes of particulate P and Si could be calculated using the same method. C_{r} is the concentrations of particulate P and Si in the river mouth water (mg L^{-1}). It is the product between the average concentrations of PIP, TPP, PISi and BSi (mg g^{-1}) at stations 38 and 39 (salinity ~ 0) in May, August and November 2004 and the average SPM content (mg L^{-1}) at station 35 (the background value of SPM from the Changjiang run-off) in February, May, August and November 2004. Afterwards, the input fluxes and annual inputs of PIP, TPP, PISi and BSi were calculated (Table 3). The annual input of PIP from the Changjiang River was less than that of DIP, the former was 55.9% of the latter and cannot be ignored as biologically available P. The annual input of PIP of the Changjiang River was much less than that of the Amazon in 1982 and 1983 (17.050×10^4 and 30.690×10^4 t a^{-1}, respectively). The annual input of PIP was 2.3–2.1 times of that of DIP in the Amazon (Edmond et al. 1981, 1985; Fox et al. 1986; Froelich 1988). The ratio of annual input of PIP to DIP in the Ochlockonee River was 0.6 (Froelich 1988) similar to that in the Changjiang River. The difference between TP and TPP + DIP is dissolved organic P (DOP), and the difference between TP and TPP is total dissolved P (TDP). The input fluxes and annual inputs of DOP and TDP were 0.13, 0.81 kg s^{-1} and 0.396×10^4, 2.537×10^4 t, respectively. These results show that the input flux of DIP accounted for 81.9% of

Table 3 Mass balances of P and Si in the TMZ

	River input		Precipitation input		Dilution and diffusion intercepted		Sediment output		Output to East China Sea	
	kg s^{-1}	10^4 t a^{-1}	kg s^{-1}	t a^{-1}	kg s^{-1}	10^4 t a^{-1}	kg s^{-1}	10^4 t a^{-1}	kg s^{-1}	10^4 t a^{-1}
TP	1.79	5.631	0.0017	52.8	0.57	1.802			1.22	3.834
TPP	0.98	3.094					0.35	1.097	0.63	1.996
TIP	1.05	3.326	0.0013	40.8	0.14	0.450	0.23	0.721	0.68	2.160
DIP	0.68	2.141	0.0013	40.8	0.14	0.450			0.54	1.696
PIP	0.38	1.185					0.23	0.721	0.14	0.464
TISi	88.89	280.326	0.00053	16.6	49.26	155.335	0.64	2.012	39.00	122.979
DISi	84.92	267.819	0.00053	16.6	49.26	155.335			35.67	112.486
PISi	3.97	12.507					0.64	2.012	3.33	10.495
BSi	3.13	9.874					0.51	1.604	2.62	8.269
TPSi	7.10	22.380					1.15	3.616	5.95	18.765

TDP, being the main form of dissolved P, and was 64.4% of TIP or 38.0% of TP. The input flux of PIP accounted for 35.6% of TIP or 21.2% of TP. The sum of DIP and PIP is the total active inorganic P (TIP) accounting for 59.2% of TP. The input flux of TPP accounted for 54.9% of TP, and particulate active inorganic P (PIP) was 38.3% of TPP. The input flux of DISi accounted for 95.5% of TISi and PISi was only 4.5%. Among the TPSi flux, PISi and BSi accounted for 55.9 and 44.1%, respectively, and PISi flux was greater than BSi. The annual input of PISi from the Changjiang River mouth was much smaller than DISi, the former was only 3.5% of the latter, which is largely different from the case of P, showing that particulate-adsorbed Si was much less important than particulate-adsorbed P.

6.3 Dilution and Diffusion Fluxes of P and Si Intercepted in the TMZ

The statistics for all data of DIP, TP, DISi and salinity in the study area in February, May, August and November 2004 show strong negative linear relationships:

$$\text{DIP}\ (\mu\text{mol L}^{-1}) = 0.942 - 0.009\ \text{S}\ (r = 0.315, n = 251, p = 3.35 \times 10^{-7})$$
$$\text{TP}\ (\mu\text{mol L}^{-1}) = 2.463 - 0.034\ \text{S}\ (r = 0.323, n = 242, p = 2.69 \times 10^{-7})$$
$$\text{DISi}\ (\mu\text{mol L}^{-1}) = 126.7 - 3.226\ \text{S}\ (r = 0.876, n = 252, p = 2.89 \times 10^{-81}).$$

It shows that their behaviours depend mainly on dilution and diffusion of sea water in the estuary, and parts of the P and Si were intercepted in the TMZ during diffusion process. According to the average salinity of 22.82 at the sea water end-member in the TMZ, the average concentrations for DIP, TP and DISi were calculated to be 0.74, 1.68 and 53.1 μmol L^{-1}, respectively, using above equations. Thus, the ratios of the concentrations of DIP, TP and DISi in the freshwater end-member could be thought to be the input flux ratios of them at the river mouth. In other words, 21% of DIP, 32% of TP and 58% of DISi were intercepted in the TMZ. The intercepted and annual intercepted fluxes of DIP, TP and DISi through dilution and diffusion in the TMZ were calculated and listed in Table 3. The maximum interception flux was in DISi. The dilution and diffusion of TP included two parts. Part 1 was dissolved P which was intercepted (0.14 kg s^{-1}) mainly through dilution and diffusion, and the concentration decreased with the increase in salinity; Part 2 was particulate P that removed mainly through deposition during dilution and diffusion (Table 3).

6.4 Output of P and Si from the TMZ to the East China Sea

According to above calculation results, P and Si amounts in various forms transported from the TMZ to the East China Sea were listed in Table 3. The output flux and annual output of DOP were 0.05 kg s^{-1} and 0.142×10^4 t and those of TDP were 0.58 kg s^{-1},

1.838×10^4 t, respectively. It shows that the output flux of DIP accounted for 92.3% of TDP, dominating dissolved P, and was 78.5% of TIP or 44.3% of TP. The output flux of PIP accounted for 21.5% of TIP or 12.1% of TP, and TIP was 56.4% of TP. The output flux of TPP accounted for 52.6% of TP, and particulate inorganic active phosphorus (PIP) accounted for 23.3% of TPP. Among various forms of Si transported from the TMZ to the East China Sea, the output flux of DISi accounted for 91.5% of TISi, and PISi accounted for 8.5%. For TPSi, the PISi and BSi accounted for 55.9 and 44.1%, respectively, and PISi was more than BSi.

Table 3 shows that during the transportation of P and Si to the East China Sea, the fluxes of PIP, DIP, TIP, DOP, TDP, TPP and TP intercepted in the TMZ accounted for 60.8, 21.0, 35.2, 64.4, 27.8, 35.5 and 32.0% of those from the river mouth, respectively. It shows also that among intercepted P, the ratio of particulate P was greater than that of dissolved P; and the most of particulate-adsorbed inorganic P and over one-third of total particulate P were intercepted in the TMZ via deposition, well reflecting the role of filtration that the TMZ played, which could be important in preventing eutrophication in estuarine waters. In terms of Si, the fluxes of TISi, DISi, PISi, BSi and TPSi intercepted in the TMZ accounted for 56.1, 58.0, 16.1, 16.2 and 16.2% of those from the river mouth, respectively. Different from P, among intercepted Si, the ratio of the dissolved Si was clearly higher than that of the particulate Si. Most of particulate Si was transported to the East China Sea, and among particulate Si, the proportions of PISi and BSi were similar. The difference in existence form between Si and P was probably related to the original ratios at the river mouth. Among the input fluxes of P and Si at the river mouth, the ratio of TDP/TPP was 0.82, and the amount of particulate P was higher than that of dissolved P; the ratio of DISi/TPSi was 11.96, indicating dissolved Si was much higher than that of particulate Si.

Moreover, the ratio of particulate P flux deposited in the TMZ to that of discharged from the river mouth was much higher than that of particulate Si case. Therefore, P can be adsorbed more easily by suspended matter than Si. In the TMZ, adsorbed and deposited P and Si would be released into sea water through sediment resuspension and take part in a new material cycle. Among the particulate P transported from the river mouth into the East China Sea, 39.2% were potential biologically available P. They are important for phytoplankton growth and were also a potential reason of eutrophication in coastal environments.

To sum up, the fluvial suspended particulate matter of the Changjiang River and the resuspension of estuarine sediment play major roles in removing and transporting P and Si. In addition to dilution and diffusion, the removal of DIP and DISi in the estuary includes biological and non-biological aspects. The biological removal of DIP and DISi took place mainly in high-salinity area of the open sea, and the non-biological removal acts in adsorption and release of DIP and DISi by suspended matter mainly in the TMZ (low salinity area). Compared to DIP, DISi was controlled mainly by sea water dilution. Influenced by buffering of suspended matter and sediment resuspension in the TMZ, the DIP concentrations were kept in the levels of 0.48–1.2 μmol L^{-1}.

The fluxes of DIP, TP and DISi from the Changjiang River to the TMZ were estimated at 0.68, 1.79 and 84.92 kg s^{-1}, and those of PIP, TPP, PISi and BSi were 0.38, 0.98, 3.97 and 3.13 kg s^{-1}, respectively. The input flux of PIP was 55.9% of DIP that is important as biologically available P. Total active inorganic P (TIP) accounted for 59.2% of TP, being a main component of P, while the input flux of PISi was only 3.5% of DISi, showing that particulate-adsorbed Si was much less important than particulate-adsorbed P. Among P and Si transported from the Changjiang mouth to the TMZ, the dissolved component was intercepted mainly during dilution and diffusion, and the particulate component was removed mainly by deposition during dilution and diffusion. In the TMZ, over half of the sedimentation fluxes of particulate matter and bearing P and Si came from sediment resuspension. Most particulate-adsorbed inorganic P and over one-third of the total particulate P from the Changjiang River were intercepted in the TMZ through deposition. The particulate-adsorbed inorganic P accounted for 21.7% of total active inorganic P, which well indicates the role as a filter that the TMZ plays for potential prevention from eutrophication in estuarine waters.

Computation in mass balances was conducted for estimating the output fluxes and annual outputs of various forms of P and Si from the TMZ to the East China Sea, in which total active inorganic P accounted for 56.4% of TP, and PIP was 21.5% of TIP or 12.1% of TP, while PISi was only 8.5% of the TISi. The active inorganic P transported to the East China Sea, which could be a possible reason for eutrophication in coastal environments.

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Nutrient Dynamics of the Upwelling Area in the Changjiang Estuary

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Abstract Nutrient dynamics and its influence on the distribution of chlorophyll-a in the upwelling area of the Changjiang (Yangtze) River estuary were investigated in the spring (May) and summer (August) of 2004. The spring upwelling was apparent in the region of 122°20′–123°00′ E, 31°00′–32°00′ N and was associated with low temperature (16–21 °C), high salinity (24–33), and low dissolved oxygen (2.5–6.0 mg L^{-1}) in the upper 10 m of the water column. The spring upwelling increased the mixed-layer phosphate, nitrate, and silicate concentrations to roughly 1, 15, and 15 μmol L^{-1}, respectively, and improved the light transparency in the euphotic zone. This improvement in phytoplankton-growing conditions was followed by an increase in chlorophyll-a concentrations. The summer upwelling was weaker and occurred over a smaller geographical area (122°20′–123°00′ E, 31°15′–31°50′ N). Strongly influenced by turbid Changjiang diluted water (CDW), it had little impact on the upper 10 m of the water column but instead increased nutrient concentrations at greater depths. The high concentration of particulates in the CDW reduced light transmission in the upper 10 m and, hence, limited phytoplankton growth throughout the water column. Chlorophyll-a concentrations in the summer upwelling area were roughly an order of magnitude lower than in the spring. Water clarity, as influenced by the CDW, appears to be the principal factor limiting the impact of upwelling on phytoplankton biomass in this area.

Keywords Upwelling · Dynamics · Nutrient · Chlorophyll-*a* · Transparency Phytoplankton · Changjiang estuary

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Upwelling is important to the ecology of coastal marine ecosystems and ultimately to fish production (Cui and Street 2004; Oleg et al. 2003; Ryther 1969) because it can bring nutrients from intermediate depths into the euphotic zone and hence stimulate the phytoplankton community and primary production (Blasco et al. 1980, 1981; Margalef 1978a, b). Numerous previous studies have explored the dynamics and impacts of upwelling systems (e.g., Barber and Smith 1981; Smith et al. 1983). Most recently, Ramírez et al. (2005) reported an intense wind-driven spring upwelling event in the NW Alboran Sea, which temporally eased the nitrogen (N) limitation of the phytoplankton community, and Skliris and Djenidi (2006) pointed out that the upwelling of nitrate-rich deep water, both upstream and downstream of a submarine canyon off the NW Corsican coast, enhanced local primary production.

Coastal upwelling occurs along many parts of the Chinese coast and especially in the East China Sea. Hu (1994) anticipated the existence of summer upwelling there in an area between 27°30′ N and 30°30′ N and bordering 124°00′ E. Chen et al. (2004) surveyed the upwelling between 26°00′ N and 30°30′ N in the East China Sea during the summer of 1998 and evaluated the effects of the upwelling on primary production and nitrate-based new production. Wang and Wang (2007) studied the seasonal variations of coastal upwelling on the inner shelf of the East China Sea and estimated nutrient fluxes into the euphotic zone during the summer upwelling period.

In recent years, frequent outbreaks of red tides in the East China Sea have become a growing concern (Chen et al. 2003; Wang 2006). About 75% of those outbreaks have taken place in the Changjiang (Yangtze) River estuary (122°15′–123°10′ E, 30°30′–32°00′ N) (Chen et al. 2003). However, the upwelling in this area has received less attention than the well-known summer coastal upwelling in the East China Sea between 26°00′ N and 30°30′ N (Chen et al. 1999, 2004; Zhou et al. 2003). Upwelling in the estuary has been observed and documented since the early 1980s (Beardsley et al. 1983; Limeburner et al. 1983; Yu et al. 1983). Persistent upwelling in the region of 122°20′–123°10′ E, 31°00′–32°00′ N has been observed from May to August (Zhao 1993; Zhao et al. 1992, 2001). Zhao et al. (2001) concluded that summer upwelling in the estuary could transport high concentrations of nitrate, phosphate, and silicate into the upper 10 m of the water column, and the physical dynamics of this summer upwelling have been simulated mathematically (Pan and Sha 2004; Zhu 2003; Zhu et al. 2003b). There is little information, however, on the dynamics of nutrients or their influence on the distribution of chlorophyll-*a* (Chl-*a*) in the Changjiang River estuary during either the spring or summer upwelling periods.

In this section, we report data collected during two cruises to the Changjiang River estuary during May and August 2004 to quantify the impact of upwelling on the ecology of this ecosystem. The distributions of nutrients and nutrient structure, their effect on Chl-*a* concentrations, and the seasonal difference in Chl-*a* distributions were investigated. In addition, we estimated nutrient fluxes into the euphotic zone during the spring upwelling period and summarized spatial variations of hydrological parameters in the upwelling area as a reference for future studies concerned with the increasingly serious eutrophication and occurrence of harmful algal blooms in the Changjiang River estuary.

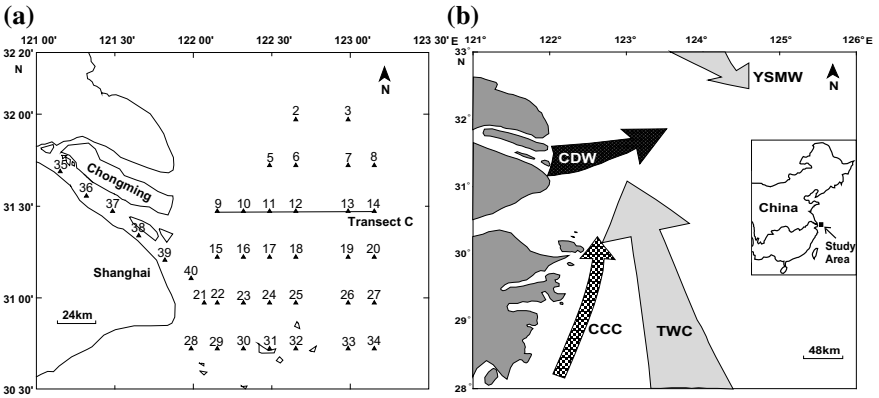

Fig. 1 **a** Sampling stations in the Changjiang estuary; **b** Distribution of water masses in Changjiang coastal area: TWC, Taiwan warm current; CDW, Changjiang diluted water; YSMW, Yellow sea mixing water; CCC, China coastal current

1 Study Area and Methods

The study area and sampling stations are shown in Fig. 1a. The current system in the area is complex (Katoh et al. 2000; Naimie et al. 2001; Su 1998; Zhang and Wang 2004), with two major currents, the Changjiang diluted water (CDW) and Taiwan warm current (TWC) (Fig. 1b), interacting and causing nutrient freshening and redistribution (Guo et al. 2003). These current interactions are modified locally by several other minor water masses: the China coastal current (CCC), the Yellow Sea mixing water (YSMW), and the Yellow Sea cold water mass (Zhou et al. 2003).

The CDW, as the name indicates, is the result of mixture of Changjiang River water with seawater in the deltaic region, which is rich in nutrients derived from land runoff. The CDW flows generally toward the northeast from May to October as indicated in Fig. 1b (Zhu 2003). The nutrient loads from the river have increased dramatically in past two decades as a result of the overuse of fertilizer and ill-managed discharges of industrial and household sewage (Gao and Song 2005; Shen et al. 2001; Wang 2006).

The TWC is characterized by high salinities (>29), temperatures ranging from 16 to 29.5 °C (Chen et al. 2003), and low dissolved oxygen (DO) concentrations. In the summer, the TWC originates mainly in the Taiwan Strait, but in the winter, most of the TWC originates in the Kuroshio Current, which moves onto the East China Sea shelf northeast of Taiwan (Chen and Sheu 2006). The TWC is rich in nutrients and a major source of nutrients in the study area (Zhou et al. 2003).

In summer, the TWC flows directly northeastward, passes through the Changjiang coastal area, reaches near 32°N, and induces upwelling in the Changjiang estuary (Bai and Hu 2004; Zhao 1993; Zhao et al. 1992, 2001; Zhu 2003). The upwelling in the study area is driven by several factors, including winds, submarine topography, and

currents. In general, the flow of the TWC as it moves northward along the slope of the submerged river valley off the mouth of the Changjiang River is primarily responsible for the upwelling, in combination with submarine topography and baroclinic effects resulting from the mixing of river water and seawater (Zhao 1993; Zhu 2003).

Cruises were carried out in May and August of 2004 to the Changjiang estuary and adjacent coastal waters. Water samples from 38 stations (Fig. 1a) were collected with Nansen samplers at depths of 0, 5, 10, 20, and 30 m and within the bottom layer of the water column and were then filtered through pre-combusted (450 °C for 6 h) Whatman GF/F filters (25 mm in diameter). Afterward, all samples were preserved with 0.3% chloroform in polyethylene bottles pretreated with 1:10 hydrochloric acid by volume for 24 h and then stored in an icebox at −25 °C before laboratory analysis.

Nutrients and Chl-*a* were measured using the methodologies of Shen et al. (2006), and DO using the Winkler method. Dissolved inorganic nitrogen (DIN) was calculated as the sum of NO_3–N, NO_2–N, and NH_4–N.

2 Nutrient Dynamics of the Upwelling Area in Spring

In the spring of 2004, river runoff increased sharply from an average of 18,000 m^3 s^{-1} in April to 35,700 m^3 s^{-1} in June as recorded at the Datong Hydrographic Station, which is located at the tidal limit of the Changjiang estuary, approximately 650 km upstream from the river mouth. This discharge was associated with a large influx of nutrients into the coastal zone. Profiles of temperature (T), salinity (S), and DO were used to determine the extent of coastal upwelling. The distribution of nutrients, nutrient ratios, and Chl-*a* in the upwelling area was examined as a function of depth (vertical profiles) and horizontally in typical water layers.

2.1 Vertical Distributions of Nutrient and Nutrient Ratio

Transect C (31°30′ N, Fig. 1a) was found to be representative with respect to system characteristics. Upwelling is evidenced by concave isolines of T, S, and DO along 122°20′–123°00′ E (Fig. 2a, c). Isotherms, between 16.5 and 20 °C, rise from the bottom toward the surface (Fig. 2a); the 16.5 °C line extends from ~30 to ~10 m; and the 19.5 °C isotherm extends almost to the surface. Isohalines ranging from 30 to 33 also show notable concavity; the 33 isohaline rises from almost 30 to 10 m (Fig. 2b). Dissolved oxygen isolines between 2.5 and 4 mg L^{-1} are notably concave (Fig. 2c), and the 4 mg L^{-1} isoline rises from ~15 to < 5 m. The direction of gradients between the isolines indicates that upwelled water is characterized by low temperature, high salinity, and low DO along 122°20′–123°00′ E and that this water reaches the euphotic zone above 5 m in the spring. Zhao (1993) documented similar phenomena. Moreover, influenced by upwelling, the thermocline shoaled by 10 m

and became thinner (Fig. 2a), and there was virtually no mixed layer in the region of most intense upwelling.

Upwelling clearly influenced the distribution of nutrients (Fig. 2d, i). The enrichment of near-surface waters with upwelled phosphate (PO_4–P) (Fig. 2d) resulted in closed elliptical phosphate isocontours between depths of ~25 and 8 m and longitudes of 122°25′ E to 122°38′ E. Peak PO_4–P concentrations were greater than 1.05 μmol L^{-1}, which is much higher than the concentration of ~0.5 μmol L^{-1} in waters surrounding the region of upwelling.

The distributions of nitrate (NO_3–N) and silicate (SiO_3–Si) were similar to that of PO_4–P with one noteworthy exception: The concentrations of NO_3–N and SiO_3–Si in the upwelled water were lower than the corresponding concentrations in the CDW (Fig. 2e, f). As a result, surface water NO_3–N and SiO_3–Si concentrations declined more or less monotonically in an onshore–offshore direction along Transect C, whereas PO_4–P concentrations peaked over the center of upwelling. This pattern contrasts with the earlier work of Zhao et al. (2001), which characterized the upwelling core as a center of maximum inorganic nutrient concentrations. This appears to be true for PO_4–P but not for NO_3–N and SiO_3–Si. Upwelled waters contained 13–18 μmol L^{-1} and 17–20 μmol L^{-1} of NO_3–N and SiO_3–Si, respectively, much lower than the corresponding concentrations in the CDW. The offshore transport of upwelled water did, however, produce a clearly discernible maximum in NO_3–N and SiO_3–Si at longitude 122°40′ E at a depth of ~5 m (Fig. 2e, f).

Dissolved inorganic nitrogen (DIN): PO_4–P ratios were relatively high (>40) in the CDW compared with upwelled water (<20) and offshore water (~20). There was consequently a more or less monotonic onshore–offshore decline in surface water DIN: PO_4–P ratios and a local minimum between roughly 10 and 30 m in the upwelling core (Fig. 2g). SiO_3–Si: DIN ratios, on the other hand, were lowest in the CDW water (<0.8) and highest in offshore water (~2.8). There was, consequently, a monotonic onshore–offshore increase in SiO_3–Si: DIN ratios and a localized maximum at depths of 10–20 m in the core of the upwelled water (Fig. 2h). The SiO_3–Si: PO_4–P ratios were lowest in upwelled water (~16) and highest in offshore water (~50). There was, consequently, a local minimum of SiO_3–Si: PO_4–P ratios in the core of the upwelled water at a depth of 10–15 m and a more or less monotonic onshore–offshore increase in surface water SiO_3–Si: PO_4–P ratios, punctuated by a local minimum near the center of the upwelling region (Fig. 2i).

Inorganic nutrient concentrations are not conservative quantities, and in this system, phytoplankton uptake had a discernible effect on nutrient concentrations within the euphotic zone in the vicinity of upwelling. Maximum Chl-*a* concentrations were ~16 μg L^{-1} (Fig. 2j). Assuming C:N and C:P ratios of 5.7 and 41 by weight, respectively (Redfield et al. 1963), and a C: Chl-*a* ratio of ~40 by weight (Riemann et al. 1989), a Chl-*a* concentration of 16 μg L^{-1} would be associated with phytoplankton N and P concentrations of 8 and 0.5 μmol L^{-1}, respectively. Thus, phytoplankton uptake very likely accounts for much of the vertical gradient in PO_4–P between the subsurface maximum of ~1.05 μmol L^{-1} and the surface concentration of ~0.6 μmol L^{-1} directly over the center of upwelling (Fig. 2d). Along Transect C surface Chl-*a* concentrations increased from 10 μg L^{-1} in the CDW to ~16 μg L^{-1} over the center

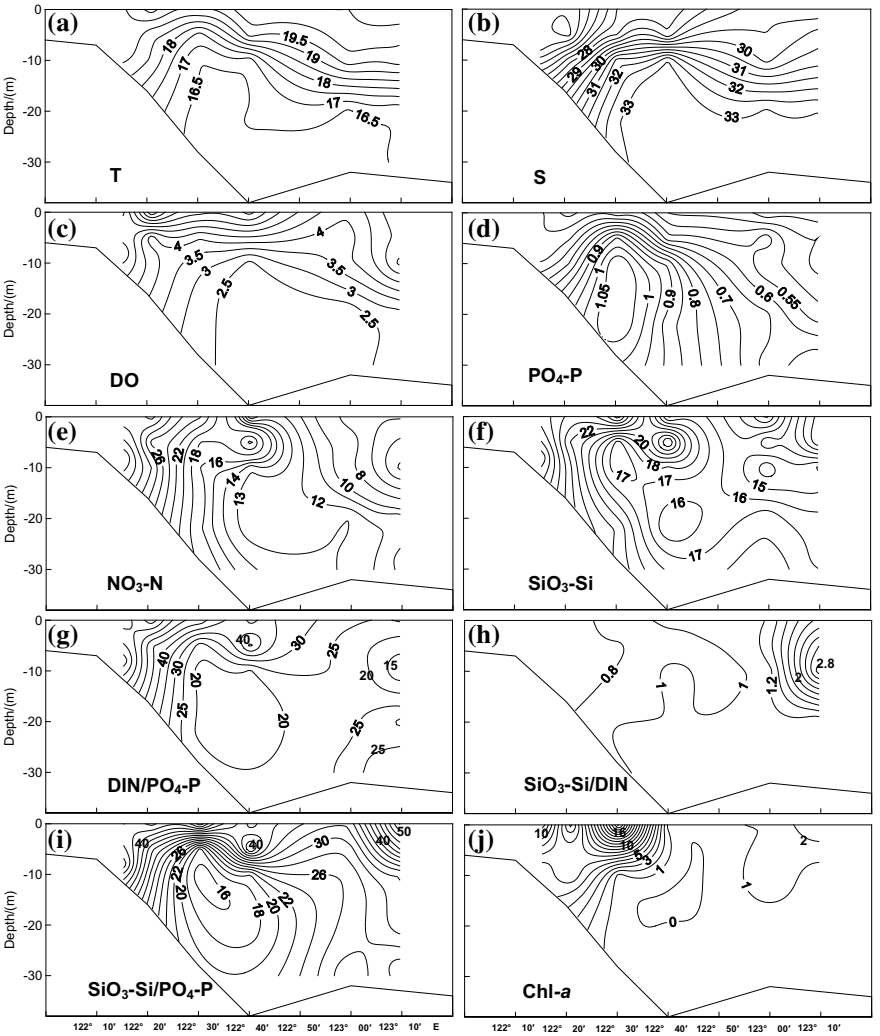

Fig. 2 Vertical distributions of temperature (T), salinity (S), dissolved oxygen (DO), nutrients, nutrient ratios, and chlorophyll-*a* (Chl-*a*) in Transect C in spring: **a** T (°C); **b** S; **c** DO (mg L^{-1}); **d** PO_4–P (μmol L^{-1}); **e** NO_3–N (μmol L^{-1}); **f** SiO_3–Si (μmol L^{-1}); g DIN: PO_4–P; h SiO_3–Si: DIN; i SiO_3–Si: PO_4–P; j Chl-*a* (μg L^{-1})

of upwelling. Nitrate concentrations along this same segment of the transect declined from ~26 to ~18 μmol L^{-1}. Roughly half of this decrease in NO_3–N was probably due to phytoplankton uptake.

2.2 Horizontal Distributions of Nutrient and Nutrient Ratio

The areal extent of the influence of upwelling is clearly shown in the horizontal pattern of water column properties at a depth of 10 m (Fig. 3). Upwelling of relatively cold and salty water with a low DO concentration is apparent in the area 122°20′–123°00′ E, 31°00′–32°00′ N, which includes Transect C (31°30′ N). A large, cooler area is evidenced by semienclosed isotherms of (<16.5–18 °C), whereas temperatures in the surrounding area were >18.5 °C (Fig. 3a). An onshore–offshore increase in salinity was punctuated by a local maximum of >32 at the center of upwelling (122°40′ E, 31°30′ N) and closed isohalines at 31 and 32 (Fig. 3b), consistent with an earlier report by Zhu et al. (2003a). Isocontours of DO between <2.5 mg L^{-1} and 3.5 mg L^{-1} formed ellipses around a minimum DO of ~2 mg L^{-1}, much lower than the DO of >4 mg L^{-1} in the surrounding area (Fig. 3c). The pattern of DO isolines is very similar to the pattern of isotherms in Fig. 3a. Moreover, horizontal extensions of isotherms, isohalines, and DO isolines indicate that the upwelling water extended into the area north of 32°00′ N.

Within the upper 10 m of the water column, both physical and biological processes influenced inorganic nutrient concentrations, but at depths ≤10 m, phytoplankton concentrations were too low to have a significant impact on the distribution of nutrients (Fig. 2j). At the surface, a large area with PO_4–P concentrations as high as 0.7–1.0 μmol L^{-1} appeared near the river mouth, whereas in the upwelling area, surface PO_4–P concentration was lower (0.4–0.6 μmol L^{-1}) (Table 1), undoubtedly a reflection of phytoplankton uptake (see above). At a depth of 10 m, two notable PO_4–P local maxima were apparent (Fig. 3d). One was located in the northern upwelling area, where PO_4–P concentrations were 0.7–1.0 μmol L^{-1}, and even >1.0 μmol L^{-1} in the center of upwelling. Another local maximum was located in the southwest part (122°00′–122°15′ E, 30°45′–31°00′ N) of the study area, where PO_4–P concentrations were >1.1 μmol L^{-1} and were probably released from the suspended particulate matter (SPM) in the north of Hangzhou Bay, where tides, such as the famous Qiantang tide, are exceptional (Shen et al. 2008). In the bottom layer, a single area of phosphate-rich water was apparent in the area of upwelling (Table 1, figure not shown), with elliptical isolines corresponding to PO_4–P concentration >1.0 μmol L^{-1} and semienclosed isolines associated with PO_4–P concentrations of 0.8–0.9 μmol L^{-1}.

Throughout most of the study area, and certainly at depths greater than 10 m, physical processes and the high concentrations of nutrients in source waters (i.e., CDW and upwelled water) largely determined the distributions of NO_3–N and SiO_3–Si. Thus, surface water NO_3–N and SiO_3–Si concentrations generally declined in an onshore–offshore direction (Fig. 3e, f). However, there was a local minimum of 10–15 μmol L^{-1} in surface water NO_3–N concentrations (Fig. 3e) near the center of upwelling. This minimum appears attributable to phytoplankton uptake. Chl-*a* concentrations peaked in the same area at 10–14 μg L^{-1}. These high Chl-*a* values would be associated with a phytoplankton biomass of 5–7 μmol L^{-1} (see above) and could thus easily account for the local minimum in nitrate concentrations. A

Table 1 Spatial variations of T, S, DO, nutrient concentrations, and nutrient ratios in all layers of upwelling in spring and summer

Months	Layers	T	S	DO	NO_3–N	PO_4–P	SiO_3–Si	DIN:P	Si:DIN	Si:P	Chl–a
		°C		mg L^{-1}	μmolL^{-1}	μmolL^{-1}	μmolL^{-1}				μg L^{-1}
May	0 m	19.8–20.8	24–30	4–6	10–30	0.4–0.6	15–30	30–70	0.8–1.5	30–45	1–19.5
	10 m	<16.5–18	24–32.5	< 2.5–3.5	10–20	0.7–1.1	10–20	< 20–30	0.7–1.5	<15–25	1–16.6
	20 m	16.2–16.6	31–34	2–2.8	10–15	0.7–1.1	10–18	15–22	0.8–1	12–25	0.15–0.5
	Bottom	≤16.5	31–34	< 2.5	10–20	0.8–1.1	10–20	20–30	0.7–1	10–25	0.25–0.5
August	0 m	25.8–26.2	14–30	6.4–7.2	5–50	0.4–0.6	20–100	20–70	2.2–3	40–160	0.5–2.5
	10 m	24–25.4	24–32	3.5–5.5	3–20	0.4–0.6	15–40	5–45	1.6–3	15–70	0.5–1
	20 m	21.6–24	28–34	< 2.5–4	3–10	0.7–1.2	15–30	10–20	2.3–3	20–40	0.1–0.5
	Bottom	22–23.5	28–34	< 2.5–4	5–15	0.7–1.4	25–40	10–20	2.4–2.6	20–40	0.5

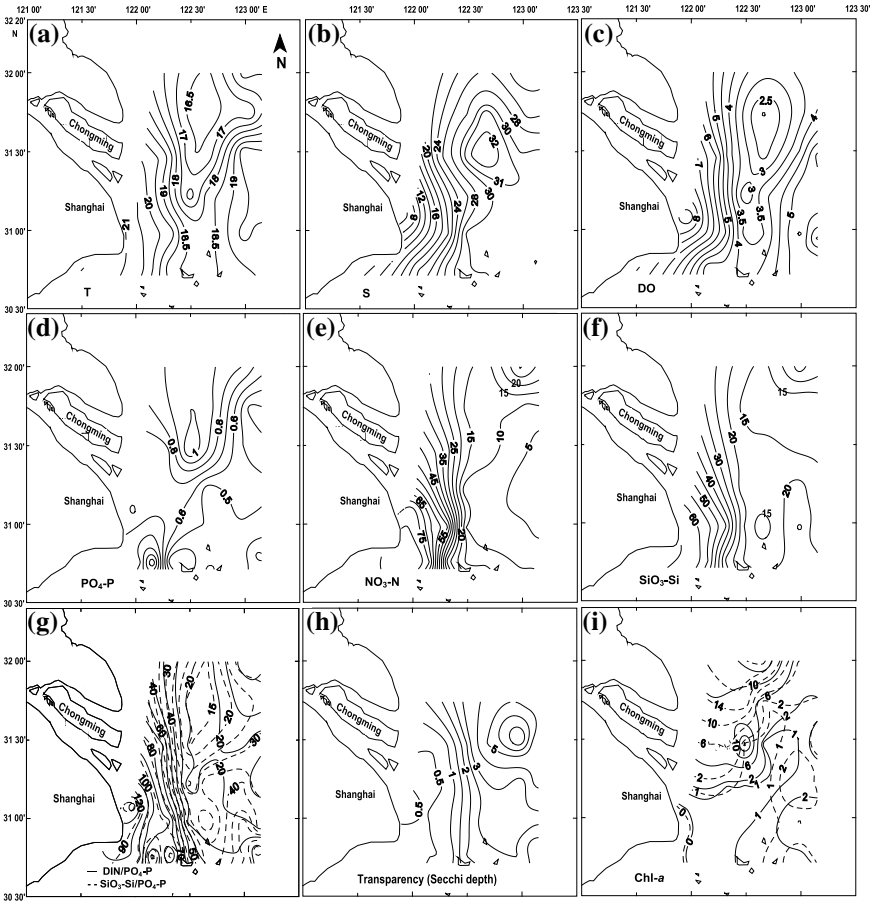

Fig. 3 Horizontal distributions of T, S, DO, nutrients, nutrient ratios, transparency (Secchi depth), and Chl-*a* in spring: **a** T (°C); **b** S; **c** DO(mg L^{-1}); **d** PO_4–P (μmol L^{-1}); **e** NO_3–N (μmol L^{-1}); **f** SiO_3–Si (μmol L^{-1}); **g** DIN: PO_4–P(—), SiO_3–Si: PO_4–P (----); h transparency (Secchi depth [m]); i Chl-*a* (μg L^{-1}) in the surface layer (—) and in the 10 m layer (----)

local minimum in surface water SiO_3–Si concentrations (< 15 μmol L^{-1}) in roughly the same area (Fig. 3f) may also reflect biological uptake. Under nutrient-replete conditions, the Si: N atomic ratio in diatoms is about 1 (Brzezinski 1985). If diatoms accounted for most of the high Chl-*a* biomass, then the associated uptake of NO_3–N and SiO_3–Si should be roughly equal.

The patterns of DIN: PO_4–P and SiO_3–Si: PO_4–P (Fig. 3g) both show local minima near the center of upwelling. These minima reflect the lower DIN: PO_4–P and SiO_3–Si: PO_4–P ratios in the upwelled water than in the CDW (Fig. 2g, i). With the exception of these local minima, DIN: PO_4–P and SiO_3–Si: PO_4–P ratios declined in

an onshore–offshore direction, a reflection of the higher DIN: PO_4–P and SiO_3–Si: PO_4–P ratios in the CDW than in the offshore waters of the East China Sea.

2.3 *Chlorophyll-a Distribution in Spring*

The roughly twofold difference in Chl-*a* concentrations between the mouth of the Changjiang River (~5–10 μg L^{-1}) and the center of upwelling (15–20 μg L^{-1}) (Fig. 3i) appears to reflect largely physical factors because inorganic nutrient concentrations in both areas were more than adequate to support rapid phytoplankton growth. Near the river mouth, Secchi depths were only ~0.5 m (Fig. 3h), which means that the depth of the euphotic zone (1% irradiance) was only ~1.4 m. Clearly, photosynthetic rates were severely light-limited near the river mouth, a conclusion consistent with the earlier study of Chen et al. (2003). In the upwelling area, on the other hand, Secchi depths ranged between 1.5 and >4.9 m, implying euphotic zone depths of 4 to >13 m. Thus, there was considerably less light limitation in the vicinity of the upwelling. Compounding the effect of slow growth rates in the mouth of the river is the increasingly rapid rate of river discharge, from 18,000 m^3 s^{-1} in April to 35,700 m^3 s^{-1} in June. The increase in discharge would tend to flush slowly growing cells out to sea.

3 Nutrient Dynamics of the Upwelling Area in Summer

Previous numerical studies (Zhu 2003; Zhu et al. 2003b) have suggested the existence of upwelling along the west side of the Changjiang submarine river valley in summer, driven mainly by the TWC as it ascends the submarine slope of the East China Sea. However, the numerical study of Pan and Sha (2004) has indicated that the greater the CDW discharge, the weaker the upwelling in the estuary. The Changjiang River discharge in August averages 43,000 m^3 s^{-1} (Chen et al. 2003) and in August of 2004 was considerably higher than in May. The resultant vertical salinity gradient depressed upwelling. A comparison of temperature isotherms in spring and summer (Figs. 2a and 4a) reveals that the temperature difference between the surface and upwelled water was about the same (~3 °C) in both seasons. However, along Transect C, salinity in the upper 10 m of the water column over the submarine slope was about 3–5 lower in summer than in spring (Fig. 4b vs. Figure 2b), and during the summer, water containing less than 4 mg L^{-1} DO never penetrated shallower than 10 m (compare Figs. 2c and 4c). Summer upwelling was clearly weaker than spring upwelling in 2004, although the size and flow of the TWC in summer were much greater (Bai and Hu 2004; Jan and Chao 2003; Zhang and Wang 2004). Summer upwelling in 1985 (Zhao et al. 2001) penetrated to shallower depths than in 2004; the difference may reflect annual variations in ocean currents.

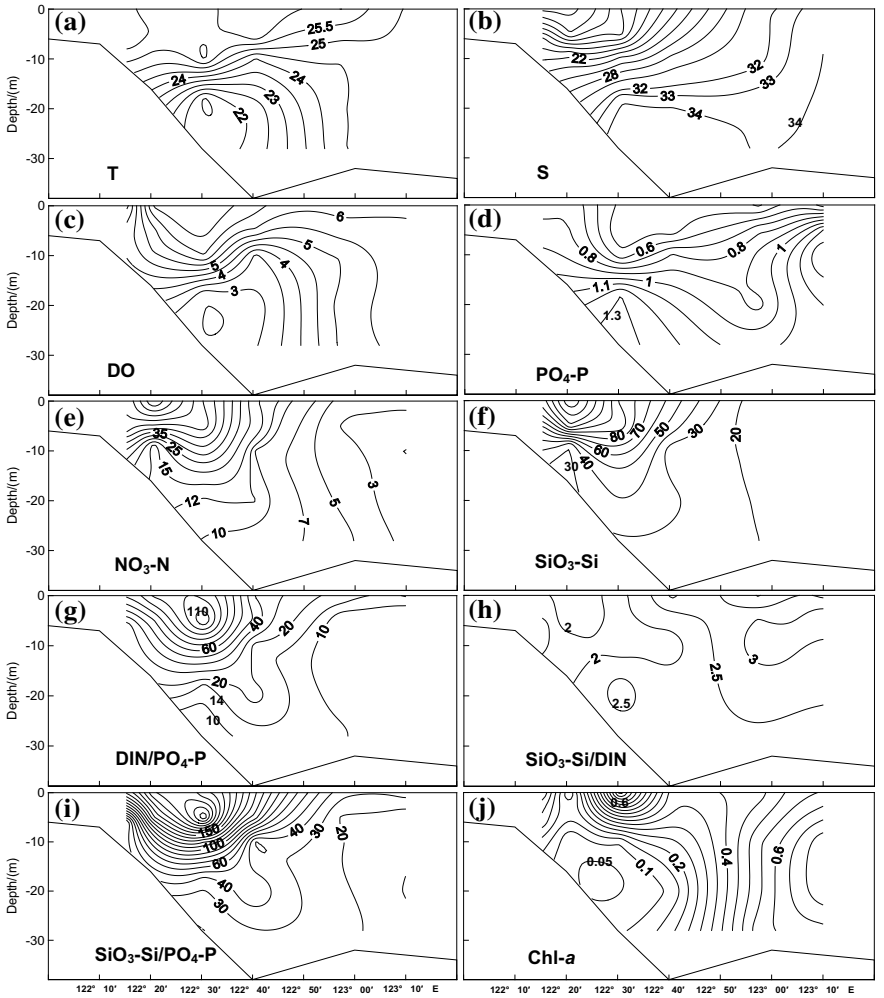

Fig. 4 Vertical distributions of T, S, DO, nutrients, nutrient ratios, and Chl-*a* in Transect C in summer. **a** T (°C); **b** S; **c** DO (mg L^{-1}); **d** PO_4–P (μmol L^{-1}); **e** NO_3–N (μmol L^{-1}); **f** SiO_3–Si (μmol L^{-1}); **g** DIN: PO_4–P; **h** SiO_3–Si:DIN; **i** SiO_3–Si: P O_4–P; **j** Chl-*a* (μg L^{-1})

3.1 Vertical Distribution of Nutrient

As in the spring, upwelling during the summer was very apparent along 122°20′–123°00′ E (Fig. 4). However, the salinity gradient in the upper water column prevented upwelled water from penetrating shallower than ~10 m. The doming of nutrient isolines indicates that summer upwelling carried TWC waters to depths of 10–15 m (Fig. 4d, f). However, the concentrations of NO_3–N and SiO_3–Si in the upwelled water were clearly less than the corresponding concentrations in the

CDW (Fig. 4e, f). The upwelled water contained higher nutrient concentrations than the CDW only in the case of PO_4–P. Isolines of PO_4–P progressed upslope east of 122°20′ E (Fig. 4d) and reached concentrations of 1.0–1.3 μmol L^{-1} at depths of 15–25 m, much higher than in the surface waters (~0.5 μmol L^{-1}). Concentrations of NO_3–N and SiO_3–Si decreased with increasing depth over the slope, reflecting higher nutrients concentrations in the CDW than in the upwelled water. This pattern contrasts with the distribution of nutrients reported by Zhao et al. (2001) during the summer of 1985, when upwelled waters contained higher concentrations of all nutrients relative to the CDW and surrounding waters. This undoubtedly reflects the roughly threefold increase in DIN and PO_4–P concentrations in the Changjiang River between 1985 and 2004 (Wang 2006).

3.2 Horizontal Distribution of Nutrient

Driven by the upslope flow of the TWC, upwelled waters intruded onshore from 122°25′ E to 122°20′ E. This is apparent not only in Transect C (Fig. 4) but also in horizontal isolines of T, S, and DO at different depths (Fig. 5). In the bottom layer, upwelled waters were apparent to the east of 122°25′ E as semienclosed isolines of low T, high S, and low DO. Temperature in the central upwelling area was <22 °C, 3 °C lower than in the surrounding water (Fig. 5a). The 34 isohaline extended shoreward in a tongue-like shape, evidence of the intrusion of high-salinity upwelled water (Fig. 5b). Dissolved oxygen concentrations in the upwelling area were <2.5 mg L^{-1}, compared with 5 mg L^{-1} in surrounding waters (Fig. 5c). At a depth of 20 m, upwelling was evidenced by semienclosed isolines of low T and low DO (Table 1, figure not shown). The area of cooler water became noticeably smaller at shallower depths. In the upper 10 m of the water column, few hydrological effects associated with upwelling were observed, but a local minimum in temperature (25.8–26.2 °C) was apparent at the surface in the area 122°10′–122°40′ E, 31°10′–31°45′ N (Fig. 5a). This likely reflects the divergent flow of surface waters in response to the upwelling. Similar cases of cold surface waters during the summer have been recorded many times by satellite remote sensing in the past (Zhu 2003).

At the surface, PO_4–P concentration decreased in an onshore–offshore direction, similar to the pattern observed during the spring (Figs. 3d and 5d). Surface PO_4–P concentrations were highest near the river mouth (~1.4 μmol L^{-1}), comparable to the values observed in the bottom layer in the upwelling area but clearly higher than the surface water PO_4–P concentrations in the vicinity of upwelling. In this case, phytoplankton uptake had little impact on inorganic nutrient concentrations. Peak Chl-*a* concentrations were only ~4 μg L^{-1}, which would imply uptake of roughly 2 μmol L^{-1} DIN and 0.125 μmol L^{-1} PO_4–P.

In all horizontal layers, the concentrations of NO_3–N and SiO_3–Si decreased from the river mouth to the open sea eastward (Fig. 5e, f). Because of the strong influence of the nutrient-rich CDW, surface concentrations of NO_3–N and SiO_3–Si were high in the river mouth, 60–75 μmol L^{-1} and 100–140 μmol L^{-1}, respectively.

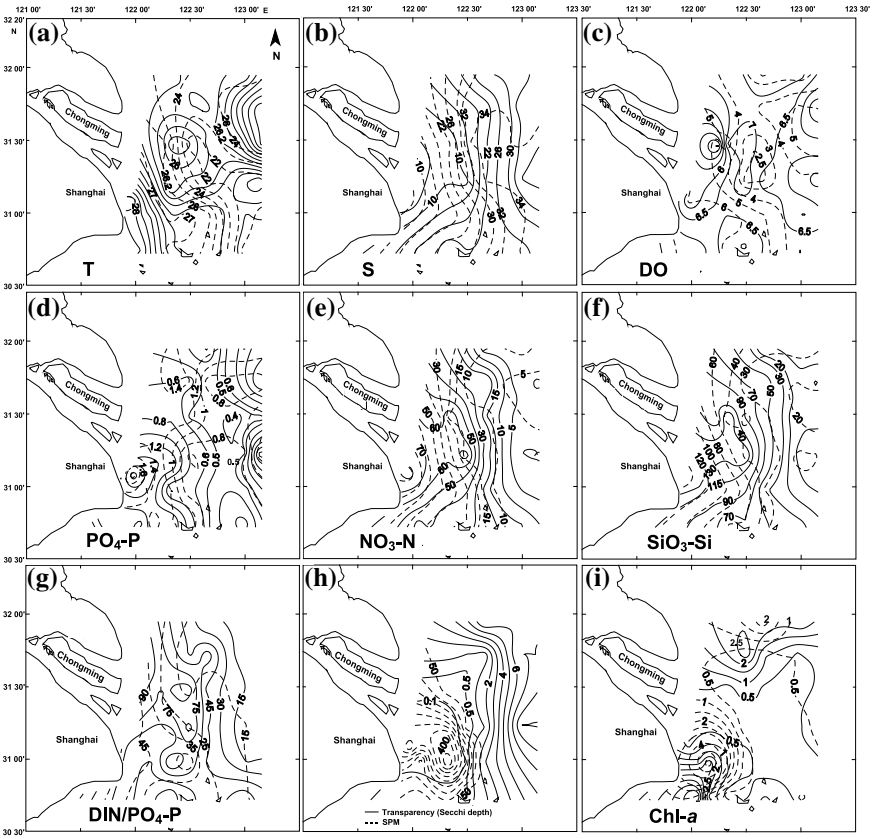

Fig. 5 Horizontal distributions of T, S, DO, nutrients, nutrient ratio, transparency (Secchi depth), suspended particulate matter (SPM), and Chl-*a* in summer. **a** T (°C); **b** S; **c** DO (mg L^{-1}); **d** PO_4–P (μmol L^{-1}); **e** NO_3–N (μmol L^{-1}); **f** SiO_3–Si (μmol L^{-1}); **g** DIN: PO_4–P; (**a–g** in the surface layer [—], in the bottom layer [----]); **h** transparency (—) (Secchi depth [m]), SPM (----) (mg L^{-1}); i Chl-*a* (μg L^{-1}) (in the surface layer [—], in the 10 m layer [----])

Corresponding surface concentrations in the upwelling area were 5–50 μmol L^{-1} and 20–100 μmol L^{-1}. From 10 m to the bottom in the upwelling area, NO_3–N and SiO_3–Si concentrations ranged from 3 to 20 μmol L^{-1} and 15 to 40 μmol L^{-1}, respectively (Table 1).

The foregoing analysis indicates that upwelling during the summer occurred below 10 m primarily in the region 122°20′–123°00′ E, 31°15′–31°50′ N. Throughout the study area, the nutrient distributions of PO_4–P, NO_3–N, and SiO_3–Si in the surface layer were controlled by the CDW (Fig. 5d, f). Below 10 m, they were influenced considerably by upwelling.

3.3 *Chlorophyll-a Distribution in Summer and Its Seasonal Difference*

Inorganic nutrient concentrations in the upper 10 m of the water column were clearly adequate to support phytoplankton blooms, but the highest Chl-*a* concentrations in the upwelling area were only ~0.5–1.0 μg L^{-1} (Figs. 4j and 5i). Surface water PO_4–P concentrations were at least 0.4 μmol L^{-1}, which is adequate to support a phytoplankton biomass of ~13 μg L^{-1} Chl-*a* (see above). Nitrate and SiO_3–Si were present in even greater abundance relative to the needs of phytoplankton. Dissolved inorganic nitrogen: PO_4–P was above 60 (Figs. 4g and 5g); SiO_3–Si: DIN was from 2 to 2.4 (Fig. 4h), and SiO_3–Si: PO_4–P was from 100 to 160 (Fig. 4i). Clearly, phytoplankton biomass was not nutrient-limited. Why was the phytoplankton biomass so much higher in the spring than in the summer?

The answer appears to be extreme light limitation during the summer upwelling period. Secchi depths in the upwelling area were only ~0.5 m in the summer (Fig. 5h), the depth of the euphotic zone, therefore, being only about 1.4 m. Surface Chl-a concentrations increased from 0.5 to 2.5 μg L^{-1} at 31°30′ N (Fig. 5i), where Secchi depths were greater than 5 m. The low transparency during the summer was caused by the strong discharge of low salinity and turbid waters from the CDW (SPM is 50 to >400 mg L^{-1}) (Fig. 5h), which overflowed clearer TWC waters and prevented upwelling from penetrating to depths shallower than 10 m.

4 Compared the Spring Upwelling with the Summer Upwelling

Spatial variations of hydrological parameters in the upwelling area in spring and summer are summarized in Table 1.

In the spring, upwelling was apparent in the region of 122°20′–123°00′ E, 31°00′–32°00′ N and was characterized by low temperature (16–21 °C), high salinity (24–33), and low DO (2.5–6.0 mg L^{-1}) in the upper 10 m of the water column. The spring upwelling increased mixed-layer PO_4–P, NO_3–N, SiO_3–Si concentrations and improved light transparency in the euphotic zone. This improvement in phytoplankton-growing conditions was followed by an increase in Chl-*a* concentrations. The summer upwelling was weaker and occurred over a smaller geographical area (122°20′–123°00′ E, 31°15′–31°50′ N). Strongly influenced by turbid CDW, it had little impact on the upper 10 m of the water column but, instead, increased nutrient concentrations at greater depths.

The impact of upwelling on phytoplankton biomass over the submarine slope offshore of the Changjiang River is modulated very much by the discharge of turbid water from the river. During May 2004, the depth of the euphotic zone in the mouth of the river was only ~1.4 m, and phytoplankton biomass was very much constrained by light limitation. The plume of turbid CDW, however, did not extend far enough from

shore to restrict upwelling or prevent a bloom of phytoplankton from developing in the vicinity of 122°20′ E, where the depth of the euphotic zone was 4–13 m. By August 2004, the plume of turbid CDW extended far enough from shore to prevent upwelled waters from reaching the euphotic zone, which was only ~1.4 m deep.

5 Estimation of Nutrient Fluxes in the Spring Upwelling

Our foregoing analyses suggest that coastal upwelling was most obvious in spring and carried rich phosphate but relatively low-content nitrate and silicate into the upper layers, which optimized local nutrient supplies to a relatively large extent and thus stimulated the growth of phytoplankton. However, compared with the Changjiang runoff, which one carried a higher concentration of nutrients? And which one had a more significant impact? Little study has been carried out on these questions. Nutrient fluxes of spring upwelling were estimated in this section and were compared with the historical data of the nutrient fluxes from the Changjiang runoff in order to provide valuable references for the future study of eutrophication and the mechanism of red tides.

5.1 Calculation Method and Result

In this section, we followed the method reported by Chen and Ruan (1996) for the estimation of nutrient fluxes in the upwelling area of Taiwan Strait to estimate the vertical fluxes of nitrogen, phosphorus, and silicon in the upwelling area of the Changjiang estuary. The equation is:

$$P = a \cdot C \cdot W \tag{1}$$

where P (g m^{-2} d^{-1}) is the nutrient vertical flux from the bottom into the upper layer carried by upwelled water, a is a unit conversion factor, C (μmol L^{-1}) is the concentration of nutrient, and W (m s^{-1}) is the speed of upwelling.

Since the upwelling speed ranged between 1.0×10^{-5}–5.0×10^{-5} m s^{-1} according to the calculation of Zhao (1993), the nutrient vertical fluxes can be estimated as a range accordingly. In addition, the upwelling region and its corresponding average nutrient concentrations are able to be calculated in accordance with the nutrient distributions which were influenced significantly by upwelling at the 10 m depth. The estimated ranges of nutrient fluxes (kg s^{-1}) by Eq. (1) are listed in Table 2.

The estimation of PO_4–P vertical flux was calculated individually for four subzones defined by the variation of average concentration in the layer of 10 m, and then the total PO_4–P flux at the 10 m depth was calculated to be 1.4–7.0 kg s^{-1} (or

Table 2 Comparison nutrient vertical fluxes in the upwelling area with input fluxes from the Changjiang runoff

Nutrients	Areas	Average concentrations	Speeds	Vertical fluxes	Fluxes	Changjiang runoff Shen (1993)
	$\times 10^6$ m^2	μmol L^{-1}	$\times 10^{-5}$m s^{-1}	mg m^{-2} d^{-1}	kg s^{-1}	kg s^{-1}
PO_4–P	268.53	1.0	1–5	26.76–133.8	1.4–7.0	0.43
	2612.02	0.95	1–5	25.42–127.1		
	1379.25	0.85	1–5	22.75–113.75		
	805.58	0.75	1–5	20.07–100.35		
SiO_3–Si	5065.37	14.62	1–5	354.77–1773.85	20.8–104	63.3
NO_3–N	5065.37	13.38	1–5	161.92–809.6	9.49–47.45	20.0
DIN	5065.37	16.42	1–5	198.71–993.55	11.65–58.25	27.9

23.91–119.57 mg m^{-2} d^{-1}) by the weighted sum for four subzones. Our estimation is obviously higher than 10.03–50.16 mg m^{-2} d^{-1} reported by Yang et al. (2005) according to the investigation result of East China Sea in 1998.

5.2 Nutrient Fluxes Comparison

The estimated PO_4–P flux above in the spring upwelling was much higher than the Changjiang runoff inputting calculated by Shen (1993) based on investigations during 1985 and 1986 (Table 2), and the estimated minimum was more than twice higher than the flux from the Changjiang runoff, which might affect the distribution of PO_4–P and the growth of phytoplankton and therefore become a factor worth paying attention to. Comparatively, the fluxes of SiO_3–Si, NO_3–N, and DIN were less in the upwelled water, since their minima only accounted for 33.3, 47.6 and 41.7%, respectively, of the corresponding fluxes from the Changjiang runoff. It is noteworthy that only nutrient fluxes in spring were calculated in this chapter, and it is possible that the nutrient fluxes in spring were higher than the annual average nutrient fluxes in the upwelling area. Calculated results above are consistent with the observation of nutrient distribution patterns. The upwelled water with high PO_4–P but relatively low NO_3–N and SiO_3–Si were able to change the nutrient structure in this area and subsequently impacted on the phytoplankton growth. Our current results show that the ratios of nutrient fluxes in the upwelling to those from the Changjiang runoff ranged 3.3–16.2, 0.33–1.6, 0.47–2.4 and 0.42–2.1 for PO_4–P, SiO_3–Si, NO_3–N, and DIN, respectively (Table 2). So many amounts of nutrients, especially PO_4–P, were carried from the bottom into the upper layers by the upwelled water that upwelling becomes one of the major nutrient sources in the studied area and probably exerts an

Table 3 Comparison nutrient fluxes (mg m^{-2} d^{-1}) in the upwelling area of the Changjiang River estuary with other coastal upwelling areas (Chen and Ruan 1996)

Nutrients	Changjiang estuary	Zhoushan and Yushan Fisheries	Middle and north Taiwan Strait	Southern Fujian and Taiwan Shallow fisheries	Zhejiang coastal	East Guang-dong coastal
PO_4–P	23.91–119.57	38–189	23.6	13.2		46.5
SiO_3–Si	354.77–1773.85	669–3348	302	264		
NO_3–N	161.92–809.6	165–824	223	88.5	33.87–2143.7	
years	2004	1984	1988	1988	1981	
References	This section	Wang and Zang (1987)	Chen and Ruan (1996)	Wu and Ruan (1991)	Lei (1984)	Han and Ma (1988)

impact that cannot be ignored on the eutrophication in the Changjiang River estuary. Of course, it is different in nutrient fluxes from the Changjiang runoff in different years. Previous study showed that there were clear positive relationships between the nutrient export fluxes in the Changjiang mouth and the river's runoff (Shen 1993; Shen et al.2003, 2009). Therefore, the nutrient fluxes from the Changjiang runoff change with the change of the Changjiang runoff. For example, in 1998 of especially heavy flood, the PO_4–P, NO_3–N, and DIN fluxes from the Changjiang runoff were 0.74, 45.59, and 55.38 kg s^{-1}, respectively, being 1.7, 2.3, and 2.0 times of those in 1985–1986.

Comparison of nutrient fluxes in the upwelling area of the Changjiang River estuary with other upwelling areas (Table 3) shows that all calculated results are of the same order of magnitude. The nutrient fluxes in the upwelling areas of Zhoushan Fishery and Yushan Fishery were relatively high, and fluxes were relatively high in the upwelling area of Changjiang River estuary as well, compared with other coastal upwelling areas.

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A New Method for Estimating Fine-Sediment Resuspension Ratios in Estuaries—Takes the Changjiang Estuary as an Example

Zhiliang Shen

Abstract Based on the principle of conservative matter removal in estuary, a new method is proposed for estimating the ratio of sediment resuspension in estuaries with fine-suspended sediments. Nearly half of the particulate matter in the turbidity maximum zone (TMZ) of the Changjiang (Yangtze) estuary originates from sediment resuspension, indicating that sediment resuspension is one of the major mechanisms involved in formation of the TMZ. Compared with traditional method for calculating these ratios in the estuary, this new method evaluates the dynamic variation of SPM content carried by river runoff from the river mouth to the ocean. The new method produced more reliable results than the traditional one and could produce a better estimation of resuspension flux for particulate matter in estuaries.

Keywords Sediment · Suspended particulate matter · Resuspension ratio Estimate method · Turbidity maximum zone · Changjiang (Yangtze) estuary

The turbidity maximum zone (TMZ) is a prevalent phenomenon in rivers within estuaries, and it plays many important roles in sediment processes in estuarine environments (Pan et al. 1999). The study of suspended matter in estuaries has become a hot topic in marine sciences (Allen et al. 1980; Herman and Heip 1999; Turner and Millward 2002; Webster and Lemckert 2002; Suzumura et al. 2004). The study on measuring sediment resuspension is an important subject. Current methods to measure sediment resuspension involve using optical and acoustical instruments, instantaneous multiple point water samplers, sediment traps, sediment cores and grabs, radiotracers (e.g., Pb-210, Cs-137 and Be-7), mass balance calculations, various modeling approaches, statistical methods (correlation analysis), and laboratory experiments (Bloesch 1994).

Globally, the Changjiang (Yangtze) River is the third largest river in length (6300 km) and the fourth largest in sediment discharge (5×10^8 t a^{-1}). Thus, the study of SPM in the TMZ of the Changjiang estuary has received much attention

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from oceanographers. These studies include, for example, the distribution, transport, and diffusion of SPM (Milliman et al. 1985; Su and Wang 1986; He and Yun 1998) and sediment resuspension (Li and Zhang 1998; Li et al. 2000). However, there are few reports on measuring sediment resuspension in the Changjiang estuary. Chen et al. (2004) estimated the ratio of sediment resuspension in the Changjiang estuary using a traditional method based on a constant suspended sediment load along the estuary. Shen et al. (2008) suggested a new method to calculate the ratio of sediment resuspension in the TMZ in the Changjiang estuary. This section takes the TMZ of the Changjiang estuary as an example, the two estimation methods (Shen's and traditional methods) are compared, and the principles of Shen's method are introduced herein. These principles underpin a better approach for estimating the ratio.

1 Study Area and Sampling

The average runoff of the Changjiang River to the East China Sea is about 29,000 m^3 s^{-1} or 9282 $\times$ 10^8 m^3 a^{-1}, most of which occurs in the flood season from May to October, accounting for over 70% of the annual total of runoff. Investigations were carried out on February, May, September, and November, 2005. Water samples were collected for SPM and salinity (S) from the surface layer at 40 stations, from station 35 in downstream Xuliujing to 123° 20′E and 30° 45′–32° 00′N (Fig. 1). Near Xuliujing at the river mouth, Changjiang River divides into South and North Branches, with runoff and SPM being transported to the ocean mainly through the South Branch (Milliman et al. 1985). A special high SPM content zone was found in the river mouth-bar area, where the TMZ exists all year round. Tides in the Changjiang estuary are of moderate intensity and are of regular semi-diurnal type, with an average tidal difference of 2.67 m at the river mouth. The turbidity maximum in Changjiang estuary is induced by runoff-tidal current interaction and salt and freshwater mixing. The space-time distribution of the turbidity maximum changes with changes in runoff, tidal currents, and salt and freshwater mixing (Pan et al. 1999). Maximum water depths are about 50 m over the whole observation area and 12 m in the TMZ itself. The TMZ is often stratified in the flood season at water depths of more than 10 m. Seasonal variations in wind-driven waves in the estuary are apparent: in winter northern wind waves are vigorous, while in summer southeast and southern ones are dominant but less vigorous. Average wave height is 10 cm higher in winter than in summer, with wind waves greater than Scale 5 in winter, which is 3 times more than those in summer (Luo and Shen 1994). Influenced by wind, tides, and currents, SPM in the TMZ of the estuary is frequently disturbed by cycles of suspension, sedimentation, resuspension, and resedimentation (Shen and Pan 2001). Much previous research has reported that sediment resuspension occurs 3–4 times in a tidal cycle in the river mouth-bar area (Pan et al. 1999; Li et al. 2000). Hence, sediment resuspension is important with respect to changing SPM content in the estuarine waters.

2 Calculation Method

2.1 Calculation Method and Principle

The new method introduced in detail in this paper is based on the principle of conservative matter removal from the estuary, using potential mixing/dilution lines (theoretical dilution lines) for fresh- and salt-water in Changjiang estuary, and comparing this to measured values, in order to calculate the ratios of sediment resuspension in the TMZ (see shaded area in Fig. 1). The method is expected to be applied only for fine-grained material in estuaries, as their behaviors in estuaries are close to that for conservative matter. Correlation statistics show that there are strong negative linear relationships between SPM and salinity with the correlation coefficients r of 0.491 (p = 0.003), 0.356 (p = 0.036), 0.604 (p = 0.00041), and 0.641 (p = 0.000059) in February, May, September, and November, respectively, suggesting that the behaviors of SPM in the Changjiang River estuary were conservative to a great extent. Due to the mixing of river water and seawater, SPM carried by river runoff is diluted and diffused, and its content decreases gradually in the transport from the river mouth

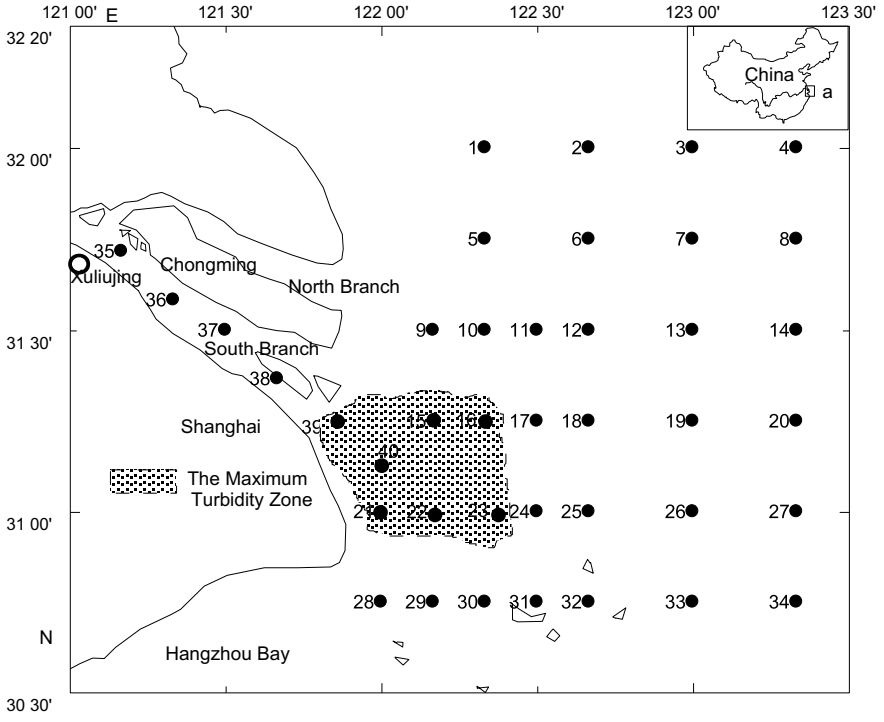

Fig. 1 Sampling stations in the Changjiang estuary: The shaded area is the TMZ (Shen and Pan 2001); a observation area

to ocean. It is a dynamic variation process. The freshwater end-member is at station 35 in downstream Xuliujing (salinity ≈ 0), whereas the seawater end-member varies seasonally with Changjiang runoff. Average salinities in seawater end-members were 33.26 in February (winter, stations 19 and 20), 33.63 in November (autumn, stations 8, 13, 14, 19, 20, 26, 27, 33, and 34), 31.13 in May (spring, station 20), and 32.89 in September (summer, stations 26 and 27). The line between fresh and seawater end-members represents the fresh–saltwater mixing/dilution line.

2.2 Method for Estimating the Resuspension Ratio of Fine-Grained Sediments

The SPM in the TMZ of Changjiang estuary includes sediments from both river runoff and resuspension. After SPM from river runoff arrives at the river mouth area, a portion is intercepted in the TMZ, influenced by runoff, tides, salt–freshwater, and circumfluence (Shen and Pan 2001). Sediment in the TMZ is mainly composed of fine-grained clayey silt and silty clay, existing as mud with high-water content when depositing from seawater to seabed (Yang et al. 1992). This sediment resuspends easily, and is reworked by wind, tides, and currents. Xuliujing is located at the fork between the South and North Branches, about 140 km from the river mouth. The SPM content in Xuliujing was similar to that in Datong (about 640 km from the river mouth) and increased with SPM increases in Datong (Chen et al. 2004). Therefore, SPM content in Xuliujing is thought to be controlled by river runoff in the same manner as at Datong, rather than by oceanic dynamical factors (Chen et al. 2004). The relationships of SPM to salinity in the entire observation area are indicated in Fig. 2. Taking SPM content at station 35 in downstream Xuliujing as the background value of river runoff, four theoretical dilution lines (Fig. 2) between the freshwater end-member (station 35) and the seawater end-member can be drawn as follows:

February: SPM (mg L^{-1}) = − 1.9159 S + 66.322
May: SPM (mg L^{-1}) = − 0.9906 S + 40.916
September: SPM (mg L^{-1}) = − 3.9699 S + 132.57
November: SPM (mg L^{-1}) = − 1.0867 S + 42.747.

Without sedimentation or resuspension, SPM content carried by Changjiang River should plot on the theoretical dilution lines. In contrast, in the case of resuspension or resedimentation, SPM values should fall either above or below these lines. Because there is little combustible particulate matter (only 7% of the total suspended particles in the estuary in 2004), biological influence is not considered herein. Thus, difference in SPM content between measurement at each station and its corresponding point on the theoretical dilution line should be equal to the resuspension or deposition amount. The resuspension ratio R can be computed as follows (Shen et al. 2008):

$$R = (\mathrm{SPM}_1 - \mathrm{SPM}_2) / \mathrm{SPM}_1 \times 100\%$$

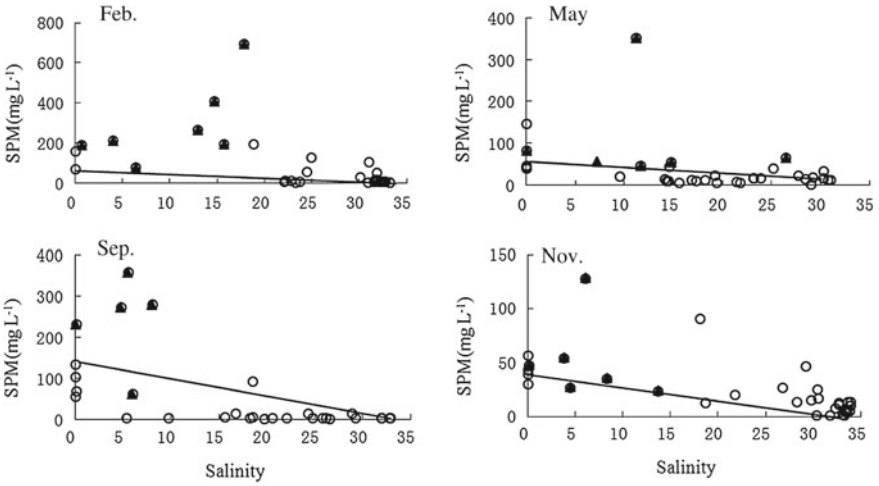

Fig. 2 The relationships of SPM to salinity in the Changjiang estuary: circle All data; filled triangle Data for the turbidity maximum zone; large dash lines Theoretical dilution lines between freshwater end-member (station 35) and seawater end-member ($r^2 = 1$, $n = 2$)

where, SPM_1 is the SPM content measured at a station in the TMZ, and SPM_2 is the corresponding SPM value at the theoretical dilution line. When R is positive, resuspension is indicated, and when R is negative, deposition is indicated.

3 Calculation Result

Based on observation data of SPM in the TMZ in February, May, September, and November, 2005, using the above method, the resuspension ratio of sediment in surface water of the TMZ was between $18.7 \pm 27.9\%$ and $73.9 \pm 22.5\%$, with an annual average of 49.2% (Table 1). The maximum resuspension ratio of sediment occurred in winter, as expected. Changjiang estuary waters are predominantly controlled by strong Changjiang runoff, and marine dynamics (tides and waves) are relatively weak in summer. In winter, runoff decreases greatly and marine dynamics are relatively strong, with greater storm frequency (Chen et al. 2004). In winter, spring, and summer, nearly half of the SPM in surface waters of the TMZ came from sediment resuspension (Table 1), illustrating that sediment resuspension is one of the major mechanisms maintaining the TMZ (Li and Zhang 1998; Pan et al. 1999). Using the new method, the resuspension ratio of sediment in surface waters of the TMZ in 2005 was a little smaller than that in 2004 at 55.7% (Shen et al. 2008).

Table 1 Resuspension ratios of sediment in surface waters of the TMZ

Month	New method		Traditional method	
	Ratios (%)	S.D. (%)	Ratios (%)	S.D. (%)
February	73.9	22.5	65.7	25.4
May	57.4	22.1	39.2	27.5
September	46.7	27.9	41.8	24.4
November	18.7	27.9	16.0	26.0
Average	49.2		40.7	

S.D. Standard deviation

4 Comparison with Traditional Method

Chen et al. (2004) estimated the ratio of sediment resuspension in Changjiang estuary using a traditional method, which took SPM content in Xuliujing as the background value of the river runoff, and assumed that the difference in SPM content between the Xuliujing measurement and the measured value for a given station was equal to the resuspension amount calculated by:

$$R = (S_t - S_r)/S_t$$

[mistakenly reported as $R = (S_t - S_r)/S_r$ in the literature] where S_t is the SPM content measured at a station and S_r is the SPM content carried by river runoff (station 35). Results of the traditional method to calculate the resuspension ratio of sediment in surface waters of the TMZ in 2005 is also indicated in Table 1. Comparing calculation results of the two methods, we find that the resuspension ratios of sediment in seasonal and annual averages using the new method are ~20% higher than those obtained using the traditional method.

Comparing the two calculation methods, the traditional method regards the SPM content carried by river runoff as invariable, and the dynamic variation in SPM content during transport is not considered. In actual fact, the SPM content carried by river runoff (the background value) at Xuliujing would reduce during transport. Hence, calculation results with the new method should be higher than with the traditional method (Table 1). Furthermore, the results of the new method are more objective.

While we calculate the resuspension ratio of sediment in surface waters of the TMZ using the new method, it should be noted that not all resuspended material may reach surface waters. Commonly the resuspension ratio of sediment increases with water depth. For example, the ratio of resuspension of sediment in bottom waters of the TMZ was 66.1% of the total SPM greater than that in surface waters (55.7%), which is consistent with SPM content at the bottom being greater than that at the surface (Shen et al. 2008). In addition, sedimentation may occur in conjunction with resuspension.

Using the new method, the resuspension ratio of sediment can be estimated in waters of different areas and depths in different estuaries. In addition, based on sedimentation fluxes of various particulate materials (such as nutrients, and heavy metals) in estuaries, their resuspension and net sedimentation fluxes also can be calculated (Shen et al. 2008). The method may therefore provide a new approach for studying the biogeochemistry of various dissolved and particulate species in estuaries.

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The Removal of Zinc, Cadmium, Lead, and Copper in the Changjiang Estuary

Zhiliang Shen and Mingxing Liu

Abstract The main removal region of ion and particulate forms of zinc (Zn), cadmium (Cd), plumbum (Pb), and copper (Cu) was in the waters of salinity 10–23 in the Changjiang estuary. The positive correlationships between heavy metals and the reciprocal of transparency, chemical oxygen demand, and chlorophyll-*a* showed that the removals of Zn, Cd, Pb, and Cu closely correlate with the distribution of suspensions, the adsorptions of organic materials, and the assimilation by organisms, suggesting that the latter two are main mechanisms of heavy metals removal in the estuary. The main area of heavy metals removal in the estuary was located in the high sedimentary rate area, and sediments mainly consisted of silty clay and clayey silt. The high heavy metals content area in surface sediment was consistent with the distribution trend of heavy metals contents in the water body.

Keywords Heavy metal · Removal · Changjiang estuary

The annual transport of Zn(T) (total zinc), Cd(T) (total cadmium), Pb(T) (total lead), and Cu(T) (total copper) from the Changjiang River to the East China Sea were about 2.6×10^4, 1.5×10^3, 1.6×10^3, and 8.0×10^3 tons, respectively (Zhang et al. 1987). It is interesting how heavy metals diffuse and remove after they enter the sea. Wu (1978) researched the contents of Cu, Cr, and Hg in Changjiang estuary sediments and their removal mechanisms. Xu et a1. (1982) discussed the distributions of Hg, Cu, Pb, Zn, and Cr contents in Changjiang estuary sediments and their relationships to environmental factors. The behaviors of dissolved Cd, Cu, and Pb in the Changjiang estuary were reported by Edmond et a1. (1985) and Elbaz-Poulichet et a1. (1990). The difference between the results of the above two papers and the results reported in this section is due to the difference in analytical method. The contents of ion and

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particulate form of Zn, Cd, Pb, and Cu in the Changjiang estuary waters were determined in this work using the method of inverse polarography with anti-adsorption physically coated mercury film electrode system devised by Gu et a1. (1973, 1980). Their removal from the estuary and their relationships with environmental factors are discussed.

1 Investigation and Analysis Method

The investigation was carried out from November 19 to 26, 1985 at 29 sampling stations (Fig. 1) The surface water samples were collected and immediately filtered with 0.45 μm filters (nitrocellulose and acetate). The filtrate was collected in clean polyethylene bottles immersed in old seawater for a long time, and the filters with suspensions were stored in a culture container under low temperature.

1.1 The Determination of Ion Form of Zn, Cd, Pb, and Cu

Filtrate samples were poured into an electrolyser. No reagent was added. An anti-adsorption physically coated mercury film electrode (as working electrode) and a mercury cell (as reference electrode) were used for differential inverse polarography of the single cell.

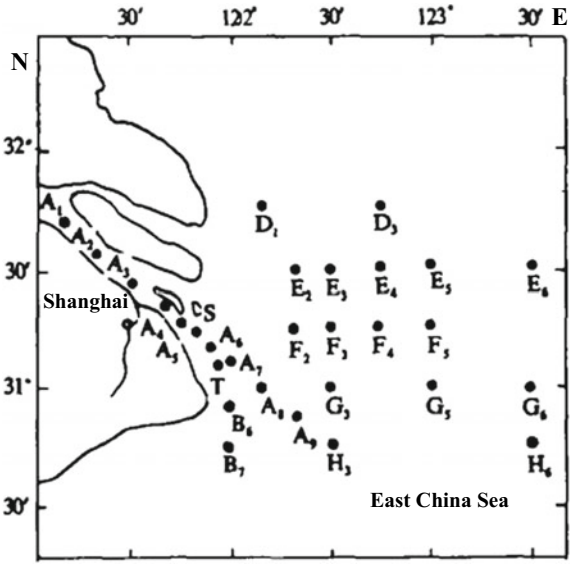

Fig. 1 Sampling stations

1.2 The Determination of Particulate Form of Zn, Cd, Pb, and Cu

The filters with suspensions were put into a digestion bomb with HC1 and HNO_3 and digested. The digested liquid was diluted with old seawater and adjusted to pH 4.5. The inverse polarography results were corrected with blanks. A British DAVIS A1660 differential cathode ray polarograph was used.

2 The Removal of Heavy Metals in the Estuary

The average contents of (and proportion to total) ion and particulate forms (P) of heavy metals in the Changjiang estuary surface seawater listed in Table 1 show that the contents of the ion form of heavy metals were low and the changes small, and that particulates comprised the main form of heavy metals there and were 4–99 times that of the ion form obviously as a result of the great quantity of particulate matter transported there by the Changjiang River.

Trace metal ions in seawater were mainly controlled by the reaction in the liquid/solid interface (Goldborg 1965). Many suspensions of clay minerals and organic matters in the Changjiang River have strong adsorption and complexation capacities for heavy metal ions. After the Changjiang River water enters the sea, because of the changes of physical and chemical environments (salinity, pH, hydrodynamics, etc.), a part of the ion form and particulate form of heavy metals are adsorbed and coagulated, and become big particles entering sediment. Investigation shows that after various heavy metals in the Changjiang River water enter the sea, all of them were removed to a certain degree (see Fig. 2). The relationships of concentrations of the ion form of heavy metals and salinity (S) were indicated as:

$$\mathrm{Zn}^{2+}\left(\mu\mathrm{g\,L}^{-1}\right) = 6.60 + 0.0015(\mathrm{S} - 18)^2 (S = 0{-}33.4)(r = 0.430,\ n = 23)$$
$$\mathrm{Cd}^{2+}\left(\mu\mathrm{g\,L}^{-1}\right) = 0.082 + 0.00008(\mathrm{S} - 14)^2 (S = 0{-}33.4)(r = 0.584,\ n = 23)$$
$$\mathrm{Pb}^{2+}\left(\mu\mathrm{g\,L}^{-1}\right) = 0.0255 + 0.000015(\mathrm{S} - 14)^2 (S = 0{-}33.4)(r = 0.496,\ n = 23)$$
$$\mathrm{Cu}^{2+}\left(\mu\mathrm{g\,L}^{-1}\right) = 0.48 + 0.0004(\mathrm{S} - 21)^2 (S = 10{-}33.4)(r = 0.468,\ n = 19)$$

The above equations and Fig. 2 show that except for Cu^{2+} being a little different the main removal region of Zn^{2+}, Cd^{2+}, and Pb^{2+} is in the waters of salinity 10–23. The maximum removal quantities of Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} were about 9, 22, 15, and 11%, respectively. There were negative exponential correlationships between the particulate form of heavy metals and salinity as indicated in the equations:

$$\mathrm{Zn(P)}\left(\mu\mathrm{g\,L}^{-1}\right) = 44.926\ \mathrm{e}^{-0.0338\,\mathrm{S}} (r = -0.704,\ n = 23)$$
$$\mathrm{Cd(P)}\left(\mu\mathrm{g\,L}^{-1}\right) = 3.332\ \mathrm{e}^{-0.0236\mathrm{S}} (r = -0.506,\ n = 23)$$

Table 1 Contents of heavy metals in the Changjiang estuary

Heavy metals	Zn			Cd			Pb			Cu		
	Zn^{2+}	Zn(P)	Zn(T)	Cd^{2+}	Cd(P)	Cd(T)	Pb^{2+}	Pb(P)	Pb(T)	Cu^{2+}	Cu(P)	Cu(T)
Average contents ($\mu g\ L^{-1}$)	6.6 ± 1.1	27.6 ± 13.5	34.2 ± 13.1	0.09 ± 0.03	2.4 ± 0.9	2.5 ± 0.9	0.027 ± 0.005	2.7 ± 1.8	2.7 ± 1.8	0.48 ± 0.05	11.7 ± 6.1	12.1 ± 6.1
Ion or particulate Total quantity (%)	19.3	80.7		3.6	96.4		1.0	99.0		4.0	96.0	

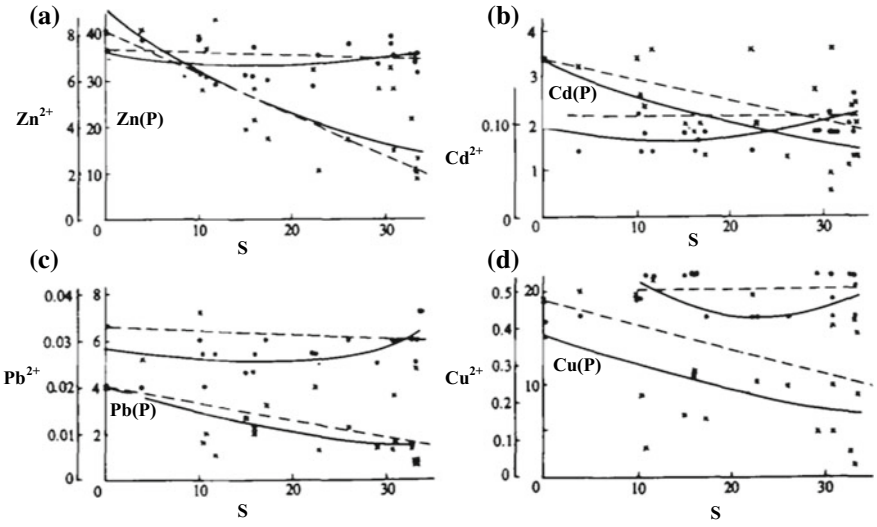

Fig. 2 Relationships of heavy metals($\mu g\ L^{-1}$) and salinity: **a** Zn–S; **b** Cd–S; **c** Pb–S; **d** Cu–S. filled circle ion form; **×** Particulate form; small dash lines theoretical dilution line; large dash lines corrective line

$$\mathrm{Pb(P)}\left(\mu g\ L^{-1}\right) = 4.030\ e^{-0.0326S} (r = -0.525,\ n = 23)$$
$$\mathrm{Cu(P)}\left(\mu g\ L^{-1}\right) = 15.152\ e^{-0.0234S} (r = -0.345,\ n = 23)$$

Figure 2 shows the similar removal processes of the ion and particulate forms of heavy metals sedimentation.

The relationships among heavy metals also show similar removal processes. The relationships between Zn^{2+}, Pb^{2+}, and Cd^{2+} were, respectively, indicated as:

$$\mathrm{Zn^{2+}}\left(\mu g\ L^{-1}\right) = 5.39 + 15.66\ \mathrm{Cd^{2+}}\left(\mu g\ L^{-1}\right) (r = 0.415,\ n = 23)$$
$$\mathrm{Pb^{2+}}\left(\mu g\ L^{-1}\right) = 0.013 + 0.160\ \mathrm{Cd^{2+}}\left(\mu g\ L^{-1}\right) (r = 0.649,\ n = 23)$$

There were obvious positive linear correlationships among the particulate forms of heavy metals:

$$\mathrm{Zn(P)}\left(\mu g\ L^{-1}\right) = 8.35 + 7.14\ \mathrm{Cd(P)}\left(\mu g\ L^{-1}\right) (r = 0.597,\ n = 23)$$
$$\mathrm{Zn(P)}\left(\mu g\ L^{-1}\right) = 17.06 + 2.90\ \mathrm{Pb(P)}\left(\mu g\ L^{-1}\right) (r = 0.432,\ n = 23)$$
$$\mathrm{Pb(P)}\left(\mu g\ L^{-1}\right) = 0.31 + 0.96\ \mathrm{Cd(P)}\left(\mu g\ L^{-1}\right) (r = 0.541,\ n = 23)$$
$$\mathrm{Zn(P)}\left(\mu g\ L^{-1}\right) = 15.32 + 0.79\ \mathrm{Cu(P)}\left(\mu g\ L^{-1}\right) (r = 0.435,\ n = 23)$$
$$\mathrm{Cu(P)}\left(\mu g\ L^{-1}\right) = 0.14 + 4.96\ \mathrm{Cd(P)}\left(\mu g\ L^{-1}\right) (r = 0.757,\ n = 23)$$
$$Cu(P)\left(\mu g\ L^{-1}\right) = 5.92 + 2.13\ \mathrm{Pb(P)}\left(\mu g\ L^{-1}\right) (r = 0.579,\ n = 23)$$

3 The Relationships of Heavy Metals and Other Hydroenvironment Factors

The relationships of total quantity of heavy metals and seawater transparency (Tr) are indicated in Fig. 3. The relationship between Zn(T) and Tr(m) was as follows:

$$\mathrm{Zn(T)}\left(\mu\mathrm{g\ L^{-1}}\right) = 18.98 + 4.12[1/\mathrm{Tr}(m)](r = 0.794,\ n = 18)$$

The high concentrations of heavy metals distributing in the <lm transparency waters show that coacervation–sedimentation and dilution–diffusion of heavy metals in the estuary occurred mainly in the waters with high contents of suspensions. In the waters with >lm transparency, the contents of heavy metals were almost constant (Fig. 3).

The adsorption of organic materials and assimilation by organisms are main mechanisms of heavy metals removal in the estuary. Gardiner (1974) showed that the adsorption ability of humus is two orders of magnitude greater than that of clay and

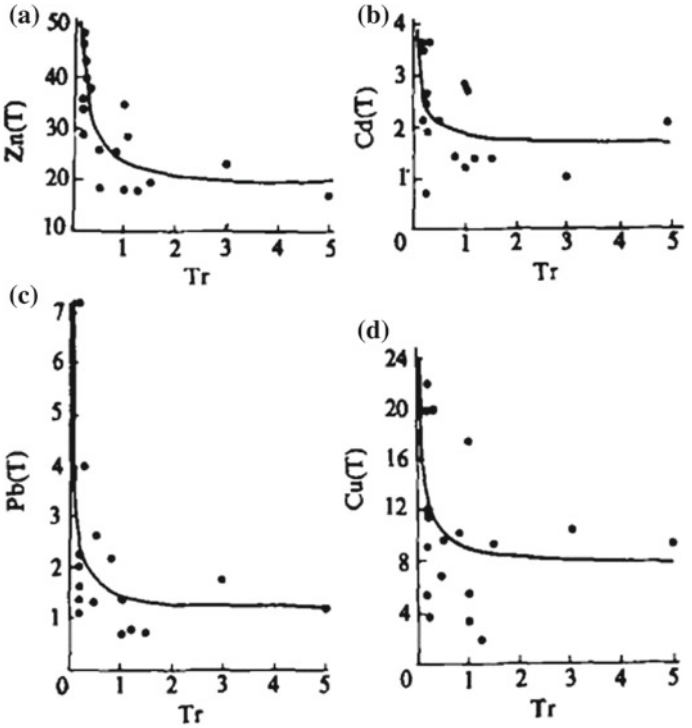

Fig. 3 Relationships between heavy metals (μg L^{-1}) and transparency (m): **a** Zn(T)—Tr; **b** Cd(T)—Tr; **c** Pb(T)—Tr; d Cu(T)—Tr

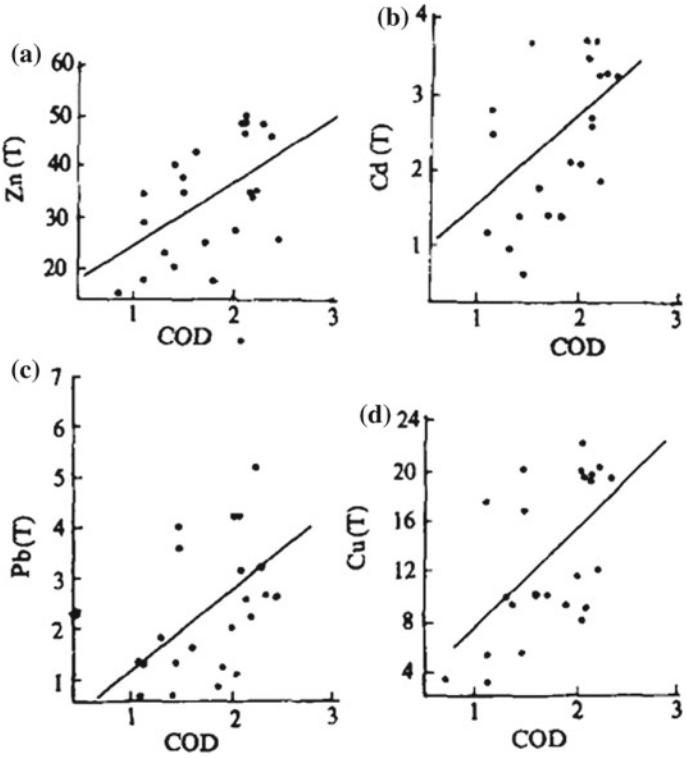

Fig. 4 Relationships between heavy metals (μg L^{-1}) and COD (mg $L^{=1}$): **a** Zn(T)—COD; **b** Cd(T)—COD; **c** Pb(T)—COD; **d** Cu(T)—COD

kaolin. Study shows that there were positive correlationships between heavy metals and chemical oxygen demand (COD) (Fig. 4) and chlorophyll-*a* (Chl-*a*) as follows:

$$\mathrm{Zn(T)}\left(\mu\mathrm{g\ L^{-1}}\right) = 11.65 + 12.94\ \mathrm{COD}\ \left(\mathrm{mg\ L^{-1}}\right)(r = 0.531,\ n = 23)$$

$$\mathrm{Cd(T)}\left(\mu\mathrm{g\ L^{-1}}\right) = 0.38 + 1.20\ \mathrm{COD}\ \left(\mathrm{mg\ L^{-1}}\right)(r = 0.476,\ n = 23)$$

$$\mathrm{Pb(T)}\left(\mu\mathrm{g\ L^{-1}}\right) = -0.30 + 1.47\ \mathrm{COD}\ \left(\mathrm{mg\ L^{-1}}\right)(r = 0.492,\ n = 23)$$

$$\mathrm{Cu(T)}\ \left(\mu\mathrm{g\ L^{-1}}\right) = -0.23 + 7.74\ \mathrm{COD}\ \left(\mathrm{mg\ L^{-1}}\right)(r = 0.589,\ n = 23)$$

$$\mathrm{Zn(T)}\left(\mu\mathrm{g\ L^{-1}}\right) = 12.46 + 17.80\ \mathrm{Chl} - a\left(\mathrm{mg\ m^{-3}}\right)(r = 0.594,\ n = 19)$$

$$\mathrm{Cd(T)}\left(\mu\mathrm{g\ L^{-1}}\right) = 0.79 + 1.51\ \mathrm{Chl} - a\left(\mathrm{mg\ m^{-3}}\right)(r = 0.576,\ n = 19)$$

$$\mathrm{Pb(T)}\left(\mu\mathrm{g\ L^{-1}}\right) = -0.28 + 2.65\ \mathrm{Chl} - a\left(\mathrm{mg\ m^{-3}}\right)(r = 0.571,\ n = 19)$$

$$\mathrm{Cu(T)}\left(\mu\mathrm{g\ L^{-1}}\right) = 2.58 + 8.99\ \mathrm{Chl} - a\left(\mathrm{mg\ m^{-3}}\right)(r = 0.530,\ n = 19)$$

4 The Relationship Between the Removal of Heavy Metals and Sedimentary Environments

The horizontal distributions of the total quantities of heavy metals are indicated in Fig. 5. From stations A_7 in the mouth to H_3 (122°30′ E, 30°45′ N), heavy metals decrease from 46.7 to 17.9 μg L^{-1} (61.7% decrease) for Zn(T), 3.5–2.1 μg L^{-1} (40% decrease) for Cd(T), 7.2–1.3 μg L^{-1} (81.9% decrease) for Pb(T) and 19.9–9.8 μg L^{-1} (50.8% decrease) for Cu(T). Surface waters increasing in salinity from 11.486 to 22.824 (bottom waters 24.972) comprised the main area of heavy metals removal in the estuary. The main characteristics of the sedimentary environments of the waters were (Yang et al. 1992):

(1) Sediments mainly consisted of silty clay and clayey silt and particles were thin, and directly transported by the Changjiang River water.
(2) Determination by ^{210}Pb showed that the sedimentation rate of the waters in the high sedimentary rate area outside the Changjiang River estuary was 2–5 cm a^{-1}.

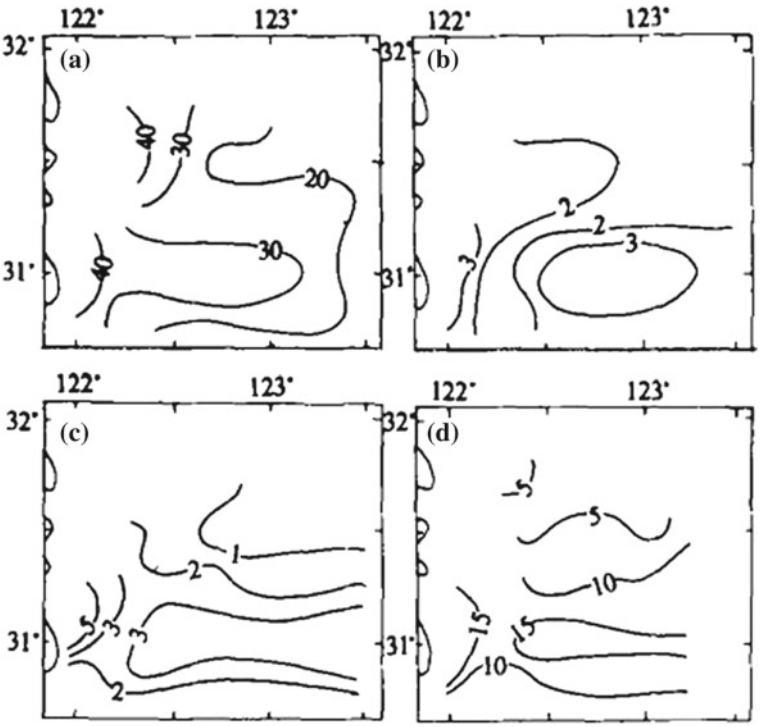

Fig. 5 Horizontal distributions of heavy metals (μg L^{-1}): **a** Zn(T); **b** Cd(T); **c** Pb(T); **d** Cu(T)

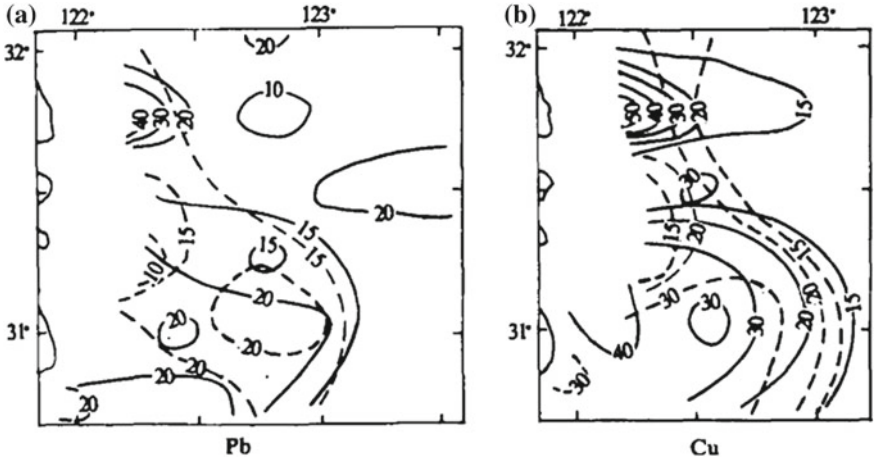

Fig. 6 Distributions of Pb and Cu content (10^{-6}) in sediments: **a** Pb; **b** Cu. Large dash lines September, 1985; small dash lines January, 1986

(3) This high heavy metals content area in surface sediment in the Changjiang River estuary (Fig. 6) was consistent with the distribution trend of heavy metals contents in the water body.

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Distributions and Removals of Nutrients in Seawater and Interstitial Water of the Sediments in the Huanghe River Estuary

Zhiliang Shen, Xingjun Liu and Jiaping Lu

Abstract The concentration of nitrate in the Huanghe River estuary was controlled by a physical mixing process and was also related to biological processes. The change in phosphate concentration was less between 0.3 and 0.7 μmol L^{-1}, due to affected by the buffering of suspensions and sediments on the removal of phosphate from estuarine waters. The annual transport from the Huanghe River mouth to the sea was 8.45×10^4 t for dissolved inorganic nitrogen and 1.45×10^3 t for phosphate. The distributions of dissolved inorganic nitrogen and silicate in interstitial water of surface sediment were similar to those in surface and bottom seawater. The nutrient concentrations in average in interstitial water were 375 μmol L^{-1} for ammonia, 1.6 μmol L^{-1} for nitrite, 6 μmol L^{-1} for nitrate, 1.2 μmol L^{-1} for phosphate, and 77 μmol L^{-1} for silicate. A cycle of phosphate in the estuary is also suggested.

Keywords Nutrient · Removal · Transport · Phosphate cycle · Seawater Interstitial water · Huanghe river estuary

The mixture of fresh and saltwater and the effects of tide, tidal current, wind, etc., result in complex physical, chemical, and biological processes in the estuary. The average discharge of water and sand of the Huanghe River are 4.428×10^{10} m^3 a^{-1} and 1.12×10^9 t a^{-1} (Ye 1982), respectively. The great changes (over 10 times) in the estuary since 1855 produced today's Huanghe River delta. The water depths near the estuary are mostly less than 15 meters. The sediments here are mainly fine sands from the middle reaches of the Huanghe River. The favorable physicochemical and biological conditions in the Huanghe River estuarine region make it a good breeding and feeding ground for fishes, shrimps, crabs, and shellfishes.

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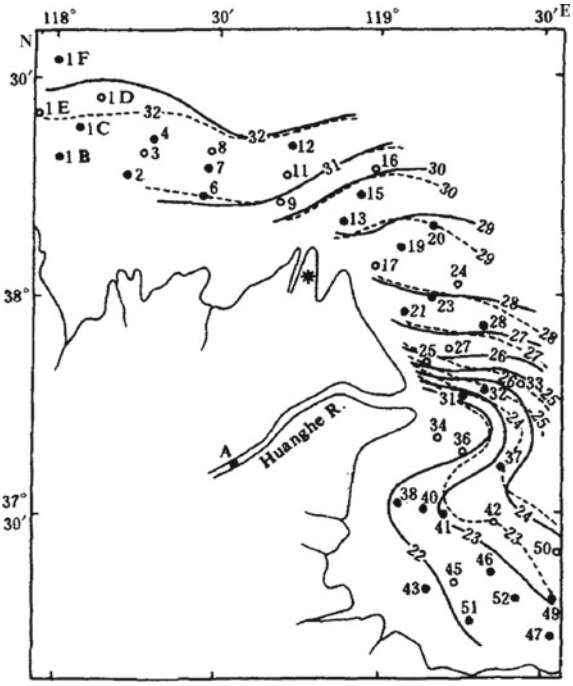

Fig. 1 Sampling stations and distribution of salinity in seawater (November): black circle Sampling stations (water); white circle sampling stations (water and interstitial water); — surface; ---- bottom

In this section, we report data collected from the Huanghe River estuary during November 21–December 2 1984 and from the Huanghe River water during April 1984–March 1985 (Fig. 1). The distributions of the nutrients in seawater and interstitial water of surface sediments, nutrient concentrations in the Huanghe River water and their removal and transport in the estuary are discussed. In addition, the cycle model of phosphate in the Huanghe River estuary is also studied in this section.

Dissolved inorganic nitrogen (DIN) is equal to the sum of nitrate (NO_3-N), nitrite (NO_2-N) and ammonia (NH_4-N) in this section.

1 The Horizontal Distributions of the Nutrients and Salinity in Seawater

The distributions of salinity, NO_3-N, NO_2-N, NH_4-N, phosphate (PO_4-P) and DIN/PO_4-P (mole ratio between DIN and PO_4-P) in surface and bottom seawater are shown in Figs. 1, 2, 3, 4, 5, and 6. Their concentration ranges and average values are listed in Table 1.

The salinity distribution shows that the Huanghe River estuarine area south of 38ºN is the main effective area of freshwater from the Huanghe River. From here on,

Fig. 2 Distribution of NO_3-N (μmol L^{-1}) in seawater (November): — surface; ---- bottom

we shall call this area the "estuarine area" and the area northwest of it, the "northwest area".

Figures 2, 3, 4, 5 show that the distributions of nutrients are converse to that of salinity. Nutrient concentrations are high in estuarine and coastal waters and low in offshore water. The concentrations of various forms of inorganic N are a little higher at the surface than at the bottom. The isopleths of concentration of inorganic N, particularly NO_3-N, are concentrated near the estuary; the concentration gradient is large, and the differences between high and low concentrations are no less than 12 times. The much higher concentration of NO_3-N in the estuarine area over that in the northwest area (Table 1) clearly indicates that the high content of NO_3-N comes from the Huanghe River water. The concentration (average 0.15 μmol L^{-1}) of NO_2-N is low in the surveyed area. The primary product of decomposed organic N—NH_4-N is influenced by the Huanghe River water and its concentration will depend on the absorption by phytoplankton, the decomposition of organisms, direct excretions from zooplankton and other aquatic life, the effect of rain, etc. Average concentrations of NH_4-N are 3.9 μmol L^{-1} for the estuarine area and 1.9 μmol L^{-1} for the northwest area. The concentration of NH_4-N in seawater is higher than that in the Huanghe River water (1.1 μmol L^{-1}). This shows that its concentration is mainly controlled by biological processes. NO_3-N is the main one of three forms of inorganic N in the surveyed area. Figure 5 shows that in the surveyed area the distribution of PO_4-P is different from that of inorganic N, it is evident that its concentration is higher in the

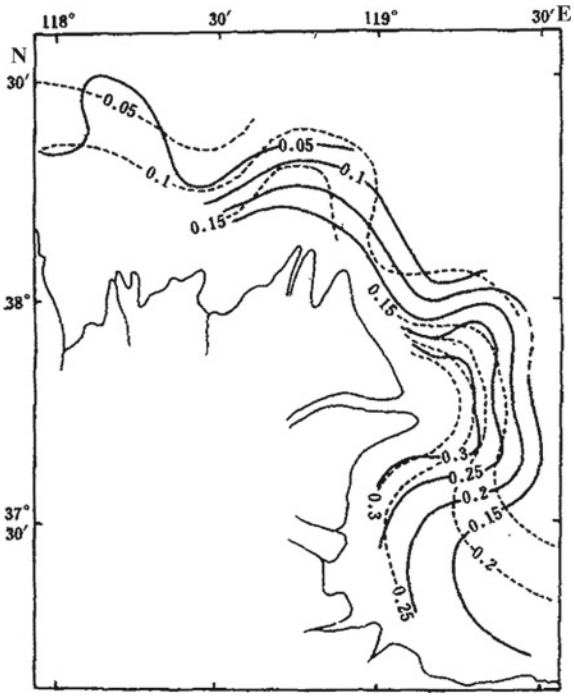

Fig. 3 Distribution of NO_2-N (μmol L^{-1}) in seawater (November): — surface; ---- bottom

northwest area than in the estuarine area and a little higher in bottom water than in surface water. This distribution pattern was also found in other months (Shen et al. 1989). According to Guo Yujie and Gao Shangwu's investigations in 1984, the total biomass of phytoplankton and zooplankton in the estuarine area is much higher than that in the northwest area. This clearly shows that the decomposition of organisms is not the main factor controlling the concentration of PO_4-P and that it is possible that the sediments and suspensions release PO_4-P.

The distributions of DIN/PO_4-P in surface and bottom water are similar to that of NO_3-N (see Fig. 6 and Table 1), varying from 3.2 to 101. DIN/PO_4-P in surface and bottom water in the estuarine area is far higher than its ordinary value of 16 in seawater. This high value is the result of the effect of the Huanghe River water and not an indication of the ratio between DIN and PO_4-P absorbed by phytoplankton or organism decomposition.

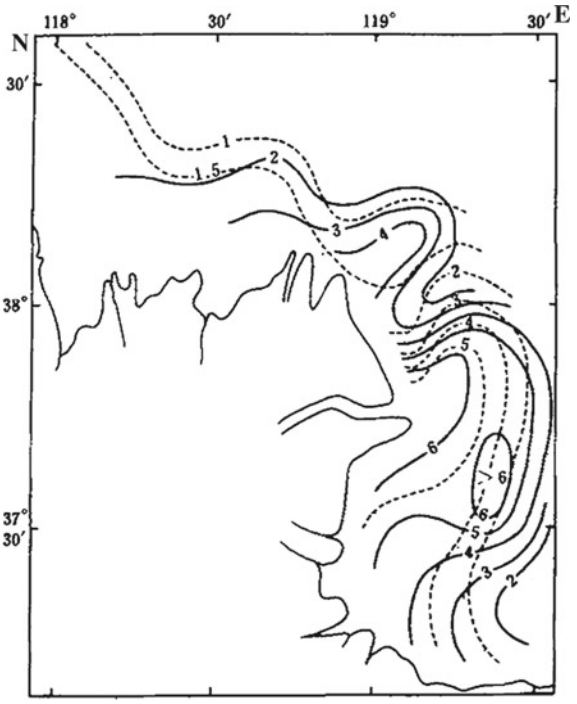

Fig. 4 Distribution of NH_4-N (μmol L^{-1}) in seawater (November): — surface; ---- bottom

2 The Relationships Between Inorganic N, Phosphate and Tide, and Their Removal from the Estuary

The circadian changes of NO_3-N, NO_2-N, NH_4-N, PO_4-P and salinity(S)in surface water at station 31 (see Fig. 7) show that the concentrations of various inorganic N and PO_4-P are converse to that of salinity in different degrees. It is particularly evident for NO_3-N during high tide (at 3:00 and 15:00 h) when salinity is highest and the concentration of NO_3-N is lowest (6.8 and 7.2 μmol $L^{-1,}$ respectively). The concentration of NO_3-N is highest during low tide (at 20:00 h).

The investigation shows that when salinity $S = 13 - 29$, there are negative linear correlationships between NO_3-N, or DIN, and salinity, respectively, and that in the range of salinity surveyed the physical mixing process is important for inorganic N. The primary productivity in the estuarine area is higher (average 116 mg C m^{-2} d^{-1} in November). It is possible that the removal of NO_3-N in the estuary of the Huanghe River is related to biological processes.

There is no linear relationship between PO_4-P concentration, and salinity. In the range of salinity surveyed, the change in PO_4-P concentration is generally less, between 0.3 and 0.7 μmol L^{-1} (the concentration of PO_4-P in river water is 0.6 μmol L^{-1}). That suspensions and sediments in the estuary are the buffers of PO_4-P in water had already been reported (Butler and Tibbitts 1972; Carritt and

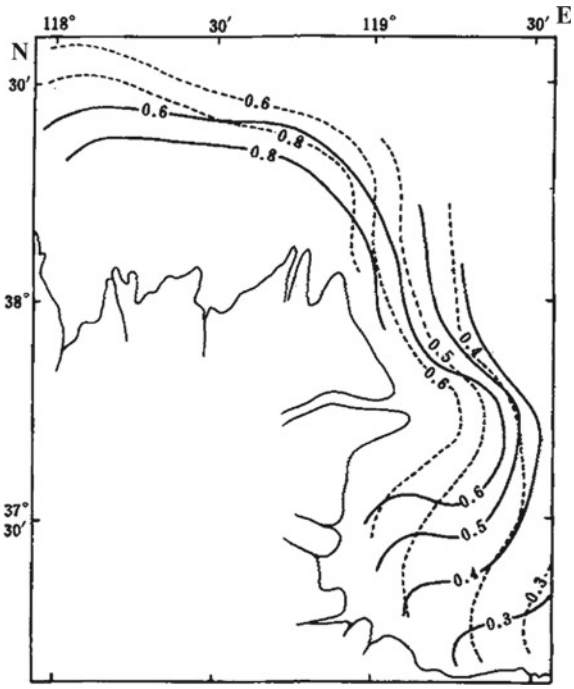

Fig. 5 Distribution of PO_4-P (μmol L^{-1}) in seawater (Nov.): — surface; ---- bottom

Goodgal 1954; Jitts 1959; Pomeroy et al. 1965). The Huanghe River transports into the Bohai Sea a large quantity of silt which absorbs PO_4-P from freshwater rich in PO_4-P and releases it into water in the mixing area of fresh and saltwater with low PO_4-P content. Besides, the resuspension (due to the actions of wind and tide) of a part of the sediments in the shallow estuarine area accelerates the exchange of PO_4-P between estuarine water and sediments. The exchange of PO_4-P will contribute to keeping its content at levels beneficial to phytoplankton growth. It is possible that the distribution of PO_4-P can be indicative of the stabilizing influence of suspensions and sediments on the removal of PO_4-P from estuarine waters.

3 The Concentrations of Inorganic N and Phosphate in the Huanghe River Water and Their Transport

Table 2 presents results from monthly investigations from April 1984 to March 1985 on the transport and concentrations of inorganic N and PO_4-P at station A (Fig. 1) in the Huanghe River. The concentration of NO_3-N in the Huanghe River water is much higher than that in the Changjiang River water (Shen et al. 1987). This is mainly due

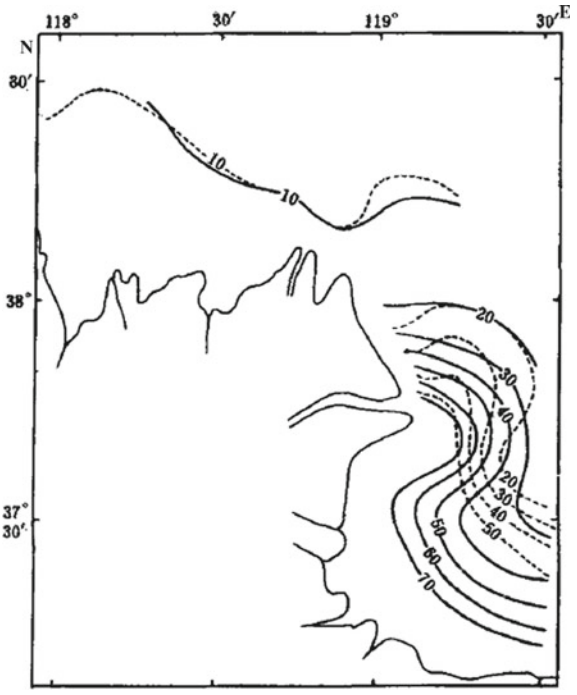

Fig. 6 Distribution of DIN/PO_4-P in seawater (November): — surface; ---- bottom

Table 1 Concentrations of nutrients (μmol L^{-1}) in seawater

Parameters	Ranges of concentration		Surface averages		Bottom averages		Total averages
	Northwest	Estuary	Northwest	Estuary	Northwest	Estuary	
Salinity	28.0–32.9	13.6–28.6	30.8	23.6	31.0	25.2	27.4
NO_3-N	4.3–10	4.0–51	6.9	18	6.7	12	11
NO_2-N	0.02–0.93	0.09–0.37	0.14	0.18	0.11	0.17	0.15
NH_4-N	0.2–6.9	0–8.1	2.1	4.1	1.6	3.5	2.9
DIN	5.4–15	7.8–56	9.1	22	8.4	16	14
PO_4-P	0.37–1.8	0.24–1.1	0.76	0.46	0.92	0.49	0.64
DIN/PO_4-P	3.2–41	13–101	12	48	9.1	33	22

to runoff, loss of water and erosion of soil in the middle reaches of the Huanghe River. Table 2 shows the annual transport is 8.45×10^4 t for total inorganic N and 1.45×10^3 t for PO_4-P.

Thus, it can be seen that the influx of Huanghe River water is of importance for the development of water productivity not only in the estuarine area but also in the Bohai Sea, and the northern part of the Yellow Sea.

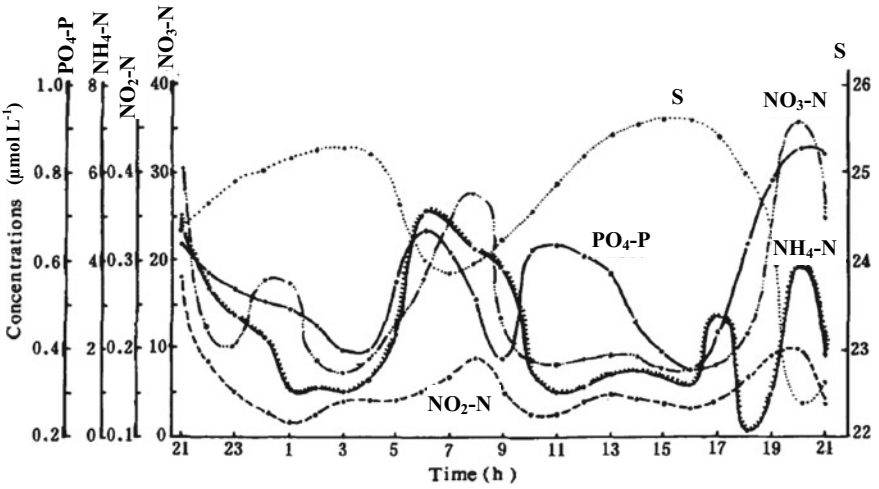

Fig. 7 Circadian changes of NO_3-N, NO_2-N, NH_4-N, PO_4-P and salinity (S) at station 31 (November. 28–29, 1984)

Table 2 Concentrations of inorganic N and PO_4-P (μmol L^{-1}) in the Huanghe River water and their transport ($\times 10^3$ t)

	River runoff ($\times 10^8 m^3$)	NO_3-N	NO_2-N	NH_4-N	DIN	PO_4-P
November concentrations		75	0.24	1.1	76	0.60
Annual average concentrations		134	0.51	13	148	0.99
November transports	25	2.6	0.008	0.036	2.7	0.047
Annual transports	468	78.2	0.28	6.1	84.5	1.45

4 The Distributions of Nutrients in Interstitial Water of Surface Sediments

The horizontal distributions of NO_3-N, NO_2-N, NH_4-N, PO_4-P, silicate (SiO3-Si), DIN/PO_4-P and DIN/SiO_3-Si in interstitial water of surface sediments are indicated in Figs. 8 and 9, 10. Their concentration ranges and average values are listed in Table 3.

Figure 8 shows that the distributions of various inorganic N in interstitial water are similar in surface and bottom seawater. Table 3 shows that the concentrations of NO_3-N and NH_4-N in the estuarine area are higher than those in the northwest area. The concentration of NH_4-N in interstitial water depends mainly on the contents of organic matter and their decomposition rate in sediments. Due to the large quantity of nutrients brought by the Huanghe River water, abundant plankton growth (particularly at the estuary) was observed in the surveyed area. The average pri-

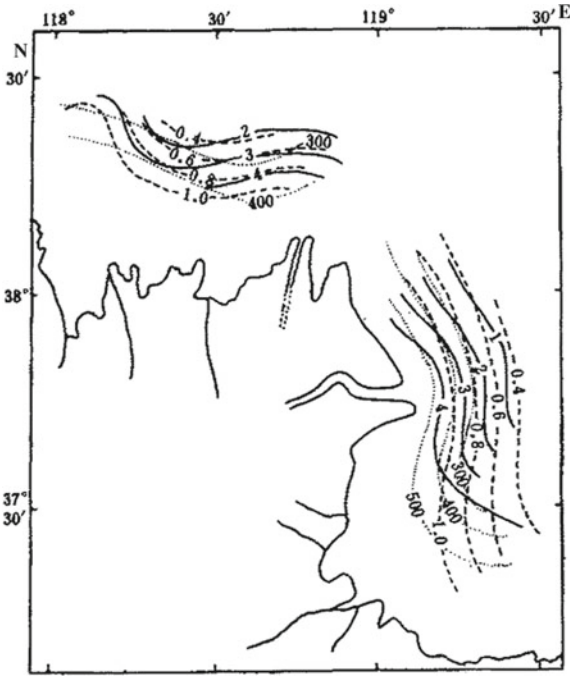

Fig. 8 Distributions of NO_3-N, NO_2-N, and NH_4-N (μmol L^{-1}) in interstitial water (November.): — NO_3-N; ···· NO_2-N; ---- NH_4-N

mary productivity was 415 mg C m^{-2} d^{-1} in the estuary from April to November 1984. Organic matter in sediments originates mainly from biological debris. It is evident that the distribution of zooplankton in seawater is positively correlated to that of nutrients in interstitial water. In the surveyed area, the content of dissolved oxygen, the saturation degree of dissolved oxygen, and water temperature in bottom water are 6.28 mL L^{-1}, 95%, and 9.8 °C, respectively. Surface sediments are mostly yellowish-brown clayey silt. According to the investigation results from 7 stations near the estuarine area in May 1984, the redox potential of surface sediments is 65–135 mv. The oxidation environment and higher temperature in the surveyed area are favorable for oxidation and decomposition of organic matter; hence, the concentration of NH_4-N in interstitial water is higher. Its average and highest values are 375 and 552 μmol L^{-1} respectively (Table 3). NH_4-N–NO_2-N–NO_3-N is an inevitable process thermodynamically, and particularly when nitrifying bacteria are present, this process is faster. The oxidation environment in this area is favorable for the continuous oxidation of NH_4-N. Therefore, there are substantial quantities of NO_2-N and NO_3-N in interstitial water. The highest concentrations are 9 μmol L^{-1} for NO_2-N, and 41 μmol L^{-1} for NO_3-N, the average concentrations are 1.6 μmol L^{-1} for NO_2-N and 6 μmol L^{-1} for NO_3-N (Table 3). The concentrations of NO_2-N and NO_3-N are much higher than those in Jiaozhou Bay which is in a strong reduction environment. The concentration of NO_3-N in interstitial water is much lower than that in seawater because of limited oxygen in the former. It is impossible for the

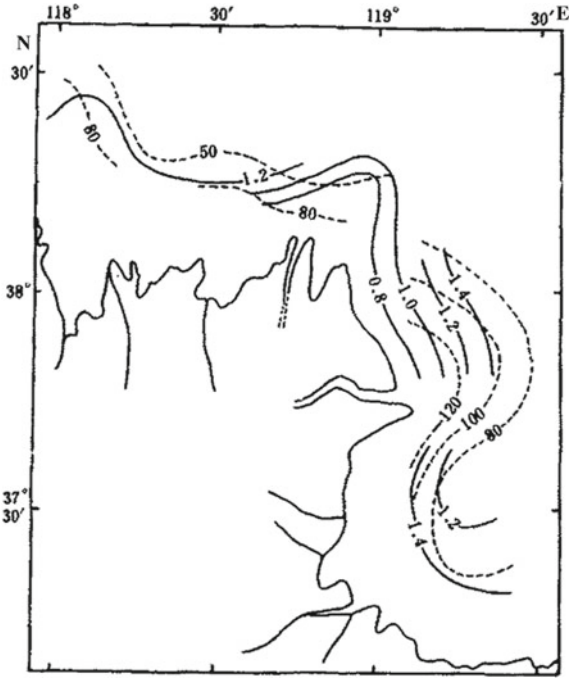

Fig. 9 Distributions of PO_4-P and SiO_3-Si (μmol L^{-1}) in interstitial water (November): — PO_4-P; ---- SiO_3-Si

three forms of inorganic N in interstitial water to reach thermodynamic equilibrium. NH_4-N accumulated in large amount is the main existence form of inorganic N in interstitial water.

Figure 9 and Table 3 show that the distribution of PO_4-P in interstitial water is more complex. The concentration of PO_4-P in the estuarine area is a little higher than that in the northwest area. The higher concentration is in the southwest area of Laizhou Bay. The distribution pattern (high offshore and low along the coast) in the northeast area of the estuary coincided with that of primary productivity during the investigation period. The concentration of PO_4-P in the interstitial water in the surveyed area is 0.73–1.6 μmol L^{-1}. Its average value of 1.2 μmol L^{-1} is lower than that in other areas of the Bohai Sea, the Yellow Sea, and the East China Sea and is higher than that in Jiaozhou Bay. The low concentration of PO_4-P is possibly related to the release of PO_4-P by sediments. For example, in the northwest area the concentrations of PO_4-P are 0.78 μmol L^{-1} for surface water, 0.94 μmol L^{-1} for bottom water, and 1.1 μmol L^{-1} for interstitial water. The low concentration difference between interstitial water and seawater reflects the exchange of PO_4-P between them. The vertical convection current of the water column promotes this exchange process.

The continental runoff is one of the main sources of SiO_3-Si in the ocean. The distribution of Sio_3-Si in interstitial water is influenced very greatly by the Huanghe River water. The following distribution trends are obvious: The concentration in the

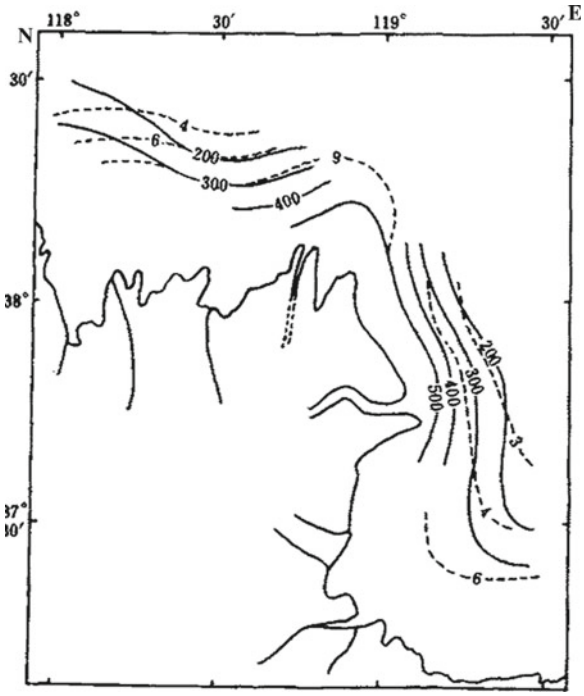

Fig. 10 Distributions of DIN/PO_4-P, DIN/SiO_3-Si in interstitial water (November): — DIN/PO_4-P; ---- DIN/SiO_3-Si

Table 3 Concentrations (μmol L^{-1}) and mole ratios of nutrients in interstitial water

Parameters	Northwest area		Estuarine area		
	Concentration ranges	Averages	Concentration ranges	Averages	Total averages
NO_3-N	0–10	4.1	0.5–41	7.7	6.0
NO_2-N	0.31–9.0	2.4	0.40–1.4	0.81	1.6
NH_4-N	269–437	361	227–552	387	375
DIN	281–446	368	229–560	396	383
PO_4-P	0.73–1.6	1.1	0.76–1.6	1.3	1.2
SiO_3-Si	41–90	57	52–139	94	77
DIN/PO_4-P	234–577	335	164–737	305	319
DIN/SiO_3-Si	3.7–11	6.5	2.3–7.5	4.2	5.0

estuary and the coast is higher than that offshore. The concentration in the estuarine area is higher than that in the northwest area (Fig. 9). The average concentration of SiO_3-Si is 77 μmol L^{-1} (highest 139 μmol L^{-1}) in the surveyed area and 5.5 times the average value in seawater.

Due to the very high content of NH_4-N, the values of 319 for DIN/PO_4-P and 5.0 for DIN/SiO_3-Si in interstitial water are much higher than those in seawater. Their horizontal distributions coincide with the distribution of inorganic N (see Fig. 10).

5 The Cycle Model of Phosphate in the Estuary of the Huanghe River

The cycle of PO_4-P in the estuary of the Huanghe River is indicated in Fig. 11. The PO_4-P carried to the sea by the Huanghe River water consists of suspended and dissolved P. The total quantity of dissolved P is 1450 t a^{-1} (see Table 2). The PO_4-P in suspensions in turbid river water is 80-90% as much as its total quantity in the river water (Baturin 1978; Jitts 1959). The PO_4-P in suspensions is taken as 90% here. So, the quantity of suspended PO_4-P entering the sea is 13,000 t a^{-1}. The PO_4-P is transported into the estuarine area by river water and exchanged among suspensions, sediments, and seawater. The exchange rate will depend on the turbulent degree of the sediments, the pH and salinity of the seawater, the concentrations of PO_4-P, and the buffering property of water and sediments (Pomeroy et al. 1965). Figure 11 shows that the PO_4-P is transformed and cycled among organisms and between organisms and seawater. The primary productivity in 1984 in the estuarine area was about 674,000 t C a^{-1}. If the annual reproduction and death of phytoplankton reach the equilibrium state, according to the atomic ratio C:P = 106, the P content in phytoplankton is 16,400 t a^{-1}, part of which is directly circulated among live organisms, that in biological debris (remains of planktons, excrements and skeletons of animals, fish scales, etc.) is regenerated to PO_4-P before entering the sea bottom. In the sediments, P will be dissociated in the mineralization process of the organic matter (Rowe et al. 1975).

Summing up, there is no shortage of PO_4-P in the surveyed area because it is continuously supplied from the suspension matter and the sediments; hence, it is not a limiting factor for phytoplankton growth here.

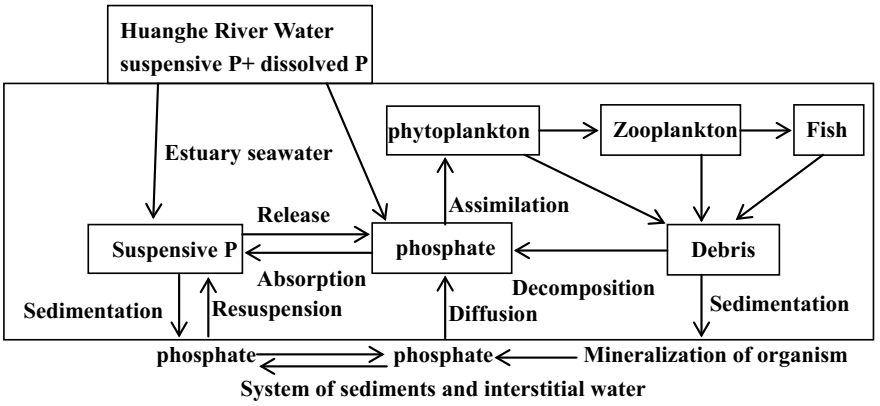

Fig. 11 Cycle of PO_4-P in the estuary

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Part III
Changes in Nutrients and Its Ecological Responses in the Changjiang River Estuary and Jiaozhou Bay

Responses of a Coastal Phytoplankton Community to Increased Nutrient Input from the Changjiang River

Mingjiang Zhou, Zhiliang Shen and Rencheng Yu

Abstract Nutrient input from the Changjiang River (Yangtze River) has been increasing dramatically since the 1960s. At the mouth of the Changjiang River, the nitrate concentration has increased about three-fold in 40 years, from 20.5 μmol/L in the 1960s to 59.1 μmol/L in the 1980s and to 80.6 μmol/L in 1990–2004. Phosphate concentration increased by a factor of 30%, from 0.59 μmol/L in the 1980s to 0.77 μmol/L in 1990–2004. The increasing nitrate input has arisen mostly from the mid and lower reaches of the Changjiang River, where the river meets one of the most strongly developed agriculture areas in China. Responses of the coastal phytoplankton community to the increasing nutrient inputs are also seen in the available monitoring data. First, a trend of increasing phytoplankton standing stock from 1984 to 2002 appeared in the Changjiang River estuary and adjacent coastal waters, especially in late spring. Secondly, the proportion of diatoms in the whole phytoplankton community showed a decreasing trend from about 85% in 1984 to about 60% in 2000. Finally, red tides/harmful algal blooms increased dramatically in this area in terms of both number and scale. About 30–80 red tide events were recorded each year from 2000 to 2005 in the East China Sea. The scale of some blooms has been in excess of 10,000 km^2.

Keywords Nutrient · Responses · Phytoplankton community · Red tide
Changjiang River estuary

The Changjiang River, with a length of about 6300 km, is the largest river flowing into the northern part of the Pacific Ocean. Annual water discharge from the Changjiang River is more than 9.0×10^{11} m^3 (Jiang and Wang 2004). It has a drainage basin area of 1.8×10^6 km^2, comprising the most important economic zones around the cities of Chongqing, Wuhan, and Shanghai, as well as important agriculture areas which annually yield about 40% of the total agricultural production in China. The rapid development of the economy and increase in the population in the drainage

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basin have significantly affected the river and consequentially affected the aquatic ecosystem in the Changjiang River estuary and adjacent coastal waters.

Like most of the estuaries in the world, the Changjiang River estuary is a very productive and resource-rich aquatic ecosystem (Ning et al. 2004). High primary production supports high fishery production in adjacent coastal waters. The nearby Zhoushan and Lusi fisheries are both important fishery grounds in China. However, the aquatic ecosystem is also quite sensitive to changes in the Changjiang River, which is now being disturbed from human activities. The construction of dams and reservoirs along the river, such as the Three Gorges Dam, has resulted in an increasing concern about the long-term changes of the Changjiang River and their impacts on the aquatic ecosystem in the estuary and adjacent coastal waters (Luo and Liu 1994).

The highly productive nature of the estuary is directly related to the large amounts of nutrients carried by the river. Shen (1991) reported that the annual fluxes of dissolved inorganic nitrogen (DIN), phosphorus (PO_4–P), and silicon (SiO_3–Si) were 7.84×10^5, 1.51×10^4, and 2.22×10^6 tonnes, respectively. In 1998, the total nitrogen (TN) and DIN fluxes reached 2.85×10^6 and 1.75×10^6 tonnes, respectively, due to the large flood that year (Shen 2004). The high loading of nutrients has resulted in serious eutrophication in this area according to the Bulletin of Marine Environmental Quality of China (State Oceanic Administration 2006). Changes in phytoplankton communities as a result of such eutrophication may negatively affect the local ecosystem, leading to adverse consequences such as harmful and nuisance algal blooms, bottom water hypoxia, and declining fishery stocks (Zhou et al. 2001, 2003a, b; Ning et al. 2004).

The relationship between nutrient availability in seawater and the dynamics of phytoplankton communities has been an important topic for a long time in biological oceanographic research. Several excellent studies have been carried out in different areas (Domingues et al. 2005; Furnas et al. 2005; Paerl 2006). However, linking nutrient biogeochemical processes and the succession of phytoplankton communities is complex. For the Changjiang River estuary and the adjacent coastal waters, analysis is restricted by the lack of systematic and long-term investigations. However, as a "hot spot" for oceanographic studies in China, the area does have large amounts of data accumulated during baseline investigations and scientific research from the 1960s to the present (Luo and Liu 1994; Zhou et al. 2003a; Ning et al. 2004). In this section, we use the data collected during the ongoing project on the oceanography and ecology of harmful algal blooms, as well as data from previous investigations, to analyze the variation and trends of nutrient loading in the Changjiang River, and the responses of the phytoplankton community, including the occurrence of red tides/harmful algal blooms.

1 Oceanographic Background

The Changjiang River estuary is located at the junction of the East China Sea (ECS) and the Yellow Sea (YS), on the continental shelf at the western rim of the Pacific Ocean. Circulation in the ECS and YS has been thoroughly investigated and char-

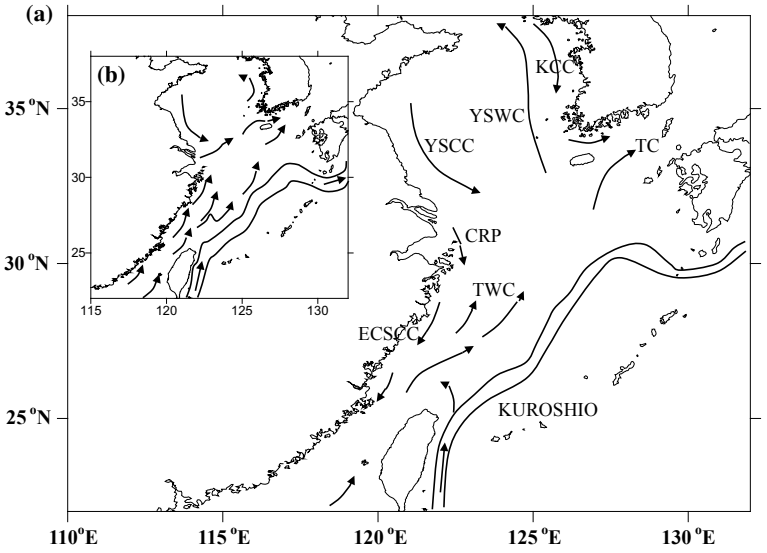

Fig. 1 Circulation pattern in the East China Sea and Yellow Sea (after Su 1998; Naimie et al. 2001): **a** winter and **b** summer circulation features. YSCC: Yellow Sea Coastal Current; CRP: Changjiang River Plume; ECSCC: East China Sea Coastal Current; TWC: Taiwan Warm Current; TC: Tsushima Current; YSWC: Yellow Sea Warm Current; KCC: Korean Coastal Current

acterized in the literature, and the circulation pattern has been summarized by Su (1998) (Fig. 1). The estuary and adjacent coastal waters are mainly affected by freshwater runoff from the Changjiang River, the coastal currents along Mainland China (East China Sea Coastal Current, ECSCC; Yellow Sea Coast Current, YSCC), the Taiwan Warm Current (TWC) from Taiwan Strait, and a branch of the Kuroshio Current extending into the area from northeast Taiwan. The circulation pattern is different in winter and in summer, due primarily to the effects of monsoons and the changing scale of the Changjiang River runoff. During the winter season, when north or northeast wind prevails, the major runoff from the Changjiang River flows southeastward along the coast of Zhejiang province. The region affected by freshwater discharge is generally confined to the area west of 123°E, bordered by the TWC in the offshore area. During the summer season, however, southwest winds prevail, and the intensified runoff of the Changjiang River normally turns eastwards or northeastwards toward Cheju Island, Korea. During this period of time, the ECSCC also moves northeastward along the coast, driven by the southwest monsoon. This forcing causes the freshwater affected area to extend northward, occupying a large area of the ECS and YS. The affected area even reached Cheju Island, during a huge flood from the Changjiang River (Wang et al. 2002).

The Changjiang River estuary and adjacent coastal waters are significantly affected by the nitrogen-rich freshwater from the outflow of the Changjiang River. According to Wong et al. (1998), a high N:P ratio and "excess nitrate" can be observed

in surface water with a salinity below 30.5, covering about one-third to one-half of the ECS in the summer of 1992. The maximum phytoplankton standing stock and productivity often appear at the front area of the freshwater plume, about 100 km away from the river mouth, at salinities between 25 and 30. Primary production there is limited by low phosphorus concentration in spring, as suggested by many field investigations and laboratory simulation experiments (Wong et al. 1998; Pu et al. 2001; Ning et al. 2004). In summer, primary productivity and Chl-*a* level are further enhanced by nutrients from the subsurface layer through upwelling. Because this subsurface water has a much lower N:P ratio, phosphorus limitation could be reduced at this time (Chen et al. 2004). Low temperatures during the winter and high turbidity at the areas close to the river mouth are also factors limiting primary production. Therefore, seasonal considerations are important when analyzing the relationships between nutrient inputs from the Changjiang River, and the responses of coastal phytoplankton communities.

2 Data Source and Methods

Data used in this report are from an ongoing project entitled "Ecology and Oceanography of Harmful Algal Blooms in China" (Zhou and Zhu 2006), our previous investigations supported by the Natural Science Foundation of China (NSFC), the Chinese Academy of Sciences, and the Three Gorges Project Construction Committee of the State Council of China, and other published references as indicated in each part. Data for analysis of long-term changes in nutrient input from the Changjiang River are based on the analysis of water samples collected from the mouth of the river as indicated in Fig. 2a. Nitrate and phosphate concentrations were determined with a Skalar flow analyzer by colorimetric methods. Detailed information for nutrient analytical methods has been described elsewhere (Shen 1997, 2004). Sampling stations selected for studies on red tides/harmful algal blooms in the Changjiang River estuary and adjacent coastal waters from 2002 to 2005 are illustrated in Fig. 2b. A detailed background of the study and the methods used are also described elsewhere (see Zhou et al. 2003a, b).

3 Changes in Nutrient Inputs from the Changjiang River

Increase in nitrogen input from the Changjiang River to the estuary and its adjacent coastal waters is apparent from the increasing concentration of nitrate at the mouth of the Changjiang River (Fig. 3). Nitrate is the major component of the DIN and TN in the Changjiang River responsible for growth of phytoplankton (Shen 2004; Xu et al. 2004). The concentration of nitrate increased about three-fold in 40 years, from 20.5 μmol L^{-1} in the 1960s to 59.1 μmol L^{-1} in the 1980s and to 80.6 μmol L^{-1} in 1990–2004, based on our results from 1985 to 2004 and on reference data collected

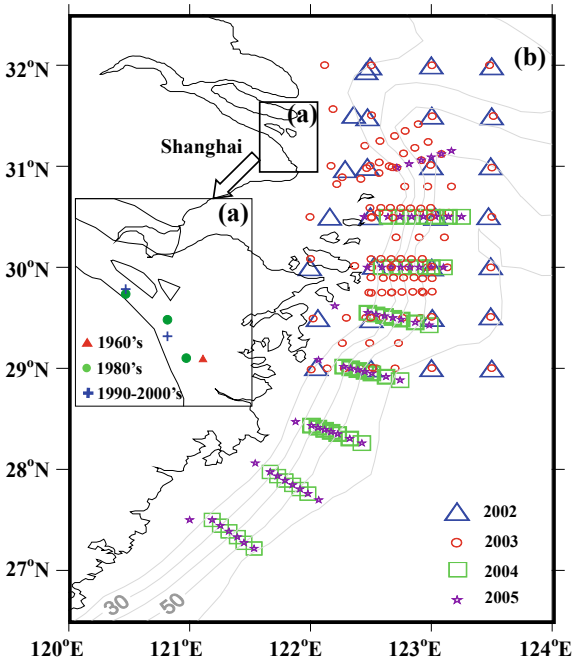

Fig. 2 Map of sampling stations in the Changjiang River estuary and adjacent coastal waters: **a** stations for nutrient analysis in the 1960s, 1980s, and 1990–2000s; **b** stations for the Chinese National Basic Research Priority Program (973) studying ecology and oceanography of harmful algal blooms, during cruises from 2002 to 2005

from 1963 to 1964. Some previous studies indicated that nitrate behaves conservatively in the area close to the mouth of the Changjiang River (Edmond et al. 1985; Tian et al. 1993). However, Zhang (1996) found a broad maximum nitrate concentration at the early stages of mixing in waters with chlorinity of 5–10% (salinity about 9–18) and a simple dilution afterward up to chlorinity of 17–18% (salinity about 31–33). It was suggested that the distribution pattern of nitrate concentration in the estuary depends on the balance of complex processes affected by both biotic and abiotic events (Zhang 1996). This phenomenon, however, would not significantly affect the long-term trend presented here, because our data were collected and compared at defined locations in the river mouth (Fig. 2a). Analysis of the riverine nitrate concentration (Liu et al. 2003; Shen 2004) and the analysis of nitrogen budget in the drainage basin of the Changjiang River (Yan et al. 2003; Bao et al. 2006) support our observations of increasing flux of nitrogen into the sea. The results of Bao et al. (2006) show that there was a 1.6-fold increase in nitrogen output to the Changjiang River during the 10-year interval from the 1980s to the 1990s, which is comparable to that derived from the analytical results of the nitrate concentration at the river mouth (Zhang et al. 1995). Those results on nitrogen budget analysis also indicate that anthropogenic nitrogen has far exceeded the natural terrestrial bio-fixed nitrogen in the drainage basin, suggesting that human activity is the major reason for the increasing nitrogen flux (Bao et al. 2006). The increased flux of nitrogen in the Changjiang River mainly came from the middle and lower reaches, especially from the river area between Dongting Lake and Boyang Lake (Shen et al. 2003).

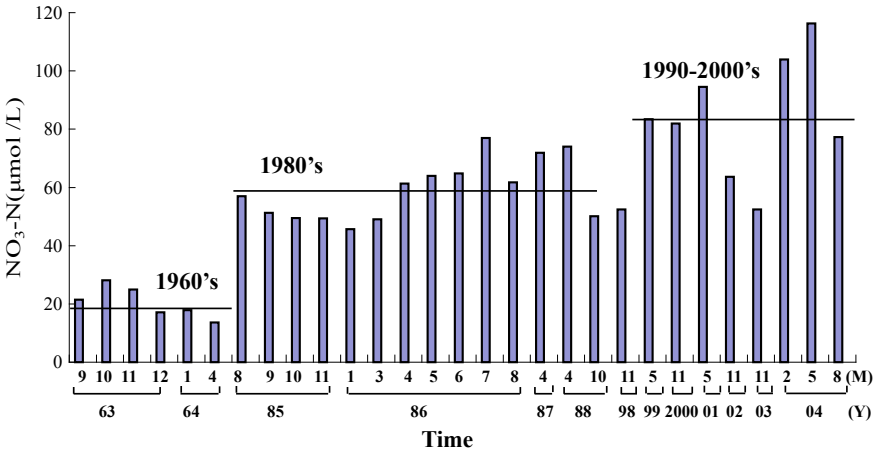

Fig. 3 Long-term variation of nitrate concentration at the mouth of the Changjiang River. (Y) and (M) are the year and the month of sample collection, respectively. The solid line in the figure indicates the averaged value of nitrate concentration during the sampling period marked above the line (data collected during the 1960s are from Prof. Gu Hongkan)

Phosphate concentration also increased at the mouth of the Changjiang River, from 0.59 μmol L^{-1} in the 1980s to 0.77 μmol L^{-1} in 1990s–2004 at the mouth of the Changjiang River (Fig. 4). Liu et al. (2003) analyzed historical trends of phosphate concentrations in the Changjiang River, but no clear trend could be found due to the limited data available. According to Jickells (2005), human mediated phosphorus discharge is mainly from sewage which, compared to nitrogen discharge, is relatively easy to control. Therefore, the flux of phosphorus in the river is expected to decrease in the long run as more sewage is treated prior to discharge. In contrast to nitrate, phosphate concentration in the Changjiang River estuary and adjacent coastal waters is affected by other important sources, such as the TWC, and branches of the Kuroshio Current. A phosphorus budget for the ECS found phosphorus fluxes from the TWC and Kuroshio Current were much higher than from the Changjiang River (Fang 2004). Also, the release of phosphorus from sediments and water column regeneration are important factors contributing to phosphate in water column (Fang 2004).

Silicon is another important macronutrient, especially for the growth of diatoms. Human activity normally has little direct effect on silicon concentration in rivers, but manipulation of river systems can alter the riverine silicon fluxes (Humborg et al. 2002). A decreasing trend for silicate was found in many rivers in North Europe after the construction of dams, which enhanced the consumption of silicate by diatom blooms (Conley et al. 2000). In the long run, a decreasing trend of silicate might occur after the construction of Three Gorges Dam on the Changjiang River. However, silicate concentration in the Changjiang River estuary and adjacent waters remain

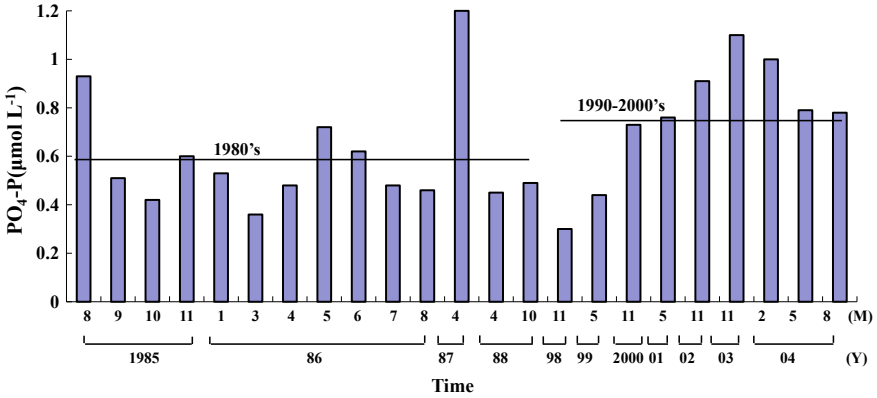

Fig. 4 Long-term variation of phosphate concentration at the mouth of the Changjiang River. (Y) and (M) are the year and the month of sample collection, respectively. The solid line in the figure indicates the averaged value of the phosphate concentration during the sampling period marked above the line

high at present and will not become a limiting factor for phytoplankton growth in the near future.

Changing nutrient fluxes of the Changjiang River have led to a shift in the nutrient regime in the estuary and adjacent coastal waters. A high N:P ratio has become a characteristic feature of coastal areas affected by freshwater discharge (Wong et al. 1998). The N:P ratio in the Changjiang River estuary and adjacent coastal waters is typically between 15 and 60 in the surface water in early spring. Increases in the N:P ratio and the N:Si ratio are expected to continue. At the same time, the increased loading of both nitrogen and phosphorus has caused the Changjiang River estuary and adjacent coastal waters to become highly eutrophic. Increasing nutrient concentrations, as well as altered nutrient ratios, could have future impacts on the phytoplankton community in this region.

4 Responses of Phytoplankton Community

Both field investigations and simulation experiments have suggested that phytoplankton abundance and community structure can be modulated by changing nutrient input (Domingues et al. 2005; Furnas et al. 2005; Paerl 2006). However, to identify the specific responses of phytoplankton community to increasing input of nutrients in the Changjiang River estuary and adjacent coastal waters is difficult, due to the lack of long-term datasets.

Phytoplankton standing stock, indicated by Chl-*a*, has increased in the Changjiang River estuary and adjacent coastal waters in the summer during the last 20 years (Table 1). These data are from a similar location, the front of the freshwater plume.

The increase of nutrient input could be a reason for the increasing Chl-*a* levels in this area. However, more data are still needed to establish a clear relationship between nutrient input and the response in phytoplankton abundance.

In late spring, the increase in phytoplankton standing stock is apparent in coastal waters of the estuary and along the coast of Zhejiang Province from the large-scale red tides/harmful algal blooms over last several years (Zhou and Zhu 2006). The red tides will be discussed in the next section.

Another response of phytoplankton communities to the changing nutrient input in this region is the decrease in the relative abundance of diatoms, accompanied by an increasing trend of dinoflagellates. Re-analysis of the previous data indicated that the percentage of diatom species in the Changjiang River estuary and adjacent coastal waters decreased from 85% in the mid-1980s to 64% in 2002 (Table 2). More significantly, the percentage of dinoflagellates in terms of cell density can reach 99% during large-scale red tides in late spring. A trend of increasing frequency of non-diatom novel phytoplankton blooms, accompanied by nutrient enrichment of coastal waters and inland seas, has been reported on a global scale (Smayda 1990). Diatoms are fast-growing species that can easily become predominant under non-limiting conditions. However, diatoms are more readily affected by phosphorus limitation than flagellates, according to Egge (1998). Egge proposed that the high phosphorus demands of diatoms, and the high efficiency in absorption of phosphorus by flagellates, were the major reasons for this nutrient-based limitation for diatoms (Egge 1998). Many authors have also indicated that high N:P ratio and phosphate limitation are characteristics of the Changjiang River estuary and adjacent coastal waters in spring (Wong et al. 1998; Pu et al. 2001; Ning et al. 2004). Therefore, the high N:P ratios arising from increasing nitrogen inputs from the Changjiang River can be an important factor affecting the relative abundance of diatoms.

Phosphate limitation and high N:P ratio have been observed in other large estuaries of China, such as the Huanghe (the Yellow River) estuary (Zhang et al. 2004) and the Pearl River estuary (Zhang et al. 1999; Yin et al. 2001), due to huge nitrogen input from the rivers. However, little information from the literature is available on the

Table 1 Trend of Chl-*a* concentration in the Changjiang estuary and adjacent coastal waters during the last 20 years

Time	Location	Maximum Chl-*a* concentration (mg m^{-3})	Average Chl-*a* concentration (mg m^{-3})	References
1984.8	28°–32°N west to 124°E	6.6	–	Ning et al. (1986)
1988.8	30°30′–31°50′N west to 124°30′E	13.0	–	Shen and Hu (1995)
1995.9	30°30′–31°30′N 121°30′–123°38′E	13.8	2.80	Liu et al. (2001)
2002.8	29°00′–32°00′N 122°00′–123°30′E	24.2	3.94	Zhou et al. (2003b)

Table 2 Variation in the percentage of diatom species to the overall species in the Changjiang River estuary and adjacent coastal waters during the last 20 years

Time	Location	Percent diatom (%)	Reference
1984	30°00′–32°10′N, 121°21′42″–124°00′E	85	Wang (2002a)
1985.8–1986.10	30°20′–32°00′N, 121°10′–124°00′E	80	Guo and Yang (1992)
1990.8-9	31°10′–31°55′N, 121°00′–122°15′E	63	Shen et al. (1995)
1996.9	31°00′–31°30′N, 121°30′–122°34′E	56	Xu et al. (1999)
1998.5,10; 1999.2-3,8; 2000.3	30°00′–32°10′N, 121°21′–124°00′E	64	Wang (2002a)

responses of phytoplankton communities to the long-term changes of nutrient regime in these estuaries. It was indicated that the replacement of diatoms by dinoflagellates was the main feature of changes of phytoplankton community in recent years in the Bohai Sea, which was probable caused by increasing N:P ratio and decreasing Si:N ratio (Wei et al. 2004). In the Pearl River estuary, it was also considered that phosphate limitation and silicate exhaustion might lead to dominance of dinoflagellates or other non-silica-requiring species (Yin et al. 2000).

In the YS, responses of phytoplankton community to the long-term changes of nutrient concentration and composition were analyzed, based on the seasonal transect maintained by the State Oceanic Administration of China during 1976–2000 (Lin et al. 2005). The percentage of diatoms decreased from 88.9% in 1986 to 69.5% in 1998, accompanied by an increased percentage of dinoflagellates from 11.1 to 30.5%. Limitation of phosphate or silicate caused by the increase in the DIN concentration and the decreases in both phosphate and silicate concentrations were considered the major reason for this shift of species. Meanwhile, a decreasing trend of phytoplankton standing stock and productivity was observed in this region, most probably due to the limitation of phosphate (Lin et al. 2005). This trend in the YS, however, differs from our observations for the Changjiang River estuary and adjacent coastal waters, where red tides/harmful algal blooms with high biomass have become an important phenomenon in late spring.

5 Red Tide/Harmful Algal Bloom

Red tide/harmful algal bloom is a common phenomenon associated with eutrophication. The frequency and intensity of red tides in some coastal areas may be good indicators of eutrophication status. In the Changjiang River estuary and adjacent coastal waters, the first recorded red tide of *Noctiluca scintillans* was in the 1930s (unpublished data of Fei H. N.). After that, there was no report of red tide in this

region until 1972, when a bloom of *Trichodesmium* spp. was reported (Chen 1982). However, from the 1980s to 2000, the frequency of red tides increased dramatically (Fig. 5), along with the rapid economic development in China. From 2001 to 2005, about 30–80 red tide events were recorded each year in the ECS, according to the Bulletin of Marine Environmental Quality of China (State Oceanic Administration 2006). Most of the red tides occur from May to June in the Changjiang River estuary and the coastal waters of Zhejiang Province (Fig. 6).

In 2000, a large-scale bloom caused by *Prorocentrum donghaiense* (synonym *P. dentatum* in this area) was reported in the Changjiang River estuary and adjacent coastal waters (Wang 2002b). Since then, a large-scale bloom of *P. donghaiense* has appeared almost every year in a similar season and location. Our yearly cruises (Zhou and Zhu 2006), beginning in 2002 (Fig. 2), revealed that the large-scale blooms can extend from the estuary of the Changjiang River down to coastal waters of Fujian Province, with an area of over 10,000 km^2 in 2004 and 2005 (Fig. 7). The cell density of *P. donghaiense* is as high as 10^7–10^8 cells L^{-1}. Besides *P. donghaiense*, other algae, such as *Skeletonema costatum, Karenia mikimotoi, Alexandrium catenella, N. scintillans*, and *Scrippsiella trochoidea*, also reach high concentrations at different times and locations. The large-scale red tide events typically last for about 1 month from late April to early June.

Since the 1980s, there has been an apparent shift of red tide causative species in the Changjiang River estuary and adjacent coastal waters (Ye and Huang 2003). From the 1980s to 1990s, the representative causative species were *S. costatum* and *N. scintillans*, a species of heterotrophic dinoflagellate that can prey on *S. costatum*. However, in the late 1990s, the representative causative species changed to dinoflagellates, including *P. donghaiense*, *K. mikimotoi*, *A. catenella*, along with *N. scintillans*. The shift in red tide causative species is believed to be a result of a high N:P ratio and of phosphate limitation caused by the increasing input of nitrogen from the Changjiang River. Egge (1998) has reported that toxic flagellate blooms occur in waters characterized by high N:P ratios and phosphate deficiency.

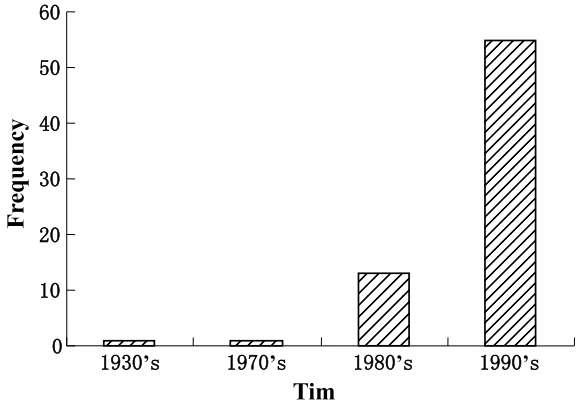

Fig. 5 Occurrence of red tides in the Changjiang River estuary and adjacent coastal waters from 1930s to 1990s

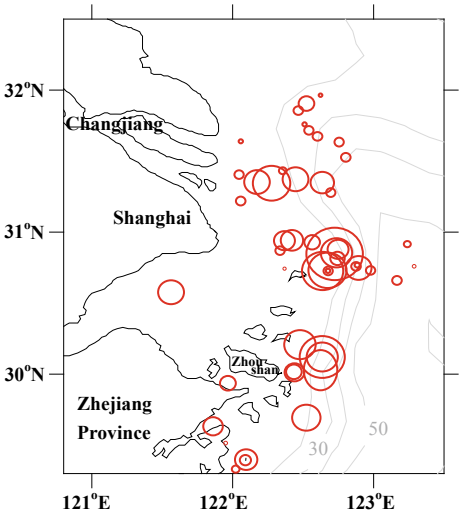

Fig. 6 Distribution of red tides in the Changjiang River estuary and the adjacent coastal waters recorded prior to 2000 (redrawn from Zhou et al. 2003a). Position and size of the circles in the figure roughly represent the location and scale of red tides

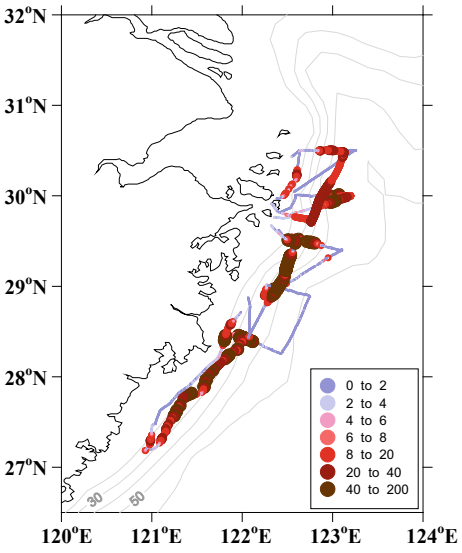

Fig. 7 Spatial distribution of a 2004 large-scale *Prorocentrum donghaiense* red tide in the Changjiang River estuary and adjacent waters. The color gradient in the figure represents the different Chl-*a* concentrations (mg m^{-3}) measured by a multiparameter water quality meter (YSI) during the CEOHAB cruise in 2004

Based on mesocosm experiments, Egge (1998) suggested that diatoms would proliferate at the beginning of the growth season when nutrient limitation did not exist. Other algae would be expected to take over only after the depletion of some nutrients like silicate. However, in the Changjiang River estuary and adjacent coastal waters, limitation of silicate does not seem to occur (Wang et al. 2003). But when phosphate concentration was low, dinoflagellate *P. donghaiense* could prevail against diatom *S. costatum* in their competition, as indicated in a mesocosm experiment in the ECS (Li et al. 2003). It was found that the growth of *S. costatum* could be limited

when phosphate concentration in seawater was lower than 0.3 μmol L^{-1} (Li et al. 2003). In our cruises in the spring of 2005, phosphate concentration decreased to about 0.2 μmol L^{-1} after the initial diatom bloom, with an elevated N:P ratio of 30–90 at the surface waters, suggesting that the growth of diatom was limited by the low concentration of phosphate in seawater (unpublished data). Under these conditions, flagellate species adapted to grow at low phosphate concentrations could proliferate to form large-scale blooms, with the "excess nitrogen" left after the initial diatom bloom. This pattern of succession was observed in our cruises in 2005, when large-scale red tides of *P. donghaiense* and *K. mikimotoi* appeared after a bloom of *S. costatum*. Therefore, phosphate limitation and "excess nitrogen" resulted from the increasing nitrogen discharged into the Changjiang River estuary, and the adjacent coastal waters promote the formation of large-scale dinoflagellate blooms in spring and lead to the shift of major red tide causative species from diatoms to dinoflagellates. However, the mechanisms for these dinoflagellate species to grow under low concentration of phosphate need further study. Possible reasons for the dinoflagellate to flourish in such a low phosphate conditions could include an intrinsically high uptake affinity for phosphate, as well as the ability to utilize organic phosphorus compounds via alkaline phosphatase (Huang et al. 2005). Mixotrophy and vertical migration capabilities of some dinoflagellates could also be possible contributing factors.

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Long-Term Changes in Nutrient Structure and Its Influences on Phytoplankton Composition in Jiaozhou Bay

Zhiliang Shen

Abstract Due to the influence of human activities, nutrient concentrations, nutrient ratios and phytoplankton composition have notably changed in Jiaozhou Bay, China, since the 1960s. From the 1960s to the 1990s, nutrient concentrations have increased 1.4 times for PO_4–P, 4.3 times for NO_3–N, 4.1 times for ammonium (NH_4–N) and 3.9 times for dissolved inorganic nitrogen (DIN). The molar ratio of DIN:PO_4–P increased from 15.9 ± 6.3 to 37.8 ± 22.9. SiO_3–Si concentration has remained at a very low level. The high ratio of DIN:PO_4–P and low ratios of SiO_3–Si:PO_4–P (7.6 ± 8.9) and SiO_3–Si:DIN (0.19 ± 0.15) showed the nutrient structure of Jiaozhou Bay has changed from more balanced to unbalanced during the last 40 years. The possibility that DIN and/or PO_4–P as limiting factors of Jiaozhou Bay phytoplankton has been lessened or eliminated and that of SiO_3–Si limiting has been increased. The changes in nutrient structure may have led to the decrease in large diatoms and a shift of phytoplankton species composition.

Keywords Nutrient · Molar ratio · Nutrient structure · Nutrient balance · Limiting Phytoplankton · Long-term changes · Jiaozhou Bay

During the last 40 years, nutrient concentrations in some Chinese estuaries and coastal waters have changed considerably. High nitrate (NO_3–N) (65 μmol L^{-1}) concentration found in the Changjiang River estuary in 1981 (Edmond et al. 1985) was about four times higher than that in 1963 (Gu et al. 1981). Between 1959 and 1983, NO_3–N and phosphate (PO_4–P) have increased 1.9 times and 1.3 times, respectively, in Bohai Bay and its eastern waters (Shen 1999). Similar changes have been observed in many estuaries and coastal areas in the world (Walsh et al. 1981; Smith et al. 1987; Marchetti et al. 1989; van Bennekom and Wetsteijn 1990; Turner and Rabalais 1991). The increase in nitrogen (N) and phosphorus (P) nutrient concentrations and ratio will cause different ecological influences in different estuaries and coastal waters. For example, in the Po River- and the Mississippi River-dominated coastal

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waters, nutrient structure has become more balanced due to N and P concentrations increasing substantially and silica (Si) only slightly increasing or decreasing. Potentially decreasing N and P limitations and increasing Si limitation for phytoplankton growth may favour a shift from diatoms to non-siliceous phytoplanktons (Justic et al. 1995). The Changjiang River carries very high concentrations of NO_3–N into the estuary waters, resulting in dissolved inorganic nitrogen (DIN)/PO_4–P molar ratios required for phytoplankton growth to be unbalanced. Monthly investigations from 1985 to 1986 showed that the DIN/PO_4–P molar ratios average between 70 and 456 for inside the mouth of the estuary and 25–43 for the plume and nearby regions (Shen et al. 1992) and are far higher than the mean ratio of nutrients contained in marine phytoplankton (Redfield et al. 1963; Brzezinski 1985). In Bohai Bay, although the concentrations of DIN and PO_4–P and net phytoplankton cell numbers increased substantially, N is still a limiting factor for phytoplankton growth since the ratio of DIN and PO_4–P has not increased (Shen 1999).

Jiaozhou Bay is a semi-enclosed bay situated in the western part of the Shandong Peninsula, China. The Bay is surrounded by Qingdao City (population 7×10^6), with an area of about 390 km^2 and an average water depth of about 7 m. The Bay mouth is narrow, only about 2.5 km wide, and connects the Bay with the South Yellow Sea. The average rainfall is 775.6 mm, with 58% of that in summer and 23% in winter. More than 10 small rivers enter the Bay, and the largest one is Dagu River, with an annual average run-off of 6.61×10^8 m^3. Most of these rivers have become discharge trenches for industrial and living wastes from Qingdao City and important sources of external nutrients entering Jiaozhou Bay. These high nutrient inputs contribute to the high annual primary production of 503 ± 184 mg C m^{-2} d^{-1} for Jiaozhou Bay (Wang et al. 1995).

Nutrient concentrations have been periodically measured in Jiaozhou Bay since 1962 (Gu et al.1982a, b) with 81 investigations during the periods 1962–1998. The data used are from the periods 1962–1963 (15 investigations, Gu et al. 1982a), 1983–1986 (41 investigations, Shen et al. 1994) and 1991–1998 (25 investigations). The samples were taken on a monthly basis during 1962–1963 and 1983–1986 and quarterly during 1991–1998. The concentrations of NO_3–N, nitrite (NO_2–N), ammonia (NH_4–N) and PO_4–P have been measured in all investigations, although SiO_3–Si has been measured only since August 1985 (altogether 37 investigations). The samples were measured using comparable analytical methods (colorimetry). The stations sampled are indicated in Fig. 1. Two major themes are discussed in this section: (1) long-term changes in nutrient concentrations and ratios in Jiaozhou Bay; and (2) the influence of nutrients on phytoplankton composition.

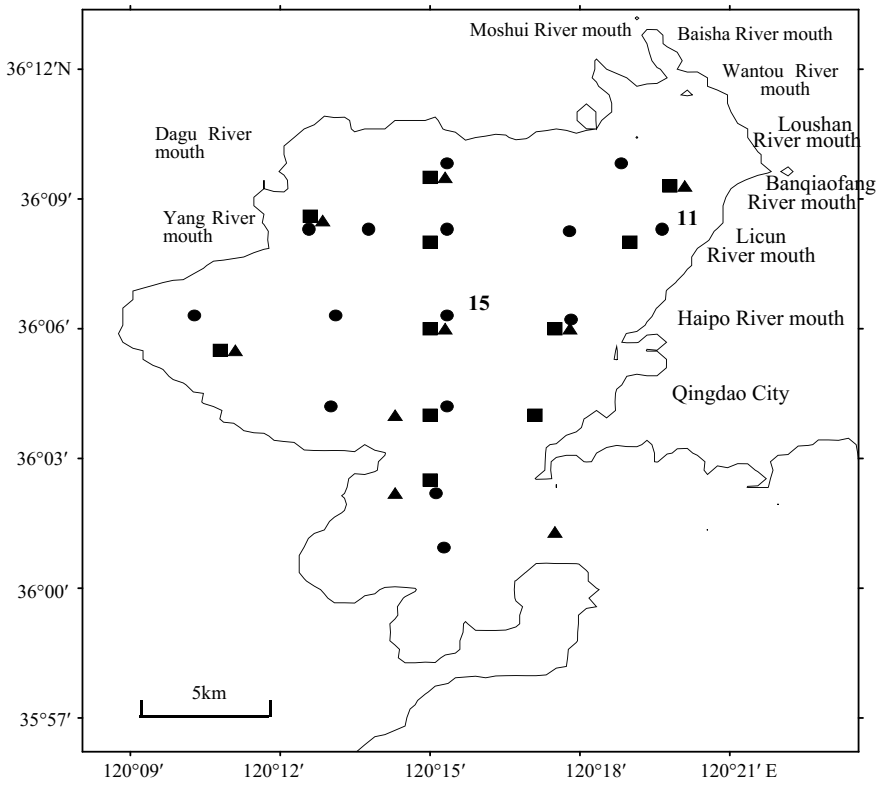

Fig. 1 Station positions

1 Long-Term Changes in Nutrient Concentrations and Structure in Jiaozhou Bay

Long-term changes in nutrient average concentrations and molar ratios in surface layer water in Jiaozhou Bay were compared on a seasonal basis during 1962–1963 (four observations), 1983–1986 (16 observations) and 1991–1998 (25 observations) (Table 1). From the 1960s (1962–1963) to the 1980s (1983–1986) and the 1990s (1991–1998), PO_4–P concentration increased 2.1 times and 1.4 times, NO_3–N concentration increased 3.7 times and 4.3 times, NH_4–N concentration increased 3.1 times and 4.1 times, and DIN concentration increased 3.0 times and 3.9 times, respectively. The DIN/PO_4–P molar ratio in Jiaozhou Bay increased from 15.9 to 26.5 between the 1960s and the 1980s and increased from 26.5 to 37.8 between the 1980s and the 1990s. The ratio of NO_3–N/NO_2–N/NH_4–N has not changed between the 1960s and the 1990s, and NH_4–N was found to be the main form of DIN (72–76% of DIN) all along Jiaozhou Bay. In comparison with 1991–1998 to 1986, SiO_3–Si average concentration decreased somewhat from 2.4 μmol L^{-1} in 1986 to

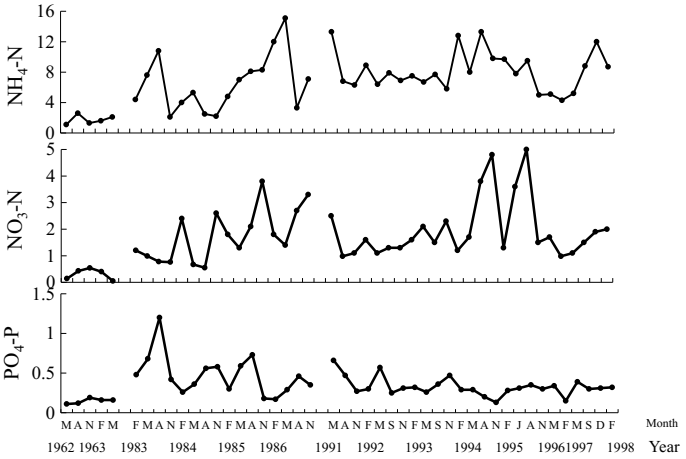

Fig. 2 Long-term changes in N and P concentrations (μmol L^{-1}) in surface water in Jiaozhou Bay, F, February; M, May; J, June; A, August; S, September; N, November; D, December

2.0 μmol L^{-1} in 1991–1998. The molar ratios of SiO_3–Si/DIN and SiO_3–Si/PO_4–P have not changed (Table 1). The long-term changes in nutrient concentrations during 1962–1963, 1983–1986 and 1991–1998 in Jiaozhou Bay are indicated in Fig. 2.

2 N and P in Jiaozhou Bay

During the last 40 years, a significant increase in N and P concentrations in Jiaozhou Bay has been observed and is the direct result of human influences. From 1962 to 1998, the population of Qingdao City increased from 4.6×10^6 to 7.0×10^6 and the gross value of industrial output increased 80 times. Particularly, the eastern shore of Jiaozhou Bay is the main industrial part and densely populated area in Qingdao City where five small rivers, Haibo River, Licun River, Banqiaofang River, Lousan River and Waitou River, have become discharge rivers of industrial wastes and sewage from urban districts. The discharge of industrial waste and sewage in urban districts was 70.2×10^6 t a^{-1} and 14.4×10^6 t a^{-1}, respectively, in 1980 and increased to 145.6×10^6 t a^{-1} for the total amount of wastes (100.6×10^6 t a^{-1} for industrial wastes) in 1987 (MEMC, NSB, SOA 1992). Sea farming along the beach of Jiaozhou Bay also contributes N and P to the Bay. From 1978 to 1987, the area of shrimp culture in Qingdao City increased 302 times. The amounts of fertilizers and detergents used have greatly increased; for example, the use of fertilizers has increased by a factor of three during 1980–1998 (Qindao Yearbook Editorial Office 1998).

Table 1 shows that inorganic N concentration increased from the 1960s to the 1990s and the different N forms increased at a similar ratio: 4·3 times for NO_3–N and 4.1 times for NH_4–N. NH_4–N was the major form of inorganic N (72–76% of

Table 1 Long-term changes in nutrient concentrations (μmol L^{-1}) and molar ratios in surface water in Jiaozhou Bay

	PO_4–P	SiO_3–Si	NO_3–N	NO_2–N	NH_4–N	DIN	NO_3–N / DIN	NO_2–N / DIN	NH_4–N / DIN	DIN / PO_4–P	SiO_3–Si / PO_4–P	SiO_3–Si / DIN
1962–1963	0.14		0.38	0.17	1.6	2.2	0.17	0.08	0.75	15.9		
(n = 4)	± 0.03		± 0.15	± 0.13	± 0.6	± 0.6	± 0.05	± 0.06	± 0.09	± 6.3		
1983–1986	0.43	2.4[a]	1.8	0.39	6.5	8.7	0.23	0.05	0.72	26.5	7.5[a]	0.20[a]
(n = 16)	± 0.17	± 1.1	± 1.0	± 0.23	± 3.7	± 3.9	± 0.12	± 0.03	± 0.14	± 23.4	± 2.0	± 0.19
1991–1998	0.33	2.0	2.0	0.66	8.2	10.8	0.18	0.06	0.76	37.8	7.6	0.19
(n = 25)	± 0.11	± 1.9	± 1.1	± 0.40	± 2.5	± 3.4	± 0.06	± 0.03	± 0.07	± 22.9	± 8.9	± 0.15

n = Number of observations
[a]*n* = 4

DIN) in Jiaozhou Bay. Most of NH_4–N in sea water in Jiaozhou Bay is imported from land, and part of it takes part in phytoplankton circulation. According to the study of NH_4–N uptake kinetics, NH_4–N assimilated by phytoplankton was far higher than NO_3–N, and NH_4–N turnover was only 16 h in Jiaozhou Bay in the summer (Jiao and Wang 1993). Because of shallow water and richer phytoplankton in Jiaozhou Bay, there is not enough time to convert NH_4–N into NO_3–N and a direct cycle between NH_4-N and phytoplankton is formed. A similar situation also takes place in some other Chinese coastal waters, for example in Bohai Bay in summer and autumn (Shen 1999).

NO_3–N and NH_4–N are consumed by phytoplankton simultaneously. In the 1960s (Gu et al. 1982a), NO_3–N was often exhausted in Jiaozhou Bay sea water, particularly during phytoplankton blooms. The annual average molar ratio NO_3–N/PO_4–P was only 2.8, and phytoplankton growth was mainly dependent upon NH_4–N. In the 1980s, because of increases in the external load of NO_3–N, only a few stations where NO_3–N concentration was to be found were below the detection limit (<0.07 μmol L^{-1}) (Shen et al. 1994), and the molar ratio of NO_3–N/PO_4–P (4.2) was still very low (Table 1). In the 1990s, NO_3–N concentrations were not observed below the detection limit and the molar ratio of NO_3–N/PO_4–P was only 6.0 (Table 1). In Jiaozhou Bay ecosystem, due to high concentration of NH_4–N, N is not the limiting factor for phytoplankton growth.

Because the increase in concentrations of PO_4–P was slower than that of DIN, the molar ratio of DIN/PO_4–P increased very rapidly and averaged from 15.9 in the 1960s, to 26.5 in the 1980s and 37.8 in the 1990s (Table 1). These ratios are higher than the average ratio of about 16 in phytoplankton. The molar ratios of DIN/PO_4–P have changed from being close to Redfield ratios to being unbalanced. This change in nutrient ratios with time is opposite to that observed for the Po River and the Mississippi River (Justic et al. 1995). The molar ratio of N/P in the Po River decreased from 62 to 37 between 1968–1970 and 1981–1984, and that in the Mississippi River increased from 9 to 15 between 1960–1962 and 1981–1987. In these river-dominated coastal waters, the northern Adriatic Sea and the northern Gulf of Mexico, nutrient ratios now approach the approximate ratios of nutrient-replete diatoms (Si/N $\approx$ 1; Si/P $\approx$ 16) (Justic et al. 1995).

3 SiO_3–Si in Jiaozhou Bay

SiO_3–Si in sea water is mainly transported through rivers. SiO_3–Si concentration in the sea water in Jiaozhou Bay is low because there is not a large freshwater flow into Jiaozhou Bay. There were no data on SiO_3–Si concentration in sea water in Jiaozhou Bay until August 1985 (Shen et al. 1994). It was possible that the SiO_3–Si concentration has decreased during the last 40 years in Jiaozhou Bay due to building irrigation in rivers, similar to in the Nile River, Egypt (Wahby and Bishara 1980), Mississippi River, USA (Turner and Rabalais 1991) and Danube River, Europe (Humborg et al. 1997). In these rivers, a significant decrease in riverine SiO_3–Si concentration has

been observed after completion of dams and led to a decline in a transport of SiO_3–Si to the oceans. This is due to the construction of dams in rivers which causes considerable reductions in nutrient loads owing to the removal of these nutrients in reservoir sediments, whereas this removal might be overcompensated by anthropogenic N and P inputs downstream of the reservoirs; no such compensation has been observed for silicate (Humborg et al. 1997).

The seasonal cycle in SiO_3–Si concentration in surface water in Jiaozhou Bay was in good agreement with monthly precipitation during August 1985–November 1986, and an obvious opposite linear correlation between SiO_3–Si concentration and salinity was found during September 1985–August 1986 (Fig. 3), which reveals the effect of freshwater run-off on SiO_3–Si concentration in sea water. The long-term changes in salinity in surface water in Jiaozhou Bay show that salinity was higher and higher from the 1960s to the 1980s and the 1990s (Fig. 4); it may be the result of the decrease in freshwater input into Jiaozhou Bay in relation to reservoir construction. For example, when annual precipitation in 1962 in Jiaozhou Bay was 1056 mm, the water discharge in Dagu River was 49.6 $m^3\ s^{-1}$, but when annual precipitation in 1975 was 1227 mm, the water discharge was only 25.4 $m^3\ s^{-1}$. Due to constructing reservoir, the annual average run-off and annual average sediment discharge in Dagu River were 23.856 $m^3\ s^{-1}$ and 170.03 $\times$ 10^4 t, respectively, during 1952–1958, but they declined to 21.275 $m^3\ s^{-1}$ and 71.21 $\times$ 10^4 t, respectively, during 1959–1978 (HL, FIO, SOA 1984). The decreases in freshwater and sediment into Jiaozhou Bay may lead to an increase in salinity and a decline in SiO_3–Si concentration in Jiaozhou Bay.

SiO_3–Si concentration in Jiaozhou Bay had obvious seasonal variation, high concentration in summer and autumn and low in winter and spring. SiO_3–Si concentration in Jiaozhou Bay is mainly controlled by river run-off in summer when SiO_3–Si concentration is the highest. The highest primary production was also found in sum-

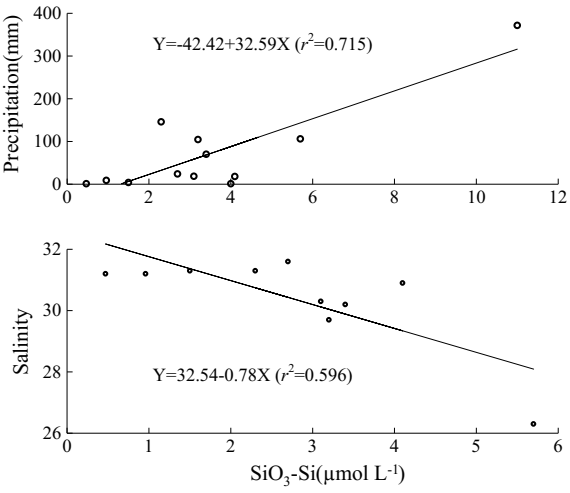

Fig. 3 Relationships between SiO_3–Si concentration and precipitation, salinity in Jiaozhou Bay in 1985–1986

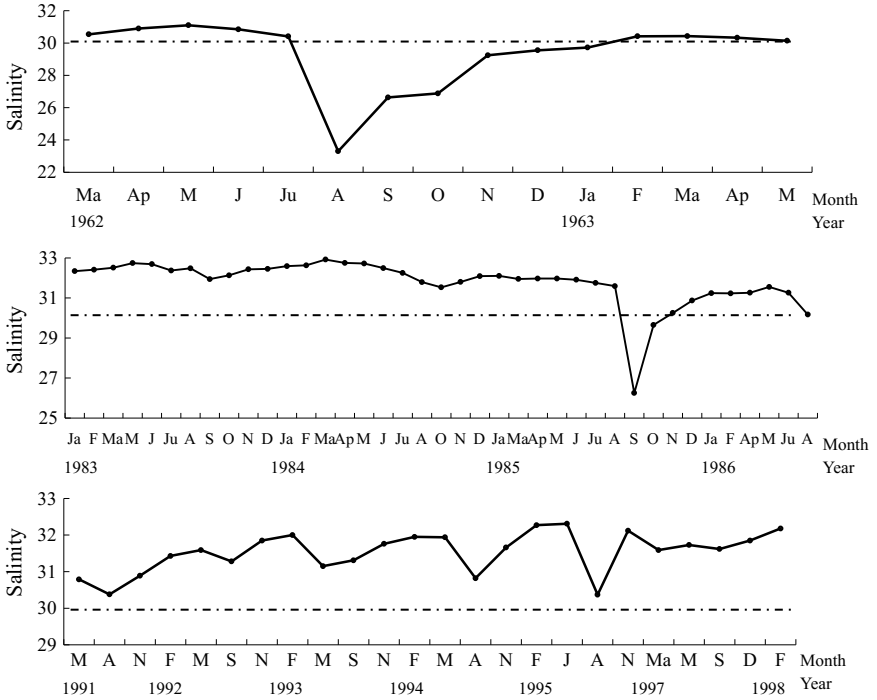

Fig. 4 Long-term changes in salinity in surface water in Jiaozhou Bay. Ja, January; F, February; Ma, March; Ap, April; M, May; J, June; Ju, July; A, August; S, September; O, October; N, November; D, December

mer (Guo and Yang 1992a; Wang et al. 1995; Wu and Zhang 1995). SiO_3–Si was consumed by diatoms and buried with dead diatoms, and the SiO_3–Si concentration was reduced to a minimum in winter and spring and could not often be detected. This occurs every year (Fig. 5).

Since the 1960s, DIN and PO_4–P concentrations have increased and SiO_3–Si concentrations have sometimes decreased or remained at a low level of 2.4 ± 1.1 μmol L^{-1} for 1985–1986 and 2.0 ± 1.9 μmol L^{-1} for the 1990s (Table 1). The average molar ratios in the 1990s were only 7.6 ± 8.9 for SiO_3–Si/PO_4–P, 0.19 ± 0.15 for SiO_3–Si/DIN and 37.8/7.6/1 for DIN/SiO_3–Si/PO_4–P (Table 1). To determine the stoichiometric nutrient limitation, the following criteria were applied: SiO_3–Si/PO_4–P >22 and DIN/PO_4–P >22 for PO_4–P limitation; DIN/PO_4–P <10 and SiO_3–Si/DIN >1 for DIN limitation; SiO_3–Si/PO_4–P <10 and SiO_3–Si/DIN<1 for SiO_3–Si limitation (Justic et al. 1995). Threshold values for nutrient of phytoplankton growth of SiO_3–Si = 2 μmol L^{-1}, DIN = 1 μmol L^{-1} and PO_4–P = 0·1 μmol L^{-1} were applied and are taken from many studies of nutrient uptake kinetics (Rhee 1973; Harrison et al. 1977; Brown and Button 1979; Perry and Eppley 1981; Goldman and Glibert 1983; Nelson and Brzezinski 1990). The long-term changes of nutrient concentra-

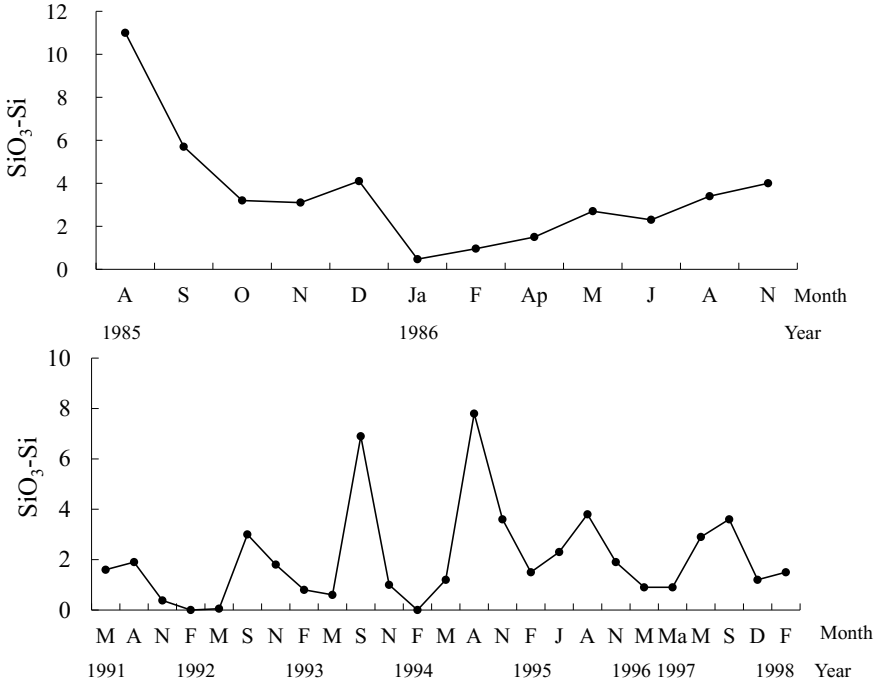

Fig. 5 Long-term changes in SiO_3-Si concentration ($\mu mol\ L^{-1}$) in Jiaozhou Bay. Ja, January; F, February; Ma, March; Ap, April; M, May; J, June; A, August; S, September; O, October; N, November; D, December

tions and ratios in Jiaozhou Bay showed that the possibility of DIN and PO_4–P as limiting factors of Jiaozhou Bay phytoplankton in the 1990s has been lessened or eliminated due to increases in nutrient loading. From the mid-1980s to the early 1990s, the frequency of Si limitation has increased from 36·6 to 69·6% (Zhang and Shen 1997), and during 1991–1998, the probable SiO_3–Si limitation was 76% and Si limitation was mainly found in the winter, spring and autumn.

4 Influences of the Changes in Nutrient Concentrations and Ratios on Phytoplankton Composition in Jiaozhou Bay

The importance of Si has been underrated in past studies because it was thought to rarely limit phytoplankton production, and it was only assumed to cause a shift in species composition, but not necessarily productivity (Dortch and Whitledge 1992). However, interest in the importance of SiO_3–Si for marine ecosystems has increased. Smayda (1989,1990) proposed that long-term declines in Si/P ratios in various coastal

waters (Baltic Sea, Kattegat, Skagerrak, Dutch Wadden Sea, North Sea, Black Sea) have resulted in increases of blooms of non-siliceous algae. Conley and Malone (1992) showed that the magnitude of the spring phytoplankton bloom in the nutrient-enriched Chesapeake Bay was controlled by SiO_3–Si and SiO_3–Si limitation leading to the collapse of the spring bloom and changes in the phytoplankton community. Dortch and Whitledge (1992) further discussed the influence of SiO_3–Si in phytoplankton production, phytoplankton size and species composition and the fate of carbon.

Between the 1960s and the 1990s, nutrient ratios have changed in Jiaozhou Bay. DIN and PO_4–P concentrations have continuously increased and SiO_3–Si concentrations have remained stable, resulting in changes in the molar ratios between DIN, PO_4–P and SiO_3–Si. High ratios of DIN/PO_4–P and low ratios of SiO_3–Si/PO_4–P and SiO_3–Si/DIN may have resulted in large changes in the Jiaozhou Bay ecosystem. The most obvious changes are the decreases of net phytoplankton (64–77 μm in net mesh) cell numbers and the alteration in the dominant species phytoplankton. The changes of net phytoplankton cell numbers from the 1960s to the 1990s (Fig. 6) showed that net phytoplankton cell numbers during 1977–1978 (Qian et al. 1983) decreased about one order of magnitude as compared to 1962–1963 (Gu et al. 1982b). In comparison with 1977–1978, net phytoplankton numbers during 1980–1981 (Guo and Yang 1992b) again decreased about one order of magnitude and further decreased in the 1990s.

Along with a decrease in net phytoplankton numbers, dominant species composition of net phytoplankton also changed notably. Table 2 shows all numbers of the four dominant species during the annual blooms in February. Between 1977 and 1981 to the early 1990s, large differences in cell number and in dominant species composition were observed. The major dominant species universally found year round in Jiaozhou Bay were *Skeletonema costatum*, *Chaetoceros debilis*, Ch. *curvisetus*, Ch. *compressus* and *Nitzschia pungens* for February 1977–January 1978 (Qian et al. 1983) and *Skeletonema costatum*, *Chaetoceros compressus*, Ch. *affinis*, *Nitzschia pungens* and *Asterionella japonica* for June 1980–November 1981 (Guo and Yang 1992a). Since the early 1990s, most of the dominant species above have not been found in Jiaozhou Bay in many investigations. Then, what were the reasons for the changes of phytoplankton? Investigations showed that temperature and salinity of sea water were similar in both periods, 2.26–3.00 °C and 31.52–32.07 for February 1981, 2.97–4.66 °C and 31.28–32.07 for February in the early 1990s. Heavy metal pollution was also unimportant in Jiaozhou Bay. Except for a part of estuary and coastal waters, most of the water and sediment environment quality was better (Chen 1991; MEMC, NSB, SOA 1992). Hence, it is likely that the changes in phytoplankton number and composition were affected by the changes in nutrient concentrations and nutrient ratios.

Officer and Ryther (1980) hypothesized that SiO_3–Si limitation in highly eutrophic estuaries will cause shifts in phytoplankton species composition to non-diatom phytoplankton. They used ocean, estuary and inland water bodies as examples to illustrate that Si is often the controlling nutrient in altering from a diatom-dominated community to a flagellate community. Since Officer and Ryther (1980), the importance of small phytoplankton and the microbial loop has become

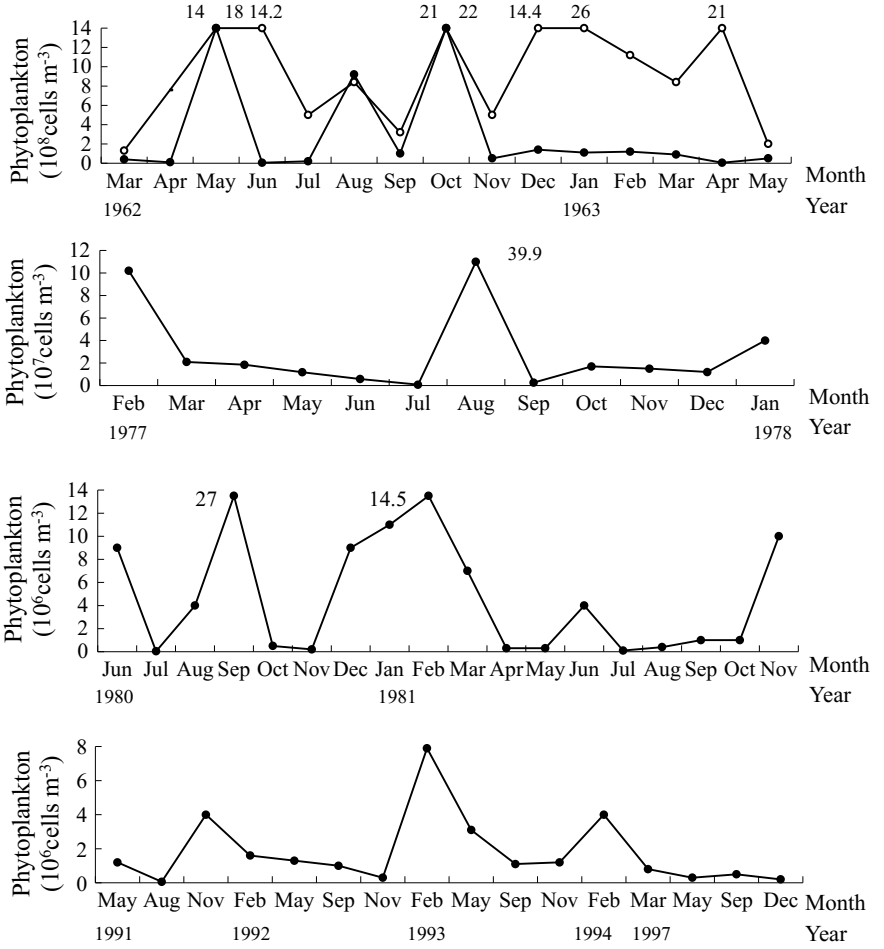

Fig. 6 Long-term changes in net phytoplankton cell numbers in Jiaozhou Bay: circle Station 11; filled circle Station 15 (for 1962–1963)

apparent (Dortch and Whitledge 1992). Dortch and Whitledge (1992) thought that decreasing SiO_3–Si would decrease the dominance of large diatoms. Net phytoplankton was dominated by diatoms in Jiaozhou Bay, and non-diatom phytoplankton cell numbers contributed less than 1% to the total phytoplankton. The species shift from diatom to non-diatom communities has not been found in the net phytoplankton. If the proportion of net phytoplankton were reduced in Jiaozhou Bay. Due to the life period of smaller phytoplankton being shorter than large phytoplankton, reduction in the proportion of large phytoplankton would accelerate the turnover of N and P. Increases in N and P concentrations would favour a small-cell phytoplankton community. Little research has been done on nanophytoplankton in Jiaozhou Bay.

Table 2 Long-term changes of dominant species composition in February in Jiaozhou Bay

Year	1977[a]	1981[b]	1992[c]	1993[c]	1994[c]
	Skeletonema	*Asterionella*	*Skeletonema*	*Phizosolenia*	*Phizosolenia*
	costatum	*Japonica*	*costatum*	*delicatula*	*delicatula*
		(3261 ± 2674)*	(650 ± 964)	(5562 ± 7170)	(3847 ± 8987)
Main dominant species	*Chaetoceros*	*Chaetoceros*	*Rhizosolenia*	*Asterionella*	*Nitzschia*
	compressus	*affinis*	*alata f. indica*	*Japonica*	*pungens*
		(2362 ± 4526)	(288 ± 206)	(706 ± 549)	(20.5 ± 15.7)
	Ch. debilis	*Ch. compressus*	*Nitzschia*	*A. Kariana*	*Chaetoceros*
			pungens		*compressus*
		(2209 ± 2188)	(124 ± 99)	(504 ± 241)	(7.3 ± 17.0)
	Ch.curvisetus	*Ch. subsecundus*	*Asterionella*	*Thalassionema*	*Guinardia*
			Japonica	*nitzschioides*	*flaccida*
		(1606 ± 1649)	(99 ± 138)	(221 ± 150)	(6.8 ± 4.9)

* The data in bracket are cell number of dominant species ($\times 10^3$)
[a] Qian et al. (1983)
[b] Guo and Yang (1992b)
[c] Wu Yulin (Pers. Comm.)

Chen and Qian (1992) found that nanophytoplankton (3–20 μm in cell size) was the major size fraction which contributed 63.4% to phytoplankton standing crop (chlorophyll-*a*) in eastern Jiaozhou Bay during May 1989–April 1990, and net phytoplankton (>20 μm) and picophytoplankton (0.2–3 μm) contributed 26.8 and 9.8% to chlorophyll-*a*, respectively. Jiao and Gao (1995) investigated nanoplanktonic diatoms in Jiaozhou Bay and showed that nanoplanktonic diatom cells (2–20 μm) accounted for 85.8% of total diatom numbers (2–200 μm) in August 1993. The average cell numbers of nanodiatom reached 221.38×10^6 cells m^{-3} close the level of net phytoplankton growth in August 1977. Therefore, it seems possible that there has been a reduction in the proportion of large diatoms in Jiaozhou Bay.

To sum up, during the last 40 years, nutrient concentrations have obviously changed in many estuaries and coastal waters in the world due to the influence of human activities. The increase in dissolved N and P concentrations and the relative decrease in dissolved Si may result from two different situations. In one nutrient structure has become more balanced for phytoplankton growth, as the northern Gulf of Mexico dominated by the Mississippi River (Justic et al. 1995). In the other nutrient structure was changed from more balanced to unbalanced, as the Jiaozhou Bay. Because of the increase in N/P ratios and the decrease in Si/N and Si/P ratios, N and P limitation for phytoplankton growth has been lessened or eliminated and SiO_3–Si limitation has increased in coastal waters. It would lead to a decrease in the number of large diatoms and change the phytoplankton species composition. Today, some

coastal ecosystems in the world are experiencing eutrophication and Si deficiency, so the role of SiO_3–Si would become more and more important.

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Ecological Responses of Phytoplankton to Nutrient Structure of Seawater in Jiaozhou Bay

Zhiliang Shen, Qun Liu, Yulin Wu and Yun Yao

Abstract Nutrient concentrations in seawater, and C, N, P, Si and chlorophyll-a content in different-sized particulates were measured in Jiaozhou Bay, and C, N, P, Si composition in different-sized fractions of phytoplankton and their ecological responses to nutrient structure of the seawater were studied. Microphytoplankton and nanophytoplankton were dominant in Jiaozhou Bay. High C (16.50–20.97 μmol L^{-1}), N (2.46–2.99 μmol L^{-1}), and low P (0.06–0.12 μmol L^{-1}), Si (0.18–0.57 μmol L^{-1}) content, and high N/P (24.7–64.6) and low Si/P (4.4–10.8) and Si/N (0.06–0.20) ratios were found in all sized groups of particulates. These values reflected the elemental compositions of different-sized fractions of phytoplankton as being an ecological response to the nutrients in the seawater. The ratios deviated significantly from the Redfield values. The nutrient composition of seawater and particulates and their relationship to chlorophyll-a showed that phytoplankton growth was possibly limited by Si. Si limitation appears favorable for controlling the ecological equilibrium of Jiaozhou Bay. Different-sized fractions of phytoplankton had different suitability to nutrient structures of the seawater. Among phytoplankton-sized groups, nanophytoplankton and microphytoplankton growths were more adaptable in eutrophic Jiaozhou Bay, and more competitive for assimilation of Si. This is consistent with their diatom-dominated composition, controlling the biomass and productivity of phytoplankton in Jiaozhou Bay.

Keywords Nutrient structures of seawater · Particulate nutrients · Phytoplankton Si limitation · Ecological responses · Jiaozhou Bay

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Previous analysis of the elemental composition of phytoplankton has indicated that the atomic ratio of N and P was about 16/1 in a spatially and temporally averaged value (Redfield 1934). Thus, the limitations of P or N to phytoplankton and primary production in waters can be estimated. Later, by proposing a ratio of dissolved C/N/P/O at 106/16/1/138, Redfield et al. (1963) found that this ratio is about the same as that in marine organic matter in average. The N/P ratio in seawater is an important index widely used by oceanographers in the world. However, studies on Si/N and Si/P ratios are very limited. Redfield et al. (1963) and Brzezinski (1985) pointed out that when nutrient levels are sufficient; the atomic Si/N/P ratio of marine diatoms is about 16/16/1. These have triggered subsequent studies on the ratios of nutrients in seawaters using stoichiometric calculation. Due to the influences of human activities, within only a few decades, numerous previously pristine, oligotrophic estuarine and coastal waters have undergone a transformation to more mesotrophic and eutrophic conditions (Nixon 1995; Paerl 1997). Eutrophic waters could change the molar ratios among key limiting nutrients, change the nutrients balance, and cause environmental deterioration (Turner and Rabalais 1994; Shen 2001). Many studies have been done on this, including long-term changes and its consequences for nutrient structure in the Mississippi River estuary and Adriatic Sea (Justic et al. 1995) and the response of phytoplankton community to the ratios for nutrient limitation (Lavrentyev et al. 1998). The importance of Si has been underrated in past studies because it was thought to rarely limit phytoplankton production (Dortch and Whitledge 1992). Smayda (1990) proposed that long-term declines in Si/P ratios in various coastal waters had resulted in increases of blooms of non-siliceous algae, which greatly increased the study of the importance of silicate in marine ecosystems (Conley and Malone 1992; Justic et al. 1995; Dugdale and Wilkerson 1998). In the past 50 years, a lot of reservoirs have been constructed in rivers. Silicate concentration may be reduced by as much as 50% due to hydrologic changes in the watershed (Correll et al. 2000; Humborg et al. 2000). As a result of an increase in N and a decrease in Si, it has been suggested that aquatic systems are moving toward lower Si/N and higher N/P ratios and that nutrient limitation of phytoplankton growth is moving toward a higher incidence of P and Si limitation (Turner et al. 2003).

The ecological study of phytoplankton has advanced into the aspect of particle size distribution and its effects. Biological and chemical processes of marine phytoplankton are related to their size to a considerable degree (Suttle et al. 1991; Ray et al. 2001). An important area of the nutrient structure of phytoplankton in different-sized fractions in the natural seawater has, however, been largely ignored. Studies on nutrient composition of phytoplankton in different-sized fractions have concentrated mainly on indoor-cultured phytoplankton strains, for example, relationships between cell volume and carbon and nitrogen contents of marine photosynthetic nanoplankton (Verity et al. 1992); the effect of variable CO_2 concentrations on the elemental composition of *Skeletonema costatum* (Burkhardt and Riebesell 1997); elemental (C, N, P, etc.) determination of marine phytoplankton cells (Ho et al. 2003); elemental composition of picophytoplankton cells and its biogeochemistry supplies (Heldal et al. 2003). There are few reports on natural population (Tada et al. 2000). Major nutrients of C, N, and P have been extensively studied (Geider and La Roche 2002; Vrede

et al. 2002), but less work has been done on Si. There are, however, large differences in phytoplankton in laboratory culture and natural population. So far, scientists have not separated phytoplankton directly in particle size from seawater for determining elemental composition. Because this particulate matter includes components from zooplankton and organic debris as well as phytoplankton, it is not possible to directly determine the nutrient.

In the past 40 years, human activities have increased the nutrient concentrations of seawater in Jiaozhou Bay substantially, especially N. DIN/DIP molar ratio is now obviously higher than the Redfield value, and the nutrient structure has become unbalanced, resulting in changes in phytoplankton population structure (Shen 2001). This section determines chlorophyll-*a* content and C, N, P, Si compositions of suspended particulate matters and their size distribution in the eutrophic Jiaozhou Bay. It discusses nutrient composition and distribution of phytoplankton in different-sized fractions, and the nutrient structure of the seawater and its ecological response. In this section, nutrient structure includes the nutrient structures in seawater and in particulate, and the nutrient balance in between.

1 Investigations and Methods

1.1 Sampling and Sample Treatment

Four seasonal investigations (February, May, August, and November) were carried out from November 2001 to August 2002. Ten observation stations were set—nine inside the bay and one outside the bay (Fig. 1). Water samples were collected for measuring nitrate (NO_3-N), nitrite (NO_2-N), ammonia (NH_4-N), phosphate (DIP), and silicate (DSi). Surface layer water samples were taken at stations 10, 7, 5, and 3 and filtered in situ with 200-μm mesh for removing larger zooplankton and other particulate matter. Then, 500 ml water samples were taken from each of these water samples and filtered with 20-μm mesh, 2- and 0.45-μm Millipore filters for determination of chlorophyll-*a* (Chl-*a*). The > 20 μm particulates were for microphytoplankton, those 20–2 μm for nanophytoplankton and < 2 μm ones for picophytoplankton. In addition, three 500 ml water samples per station were taken and filtered with a 20-μm mesh. The filtrates for determining C and N were filtered sequentially with pre-ignited (450 °C, for 6 h) Whatman GF/D (2.7 μm) and GF/F(0.7 μm) filters (25 mm in diameter) in order, and the filtrates for determining P and Si were filtered sequentially with 2 and 0.45 μm Millipore filters in order. All the suspended matter blocked by 20-μm mesh was washed down on a GF/F filter or 0.45-μm Millipore filter. Filtered membranes and blank membranes were stored in an icebox for further analysis.

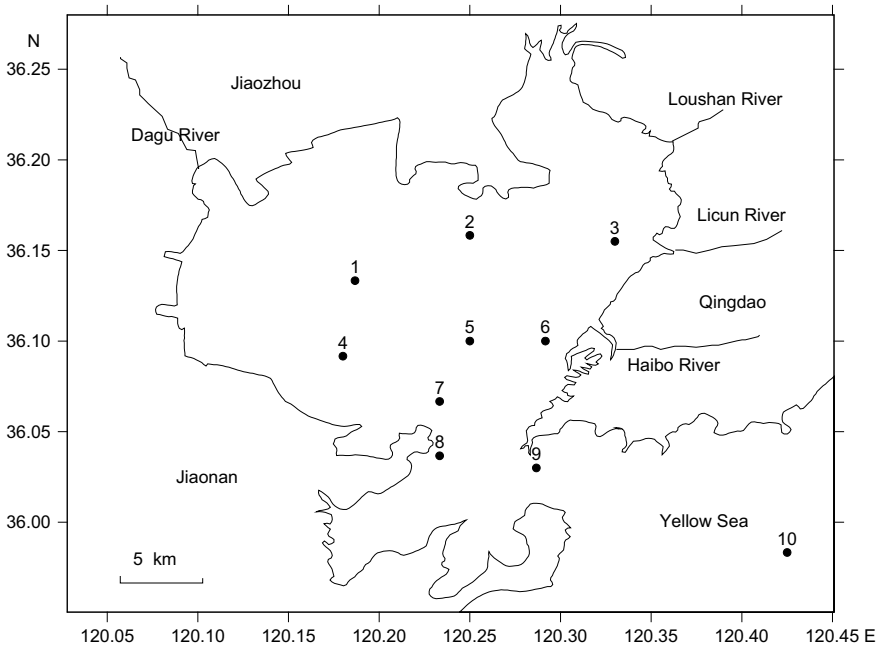

Fig. 1 Station positions

1.2 Sample Analysis

NO_3-N was measured using the cadmium-copper reduction method, NO_2-N using the Griess–Ilosvay method, NH_4-N using the indophenol blue method, DIP using the molybdenum–antimony–ascorbic method, and DSi with the silicon–molybdenum blue method. Dissolved inorganic nitrogen (DIN) was calculated as the sum of NO_3-N, NO_2-N, and NH_4-N. The sample of particulate P (PP) was digested referring to Koroleff's (1976) method and measured with the potassium peroxodisulfate oxidation colorimetry. The sample membrane or blank membrane, 2 ml of 5% $H_2SO_4/K_2S_2O_8$ solution, and 10 ml of distilled water were put into a polyfluortetraethylene digestion bottle for 1 h at 115 °C in a pressure cooker, and then measured with colorimetry. The sample of particulate Si (PSi) was measured referring to Treguer and Gueneley's (1988) method, putting sample membrane or blank membrane and 10 ml of 5% Na_2CO_3 digestion solution into a polyfluortetraethylene digestion bottle, then was digested and measured in the procedure described above. Particulate C (PC) and N (PN) were measured using a model 240C Element Analyzer. Chl-*a* was measured with spectrophotometry (Scor-Unesco 1966) and calculated using Jeffery and Humphrey's (1975) formula.

2 Concentration and Structure of Nutrient in Seawater

Average concentrations and molar ratios of nutrients in surface layer seawater in four seasons during 2001–2002 (Table 1) showed that the average concentrations of NH_4-N were 9.2 ± 5.6, 23.0 ± 12.2, 18.8 ± 5.6, and 15.1 ± 8.3 μmol L^{-1} in February, May, August, and November, respectively, taking 53.6–77.2% of DIN and being the main form of DIN. The concentrations of NO_3-N and NO_2-N were 18.5–39.6 and 4.2–7.5% of DIN, showing that three forms of inorganic N did not reach thermodynamic equilibrium. The average monthly concentrations of DIP and DSi were between 0.39 ± 0.18 and 0.62 ± 0.22 μmol L^{-1}, and 3.4 ± 1.1 and 8.8 ± 4.0 μmol L^{-1}, respectively. All the DIN, DIP and DSi concentrations were high in summer and low in winter. The highest of DIN/DIP ratio and the lowest of DSi/DIN ratio occurred in summer resulted from summer high concentration of DIN. The highest concentration of DSi caused the highest DSi/DIN and DSi/DIP ratios in autumn. The lowest of DIN/DIP and DSi/DIP ratios appeared in winter due to low concentrations of DIN and DSi. The molar ratios of nutrients moved away from the mean ratio (DIN/DIP/DSi = 16:16:1) of nutrients contained in marine diatoms (Redfield et al. 1963; Brzezinski 1985). Among these ratios, the annual average of DIN/DIP ratio was 50.5 ± 16.0, much higher than the Redfield value; DSi/DIP ratio remained small, below 16, except for the autumn one, and DSi/DIN ratio remained much smaller than 1. Average annual concentrations of nutrients in surface seawater at station 10 outside the bay and stations 7, 5, 3 inside the bay (Table 2) showed that the values were higher at station 3 than other stations, and higher inside the bay than outside, resulting from industrial wastes and residential sewage from Qingdao City coming from mainly the bay's east and northeast directions (Shen 2001). The average annual concentrations of nutrients and their ratios at stations 7, 5, and 3 were very consistent with the bay-wide average values, based on all sampling stations. The average status of the three stations could therefore represent that of the whole bay.

3 C, N, P, Si Composition in Different-Sized Particulates

Average annual contents of particulate (<200 μm) C, N, P, Si at stations 10, 7, 5, and 3 are shown in Table 3. The variations of their contents were between 27.22 and 86.73 μmol L^{-1} for PC, 3.89 and 11.80 μmol L^{-1} for PN, 0.06 and 0.30 μmol L^{-1} for PP, and 0.42 and 2.09 μmol L^{-1} for PSi. The ratios of PC/PN, PN/PP, PSi/PP, and PSi/PN were between 4.4–9.7, 22.6–70.6, 3.6–9.8, and 0.08–0.25, respectively. In composition of particulate C, N, P, and Si at the four stations, station 3 was exceptional one, where it had higher PC and PN contents due to high Chl-*a*, little higher PP and lower Si contents and lower PN/PP, PSi/PP and PSi/PN ratios than those from other in-bay stations, but PC/PN ratio that were equal or close to each other.

Table 1 Average concentrations (μmol L^{-1}) and molar ratios of nutrients in surface layer seawater in Jiaozhou Bay

Months	NO_3-N	NO_2-N	NH_4-N	DIN	DIP	DSi	DIN/DIP	DSi/DIP	DSi/DIN
2	2.97 ± 1.33	0.53 ± 0.15	9.17 ± 5.60	12.69 ± 6.74	0.47 ± 0.10	3.37 ± 1.05	27.7 ± 13.6	7.4 ± 2.6	0.32 ± 0.16
5	5.48 ± 5.50	1.35 ± 0.62	23.00 ± 12.15	29.80 ± 17.73	0.60 ±0.06	6.36 ± 2.09	50.9 ± 32.4	10.7 ± 3.8	0.25 ± 0.08
8	13.94 ± 4.63	2.34 ± 0.41	18.77 ± 5.62	35.07 ± 9.36	0.62 ±0.22	8.18 ± 3.14	61.6 ± 24.1	13.7 ± 3.8	0.23 ± 0.05
11	5.33 ± 3.90	1.66 ± 0.62	15.09 ± 8.26	22.09 ± 10.09	0.39 ±0.18	8.76 ± 4.00	61.6 ± 23.8	23.1 ± 5.5	0.44 ± 0.27
Averages	6.93 ± 4.82	1.47 ± 0.75	16.50 ± 5.85	24.91 ± 9.74	0.52 ±0.11	6.66 ± 2.42	50.5 ± 16.0	13.7 ± 6.7	0.31 ± 0.10

Table 2 Average annual concentrations (μmol L^{-1}) and molar ratios of nutrients in surface seawater

Stations	DIN	DIP	DSi	DIN/ DIP	DSi/ DIP	DSi/DIN
10	18.35 ± 4.96	0.41 ± 0.11	4.60 ± 1.71	47.5 ± 18.5	13.1 ± 9.6	0.26 ± 0.10
7	17.50 ± 5.73	0.47 ± 0.20	5.45 ± 1.35	45.5 ± 29.6	13.5 ± 6.9	0.32 ± 0.06
5	20.75 ± 13.99	0.51 ± 0.16	5.80 ± 1.47	46.9 ± 35.1	12.9 ± 6.9	0.36 ± 0.18
3	34.88 ± 14.92	0.64 ± 0.22	9.53 ± 5.51	54.1 ± 14.7	14.0 ± 5.7	0.27 ± 0.13
Averages for inside bay	24.38 ± 13.60	0.54 ± 0.19	6.93 ± 3.62	48.8 ± 25.5	13.5 ± 5.9	0.32 ± 0.13

Seasonal distributions of average content of C, N, P, Si in different-sized particulates in Jiaozhou Bay (Table 4) showed that higher content of PC and PN were mostly in nanoparticles, followed by microparticulates for PC content in most seasons, and that the highest content of PP and PSi was commonly also in nanoparticles, and higher content of PSi was in microparticulates. The ratios of C, N, P, and Si in different-sized particulates showed that PC/PN and PSi/PN ratios of microparticulates and nanoparticles were higher than those of picoparticulate. The smallest PN/PP ratio was in nanoparticles, and the highest PSi/PP ratio was in microparticulates or nanoparticles. Average annual contents of C, N, P, Si and their ratios showed similar patterns in different-sized particulates (Table 5).

4 Composition of Phytoplankton in Particle Size

Seasonal variations in average composition of phytoplankton (Chl-*a* content) in different-sized fractions in Jiaozhou Bay are listed in Table 6. Of the total Chl-*a* content of phytoplankton, microphytoplankton was dominant, amounting to 52.4–79.8 and 38.7–52.5%, in winter and spring, respectively, followed by nanophytoplankton, 17.3–38.2 and 30.7–44.5%, while picophytoplankton accounted for the least, 2.9–14.4 and 3.0–28.1%. In summer and autumn, however, major contributions came from nanophytoplankton, 35.5–55.2 and 42.1–53.4%, respectively, next to it was microphytoplankton, 28.0–51.0 and 24.0–38.7%, with the least in picophytoplankton, 13.5–17.1 and 17.6–31.5%. The average annual Chl-*a* percentages of microphytoplankton, nanophytoplankton and picophytoplankton in total phytoplankton were 46.1, 37.5, and 16.5% in turn. These data are consistent with Wang's (2001, unpublished) results that taken from 12 surveys from December 1997 to August 2000, being 42.1, 40.9, and 17.0% for the three fractions, in same stations in Jiaozhou Bay. It showed that the composition of phytoplankton consisted mainly of microphytoplankton and nanophytoplankton in the bay. Table 6 also shows that picophytoplankton proportion was minimum in winter, taking only 6.1% of Chl-*a* content of the total phytoplankton, which agrees to the investigations on Cyanobacteria (Xiao et al. 1995) and Synechococcus (Yang and Jiao 2001) in the bay showing that picophytoplankton growth was controlled largely by temperature (Agawin et al. 2000). The size-graded

Table 3 Average annual contents (μmol L^{-1}) of particulate C, N, P, Si and their molar ratios

Stations	PC	PN	PP	PSi	PN/PP	PSi/PP	PSi/PN	PC/PN
10	55.97 ± 12.17	8.02 ± 3.47	0.27 ± 0.11	0.84 ± 0.30	30.4 ± 6.9	3.7 ± 2.2	0.13 ± 0.10	7.6 ± 1.8
7	56.42 ± 14.93	8.37 ± 1.97	0.21 ± 0.06	1.14 ± 0.31	44.5 ± 19.9	5.7 ± 1.0	0.14 ± 0.06	7.0 ± 2.1
5	56.14 ± 11.61	7.39 ± 1.88	0.21 ± 0.07	1.40 ± 0.49	38.2 ± 19.9	6.8 ± 2.2	0.20 ± 0.06	7.7 ± 0.8
3	71.75 ± 14.18	9.37 ± 2.05	0.25 ± 0.04	1.03 ± 0.23	37.6 ± 9.2	4.0 ± 0.6	0.11 ± 0.03	7.7 ± 0.3
Averages for inside bay	61.44 ± 14.51	8.37 ± 1.97	0.22 ± 0.06	1.19 ± 0.36	40.1 ± 15.8	5.5 ± 1.8	0.15 ± 0.06	7.5 ± 1.2

Table 4 Average contents (μmol L^{-1}) of particulate C, N, P, Si in different-sized particulates and their mole ratios in Jiaozhou Bay

	February seawater	Particulates (μm)				May seawater	Particulates (μm)				August seawater	Particulates (μm)				November seawater	Particulates (μm)			
		20–200	2–20	<2	Total		20–200	2–20	<2	Total		20–200	2–20	<2	Total		20–200	2–20	<2	Total
C	2200[a]	21.54	26.93	17.36	65.83	2200[a]	17.22	29.13	16.16	62.51	2200[a]	21.42	11.63	14.50	47.55	1930[a]	23.69	28.20	17.97	69.86
N	12.2	2.27	3.63	3.02	8.92	24.8	2.66	2.59	3.22	8.47	38.2	2.65	2.67	2.40	7.72	22.4	2.26	3.08	2.57	7.91
P	0.47	0.06	0.11	0.03	0.20	0.64	0.07	0.13	0.08	0.28	0.68	0.05	0.11	0.07	0.23	0.36	0.04	0.11	0.04	0.19
Si	3.7	0.61	0.53	0.20	1.34	6.6	0.59	0.61	0.29	1.49	10.0	0.43	0.58	0.06	1.07	7.5	0.16	0.54	0.15	0.85
N/P	26.0	37.8	33.0	100.7	44.6	38.8	38.0	19.9	40.3	30.3	56.2	53.0	24.3	34.3	33.6	62.2	56.5	28.0	64.3	41.6
Si/P	7.9	10.2	4.8	6.7	6.7	10.3	8.4	4.7	3.6	5.3	14.7	8.6	5.3	0.9	4.9	20.8	4.0	4.9	3.8	4.5
Si/N	0.30	0.27	0.15	0.07	0.15	0.27	0.22	0.24	0.09	0.18	0.26	0.16	0.22	0.03	0.14	0.33	0.07	0.18	0.06	0.11
C/N	180.3	9.5	7.4	5.7	7.4	88.7	6.5	11.2	5.0	7.4	57.6	8.1	4.4	6.0	6.2	86.2	10.5	9.2	7.0	8.8

[a]Average concentrations of carbon dioxide in Jiaozhou Bay seawater in August and November, 1991, and February and May, 1992 (Shen and Liu 1997)

Table 5 Average annual contents ($\mu mol\ L^{-1}$) of particulate C, N, P, Si in different-sized particulates and their molar ratios

Elements and ratios	Seawater	Particulates (μm) 2–20			Total particulates
		20–200	2–20	<2	
C	2132.5 ± 135.0[a]	20.97 ± 6.09	23.97 ± 10.30	16.50 ± 3.17	61.44 ± 14.51
N	24.38 ± 13.60	2.46 ± 0.78	2.99 ± 1.52	2.78 ± 0.52	8.37 ± 1.97
P	0.54 ± 0.19	0.06 ± 0.03	0.12 ± 0.04	0.06 ± 0.03	0.22 ± 0.06
Si	6.93 ± 3.62	0.45 ± 0.26	0.57 ± 0.16	0.18 ± 0.09	1.19 ± 0.36
N/P	45.8 ± 16.5	56.8 ± 31.9	34.7 ± 38.5	64.6 ± 37.4	40.1 ± 15.8
Si/P	13.4±5.7	10.8±10.3	5.4±2.6	4.4±3.1	5.5±1.8
Si/N	0.29±0.03	0.20±0.14	0.25±0.17	0.06±0.03	0.15±0.06
C/N	103.2±53.3	8.8±1.9	8.7±2.7	5.8±0.9	7.5±1.2

[a]Average concentrations of carbon dioxide in Jiaozhou Bay seawater in August and November, 1991, and February and May, 1992 (Shen and Liu 1997)

composition of phytoplankton was related to the eutrophication and higher productivity in the Bay, similar to many other marine areas in the world (Agawin et al. 2000).

Average annual Chl-*a* content in different size fractions of phytoplankton (Table 7) showed that the Chl-*a* contents of microphytoplankton and nanophytoplankton were high at station 3 and low at other stations and high inside the bay and low outside. On the other hand, outside the bay, there was higher Chl-*a* content in picophytoplankton being 28.2% of the total phytoplankton, but lower that at the stations inside the bay, which may be related to nutrient concentration. With decrease in nutrient concentration from inner bay to outer bay, microphytoplankton and nanophytoplankton decreased and but picophytoplankton increased.

5 Comparison of Nutrient Composition in Different-Sized Particulate with Nutrient Structure of Seawater

Suspended particulate matter smaller than 200 μm includes almost all phytoplankton, microzooplankton, bacteria, and organic debris. Different forms of particulate C (filtered using GF/C filters) studied by Shen et al. (1997) showed that biological organic C and debris organic C were 56.4 and 43.6% of the total, respectively. Of biological organic C, phytoplankton C, zooplankton C, and bacteria C were 88.2, 5.0, and 6.8%, respectively. Because many organic debris and large zooplankton were removed from suspended particulate matter, phytoplankton was thought the major component in particulates smaller than 200 μm.

Concentrations of DIC, DIN, DIP and DSi in the seawater were much higher than those of C, N, P, and Si in different-sized particulates (Table 4). In particular, DIC concentration in the seawater was two orders of magnitude higher than C in particulates,

Table 6 Average compositions of phytoplankton (Chl-*a* contents) in different-sized fractions in Jiaozhou Bay

Months	Size	Chl-*a*	Percent	Size	Chl-*a*	Percent	Size	Chl-*a*	Percent	Total Chl-*a*
	μm	μg L^{-1}	%	μm	μg L^{-1}	%	μm	μg L^{-1}	%	μg L^{-1}
2	20–200	3.497	69.4	2–20	1.238	24.6	<2	0.305	6.1	5.040
5	20–200	0.678	43.1	2–20	0.553	35.1	<2	0.343	21.8	1.574
8	20–200	0.807	41.1	2–20	0.849	43.3	<2	0.306	15.6	1.962
11	20–200	0.654	30.7	2–20	1.001	47.0	<2	0.477	22.4	2.132
Averages	20–200	1.409	46.1	2–20	0.910	37.5	<2	0.358	16.5	2.677

Table 7 Average annual Chl-*a* contents (μg L^{-1}) in different-sized particulates

Stations	20–200 μm		2–20 μm		<2 μm	
	Chl-*a*	%	Chl-*a*	%	Chl-*a*	%
10	0.624	33.0	0.732	38.8	0.532	28.2
7	0.927	47.7	0.786	40.5	0.229	11.8
5	0.992	43.3	0.829	36.2	0.470	20.5
3	2.309	60.8	1.116	29.4	0.374	9.8

and DIN, DIP and DSi were about one order higher. No big difference was found in their molar ratios, except for C/N ratio. The difference in N/P ratios of various-sized particulates reflected probably different adaptability of different-sized phytoplankton to DIN/DIP ratio in the seawater. Dissolved N/P ratio in annual average in the seawater was higher than that of particulate including phytoplankton, due to mainly the N excess in the seawater. Different from DIN/DIP ratio, the low concentration of DSi in the seawater resulted in low DSi/DIP and DSi/DIN ratios, particularly the latter (Table 1). Phytoplankton assimilates nutrients in the seawater in certain proportions, so PSi content and PSi/PP, PSi/PN ratios in suspended particulates were lower. The average monthly contents of PSi in various-sized particulates were between only 0.06 and 0.61 μmol L^{-1}, and PSi/PP, PSi/PN ratios were between 0.9 and 10.2, 0.03, and 0.27, respectively (Table 4). The Si content and Si/P, Si/N ratios in particulates lower than those in the seawater showed that those in phytoplankton were also lower than those in the seawater. Similar to the seawater, all these ratios in phytoplankton were greatly different from the mean ratios (N/P = 16, Si/P = 16, Si/N = 1) of nutrients contained in marine diatoms (Redfield et al. 1963; Brzezinski 1985). Of these ratios, PN/PP ratio was much higher; PSi/PP and PSi/PN ratios were lower than the Redfield value, particularly PSi/PN ratio. Only PC/PN ratio was close to the Redfield value (6.6) (Table 3). Therefore, high contents of C and N, low P and Si contents, high C/P and N/P ratios, and low Si/P and Si/N ratios in phytoplankton were a response to abundance in C and N, and relative scarcity in P and Si in the seawater, which also illustrated that P and Si possibly became limiting factors to phytoplankton growth, particularly Si. During the last 40 years, along with nutrient structure in the seawater in Jiaozhou Bay greatly changed, the composition of phytoplankton population also changed correspondently (Shen 2001). At present, some phytoplankton-dominant species in the bay, such as microphytoplanktonic diatom *Thalassiosira rotula* and nanophytoplanktonic diatom *S. costatum,* can grow in the conditions of high C, N and low P, Si contents, high C/P and N/P ratios, and low Si/P and Si/N ratios, which is the result of long-period adaptability of these phytoplankton to the nutrient structure of the seawater.

6 The Response of Different-Sized Fractions Phytoplankton to Si Limitation in Jiaozhou Bay

Study on long-term change in nutrient structure of the seawater in Jiaozhou Bay showed that from 1962 to 1998, DIN and DIP concentrations had increased 3.9 times and 1.4 times, respectively, and DSi concentration remained at a very low level (2.0 ± 1.0 μmol L^{-1} on an average in the 1990s), and the possibility that DIN and/or DIP as limiting factors of phytoplankton has been lessened or eliminated and that of DSi limiting has been increased (Shen 2001). In recent years, duo to rapid economic developments, including city construction, which has been increasing at 15% per year since 1997 with corresponding increases in cement consumption in Qingdao city. The waste entering the bay by surface runoff has increased the DSi concentration in the seawater. However, DSi concentration was still low relative to DIN and DIP, especially in winter. The investigations by the authors showed that the average DSi concentrations in winter were 1.0, 1.2, and 2.2 μmol L^{-1}, respectively, in 2000, 2001, and 2003. In this investigation, the concentration of DSi was 3.4 ± 1.1 μmol L^{-1} in average in winter (Table 1), but at some stations, it was below the threshold value for diatom growth (2.0 μmol L^{-1}) (Brown and Button 1979; Perry and Eppley 1981; Goldman and Glibert 1983; Nelson and Brzezinski 1990). The annual average and a majority of seasonal DSi/DIP ratios were smaller than Redfield value (16), and DSi/DIN ratios were far smaller than Redfield value (1) (Redfield et al. 1963; Brzezinski 1985) (Table 1). Therefore, DSi was still potential limitation factor to phytoplankton growth, particularly in winter.

The correlative study between Chl-*a* content and PC, PN, PP, PSi contents in different-sized particulates show that there were no relationship between them, but positive linear correlation between Chl-*a* and PSi ($r = 0.387$, $p = 0.0262$), implying that more Si was absorbed by phytoplankton, yielding higher Chl-*a* content. Most of particulate Si was biological origin, showing the importance of Si to phytoplankton growth, especially to diatoms, which were more than 90% of total phytoplankton cell number in the bay. On the other hand, no correlation was found between Chl-*a* content and various forms of DIN and DIP in the seawater, but there was a negative linear correlation between Chl-*a* and DSi ($r = -0.381$, $p = 0.0241$). Also, there was no relation between Chl-*a* content and DIN/DIP ratio in the seawater. However, Chl-*a* content was negatively related to the DSi/DIP ($r = -0.349$, $p = 0.0369$) and DSi/DIN ($r = -0.424$, $p = 0.0099$) ratios, the same to the relation between Chl-*a* and DSi. It reflects close relations of growth and decay of phytoplankton, and DSi in the seawater and Si in phytoplankton, and showed that Si was most likely to limit phytoplankton growth among various nutrients. In recent years, N and P concentrations increased considerably in Jiaozhou Bay, but the Chl-*a* content did not (Wu et al. 2004), which might closely related to Si limitation to phytoplankton. Once DSi concentration increases in the seawater, it would lead to abnormal growth of phytoplankton and trigger red tides. In winter 2004, DSi concentration reached very high level at 97.7 μmol L^{-1} at station 3 in the bay where phytoplankton grew rapidly and resulting in the red tide of *Lauderia annulata*. When DSi concentration decreased

to 0.49 μmol L^{-1}, DSi/DIP and DSi/DIN ratios were 1.59 and 0.03, respectively, the red tide was finally controlled. Therefore, from this viewpoint, Si limitation is favorable for keeping ecological equilibrium of Jiaozhou Bay, and it is an ecological significance on nutrient limitation of phytoplankton in eutrophic condition. This is similar to nutrient-enriched Chesapeake Bay, where the spring phytoplankton bloom was controlled by dissolved Si (Conley and Malone 1992).

The average monthly and annual contents of particulate nutrients (Tables 4 and Table 5) showed small changes in PN and the average annual contents in order of nanoparticles > picoparticles > microparticulates, PP content of nanoparticles were obviously higher than those of microparticulate and picoparticle fraction, and PSi were in order of nanoparticles > microparticulates > picoparticles. The monthly average molar ratios of nutrient in various-sized particulates (Table 5) showed that PN/PP ratios were the highest commonly in picoparticle fraction, followed by microparticulate and nanoparticle, and all of them were above the Redfield value (16). PSi/PP ratios were between 0.9 and 10.2 below the Redfield value (16), and the smallest those occurred in picoparticle fraction, between 0.9 and 6.7 with an average of 4.4 ± 3.1. PSi/PN ratios were between 0.03 and 0.27 far smaller than Redfield value (1), and the smallest those occurred also in picoparticle fraction between 0.03 and 0.09 with an average of 0.06 ± 0.03. These nutrient contents and ratios in various-sized particulates reflect nutrient composition in different-sized fractions of phytoplankton. A relatively high content of PN and high PN/PP ratio, and very low PP and PSi contents and PSi/PP, PSi/PN ratios in picophytoplankton indicated that little DSi relative to DIP in the seawater were assimilated by picophytoplankton and Si most possibly limited picophytoplankton growth. Nanoparticles and microparticulates Si accounted for 47.9 and 37.8% of the total particulate Si, respectively, showing that the two phytoplankton groups were more competitive in assimilating Si. This competition would benefit their growth in relative Si scarcity environment, which is consistent to the study of the composition of phytoplankton in particle size in the bay.

7 The Responses of Composition of Phytoplankton in Particle Size to Nutrient Structure

The relations of C, N, P, Si contents (Fig. 2) show that the nutrients' ratios in different-sized particulates, except for PC/PN ratio, were close to the Redfield value (6.6), most PN/PP and PC/PP ratios were much higher than the Redfield value (16 and 106). However, PSi/PP and PSi/PN ratios were opposite, much smaller than the Redfield value (16 and 1), which was similar to nutrient ratios in the seawater. Also, small variations in element contents and their ratios were found in the picoparticle fraction, and large variations in nanoparticles and microparticulates. It probably reveals the difference in adaptability of phytoplankton in different sizes to nutrient structure of the seawater, and nanophytoplankton and microphytoplankton showed

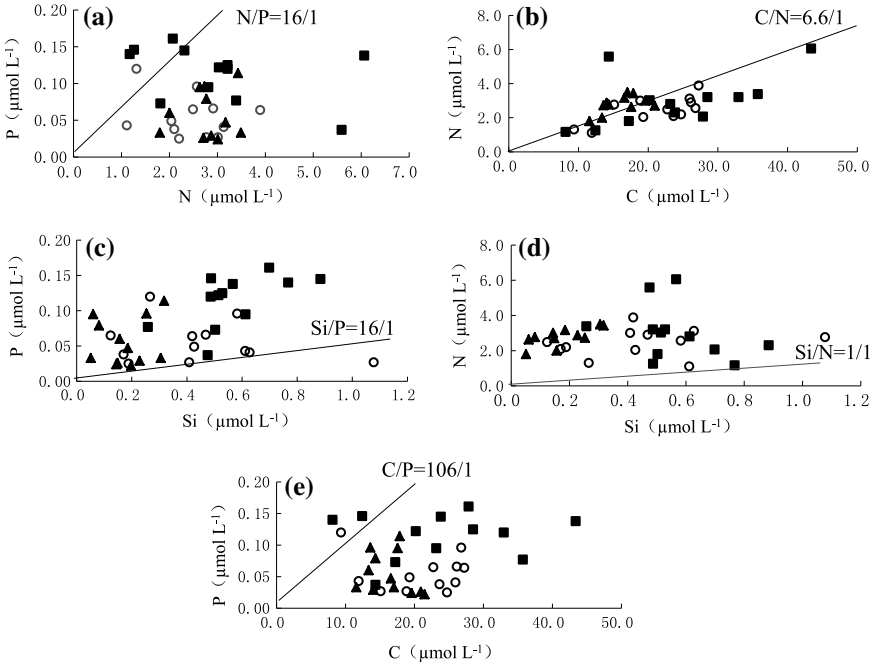

Fig. 2 Relations among C, N, P, Si contents in different-sized particulates in Jiaozhou Bay: a N–P; b C–N; c Si–P; d Si–N; e C–P. Circle microparticulates; black square nanoparticles; black triangle picoparticles

better adaptability than picophytoplankton in the eutrophic environment in the bay, which is also consistent with the composition of phytoplankton in particle size. On the contrary, picophytoplankton prefers to live in oligotrophic waters (Agawin et al. 2000). Recent blooms in the bay were purely due to the extensive proliferation of the two phytoplankton groups (nanophytoplankton and microphytoplankton), such as *S. costatum*, *Eucampia zoodiacus,* and *L. annulata*. The PC contents of the two groups showed that they two were dominant in biomass and productivity of phytoplankton in the bay.

Although the Chl-*a* content of picophytoplankton was only 16.5% of the total phytoplankton (Table 6), the contents of C, N, P of picoparticulate were higher and accounting for 26.9, 33.2, 27.3% of the total, respectively (Table 5), indicating that picophytoplankton had greater N assimilation than that of microphytoplankton, but similar P assimilation, which was probably related to their small cell size associated to small diffusion boundary layer and large surface area per unit volume (Raven 1986). The cell density of picophytoplankton was 10^3–10^4 cells ml L^{-1} (Yang and Jiao 2001), three to five orders of magnitude higher than that of total net-phytoplankton. This shows that picophytoplankton occupied important position in whole process of primary production in Jiaozhou Bay. Picophytoplankton consisted mainly of *Syne-*

chococcus and pico-eukaryotic phytoplankton, and the former had higher cell concentration obviously than that of the latter (Yang and Jiao 2001), notably different from nanophytoplankton and microphytoplankton who were dominated by diatom. This was consistent to weak Si assimilation of picophytoplankton.

At present, studies on nutrient composition of phytoplankton in different-sized fractions have focused mainly on indoor-cultured phytoplankton strains. Scientists are as yet unable to separate phytoplankton directly in particulate size from seawater. It is therefore difficult to directly measure the nutrient composition of phytoplankton-sized groups in natural seawater. We studied C, N, P, and Si compositions of phytoplankton groups and their ecological responses to nutrient structure of the seawater by measuring chlorophyll-a and C, N, P, and Si contents in different-sized suspension particulates. The differences in C, N, P, and Si compositions of different-sized particulates probably reflected different adaptability of three phytoplankton-sized groups to nutrient structure of the seawater. Si was shown to be a potential limitation factor to phytoplankton growth. Nanophytoplankton and microphytoplankton were more competitive for assimilation Si, and more suitable for growth in eutrophic Jiaozhou Bay. The ecological study of phytoplankton has now advanced into the aspect of particle size distribution. It is very important to study nutrient composition in different-sized fractions of phytoplankton in natural seawater and is becoming a pressing assignment for the ocean ecologist.

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Silica Supply and Diatom Blooms in Jiaozhou Bay

Zhiliang Shen, Yun Yao and Yulin Wu

Abstract The variations in nutrients (molar ratios) and chlorophyll-*a* in the Jiaozhou Bay were examined before and after a diatom bloom in a period that lasted from November 2003 to March 2004. Negative relationships between nutrient concentrations, Si/P, Si/N ratios, and chlorophyll-*a* content were found during the bloom, which reflected the relationship between nutrient concentrations, phytoplankton biomass, and growth. Large increase in nutrient concentrations, particularly SiO_3–Si after the late autumn, is one of major reasons inducing the diatom bloom in winter, and the bloom was finally controlled due to SiO_3–Si depletion by phytoplankton. The bloom was mainly controlled by SiO_3–Si. Before 1998, relatively low level of SiO_3–Si kept ecological balance of eutrophication waters in the Jiaozhou Bay. In recent years, however, human activities have increased SiO_3–Si concentration, which is likely one of the primary causes for the increased diatom blooms in the Jiaozhou Bay. Therefore, it is necessary to control SiO_3–Si concentration in the Jiaozhou Bay.

Keywords Nutrient · Phytoplankton · Chlorophyll-*a* · Blooms · Si supply Jiaozhou Bay

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In the past few decades, coastal marine phytoplankton blooms have increased dramatically in frequency, intensity, and geographic distribution (Smayda 1990; Hallegraeff 1993; Hodgkiss and Ho 1997; Paerl 1997; Zhou et al. 2003, 2008). It has been suggested that nutrient-impacted coastal and offshore waters are experiencing an epidemic of harmful phytoplankton blooms (Smayda 1990). However, as Hodgkiss and Ho (1997) showed, it is still not possible to conclude the extent to which the increase in blooms in coastal waters can be attributed to the increase in nutrient levels, since so many other factors are involved. Obviously, the occurrence and increase of phytoplankton blooms are related to the changes in nutrient ratios (Hodgkiss and Chan 1987; Smayda 1989; Hodgkiss and Ho 1997; Flynn 2002; Domingues et al. 2005). Diatom blooms are common in temperate aquatic systems, and their dynamics are often controlled by nutrients, especially Si (Conley and Malone 1992). As a result of increased human activities, N and P loads have considerably increased, especially N. In contrast to N and P, Si concentration may be reduced due to hydrologic changes in a watershed (Correll et al. 2000; Humborg et al. 2000). The situation has seriously affected the N:P:Si ratio and resulted in lower Si:N and higher N:P ratios in lotic systems, and it has been argued that nutrient limitation of phytoplankton growth in aquatic systems is moving toward a higher incidence of P and Si limitation (Turner et al. 2003). Similar change has been also observed in the Jiaozhou Bay (Shen 2001; Shen et al. 2006).

The study on long-term changes in nutrient structure in the Jiaozhou Bay showed that since the 1960s, due to the influences of human activities, N and P concentrations have significantly increased, while Si concentration has remained at a relatively stable or lower level due to damming of waterways, which has resulted in a change in nutrient limitation of phytoplankton growth from N and P to Si (Shen 2001). Si limitation appears favorable for controlling the ecological equilibrium of the Jiaozhou Bay (Shen et al. 2006). Ecological conditions were reasonably stable up until 1998, when accelerating eutrophication became more evident in the Jiaozhou Bay (Yao et al. 2007). In recent years, due to rapid economic developments, including city construction that has been increasing at 15% per year since 1997 with corresponding increases in cement consumption in Qingdao City. The waste entering the bay by surface runoff has increased the Si concentration in the seawater, and the occurrence of bloom increased dramatically in the Jiaozhou Bay. For example, blooms of *Skeletonema costatum* and *Eucampia zodiacus* occurred in July 1998 and June 1999, respectively, in the north-eastern part of the Jiaozhou Bay (Huo et al. 2001; Zhang et al. 2002). Subsequently, the blooms caused by *Coscinodiscus asteromphanus* and *Lauderia annulata* were found by our investigations in June 2003 and February 2004, respectively, and the latter was found in winter for the first time.

In this section, four observation stations associated with the bloom were set up in the Jiaozhou Bay (Fig. 1) and surface seawater samples were collected every ten days from November 2003 to March 2004, for determining phosphate (PO_4–P), silicate (SiO_3–Si), nitrate (NO_3–N), nitrite (NO_2–N), ammonium (NH_4–N), and chlorophyll-*a* (Chl-*a*). Dissolved inorganic nitrogen (DIN) was calculated as the sum of NO_3–N, NO_2–N, and NH_4–N. Seawater transparence was observed using a transparent scale. Phytoplankton samples were collected vertically from the bottom to surface layer

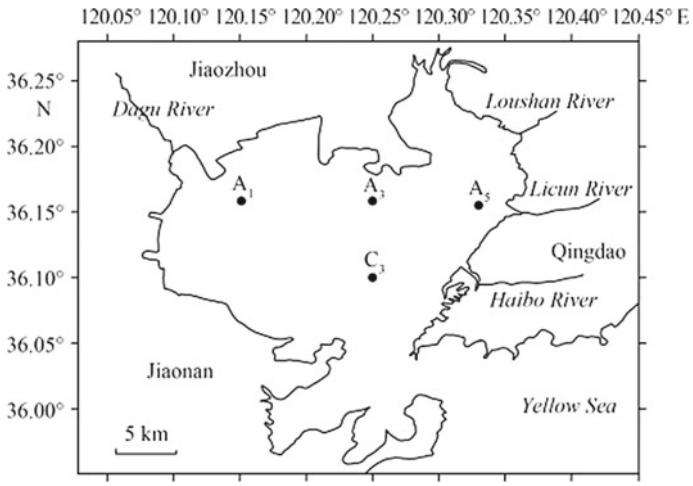

Fig. 1 Survey stations in the Jiaozhou Bay

using a phytoplankton net (37 cm diameter, 140 cm length, and 77 meshes). We use the data observed during five months before and after the bloom, as well as the data from investigations since 1991, the variations of nutrient concentrations and molar ratios, phytoplankton cell abundance, and Chl-*a* content are discussed; the relation of Si supply and diatom bloom are studied; and the causes of diatom bloom increasing in recent years are explored.

1 Nutrient Concentrations and Molar Ratios

The average concentrations and molar ratios of nutrients in the surface layer water during investigations are listed in Table 1. Particularly high nutrient concentrations were found at station A_5 situated in the north-eastern part of the bay with a weak water exchange (Zhao et al. 2002), which is near the main industrial and residential areas of Qingdao City. Very high DIN/PO_4–P (N/P) ratio and higher SiO_3–Si/PO_4–P (Si/P) ratio were also found at station A_5, as a result of very high DIN and higher SiO_3–Si concentrations. Station C_3 is situated in the middle part of the bay with relatively low nutrient concentrations and ratios. Stations A_1 and A_3 are located in the marine aquaculture areas and were influenced by waste from agricultural nonpoint sources along the coast. Moreover, station A_1 was also influenced by the discharge of the Dagu River water. The concentrations and ratios of nutrient at stations A_1 and A_3 were relatively high and between stations A_5 and C_3. The SiO_3–Si/DIN (Si/N) ratio was low in the four stations due to high concentrations of DIN and relatively low concentrations of SiO_3–Si.

Table 1 Temperature (°C), salinity, nutrient concentrations (μmol L^{-1}), and ratios (mean ± standard deviations) in surface seawater

Stations	Temperature	Salinity	DIN	PO_4–P	SiO_3–Si	N/P	Si/P	Si/N
A_1	5.70 ± 3.38	30.87 ± 1.48	32.5 ± 9.3	0.71 ± 0.21	7.5 ± 2.8	50.8 ± 22.9	11.2 ± 3.8	0.27 ± 0.16
A_3	6.22 ± 2.86	31.72 ± 0.66	24.7 ± 15.9	0.86 ± 0.40	8.1 ± 7.3	28.4 ± 11.1	8.2 ± 4.9	0.33 ± 0.22
A_5	5.62 ± 3.75	31.51 ± 0.70	77.0 ± 47.5	1.2 ± 0.68	23.8 ± 28.4	68.6 ± 31.6	15.3 ± 13.5	0.24 ± 0.22
C_3	7.24 ± 3.64	31.84 ± 0.67	11.6 ± 3.6	0.60 ± 0.17	4.6 ± 2.9	19.4 ± 4.2	6.9 ± 3.8	0.36 ± 0.20

2 Variations in Nutrient Concentrations and Ratios During Ten-Day Period

Variations in nutrient concentrations in the surface water at stations A_1, A_3, A_5, and C_3 during ten-day period from November 2003 to March 2004 (Fig. 2) showed that the maximum changes in DIN, PO_4–P, SiO_3–Si concentrations were at station A_5 and the minimum changes were at station C_3. DIN concentrations reached very high values of 67.3, 160.3 μmol L^{-1} for stations A3 and A_5 on January 8, 13.2 μmol L^{-1} for station C_3 on January 17, and 44.6 μmol L^{-1} for station A_1 on January 30. After attaining high values, DIN concentrations decreased to minimum values of 7.8, 34.0, 6.4 μmol L^{-1}, respectively, at stations A_3, A_5, and C_3, and 35.9 μmol L^{-1} at station A_1 on February 9. They then increased again. PO_4–P concentrations generally showed a downward trend and declined to the lowest values of 0.33, 0.36, 0.26 μmol L^{-1} at stations A_1, A3, and A_5, respectively, and 0.27 μmol L^{-1} at station C_3 on February 18 and then recovered rapidly. The change of SiO_3–Si concentration was significant. The maximum values of 12.2 and 24.9 μmol L^{-1} at stations A_1 and A_3, respectively, occurred on January 8, and the maximum of 97.7 μmol L^{-1} at station A_5 and the second highest value of 8.1 μmol L^{-1} at station C_3 occurred on December 21. After the maximum values, the concentrations of Si decreased rapidly to the lowest values of 3.2, 1.2, 0.49, and 0.38 μmol L^{-1} at stations A_1, A_3, A_5, and C_3, respectively, on February 9 or 18.

Variations in nutrient molar ratios in the surface water at stations A_1, A_3, A_5, and C_3 during ten-day period (Fig. 3) were similar to those of nutrients. The maximum changes in N/P, Si/P, Si/N ratios were also found at station A_5, and the minimum changes were at station C_3. The highest or second highest N/P ratios occurred at stations A_1, A_3, and A_5 on February 9 or January 30 and then descended obviously. The Si/P ratios reached the highest values of 19.1, 17.2, 43.0, and 11.8 at stations A_1, A_3, A_5, and C_3 on January 8, December 30, December 10, and January 17, respectively. After the highest, the Si/P ratios decreased rapidly to the lowest values of 3.4, 1.8, 1.6 for stations A_1, A_3, and A_5, respectively, on February 18 and 1.3 for station C_3 on February 9. They then increased again. Small changes were found in Si/N ratios. After experiencing the highest values, they decreased to the lowest values of 0.09, 0.06, 0.03, and 0.05 at stations A_1, A_3, A_5, and C_3, respectively, on February 18 or 28 and then increased gradually.

3 Variation in Phytoplankton Cell Abundance and Biomass During Ten-Day Period

Variations in average cell abundances of phytoplankton at the four stations during ten-day period (Fig. 4) showed that a minimum value of 0.153×10^3 cells L^{-1} was on December 21, after which the cell abundance increased quickly and reached a maximum of 493×10^3 cells L^{-1} on February 9 and then descended quickly again.

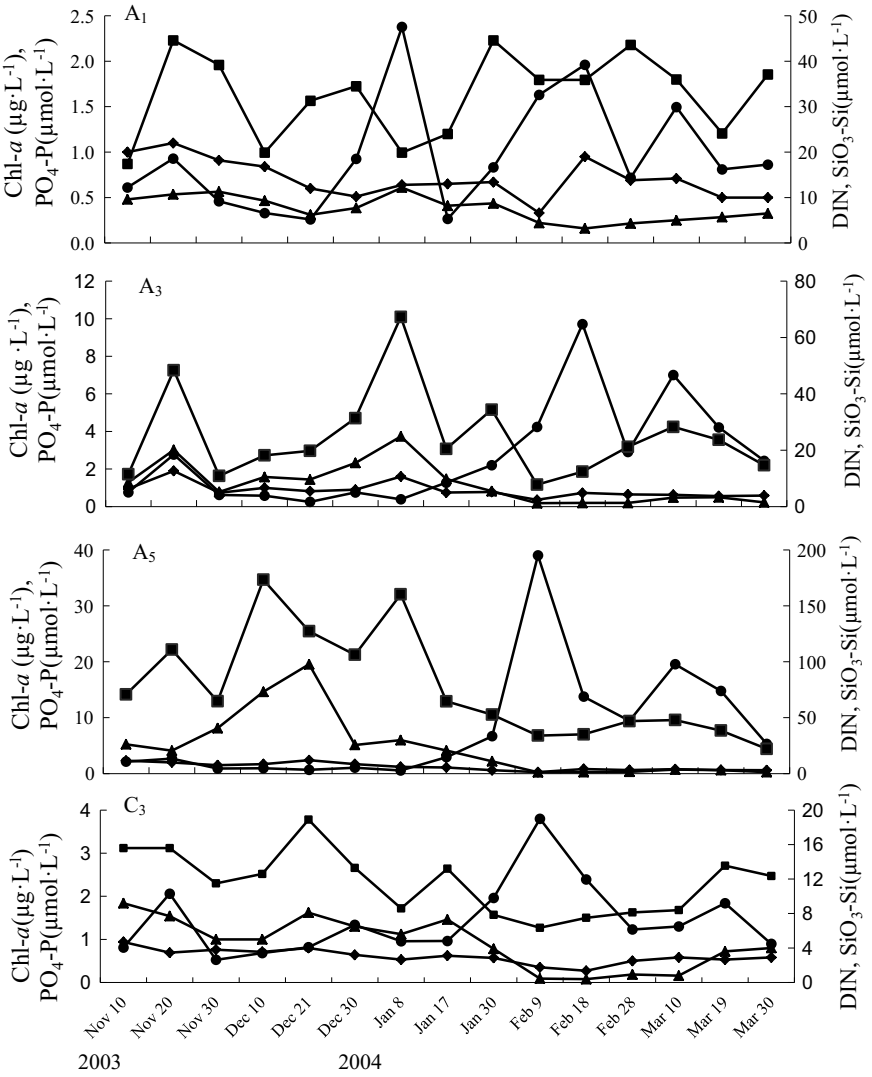

Fig. 2 Ten-day period variations in nutrients and Chl-*a* contents: filled circle—Chl-*a*; filled square—DIN; filled diamond—PO_4–P; filled triangle—SiO_3-Si

Among the four stations, the maximum change in phytoplankton cell abundance occurred at station A_5 and the maximum value of phytoplankton cell abundance reached 640×10^3 cells L^{-1} on February 9. Phytoplankton dominant species were *L. annulata*, *S. costatum*, *Rhizosolenia delicatula*, *Chaetoceros debilis*, *Asterionella kariana*, etc., suggesting that this bloom was mainly composed of the smaller cell species of *L. annulata*. At the peak of the bloom, the cell abundances of *L. annulata*

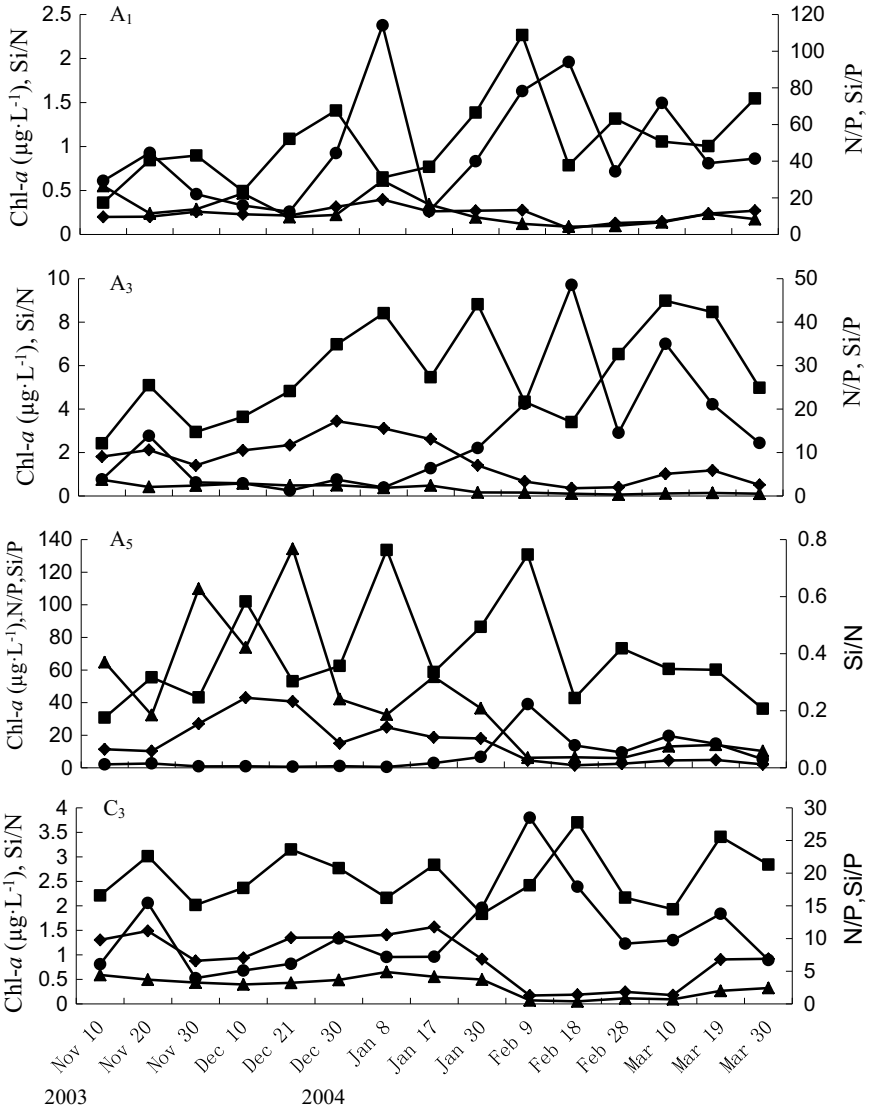

Fig. 3 Ten-day period variations in nutrient ratios and Chl-*a* content: filled circle—Chl-*a*; filled square—N/P; filled diamondt—Si/P; filled triangle—Si/N

reached 30.7×10^3, 330.7×10^3, $541.3 \times 10^{3,}$ and 75.7×10^3 cells L^{-1} and accounted for 35.4, 29.2, 84.6, and 37.1% of total cell abundances at stations A_1, A_3, $A_{5,}$ and C_3, respectively. The ten-day period changes in Chl-*a* content (Fig. 2) were consistent with those in cell abundances of phytoplankton; the most notable event occurred at stations A_3 and A_5. After December 21, Chl-*a* contents increased gradually and the

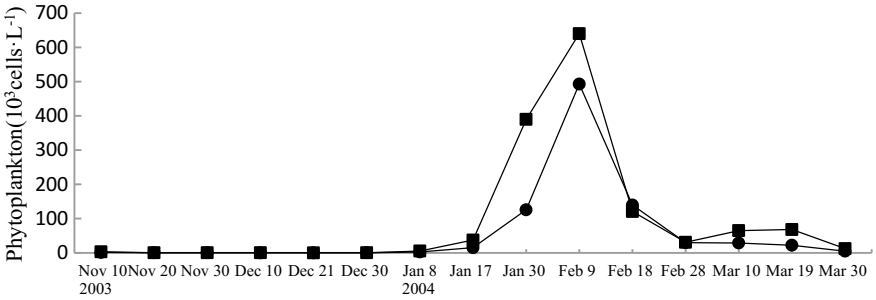

Fig. 4 Ten-day period variations in phytoplankton cell abundance: filled circle—average cell abundances for four stations; filled square—station A_5

highest Chl-*a* content of 39.03 μg L^{-1} appeared at station A_5 and the lowest that of 1.96 μg L^{-1} was at station A_1 at the peak of the bloom, suggesting that this bloom mainly occurred at station A_5.

4 Relationships Between Nutrient Concentrations and Phytoplankton Biomass

A comparison of nutrient concentrations and Chl-*a* content at the four stations during the course of this study, Chl-*a* content was very high for (8.03 ± 10.46) μg L^{-1} at station A_5, following was (2.68 ± 2.71) μg L^{-1} at station A_3. The lowest Chl-*a* content was at station A_1 for (0.96 ± 0.63) μg L^{-1}, which was consistent with the changes in cell abundances of phytoplankton, suggesting that phytoplankton growth was mainly controlled by nutrients. However, the phytoplankton growth was not only dependent on nutrient concentrations but also on other environment factors (Reynolds 1989; Hodgkiss and Ho 1997; Domingues et al. 2005). Cloern (1987) showed that the variability of phytoplankton biomass in estuaries can be related to the changes in light availability. When comparing environment conditions at station C_3 with other stations, the differences in water temperature and salinity were insignificant (Table 1). Light availability (seawater transparence) was better at station C_3 ((2.1 ± 1.0) m) than other stations ((1.3 ± 0.6) m, (1.6 ± 0.6) m, and (1.5 ± 0.4) m at stations A_1, A_3, and A_5, respectively), which was favorable for phytoplankton photosynthesis.

Chl-*a* content at station A_5 with high concentration of nutrients always kept a relative high level, even though after the peak of the bloom (Fig. 2). Pearson correlative analyses between nutrient concentrations and Chl-*a* content at every station before and after the bloom show that the most notable negative correlations were found at station A_5, following station C_3 (Table 2), which reflected the nutrient uptake and release associated with phytoplankton growth and death. The nutrients in the Jiaozhou Bay come mainly from terrestrial sources (Shen 2001; Wang et al. 2006; Sun et al. 2011b). Due to a few rainwater and wastes from agriculture and marine

Table 2 Correlationships of nutrient concentrations (μmol L^{-1}), ratios, and Chl-*a* content (μg L^{-1})

Stations	A_1		A_3		A_5		C_3	
	r	*p*	*r*	*p*	*r*	*p*	*r*	*p*
DIN	0.029	0.917	−0.208	0.457	−0.561	0.030	−0.490	0.064
PO_4–P	−0.116	0.679	−0.314	0.457	−0.671	0.006	−0.695	0.004
SiO_3–Si	−0.144	0.608	−0.522	0.046	−0.531	0.042	−0.532	0.041
N/P	0.157	0.575	0.107	0.705	0.358	0.190	0.228	0.414
Si/P	0.085	0.763	−0.661	0.007	−0.552	0.033	−0.484	0.068
Si/N	−0.019	0.947	−0.685	0.005	−0.568	0.027	−0.532	0.041

aquaculture in winter, the outer-source nutrients come mainly from industrial waste and residential sewage (including construction wastewater) from urban districts. Station A_5 is near river mouths discharged waste (sewage); nutrients discharged in a steady stream were a main cause of maintaining high Chl-*a* content there. Investigations showed that the maximum SiO_3–Si concentration was found in the Licun River mouth with 119.8 μmol L^{-1} (Yao and Shen 2006), which is possibly relative to a mass of silicious construction wastewater entering. In addition, the regeneration and accumulation of nutrients in late autumn was also an important source deriving from plankton death and decomposition. Continuous access to nutrients is essential for maintaining phytoplankton growth. Nutrient availability has frequently outweighed other factors as being the easiest way to initiate a bloom (Liu et al. 2005). As a result of negative relationships between SiO_3–Si concentration and Chl-*a* content, the clearly or more clearly negative relationships between the ratios of Si/P, Si/N, and Chl-*a* content were found at stations A_3, A_5, and C_3 (Table 2), suggesting that phytoplankton growth was related to the ratios of limiting nutrients (Shen et al. 2006). However, poor relations between N/P ratio and Chl-*a* content were found at those stations, due to N/P ratio much higher than Redfield value (16) (Redfield et al. 1963).

5 Bloom and Si Supply

Bloom is characterized by high values of Chl-*a* and phytoplankton biomass (Liu et al. 2005). As mentioned above, station A_5 was the major area of this bloom. When SiO_3–Si and PO_4–P concentrations reached the maximum values (December 21), phytoplankton cell abundance and Chl-*a* content began to increase. Particularly after January 8, phytoplankton bred rapidly, phytoplankton cell abundance increased from 5.38×10^3 to 640×10^3 cells L^{-1} (Fig. 4), and Chl-*a* content increased from 0.56 to 39.03 μg L^{-1} (Fig. 2) (February 9). Similar variations also occurred at stations A_1, A_3, and C_3. Paerl (1997) showed that particular importance in nutrient-sensitive water is the rates of new N and other nutrient supply-fundamental determinants of bloom development, maintenance, and proliferation. In the Jiaozhou Bay, phytoplankton

community composition is mainly diatom, accounting for more than 99% (Sun et al. 2011a). Because of N excess, PO_4–P plenty, and SiO_3–Si relative insufficient in the Jiaozhou Bay, continuous supply of Si was the determinant function for occurrence and development of this bloom. Along with the increasing in phytoplankton quantity, the nutrient concentrations descended quickly to the lowest values of 34.0, 0.27, and 0.49 μmol L^{-1} for DIN, PO_4–P, and SiO_3–Si respectively at the peak of the bloom. Very high N/P ratio of 130.8, lower Si/P ratio of 4.6, and very low Si/N ratio of 0.04 were found at the bloom peak, and after which, they decreased to the lowest values of 42.8, 1.6, and 0.03 for N/P, Si/P, and Si/N ratios respectively, suggesting that the changes in nutrient ratios were behind in the nutrient concentrations. Above data show that at the peak of the bloom, only SiO_3–Si concentration decreased to below the threshold value of diatom growth (2.0 μmol L^{-1}) while DIN and PO_4–P concentrations were clearly higher than their threshold values (1.0 and 0.10 μmol $L^{-1,}$ respectively) (Brown and Button 1979; Perry and Eppley 1981; Goldman and Glibert 1983; Nelson and Brzezinski 1990). Among various molar ratios of nutrients, N/P ratio was far higher than Redfield value (16) for the mean ratio of nutrients contained in marine diatom, only Si/P and Si/N ratios related to SiO_3–Si were much lower than Redfield values (16 and 1, respectively) (Redfield et al. 1963; Brzezinski 1985). The differences in Si/P and Si/N ratios were about one order of magnitude larger around the bloom. Large increase in nutrients, especially SiO_3–Si after the late autumn, led to rapid increase of diatom, which is one of major reasons arousing the bloom in winter. After which, due to SiO_3–Si was nearly exhausted by phytoplankton and very low Si/P and Si/N ratios, the bloom was finally controlled. The finding is somewhat similar to the nutrient-enriched Chesapeake Bay, where the magnitude of the spring phytoplankton bloom was controlled by SiO_3–Si (Conley and Malone 1992). The changes in nutrients and the ratios around the bloom peak showed that the occurrence and end of the bloom were not only controlled by nutrients, but also well related to the changes in nutrient ratios. Obviously, as Smayda (1989) put it, other factors will be involved in regulating bloom events, but nutrient ratios can be considered to be of major importance. Phytoplankton bloom dynamics rely on the synergistic interactions of favorable physical, chemical, and biotic conditions (Paerl 1988). Continuous supply of Si was the determinant function for occurrence and development of this bloom; however, the bloom was not happening when highest SiO_3–Si concentration. In addition to plenty of nutrients supply, suitable temperature and salinity, weather and sea conditions also play an important role in the bloom formation. At the peak of the bloom on February 9, seawater was maroon. Weather was smoke and fog, small stormy waves, and the wind speed of 2.5 m/s which were favorable to gathering phytoplankton.

According to the quarter investigations from May 1991 to May 2004, the nutrient concentrations tended to increase in the Jiaozhou Bay, especially after 1999. To take station A_5 as example (Figs. 5 and 6), the changes in DIN, PO_4–P, and SiO_3–Si concentrations were between 7.1 and 44.4 μmol L^{-1}, 0.08 and 1.8 μmol L^{-1}, below the detection limit, and 6.1 μmol L^{-1}, respectively, before 1999 (1990s). Among these three nutrients, SiO_3–Si concentration was the lowest. The probability of SiO_3–Si concentration less than 2.0 μmol L^{-1} (threshold value of diatom growth) accounting

for all investigation data was as high as 50%, while that of PO_4–P concentration less than the threshold value (0.1 μmol L^{-1}) was only 6%, and all DIN concentrations were greater than the threshold value (1 μmol L^{-1}). During 1999 and 2004 (2000s), DIN, PO_4–P, SiO_3–Si concentrations were between 7.4 and 123.7 μmol L^{-1}, 0.16 and 2.0 μmol L^{-1}, below the detection limit, and 45.4 μmol L^{-1}, respectively. Comparing with 1990s, their average values increased 0.99 times for DIN, 0.25 times for PO_4–P, and 3.2 times for SiO_3–Si, and the increasing of SiO_3–Si was the most obvious. The variations in nutrients at station A_5 were consistent with the Jiaozhou Bay (Sun et al. 2011b). SiO_3–Si is mainly from river transport. According to the data from Qingdao Observatory, annual average precipitation was 643.7 mm for the 1990s and 684.2 mm for the 2000s. The increase in precipitation means the increase in SiO_3–Si into the Jiaozhou Bay brought by precipitation surface runoff. However, it possibly shows that less increase in precipitation is insignificant for SiO_3–Si increase from the 1990s to the 2000s. The increasing of SiO_3–Si is possibly relative to rapid economic developments, especially city construction in Qingdao since the late 1990s. To take floor space of buildings completed as example, floor space of buildings completed per annum were 203×10^4–259×10^4 m^2 during 1995–1998, 474×10^4 m^2 in 1999, and 635×10^4 m^2 in 2004, suggesting that a lot of construction wastewater entering the bay increased Si concentration in the seawater. The changes in nutrient supplies are often accompanied by alterations in nutrient ratios (Yin et al. 2001). The molar ratios of nutrients also increased with the increase of nutrient concentrations (mainly N and Si). In the 1990s, the changes in N/P, Si/P, and Si/N ratios were between 15.9 and 88.4, 0 and 12.2, 0 and 0.51, respectively, and Si/P and Si/N ratios were much lower than Redfield value (16 and 1, respectively) (Redfield et al. 1963; Brzezinski, 1985). In the 2000s, N/P, Si/P, and Si/N ratios were between 22.4 and 118.1, 0 and 37.8, 0 and 0.57, respectively, and increased 0.35, 0.88, and 0.19 times, respectively, as compared with 1990s. Relative to the nutrient concentrations increased significantly, temperature and salinity in the surface seawater had no obvious changes (Fig. 7). The survey found that the season averages of temperature and salinity were (15.72 ± 7.75) °C and 31.34 ± 0.95 in the 1990s, and (14.32 ± 8.42) °C and 31.38 ± 0.87 in the 2000s, respectively. Higher temperature in the 1990s is associated with the data of a lack of winter. Many nutrient enrichment experiments have shown that marine phytoplankton blooms are often nutrient limited (Hodgkiss and Ho 1997). Although eutrophication in the Jiaozhou Bay was more serious before 1998, there were few bloom events and the bay was in relatively stable ecological condition. Low SiO_3–Si concentration and Si/P, Si/N ratios limited phytoplankton growth, especially in winter (Shen 2001) when phytoplankton reproduced frequently (Wu et al. 2004). In recent years, the nutrient concentrations showed increasing trends in the Jiaozhou Bay, especially Si limitation was alleviated compared to the 1990s due to the increasing in SiO_3–Si concentration, which supplied material base for phytoplankton growth (Sun et al. 2011b). The study showed that from the 1990s to the 2000s, net phytoplankton cell abundance increased from $(2.74 \pm 3.17) \times 10^3$ cells L^{-1} to $(13.04 \pm 27.08) \times 10^3$ cells L^{-1}, increased almost one order of magnitude (Fig. 7). After 1998, the bloom event significantly increased with the increase in nutrient concentrations, molar ratios, and phytoplankton number.

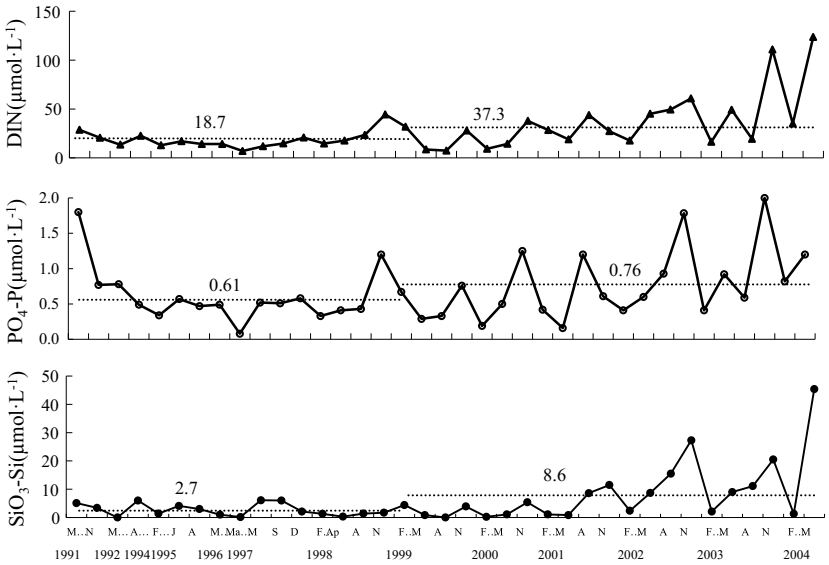

Fig. 5 Years variations in nutrient concentrations at station A_5 from 1991 to 2004. Dotted line—averaged value; F—February; Ma—March; Ap—April; M—May; J—June; A—August; S—September; N—November; D—December

According to the report of Wu et al. (2005), before the 1990s, there was not bloom event report in the Jiaozhou Bay, in the late 1990s, the rapid development of bloom, almost occurred every year, among them, two bloom events were recorded in 1999, 2003, and 2004. So the nutrient loading has an obvious relationship with increased blooms (Hallegraeff 1993). For example, in a bloom of *E. zodiacus* occurred in the north-eastern part of the Jiaozhou Bay (Zhang et al. 2002), PO_4–P and SiO_3–Si concentrations decreased from 2.1 and 19.2 μmol L^{-1} to 0.40 and 0.92 μmol $L^{-1,}$ respectively. Only when SiO_3–Si concentration decreased to below threshold value of diatom growth (2.0 μmol L^{-1}), the bloom was finally controlled. This is very similar to the development and end of the bloom found by us in winter in this section.

Here, we can suggest that SiO_3–Si kept ecological balance of eutrophication waters in the Jiaozhou Bay where Si is relatively insufficient. Once the SiO_3–Si concentration increases significantly, the equilibrium between nutrients and phytoplankton will be destructed and lead to rapid increase of diatom and arouse blooms when other conditions (such as temperature, water current state) are quite suitable. It is likely one of the primary causes for the increased blooms in recent years in the Jiaozhou Bay. In this sense, SiO_3–Si limitation is favorable for keeping ecological equilibrium of the Jiaozhou Bay (Shen et al. 2006). From a practical perspective, regulating nutrient supply is often the only feasible management approach to bloom control (Paerl 1997). Hence, we suggest that from now on, the increase of SiO_3–Si concentration should be controlled in the Jiaozhou Bay.

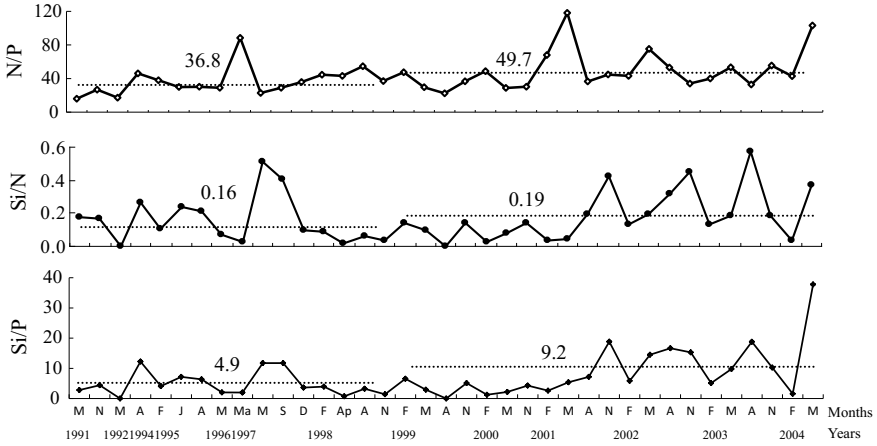

Fig. 6 Years variations in nutrient ratios at station A_5 from 1991 to 2004. Dotted line—averaged value; F—February; Ma—March; Ap—April; M—May; J—June; A—August; S—September; N—November; D—December

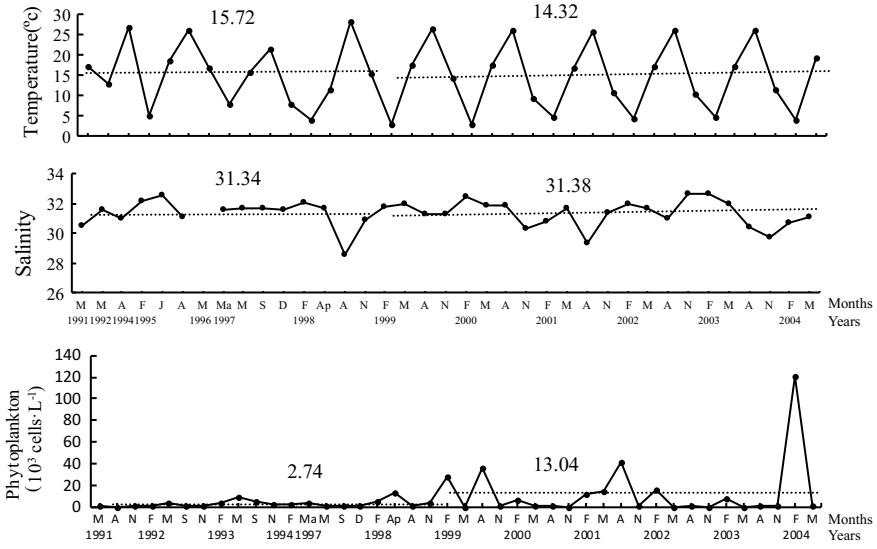

Fig. 7 Years variations in temperature, salinity, and phytoplankton cell abundance at station A_5 from 1991 to 2004. Dotted line—averaged value; F—February; Ma—March; Ap—April; M—May; J—June; A—August; S—September; N—November; D—December

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Part IV
Particulate Organic Carbon and the Composition of Nutrient of Phytoplankton

Particulate Organic Carbon and Its Composition in Jiaozhou Bay

Zhiliang Shen, Heming Yang and Qun Liu

Abstract The seasonal variations of particulate organic carbon (POC) in Jiaozhou Bay were consistent with those of chlorophyll-*a* (Chl-*a*), primary productivity, particulate nitrogen (PN) and organic matters in surface sediments, and all of the highest values were found in summer. The average mass ratio of POC and PN in seawater was 6.5. The POC contents varied between 0.050 and 1.000 mg C L^{-1} with an average of 0.282 ± 0.186 mg C L^{-1}. The contributions of detritus organic carbon, phytoplankton carbon, bacterial carbon, and zooplankton carbon were 0.123, 0.140, 0.0108, and 0.0079 mg C L^{-1}, respectively, and the ratios in POC were 43.6, 49.8, 3.8, and 2.8%, respectively.

Keywords Particulate organic carbon · Particulate nitrogen · Composition Jiaozhou Bay

Although particulate organic carbon (POC) in the seawater is only 1–10% of dissolved organic carbon (Parsons 1975), because of its importance in marine food chain and marine productivity, the study on POC has become a hot topic of marine sciences (Mendel 1967; Eppley et al. 1977; Postma and Rommets 1984; Han et al. 1991; Guo and Hong 1994).

Jiaozhou Bay is a typical half-enclosed bay situated in the western part of the Shandong Peninsula, China. The bay is surrounded by Qingdao City (7 million people) and has an area of about 390 km^2 and an average water depth of about 7 m. A great number of household and industrial wastes and organic matters from Qingdao City are one of the main sources of POC in Jiaozhou Bay.

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Ji et al. (1992) reported on POC in Jiaozhou Bay seawater from 1980 to 1981. Using a wet oxidation method (Sun et al. 1983), POC concentration was determined for 0.225 mg C L^{-1} in average and accounted for about 13% of total organic carbon. In this section, the POC in Jiaozhou Bay seawater was measured using a dry burn method and the distributions and variations of POC and the relationships between POC and chlorophyll-*a* (Chl-*a*), primary productivity (PP), particulate nitrogen (PN), nutrients, suspended matter, and organic matter (OM) in surface sediment, respectively, are discussed, and the composition of particulate organic carbon is also estimated.

1 Sampling and Analysis Method

Four seasonal investigations were carried out in Jiaozhou Bay waters in May, August, November, 1991, and February, 1992. There are nine stations indicated in Fig. 1, and the water samples were collected from the surface layer, 10 m layer, and bottom layer.

The water samples (200–500 mL) were filtered through the pre-ignited (450 °C) Whatman GF/C filter, and the blank filler was moistened in the filtrate, and then, they were stored in a low temperature ice box for analysis later at the laboratory. The POC

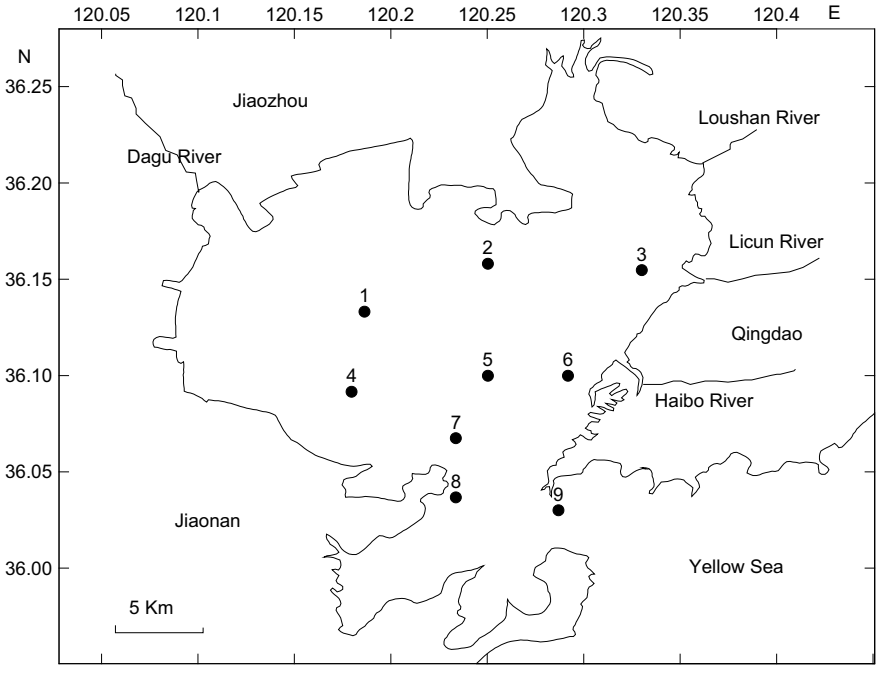

Fig. 1 Sampling stations

and PN were simultaneously determined with a PE 240C elementary analyzer, and the acetanilide was used as standard material. Strickland and Parsons (1972) used two layers filters for filter and the low layer filters for blank. Gordon and Sutcliffe (1974) pointed that two layers filters could possibly increase the blank value. We (Yang and Liu 1995) put the blank filters moistened in the filtrate into a closed container and treated for 0.5 h with HCL vapor and then dried for 3 h at 105–110 °C. The contents of POC and PN for ten blank filters were 6.09 ± 1.81 μg C L^{-1} and 1.19 ± 0.57 μg N L^{-1}, respectively. The samples filters filtered were also treated as above, and the result of removal inorganic carbon was good.

If the oxidation temperature is maintained at 750 ± 50 °C, we found that it could not reduce the transform efficiency of organic carbon, but the filters were not sintered on the sample spoon.

2 Distribution and Variation of POC

2.1 Content and Horizontal Distribution of POC

The POC contents in Jiaozhou Bay seawater were 0.050–1.000 mg C L^{-1} with an average value 0.298 ± 0.204 mg C L^{-1} for surface water and 0.050–0.700 mg C L^{-1} with an average value 0.265 ± 0.179 mg C L^{-1} for bottom water and 0.282 ± 0.186 mg C L^{-1} for annual average value. The POC content in Jiaozhou Bay seawater was lower than that in the Daya Bay (0.415 mg C L^{-1}) (Xu et al. 1989) which is located in the north of the South China Sea and the Changjiang River estuary area (0.833 mg C L^{-1}) (Xie et al. 1992) and much higher than that in the Pacific (0.030 mg C L^{-1}) and Atlantic (0.054 mg C L^{-1}) (Wangersky 1976).

Besides controlled by the organism cycle insider the bay, the horizontal distribution of POC (Fig. 2) is closely related to the transportation of the outside sources organic maters. Higher contents of POC were generally in northeastern and eastern bay because of the import of the industrial and living wastewater there. Because of the effect of the Dagu River water imported (flood season), the POC contents in August decreased from estuary toward southeastern and the highest value (1.000 mg C L^{-1} for surface and 0.700 mg C L^{-1} for bottom) were found at station 1 near the estuary. Because of the effects of seawater culture surrounding Jiaozhou Bay, the POC contents in the coastal waters were higher than those in the center waters.

2.1.1 Seasonal Variation of POC

The seasonal variations of POC (Table 1) in Jiaozhou Bay seawater showed that POC contents were higher in spring and summer than those in autumn and winter, the highest in summer, and the lowest in autumn. The seasonal variations of POC were consistent with those of Chl-*a* and primary productivity (PP) (Fig. 3), showing

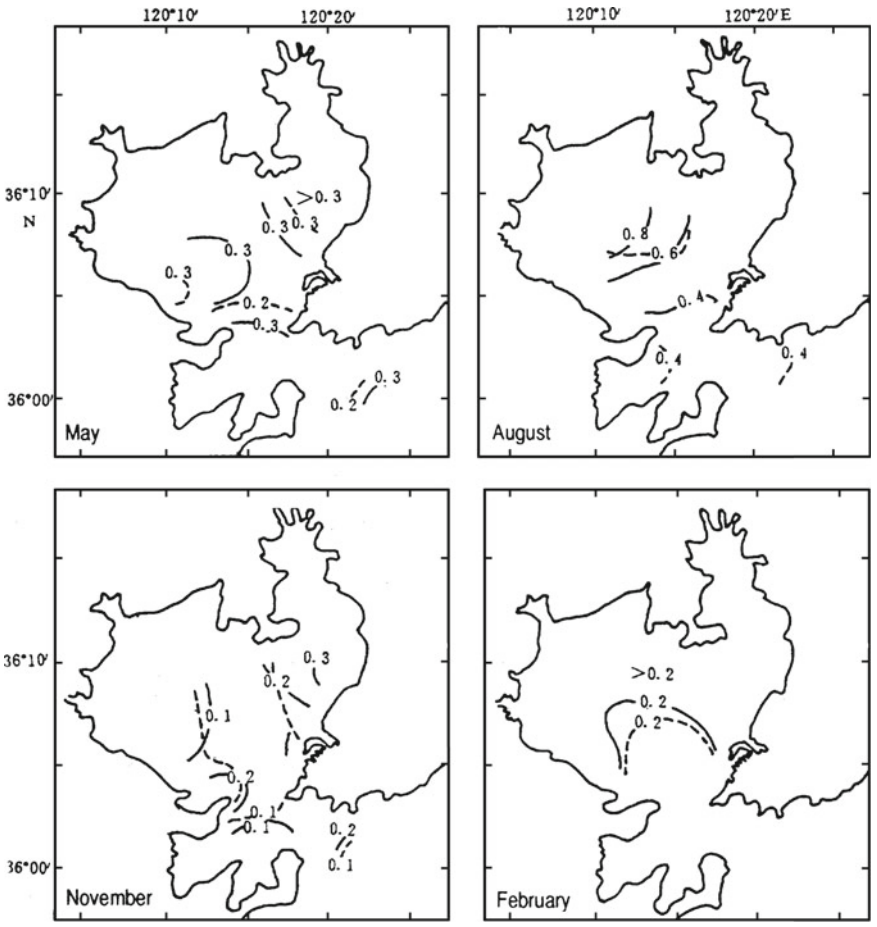

Fig. 2 Horizontal distributions of POC (mg C L^{-1}) in Jiaozhou Bay: solid line—surface; dashed line—bottom

Table 1 Seasonal variations of POC contents (mg C L^{-1}) in Jiaozhou Bay

Seasons	Surface	Bottom	Averages
Spring	0.337 ± 0.077	0.204 ± 0.090	0.274 ± 0.106
Summer	0.549 ± 0.219	0.520 ± 0.130	0.535 ± 0.177
Autumn	0.124 ± 0.090	0.162 ± 0.091	0.143 ± 0.089
Winter	0.181 ± 0.056	0.167 ± 0.087	0.174 ± 0.068

the control actions of phytoplankton and primary productivity in Jiaozhou Bay to the seasonal variations of POC and the effects of POC to the seasonal variations of primary productivity.

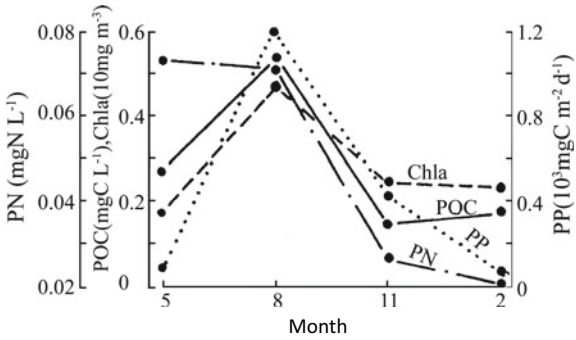

Fig. 3 Seasonal variations of POC, PN, Chl-*a*, and PP

3 The Relations of POC and Chlorophyll-*a* and Other Environment Factors

The correlation statistics to all of data (surface and bottom) showed that there was fairly good positive linear correlationship between POC and chlorophyll- *a* indicated as:

$$\text{POC (mg C L}^{-1}) = 0.123 + 0.061\ \text{Chl-}a\ (\text{mg m}^{-3})\ (r = 0.538,\ n = 61)$$

There were also fairly good positive linear correlationships between POC and PN except November. Their correlation coefficients were 0.601 (n = 18) for May, 0.669 (n = 17) for August, 0.310 (n = 17) for November, and 0.685 (n = 16) for February. The relationship (all of data) between them was as follows:

$$\text{POC (mg C L}^{-1}) = 0.136 + 2.882\ \text{PN (mg N L}^{-1})\ (r = 0.623,\ n = 68)$$

The correlation between POC and PN is closely related to their sources. The PN measurement involves three forms of nitrogen, adsorbed ammonia, and adsorbed organic nitrogen on finest particles (Meybeck 1982). Higher concentration of NH_4–N (average 7.5 μmol L^{-1}) in Jiaozhou Bay was 78% of total inorganic nitrogen (Shen 1997). The NH_4–N adsorbed in the suspended particles was possibly one factor of affecting the relationship of POC and PN. Although there were positive correlationship between POC and NH_4–N, the correlations were poor and the correlation coefficients were 0.391 (n = 18) for May, 0.320 (n = 17) for August, 0.208 (n = 17) for November, and 0.356 (n = 16) for February. The quality ratio of C and N for aquatic plants was 5.7 (Vallentyne 1973) about 10% of terrestrial plants. The ratios of POC and PN in Jiaozhou Bay in May, August, November, and February were, respectively, 3.8, 7.5, 5.3, and 9.7 with an average 6.5. It showed that phytoplankton carbon was of importance to the compositions of POC in Jiaozhou Bay. Milliman et al. (1984) thought that the low C/N ratios (less than 4) in suspended particles might be explained

by ammonia absorption onto clay particles and higher C/N ratio (greater than 12) could be expected from organic material derived from terrestrial plants and humus.

The effects of nutrients in the seawater to POC are realized mainly through phytoplankton variations. Besides living organisms, the POC also include non-living organisms example for terrestrial transportation matters and marine detritus organisms; therefore, there were not definite correlationships between POC and nutrients, but their seasonal variations (Fig. 4) showed there were certain relations of growth and decline. From May to August, the POC content reached annual maximum value, when it was also annual chlorophyll-*a* and primary productivity peek (4.62 ± 2.14 mg m^{-3} and 1192.2 ± 572.9 mg C m^{-2} d^{-1}, respectively) (Fig. 3), the concentrations of NO_3–N, NH_4–N, and PO_4–P obviously decreased then. From August to November, the POC content rapidly decreased and a little increased until February. Because of low concentration of PO_4–P greatly consumed by phytoplankton, it rose only after November. The concentrations of NO_3–N and NH_4–N gradually rose after August.

No obvious correlationship between POC and suspended matters (only observed in August) showed that the sources of suspended matters in Jiaozhou Bay at every station were different. There were no obvious relationships between POC and organic matters in the surface sediments. These are the reasons that sediments in shallow Jiaozhou Bay are easily resuspended and further removed due to the actions of wind and tide, etc., but the seasonal variations of organic matters in the surface sediments were completely consistent with those of POC (Fig. 4).

3.1 The Composition of Particulate Organic Carbon in Jiaozhou Bay

It is difficult to distinguish quantitatively the living part and non-living part in POC (Parsons 1975; Alcaraz et al. 1985). They can be estimated according to the correlationship equation between POC and chlorophyll-*a* (Parsons 1975; Eppley et al. 1977):

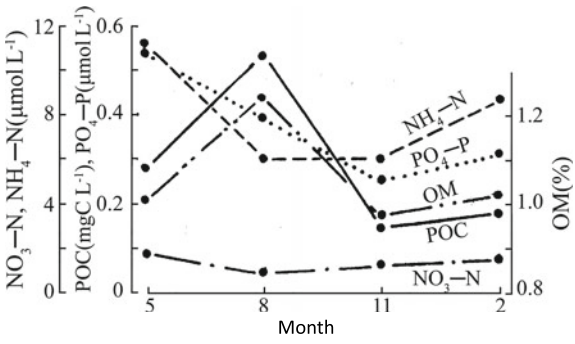

Fig. 4 Seasonal variations of nutrients, POC, and organic matters (OM) in surface sediment

$$\mathrm{POC} = \mathrm{POC\ (detritus)} + \mathrm{f} \cdot \text{Chl-}a$$

where POC (detritus) is the detritus organic carbon, f · Chl-*a* is living organic carbon, and f is about 25–250 (Parsons 1975). From above the relationship between POC and chlorophyll-*a* in Jiaozhou Bay, detritus organic carbon was 0.123 mg C L^{-1} and f was 61 which approach the paper value 60 (Horne 1969). Thus, the living organic carbon equals 0.159 mg C L^{-1}. 43.6% of POC for the detritus organic carbon and 56.4% of that for the living organic carbon showed that living organic carbon was main contributor of particulate organic carbon in Jiaozhou Bay seawater. The estimated the living organic carbon in Daya Bay seawater (Xu et al. 1989) using same way shows that the ratio (41.2%) of it in POC there is lower than that in Jiaozhou Bay, it mainly due to the annual average chlorophyll-*a* (2.78 mg m^{-3}) and primary productivity (461 mg C m^{-2} d^{-1}) in Jiaozhou Bay are two times of those in the Daya Bay (Xu et al. 1989) and suspended matters (561 mg L^{-1} for 1995) in Jiaozhou Bay was only 57% of that in the Daya Bay (Xu et al. 1989). The ratio of living organic carbon in POC in Jiaozhou Bay is higher than that in the Long Island Strait (70% for phytoplankton blooms and 10–25% usually) (Parsons 1975) and Tsugaru Strait (0.4–34%) (Nakajima and Nishzawa 1968) and southern Taiwan upwelling area (37%) (Hung et al. 1987).

In fact, in addition to phytoplankton carbon, living organic carbon includes bacterial organic carbon and zooplankton organic carbon. Investigation showed that the annual average zooplankton biomass (wet quality) was 76.2 mg m^{-3}. According to the quality transform factor 25% of dry and wet samples and transform factor 416×10^3 mg C kg^{-1} of zooplankton carbon (Bowen 1979), zooplankton carbon equals 0.0079 mg C L^{-1}, which is only 5.0% of living organic carbon and 2.8% of POC, respectively. According to bacterial average numbers 5.39×10^5 cell mL^{-1} in the Jiaozhou Bay seawater (Xiao et al. 1995) and the transform factor 20 fg C $cell^{-1}$ of bacterial carbon (Lee and Fuhrman 1987; Cho and Azam 1990), calculated bacterial carbon content equals 0.0108 mg C L^{-1} which is only 6.8% of living organic carbon and 3.8% of POC, respectively. Therefrom, phytoplankton carbon in Jiaozhou Bay is 0.140 mg C L^{-1} which 88.2% of living organic carbon and 49.8% of POC, respectively.

From the above, the POC contents in Jiaozhou Bay seawater varied between 0.050 and 1.000 mg C L^{-1} with an average value of 0.282 ± 0.186 mg C L^{-1}. The contributions of detritus organic carbon, phytoplankton carbon, bacterial carbon, and zooplankton carbon were 0.123, 0.140, 0.0108, and 0.0079 mg C L^{-1}, respectively, and the ratios in POC were 43.6, 49.8, 3.8, and 2.8%, respectively. Phytoplankton carbon, bacterial carbon and zooplankton carbon were 88.2, 6.8, and 5.0% of living organic carbon, respectively.

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Nutrient Compositions of Cultured *Thalassiosira rotula* and *Skeletonema costatum* from Jiaozhou Bay

Zhiliang Shen, Yulin Wu, Qun Liu and Yun Yao

Abstract The nutrient compositions of cultured *Thalassiosira rotula* and *Skeletonema costatum* from Jiaozhou Bay were measured. Carbon (C), nitrogen (N), phosphorus (P), and silicon (Si) contents in cell were obvious higher in *T. rotula* than in *S. costatum*, but the percents of N, P, Si contents in cell dry mass in *T. rotula* were lower than those in *S. costatum*. The dry mass concentrations of N, P, Si in *S. costatum* were much higher than those in *T. rotula*, particularly Si, the former was 6.4 times of the latter, showing that *S. costatum* could more assimilate these elements. Especially, *S. costatum* had competitive dominance for assimilation Si, which is beneficial to its becoming a major dominant species in relative short Si of Jiaozhow Bay. There were some differences in numerical value of nutrient ratios both laboratory-cultured phytoplankton and different-sized suspended particulates (mainly phytoplankton) in Jiaozhou Bay, which was caused by the changes of environment. High contents of C, N and relative low P, Si, high N/P ratio (far higher than Redfield value) and low Si/P and Si/N ratios (far lower than Redfield values) in the two diatoms and different-sized suspended particulates were consistent with those in the seawater. Relative short Si in the seawater and phytoplankton showed that Si was possibly affecting phytoplankton growth in Jiaozhou Bay.

Keywords Carbon · Nitrogen · Phosphorus · Silicon composition · Culture *Skeletonema costatum* · *Thalassiosira rotula* · Jiaozhou Bay

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Biological and chemical processes of marine phytoplankton are related to their size to a considerable degree (Ray et al. 2001; Suttle et al. 1991). At present, the ecological study of phytoplankton has advanced into the aspect of particle size distribution and its effects, and element composition of phytoplankton in different-sized fractions is an important study field. Measuring the chemical composition (carbon, nitrogen, Phosphorus, silicon, etc.) of phytoplankton is of important senses to estimate primary production of phytoplankton (Strickland 1960; Conley et al. 1989; Geider and La Roche 2002; Heldal et al. 2003), judgement nutrients limitation (Harrison et al. 1977; Sakshaug and Holm-Hansen 1977; Rhee and Gotham 1980; Brzezinski et al. 1990; Beardall et al. 2001; Claquin et al. 2002; Shen et al. 2006; De La Rocha et al. 2010; Hagstrom et al. 2011), discussion stoichiometric balance between nutrient structure of seawater and nutrient composition of phytoplankton and biogeochemistry of nutrient (Fraga et al. 1998; Heldal et al. 2003; Shen et al. 2006; Hoffmann et al. 2007; Baines et al. 2011). However, so far scientists cannot always separate phytoplankton directly by particulate size from seawater. Measurements of elemental ratios or chemical composition of natural populations of phytoplankton are prone to interference from debris and other microorganisms such as bacteria and microzooplankton that can be collected on the filters used to ample the phytoplankton (Beardall et al. 2001). Therefore, correlative studies in the international concentrated mainly on laboratory- cultured phytoplankton strains (Heldal et al. 2003; Ho et al. 2003; Burkhardt and Riebesell 1997; Verity et al. 1992). Major nutrients studied are carbon, nitrogen, Phosphorus (Menzel and Ryther 1964; Sakshaug and Holm-Hansen 1977; Nøst-Hegseth 1982; Sakshaug et al. 1983; Lirdwitayaprasit et al. 1990; Burkhardt and Riebesell 1997; Geider and La Roche 2002; Vrede et al. 2002; Loebl et al. 2010), less for silicon (Lewin and Guillard 1963; Harrison et al. 1977; Leynaert et al. 1991; Ríos et al. 1998; Marchetti and Harrison 2007; Baines et al. 2011). Researches have been reported in the elemental composition of *Skeletonema costatum,* such as the changes in chemical composition of *S. costatum* under the conditions of nitrate-, phosphate-, and iron-limited growth (Sakshaug and Holm-Hansen 1977) and CO_2 affecting elemental composition (C:N:P) of *S. costatum* (Burkhardt and Riebesell 1997).

Jiaozhou Bay is seriously affected by human activities. During the last 40 years, nitrogen and Phosphorus concentrations have largely increased in Jiaozhou Bay seawater, especially nitrogen, and silicate concentration may has remained at a relatively lower level. The molar ratio of nitrogen to phosphorus was obviously higher than Redfield value (Redfield et al. 1963) and eutrophication has become increasingly serious, resulting in changes of phytoplankton community structure (Shen 2001; Sun et al. 2002). In order to explore the change rule of phytoplankton community under eutrophication condition, carbon, nitrogen, Phosphorus, silicon compositions, and molar ratios of laboratory-cultured two different-sized phytoplankton common species of *Thalassiosira rotula* and *S. costatum* from Jiaozhou Bay were measured and compared with the nutrient structures of seawater and different-sized suspended particulates in this section.

1 Sampling and Experimental Methods

1.1 Sampling

Investigation was carried out, and nine stations were set up in Jiaozhou Bay in February 2002 (Fig. 1). Surface water samples were collected using a Niskin sampler. Unfiltered water samples were preserved (with 0.3% chloroform) in polyethene bottles and stored in a low temperature ice box (−30 °C) for analyzing nutrients (taking clear superstratum water sample) at the laboratory later. Phytoplankton water samples were collected from surface layer seawater and preserved with neutralized formalin. Phytoplankton were identified and counted under a microscope using a workshop-made Sadgwick-Rafter-like chamber at the laboratory later.

1.2 Laboratory Cultures

T. rotula and *S. costatum* were separated from phytoplankton samples collected in Jiaozhou Bay under a microscope and transferred to 200 mL triangle bottles with 100 mL f/2 medium for culture, respectively. The cultures were carried out at a

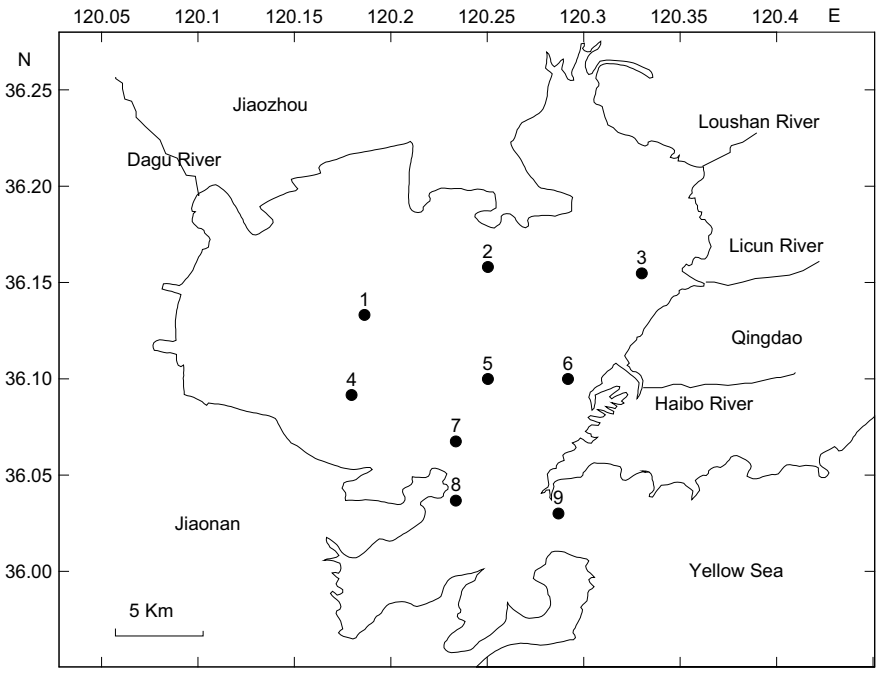

Fig. 1 Station positions

temperature of 18 ± 1 °C, an illumination of 4000LX, and a ratio of light time to dark time equaling 12 h: 12 h. After repeat separations and purifications, extending cultures were lasted 30 days for *T. rotula* and 45 days for *S. costatum,* and then they were counted. Their cell abundances were 35.2×10^3 cells mL^{-1} for *T. rotula* and 480×10^3 cells mL^{-1} for *S. costatum.* Six samples with 2 mL each were taken from every medium. The medium samples for determining phytoplankton carbon and nitrogen were filtered with preignited (450 °C, for 6 h) Whatman GF/D (2.7 μm), and the medium samples for determining phosphorus and silicon were filtered with 2 μm Millipore filter. Four millilitres medium with two shares each were taken and filtered with 0.45 μm Millipore filter for determining the dry mass of the culture cells. All filters were 25 mm in diameter. All filtered membranes and blank membranes immersed filtrates were rinsed with deionized water and stored in a low-temperature icebox for further analysis.

1.3 Analysis and Calculation

Nutrients concentrations were determined by colorimetric methods (Shen et al. 2008). Dissolved inorganic nitrogen (DIN) is equal to the sum of NO_3–N, NO_2–N, and NH_4–N. The sample of phytoplankton P was digested referring to Koroleff's (1976) method and measured with the potassium peroxodisulphate oxidation- colorimetry. Sample membrane or blank membrane, 2 mL of 5% H_2SO_4–$K_2S_2O_8$ solution and 10 mL of distilled water were put into polyfluortetraethylene digestion bottle in order and digested for 1 h at 115 °C in a pressure cooker, then measured by colorimetry. The sample of phytoplankton Si was measured referring to Treguer and Gueneley's (1988) method, putting sample membrane or blank membrane, 10 mL of 5% Na_2CO_3 digestion solution into polyfluortetraethylene digestion bottle in order, then was digested and measured by colorimetry. The samples were determined using a SKALAR Flow Analyzer made in Netherlands. Phytoplankton C and N were measured using a model 240C Element Analyzer. The dry mass of diatom cell was measured using the weight method.

The content of element in cell was calculated as:

$$Q = C \cdot F / D$$

where, Q is content of element in cell (pg $cell^{-1}$), C is molar concentration of element (μmol L^{-1}), F is conversion coefficient of unit, D is cell density in cultured medium (cell mL^{-1}). The dry mass concentration of element is calculated as:

$$M_1 = C \cdot F / M_2$$

where, M_1 is dry mass concentration of element (mg g^{-1}) and M_2 is dry mass concentration of diatom in cultured medium (mg L^{-1}).

2 Nutrient Concentrations and Structure in Jiaozhou Bay Seawater

Nutrient concentrations and molar ratios in surface seawater in Jiaozhou Bay in February 2002 (Table 1) show that there were high concentration of N and low SiO_3–Si in Jiaozhou Bay and SiO_3–Si concentrations were lower than or equal to the threshold value of diatom growth (2.0 μmol L^{-1}) (Brown and Button 1979; Perry and Eppley 1981; Goldman and Glibert 1983; Nelson and Brzezinski 1990) at station 1 or 2, respectively. Among three forms of inorganic N, NH_4–N was main existent form being 72.4% of DIN and NO_3–N was only 23.6% of DIN, which showed that three forms of inorganic N were not in thermodynamics equilibrium. The ratios of nutrients in average were 27.8 ± 13.6 for DIN/PO_4–P ratio far higher than Redfield value (16) and 7.4 ± 2.6 and 0.32 ± 0.16 for SiO_3-Si/PO_4-P and SiO_3-Si/DIN ratios, respectively, far lower than Redfield value (16 and 1, respectively) (Brzezinski 1985; Redfield et al. 1963), which showed that SiO_3-Si and PO_4–P possibly were potential limiting factor to phytoplankton growth, especially SiO_3–Si (Shen et al. 2006).

3 Distributions of *T. rotula* and *S. costatum* in Jiaozhou Bay

S. costatum was the predominant phytoplankton in Jiaozhou Bay, particularly in winter and summer. *T. rotula* was a phytoplankton common species, but its abundance had not orderliness in seasonal variation and quantity was far lower than *S. costatum.* A phytoplankton peak in quantity was often found in winter (Wu et al. 2004). Twenty-eight species of phytoplankton including 27 species of diatoms and 1 species of *Dictyocha* sp. were identified in February, 2002. The cell abundance of phytoplankton in average was 651.0 cell mL^{-1}, and the dominant species were *S. costatum* and *Thalassiosira nordenskiöldii.* Thereinto, the cell abundance of *S. costatum,* ranged between 185.0 and 822.0 cells mL^{-1} with an average of 427.8 cells mL^{-1} in seawater. The cell abundance of *T. rotula* was between 6.8 and 61.6 cells mL^{-1} with an average of 23.2 cells mL^{-1}. Their ratios in total cell abundance of phytoplankton were as high as 65.7% for *S. costatum* and only 3.6% for *T. rotula.*

4 C, N, P, Si Compositions of *T. rotula* and *S. costatum*

Dry mass and contents of C, N, P, Si in cells of *T. rotula and S. costatum* are indicated in Table 2. The dry mass of each cells of *T. rotula and S. costatum* were 3125.0 and 300.0 pg, respectively, and the former was one order of magnitude higher than the latter which was obviously related to their volumes. *T. rotula* belong to microphytoplankton and *S. costatum* was nanophytoplankton and their diameters are 20–50 and 6–20 μm commonly in Jiaozhou Bay, respectively. C, N, P, Si contents of each

Table 1 Nutrient concentrations ($\mu mol\ L^{-1}$) and their molar ratios in surface seawater in Jiaozhou Bay

Stations	PO_4–P	SiO_3–Si	NO_3–N	NO_2–N	NH_4–N	DIN	N /P	Si/P	Si/N
9	0.35	3.9	1.7	0.55	11.3	13.6	38.9	11.1	0.29
8	0.31	3.1	1.2	0.29	5.1	6.6	21.3	10.0	0.47
7	0.46	4.1	2.4	0.47	8.6	11.5	25.0	8.9	0.36
6	0.54	4.6	5.5	0.81	21.7	28.0	51.9	8.5	0.16
5	0.54	4.5	2.1	0.44	4.9	7.4	13.7	8.3	0.61
4	0.60	3.8	3.0	0.55	5.2	8.8	14.7	6.3	0.43
3	0.41	2.4	3.9	0.57	13.2	17.7	43.2	5.9	0.14
2	0.55	2.0	4.0	0.67	7.8	12.5	22.7	3.6	0.16
1	0.44	1.9	2.9	0.46	4.7	8.1	18.4	4.3	0.23
Averages	0.47	3.40	3.00	0.53	9.20	12.70	27.8	7.4	0.32
	±0.10	±1.1	±1.3	±0.15	±5.6	±6.7	±13.6	±2.6	±0.16

cell of *T. rotula* were 1812.5, 170.5, 12.00, and 4.81 pg, respectively and were 58.0, 5.5, 0.4, 0.2% of the dry mass of cell, respectively. Thereinto, C content exceeds half of the dry weight of cell and was one order of magnitude higher than N content, N content was one order of magnitude higher than P content, and Si content was the lowest. C, N, P, Si contents of each *S. costatum* cell were 97.0, 27.9, 1.63, and 2.95 pg, respectively and were 32.3, 9.3, 0.5, and 1.0% of the dry mass of cell, respectively. Comparing the compositions of C, N, P, and Si of two diatom cells, the various elemental contents in *T. rotula* were notably higher than those in *S. costatum* which was consistent with the high dry mass of the former. There were greater differences in the percent of elemental contents of two diatom cells in the dry mass of cells. The percent of C content in *T. rotula* was much higher than that in *S. costatum*, but the percents of N, P, Si contents in *T. rotula* lower than those in *S. costatum*, particularly Si. Element compositions of two diatom cells showed that the N and P contents in *T. rotula* cell were much higher than those in *S. costatum* cell and the former were 6.1 and 7.4 times the latter, respectively, but C content of the former was 18.7 times that of the latter (the dry mass of the former was only 10.4 times that of the latter). On the basis of cell volume, Sun et al. (1999) estimated the C contents in each cell of *T. rotula* and *S. costatum* in Jiaozhou Bay using the formulas suggested by Mullin et al. (1966), Strathmann (1967), Eppley et al. (1970) and Taguchi (1976), they were 736.2, 579.1, 693.7, and 338.2 pg, respectively for *T. rotula* and 16.9, 15.0, 17.8, and 9.6 pg, respectively for *S. costatum*. N contents in each cells of *T. rotula* and *S. costatum* were estimated using the formulas suggested by Taguchi (1976) being 78.0 and 3.4 pg, respectively (Sun et al. 1999). It showed that considerable differences in C and N contents were found in the two diatom cells which were consistent with the results of this section. However, C and N contents of the two diatom cells determined by the authors were much higher than the results estimated by Sun et al. (1999), which were possibly showed that there was a larger difference between the data measured using chemical method and those calculated by the models. The Si content in each cell of *S. costatum* determined by the authors was a little higher than that previously observed by Harrison et al. (1977) and Paasche (1980) being 2.1 and 2.67 pg, respectively, at 18 °C and under constant light. Brzezinski (1985) showed that there were considerable differences in the elemental compositions for two clones of *S. costatum.* In light-to- dark cycle experiments, the contents of C, N, Si in each cell of the two clones of *S. costatum* were 7.32, 0.91, 1.18 pg, and 66.0, 9.1, 17.08 pg, respectively, and the differences of both were as high as one order of magnitude. The changes of various environmental conditions including light intensity, photoperiod, temperature, nutrient limitation, and species differences can influence significantly nutrient composition of diatoms (Brzezinski 1985).

The dry mass concentrations of C, N, P, Si in *T. rotula* and *S. costatum* listed in Table 3 show that their dry mass concentrations were 580.0, 54.55, 3.85, 1.54 and 323.3, 93.05, 5.43, 9.84 mg g^{-1}, respectively. Similar to C, N, P, Si contents in the cells, there were very high mass concentration of C, higher of N and low P, Si in the two diatoms. But, comparing the two diatoms, considerable difference between the difference in the dry mass concentrations of C, N, P, Si and the difference in C, N, P, Si contents of cells was found. The dry mass concentration of C in *T.*

Table 2 C, N, P, Si contents in each cell of *T.rotula* and *S. costatum*

Diatoms	Cell dry mass	C		N		P		Si	
	pg	pg	%	pg	%	pg	%	pg	%
T. rotula	3125.0	1812.5	58.0	170.5	5.5	12.00	0.4	4.13	0.1
T. rotula		693.7[a]		78.0[b]					
S. costatum	300.0	97.0	32.3	27.9	9.3	1.63	0.5	3.81	1.3
S. costatum		17.8[a]		3.4[b]					

[a]Estimated by Sun et al. (1999) using the formula of Eppley et al. (1970)
[b]Estimated by Sun et al. (1999) using the formula of Taguchi (1976). Percentage indicate proportions of the contents of corresponding elements accounting for the dry mass of cell

Table 3 Dry mass concentrations (mg g^{-1}) and molar ratios of C, N, P, Si in *T. rotula* and *S. costatum*

Diatoms	C	N	P	Si	C/N	N/P	Si/P	Si/N
T. rotula	580.0	54.55	3.85	1.54	12.4	31.4	0.38	0.01
S. costatum	323.3	93.05	5.43	12.70	4.1	38.0	2.6	0.07

rotula was obviously higher than that in *S. costatum*, however, the difference of both was much less than the difference in C contents in cells. As opposed to C, the dry mass concentrations of N, P, Si in *S. costatum* were higher than those in *T. rotula*, which was consistent with the percentage of their contents in cells (Table 3). In considerable degree, the higher N, P, Si concentrations in *S. costatum* reflected that these elements in the seawater could be more assimilated by *S. costatum*, and was favorable for its growth, which was probably related to their small cell size associated with small diffusion boundary layers and large surface area per unit volume (Raven 1986). Particularly for Si, its dry mass concentrations in *S. costatum* were 6.4 times that in *T. rotula* showing that *S. costatum* had competitive dominance for assimilating Si. Previous studies showed that diatoms do not store sufficient Si for new valve formation (Azam 1974; Sullivan 1977; Binder and Chisholm 1980) and must accumulate most of the requisite amount immediately before cell division (Brzezinski 1985). Therefore, small unit of *S. costatum* with competitive dominance for assimilating Si could become a major dominant species under the condition of relatively low concentration of Si in Jiaozhou Bay. The ecological significance of dry mass concentrations of C, N, P, Si is that produce 1 g dry diatom, for *T. rotula,* it would assimilate 54.55 mg N, 3.85 mg P, and 1.54 mg Si (dry mass) from the seawater and simultaneously yield 580.0 mg organic C, but, for *S. costatum*, it would need more N, P, Si, however, organic C yielded was only 55.7% of the *T. rotula* (Table 3).

5 Comparing Nutrient Compositions of *T. rotula* and *S. costatum* with Nutrient Structures of Seawater and Particulates

Nutrient concentrations and their molar ratios in the seawater and different-sized particulates (Shen et al. 2006) are compared with those in laboratory-cultured phytoplankton common species (Table 4), showing that except for N/P ratio close, C/N, Si/P and Si/N ratios in laboratory- cultured *T. rotula* and *S. costatum* were much lower than those in the seawater, and that the C/N ratio in different-sized particulates were between two phytoplankton common species and the Si/P and Si/N ratios were much higher than those in phytoplankton common species, and their N/P ratio was also close. Comparing the particulates with seawater, however, besides C, the contents of N, P, Si and their molar ratios were more close. Because different-sized particulates were mainly composed of phytoplankton, similar nutrient contents and

Table 4 Nutrient concentrations and molar ratios in phytoplankton common species (mg g^{-1}), different-sized particulates (μmol L^{-1}) and seawater (μmol L^{-1})

Element ratios	Seawater	Particulates (μm)[b]			Particulates[b]	Phytoplankton common species	
		20–200	2–20	<2	Total	*T. rotula*	*S. costatum*
C	2200[a]	21.54	26.93	17.36	65.83	580.0	323.3
N	12.70	2.27	3.63	3.02	8.92	54.55	93.05
P	0.47	0.06	0.11	0.03	0.20	3.85	5.43
Si	3.40	0.61	0.53	0.20	1.34	1.32	12.70
N/P	27.8	37.8	33.0	100.7	44.6	31.4	38.0
Si/P	7.4	10.2	4.8	6.7	6.7	0.38	2.6
Si/N	0.32	0.27	0.15	0.07	0.15	0.01	0.07
C/N	173.2[a]	9.5	7.4	5.7	7.4	12.4	4.1

[a]Inorganic C content in the seawater from Shen et al. (1997)
[b]Average values of stations 3, 5, 7, mainly phytoplankton in different sized particulates (Shen et al. 2006)

their ratios both the particulates and seawater reflected an ecological response of phytoplankton to the nutrient structure of seawater to a certain extent (Shen et al. 2006). The difference in numerical value of nutrient ratios both laboratory-cultured phytoplankton and the particulates in Jiaozhou Bay reflected the difference between laboratory-cultured phytoplankton and the phytoplankton in natural seawater, which was obviously caused by natural phytoplankton cultured in the laboratory, showing the importance of environment to phytoplankton growing. However, high C, N contents and low P, Si in the two laboratory-cultured diatoms and different-sized particulates were consistent with those in the seawater. There was also obvious similitude in the molar ratios of elements. Those ratios have large deviation from the mean ratio (DIN/PO_4–P/SiO_3–Si = 16/16/1) of nutrients contained in marine diatom (Brzezinski 1985; Redfield et al. 1963). High N/P ratios were far higher than Redfield values, and low Si/P and Si/N ratios were far lower than Redfield values. It could be suggested that laboratory-cultured phytoplankton were bred under better nutritional condition, however, its nutrient structure characteristics formed long-term in Jiaozhou Bay had been not completely changed. Since the seminal work of Redfield, the elemental composition of phytoplankton, and even the composition of the water in which the organisms are growing, has been used as a potential index of nutrient limitation (Beardall et al. 2001). High contents of C, N and relative low contents P, Si, high N/P ratio and low Si/P and Si/N ratios in phytoplankton showed that P and Si were possibly potential influence on affecting phytoplankton growth, especially Si. In Jiaozhou Bay where Si was relative short, once SiO_3–Si concentration increases in the seawater, it would probably lead to abnormal breeding of diatoms (Yao and Shen 2007; Zhang et al. 2002).

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Differences in Nutrient Compositions of Cultured Marine Diatoms: Different Sea Areas, Sizes, and Seasons

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Abstract Comparing the nutrient compositions of cultured different-sized fractions of dominant phytoplankton species *Skeletonema costatum*, *Chaetoceros curvisetus*, and *Thalassiosira nordenskiöldii* collected in different sea areas in various seasons, the N content of these species was similar, while the C, P, and Si contents of *S. costatum* from eutrophic Changjiang estuary were higher than those from Jiaozhou Bay. The C, N, P, and Si contents of cultured phytoplankton from Jiaozhou Bay increased with size fraction augmentation, and the percentages of C, N, and P followed the same trend, while the percentage of Si remained constant. Moreover, *S. costatum* from small-sized fraction assimilated Si more easily than *C. curvisetus* and *T. nordenskiöldii*, which is explained by the dominance of *S. costatum* under the conditions of low SiO_3–Si concentration in Jiaozhou Bay seawater. The C, N, P, and Si contents of cultured *S. costatum* collected during winter were highest, which is consistent with the phytoplankton blooming seasons in Jiaozhou Bay. The very low SiO_3–Si concentration in the seawater during spring restrained the growth of phytoplankton, supported by the fact that the N, P, and Si contents and their ratios in cells of cultured *S. costatum* were low in spring season.

Keywords Nutrient composition · Culture · *Skeletonema costatum* *Chaetoceros curvisetus* · *Thalassiosira nordenskiöldii* · Changjiang estuary Jiaozhou Bay

In order to explore further the nutrient composition of phytoplankton in seawater and their ecological response to the nutrient structure of seawater, the C, N, P, and Si contents of cultured *Skeletonema costatum, Chaetoceros curvisetus*, and *Thalas-*

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siosira nordenskiöldii were measured in this section. The differences in C, N, P, Si contents and compositions of cultured marine diatoms in different sea areas, sizes, and seasons were evaluated.

1 Sampling and Experimental Methods

1.1 Sampling

This study was conducted at Station 5 of Jiaozhou Bay (JZB-5) (120° 15′ E, 36° 06′ N) and Station 24 of the Changjiang estuary (CJE-24) (122° 30′ E, 31° 00′ N) during November 2007 and April and August 2008. Surface water samples were collected using a Niskin sampler, and unfiltered water samples were preserved (with 0.3% chloroform) in polyethene bottles and stored in a low-temperature refrigerator (−30 °C) until subsequent analysis of their nutrient contents (taking clear superstratum water samples). Phytoplankton samples were collected from the surface layer seawater using nets (77 μm) and preserved in a cold-temperature freezer (0 °C). *S. costatum* collected in JZB-5 and CJE-24 were separated from phytoplankton samples in November 2007, while *S. costatum*, *C. curvisetus*, and *T. nordenskiöldii* collected in April 2008 and *S. costatum* collected in August 2008 were separated from phytoplankton samples of Jiaozhou Bay.

1.2 Phytoplankton Cultures

Algae species separated as described above were transferred to 1000 ml triangle bottles with 500 ml f/2 medium for culture. The cultures were conducted at a temperature of 20 ± 1 °C, an illumination of 4000 LX and a ratio of L:D = 12 h:12 h. After repeated separations and purifications, the samples were cultured for an extended period of 10–30 days, after which the organisms were counted. The cell abundances were 272×10^3 cells mL^{-1} for *S. costatum* collected from JZB-5 in November 2007, 364×10^3 cells mL^{-1} for *S. costatum* collected from CJE-24 in November 2007, 520×10^3 cells mL^{-1} for *S. costatum* collected from JZB-5 in April 2008, 150×10^3 cells mL^{-1} for *C. curvisetus* collected from JZB-5 in April 2008, 215×10^3 cells mL^{-1} for *T. nordenskiöldii* collected from JZB-5 in April 2008 and 428×10^3 cells mL^{-1} for *S. costatum* collected from JZB-5 in August 2008. In addition, nine samples of 2 ml each were collected from each medium. The medium samples for determining phytoplankton C and N were filtered with pre-ignited (450 °C, for 6 h) Whatman GF/D (2.7 μm) filters, while the medium samples for determining P and Si were filtered using 2-μm Millipore filters. A total of three 5-ml aliquots of medium were filtered through 0.45-μm Millipore filters to determine the dry mass of the culture cells. All filters were 25 mm in diameter. All filtered membranes and

blank membranes were rinsed with deionized water and stored in a low-temperature freezer until subsequent analysis.

1.3 Analysis and Calculation

Nutrients' concentrations of nitrate (NO_3–N), nitrite (NO_2–N), ammonia (NH_4–N), phosphate (PO_4–P), and silicate (SiO_3–Si) were determined to see Shen et al. (2008). Dissolved inorganic nitrogen (DIN) is equal to the sum of NO_3–N, NO_2–N, and NH_4–N. The sample of phytoplankton P was digested according to Koroleff's (1976) method and measured by potassium peroxodisulfate oxidation colorimetry (Shen et al. 2008). The sample of phytoplankton Si was measured in accordance with Treguer and Gueneley's (1988) method and measured by colorimetry (Shen et al. 2008). The samples were determined using a SKALAR Flow Analyzer made in the Netherlands. Phytoplankton C and N were measured using a model 240C Element Analyzer. The dry mass of the diatom cell was measured using the weight method.

The content of the elements in the cell was calculated as:

$$Q = C \cdot F/D$$

where Q is the content of elements in the cell (pg cell^{-1}), C is the molar concentration of the element (μmol L^{-1}), F is the conversion coefficient of the unit, and D is the cell density in cultured medium (cell mL^{-1}). The dry quality concentration of the element is calculated as:

$$M_1 = C \cdot F/M_2$$

where M_1 is the dry quality concentration of the element (mg g^{-1}) and M_2 is the dry quality concentration of diatoms in the cultured medium (mg L^{-1}).

2 Comparing Nutrient Compositions of Cultured *S. costatum* from JZB with Those from CJE

The nutrient concentrations and molar ratios of surface seawater at JZB-5 and CJE-24 in November, 2007 (Table 1) showed that the concentration of dissolved inorganic nitrogen (DIN) was higher and the SiO_3–Si and PO_4–P concentrations were lower in JZB. The DIN/PO_4–P molar ratio was far higher than the Redfield value (16) (Brzezinski 1985; Redfield et al. 1963), while the SiO_3–Si/DIN ratio was far lower than the Redfield value (1) and the SiO_3–Si/PO_4–P ratio was close to the Redfield value (16). These findings showed that there were high N concentrations and low SiO_3–Si concentrations in JZB, which was consistent with the previous results (Yao

Table 1 Nutrient concentrations ($\mu mol\ L^{-1}$) and their molar ratios in surface seawater in JZB-5 and CJE-24

Station	PO_4–P	SiO_3–Si	NO_3–N	NO_2–N	NH_4–N	DIN	DIN/PO_4–P	SiO_3-Si/PO_4–P	SiO_3–Si/DIN
JZB-5	0.28	4.1	13.2	0.77	3.8	17.8	63.6	14.6	0.23
CJE-24	0.99	55.0	49.5	0.22	1.5	51.2	51.7	55.6	1.1

and Shen 2007; Shen et al. 2006). When compared with JZB, the nutrient concentrations in the CJE were rich and the DIN, SiO_3–Si, and PO_4–P concentrations were 2.9, 13.4, and 3.5 times of those in JZB, respectively. The molar ratios of DIN/PO_4–P and SiO_3–Si/PO_4–P in CJE were far higher than the Redfield value (16), while the SiO_3–Si/DIN ratio was close to the Redfield value (1), indicating that there were high N and SiO_3–Si concentrations and low PO_4–P concentrations in CJE, consistent with previous results (Pan and Shen 2009a).

The dry mass and contents of C, N, P, and Si in cells of *S*. *costatum* from JZB and CJE are shown in Table 2. The dry mass of cells of *S*. *costatum* from JZB and CJE were 343.4 and 312.5 pg cell^{-1}, respectively, which is consistent with the results of previous studies (Shen et al. 2008). In addition, the C content was the highest, followed by the N, Si, and P contents. Shen et al. (2008) reported that the C, N, P, and Si contents in the cells of *S*. *costatum* from JZB were 97.0, 27.9, 1.63, and 2.95 pg cell^{-1}, respectively, which accounted for 32.3, 9.3, 0.5, and 1.0% of the cell dry mass, respectively. Although the N and P contents in their study were notably different from those in the present study, the Si contents were similar. Based on the cell volume, Sun et al. (1999) estimated the C and N contents in the cells of *S*. *costatum* in JZB using the formulas suggested by Eppley et al. (1970) and Taguchi (1976) to be 17.8 and 3.4 pg cell^{-1}, respectively. However, the C and N contents of cells determined in this study were much higher than the results estimated by Sun et al. (1999), while the Si content was slightly higher than the 2.1 pg cell^{-1} reported by Harrison et al. (1977) and 2.67 pg cell^{-1} reported by Paasche (1980). Differing environmental conditions (including light intensity, photoperiod, temperature, nutrient limitation), species source and research methods likely led to these differences. The C, P, and Si contents in cells of *S*. *costatum* from CJE were higher than those from JZB, but the N contents of cells from both areas were similar. Additionally, the dry mass concentrations of C, P, and Si of *S*. *costatum* from the CJE were also higher than those from JZB, while the N dry mass concentrations were similar (Table 3), which was similar to the changes in the elemental contents. The N/P molar ratios in the cells of *S*. *costatum* from JZB were higher than those from CJE, while the Si/N ratio was lower than that of CJE and the Si/P ratio was similar, which may have been due to the low Si content in cells of cultured *S*. *costatum* from JZB.

Comparison of the nutrient compositions of cultured *S*. *costatum* from JZB with those from CJE revealed great differences, which may have been due to the large differences in the shape, size, pigment, body type and number, chain-like cells, and shape and cell number in of *S*. *costatum* collected from JZB and CJE (Han et al. 2004). The N contents of samples from JZB and CJE were similar, while the contents of C, P, and Si differed greatly, which showed that the elemental contents in cells differed among cultured *S*. *costatum* collected from different sea areas under the same conditions. These differences may have been due to differences in their previous environments. When the nutrient concentrations of seawater were compared with those of cultures of *S*. *costatum* from JZB and CJE, the C, P, and Si levels of cultured *S*. *costatum* from eutrophic CJE were higher than those from JZB, except for N. Relative to N and P, the SiO_3–Si concentration in CJE was much higher than that in JZB, as was the Si content of cultured *S*. *costatum*. This was likely because the

Table 2 C, N, P, and Si contents and dry mass in each cell of cultured *S. costatum* from JZB and CJE

Station	Cell dry mass	C		N		P		Si	
	pg cell^{-1}	pg cell^{-1}	%	pg cell^{-1}	%	pg cell^{-1}	%	pg cell^{-1}	%
JZB-5	343.4 ± 10.6	74.45 ± 7.5	21.68	10.85 ± 2.3	3.16	0.57 ± 0.08	0.17	2.98 ± 0.25	0.87
CJE-24	312.5 ± 9.87	95.22 ± 8.0	30.47	9.37 ± 1.6	3.00	0.79 ± 0.10	0.25	4.05 ± 0.33	1.30

Table 3 Dry mass concentrations (mg g^{-1}) and molar ratios of C, N, P, Si of cultured *S. costatum* from JZB and CJE

Station	C	N	P	Si	C/N	N/P	Si/P	Si/N
JZB-5	216.8 ± 7.6	31.6 ± 2.1	1.65 ± 0.88	8.67 ± 1.1	8.0	42.4	5.8	0.14
CJE-24	304.7 ± 8.4	30.0 ± 1.2	2.51 ± 1.1	13.0 ± 1.2	11.8	26.5	5.7	0.22

marine planktonic diatom's demand for Si was related to diatom species as well as the sea area distribution of diatom (Li and Wang 1998), and the fact that the ability of allogeneic algae to absorb nutrients under different environmental conditions differs. Although the DIN concentration in CJE was higher than that in JZB, the N contents of cultured *S*. *costatum* from both areas of the sea were similar, which was likely caused by N saturation in cells of cultured *S*. *costatum*.

3 Comparing Nutrient Compositions of Cultured Different-Sized Phytoplankton from JZB

The DIN and PO_4–P concentrations were higher, and the SiO_3–Si concentration was much lower in JZB seawater (Table 4), while the SiO_3–Si concentration was lower than the threshold value of diatom growth (2.0 μmol L^{-1}) (Nelson and Brzezinski 1990; Goldman and Glibert 1983; Perry and Eppley 1981; Brown and Button 1979), showing that there were high N and PO_4–P concentrations and low SiO_3–Si concentrations in JZB. The molar ratios of DIN/PO_4–P, SiO_3–Si/PO_4–P, and SiO_3–Si/DIN were all lower than the Redfield value (16:16:1) (Brzezinski 1985; Redfield et al. 1963), especially the SiO_3–Si/PO_4–P and SiO_3–Si/DIN ratios, which showed that SiO_3–Si was probably the factor limiting phytoplankton growth.

The cell dry mass of cultured *C*. *curvisetus* and *T*. *nordenskiöldii* from JZB was similar, and both of these values were higher than that of *S*. *costatum* (Table 5). This difference was likely due to differences in the cell volume (the diameters of cells of *S*. *costatum*, *C*. *curvisetus,* and *T*. *nordenskiöldii* are 6–20, 7–30, and 12–43 μm, respectively). Similar to the cell dry mass, the C, N, P, and Si contents of *S*. *costatum* were lower than those of *C*. *curvisetus* and *T*. *nordenskiöldii*, which likely reflected differences in the size of these cells; however, the size order of the content of each element in the cell was the same (C > N > Si > P). Sun et al. (1999) estimated the C contents in cells of *C*. *curvisetus* and *T*. *nordenskiöldii* in JZB to be 363.7 and 759.6 pg $cell^{-1}$, respectively, using the formulas suggested by Eppley (1970). They also estimated the N contents in the cells of *C*. *curvisetus* and *T*. *nordenskiöldii* using the formulas suggested by Taguchi (1976) to be 44.3 and 88.0 pg $cell^{-1}$, respectively (Sun et al. 1999). The C and N contents of *C*. *curvisetus* estimated by Sun et al. (1999) were close to the values observed in the present study; however, those of *T*. *nordenskiöldii* were much larger than those observed in the present study, which likely showed that there was a larger difference between the data measured using the chemical method and those calculated using the models. The percentages of C, N, P, and Si in the cells of *C*. *curvisetus* and *T*. *nordenskiöldii* were similar, while those of C, N, and P were larger than those of *S*. *costatum*. However, the percentages of Si of *C*. *curvisetus* and *T*. *nordenskiöldii* were nearly the same as those of *S*. *costatum*. The dry mass concentrations of C, N, and P in *S*. *costatum* were much smaller than those of *C*. *curvisetus* and *T*. *nordenskiöldii*, but the dry mass concentrations of Si were close (Table 6), which was consistent with the elemental contents. The N/P molar

Table 4 Nutrient concentrations ($\mu mol\ L^{-1}$) and their molar ratios in surface seawater in JZB-5

Month	PO_4–P	SiO_3–Si	NO_3–N	NO_2–N	NH_4–N	DIN	DIN/PO_4–P	SiO_3–Si/PO_4–P	SiO_3–Si/DIN
4	2.0	0.66	4.4	0.76	5.5	10.6	5.3	0.33	0.06

ratios of the three algal cells were higher than the Redfield value (16:1), but the molar ratios of C/N, Si/P, and Si/N were much lower than the Redfield value (106:16:16:1), which showed that there were high N concentrations and low Si concentrations in the cells.

Shen et al. (2008) reported that the C, N, P, and Si contents of *T*. *rotula* cell were 1812.5, 170.5, 12.00, and 4.81 pg cell^{-1}, respectively, and 58.0, 5.5, 0.4, and 0.2% of the dry mass of the cell, respectively. When combined with the results of this study, this information indicates that the C, N, P, and Si contents and their percentages in cells of different-sized fractions of phytoplankton varied, and that the C, N, P, and Si contents generally increased as the phytoplankton size increased. This is likely because the biological and chemical processes that occur in marine phytoplankton are related to their size (Ray et al. 2001; Suttle et al. 1991). With respect to the specific surface area per unit volume, the ability to absorb nutrients for phytoplankton is different (Sournia 1981); therefore, physiological differences in the different-sized phytoplankton have an important influence on the nutrient compositions. The C, N, and P contents, percentages, and dry mass concentrations in cells of cultured *S*. *costatum* were lower than those of cultured *C*. *curvisetus* and *T*. *nordenskiöldii*, but the Si percentage and dry mass concentration were similar for all species. The N/P molar ratios of cultured *S*. *costatum* were lower than those of cultured *C*. *curvisetus* and *T*. *nordenskiöldii*, but the Si/P and Si/N molar ratios of cultured *S*. *costatum* were higher than *C*. *curvisetus* and *T*. *nordenskiöldii*, which may indicate that Si assimilation by the small-sized fractions of *S*. *costatum* occurred much more easily than that by *C*. *curvisetus* and *T*. *nordenskiöldii*. Moreover, N and P assimilation of the large *C*. *curvisetus* and *T*. *nordenskiöldii* occurred much more easily than for that of smaller organisms. Under nutrient conditions of high N and low SiO_3–Si concentrations in JZB, the easier absorption of SiO_3–Si by *S*. *costatum* provided advantages and combined with the results of previous studies indicates that small-sized diatoms such as *S*. *costatum* have likely been dominant in JZB recently (Liu et al. 2008).

4 Comparing Nutrient Compositions of Cultured *S*. *costatum* from JZB During Different Seasons

The average concentration of the DIN was higher, and the SiO_3–Si concentration was lower in seawater of JZB during all four seasons (Table 7), which showed that there were high N and low SiO_3–Si concentrations in JZB. The average DIN concentration was highest during summer, followed by autumn and then spring, winter. The SiO_3–Si concentration was highest during summer and lowest during spring. Moreover, the DIN/PO_4–P molar ratios during summer and autumn were higher than the Redfield value (16), but those during winter and spring were lower. The SiO_3–Si/PO_4–P and SiO_3–Si/DIN molar ratios were lower than the Redfield value (16 and 1) during all seasons, which was consistent with the low SiO_3–Si concentration.

Table 5 C, N, P, and Si contents and dry masses in phytoplankton from different size fractions in JZB

Algae	Cell dry mass	C		N		P		Si	
	pg cell^{-1}	pg cell^{-1}	%	pg cell^{-1}	%	pg cell^{-1}	%	pg cell^{-1}	%
S. costatum	326.9 ± 9.8	93.1 ± 7.5	28.5	1.9 ± 0.8	0.59	0.15 ± 0.06	0.05	0.57 ± 0.09	0.17
C. curvisetus	800.0 ± 10.2	330.7 ± 10.2	41.3	19.5 ± 0.74	2.4	1.0 ± 0.10	0.13	1.3 ± 0.21	0.16
T. nordenskiöldii	837.2 ± 11.3	321.8 ± 11.3	38.4	33.3 ± 1.2	4.0	1.2 ± 0.32	0.15	1.5 ± 0.15	0.18

Table 6 Dry mass concentrations (mg g^{-1}) and molar ratios of C, N, P, and Si in different-sized phytoplankton

Algae	C	N	P	Si	C/N	N/P	Si/P	Si/N
S. costatum	284.7 ± 9.8	5.9 ± 0.85	0.46 ± 0.11	1.8 ± 0.42	56.5	28.3	4.2	0.15
C. curvisetus	413.3 ± 11.2	24.4 ± 1.1	1.3 ± 0.62	1.6 ± 0.55	19.8	41.8	1.4	0.03
T. nordenskiöldii	384.4 ± 10.6	39.7 ± 2.3	1.5 ± 0.21	1.8 ± 0.12	11.3	60.1	1.4	0.02

Table 7 Nutrient concentrations ($\mu mol\ L^{-1}$) and their molar ratios in surface seawater during different seasons

Month	PO_4–P	SiO_3–Si	NO_3–N	NO_2–N	NH_4–N	DIN	DIN/PO_4–P	SiO_3–Si/PO_4–P	SiO_3–Si/DIN
2 (Shen et al. 2008)	0.54	4.5	0.44	4.9	2.1	7.4	13.7	8.3	0.61
4	2.0	0.66	4.4	0.76	5.4	10.6	5.3	0.33	0.06
8	0.70	5.7	21.6	2.9	7.3	31.8	45.3	8.1	0.18
11	0.28	4.1	13.2	0.77	3.8	17.8	63.6	14.6	0.23
Average	0.88	3.7	9.9	2.3	4.7	16.9	19.2	4.3	0.22

Table 8 C, N, P, and Si contents and dry mass in each cell of cultures of *S. costatum* collected during different seasons

Month	Dry mass	C		N		P		Si	
	pg cell^{-1}	pg cell^{-1}	%	pg cell^{-1}	%	pg cell^{-1}	%	pg cell^{-1}	%
2 (Shen et al. 2008)	300.0 ± 9.8	97.0 ± 7.8	32.3	27.9 ± 3.5	9.3	1.6 ± 0.21	0.50	3.8 ± 0.74	1.3
4	326.9 ± 10.2	93.1 ± 5.4	28.5	1.9 ± 0.81	0.59	0.15 ± 0.03	0.05	0.57 ± 0.21	0.17
8	186.9 ± 6.5	60.6 ± 5.5	32.4	11.8 ± 2.5	6.3	0.67 ± 0.07	0.36	1.3 ± 0.47	0.68
11	343.4 ± 8.8	74.5 ± 6.7	21.7	10.9 ± 3.1	3.2	0.57 ± 0.06	0.17	3.0 ± 0.98	0.87

The contents and percentages of C, N, P, and Si in cells of cultured *S*. *costatum* from JZB each season were consistent (Table 8), with the C content being highest, followed by N, Si, and P. The cell dry mass during autumn, winter, and spring was similar and much higher than during summer, which may have been due to differences in the cell volume of cultured *S*. *costatum*. When compared with other seasons, the contents of C, N, P, and Si in cultured *S*. *costatum* collected during winter were highest. In previous studies (Wu et al. 2004, 2005; Li et al. 2005), winter has been shown to be the season in which phytoplankton breed vigorously in JZB. The average chlorophyll-*a* concentration was 7.04 mg m^{-3} during winter 2008, which was far higher than during spring and autumn (Pan and Shen 2009b). The contents of N, P, and Si in the cells of cultured *S*. *costatum* during spring were low, while the C content was high; however, those during summer and autumn were high, while the C content was relatively low.

The dry mass concentrations of C, N, P, and Si in cells of cultured *S*. *costatum* from JZB varied among seasons (Table 9). The dry mass concentrations of C, N, and P in cells of cultured *S*. *costatum* collected during summer and winter were higher than those of *S*. *costatum* collected during spring and autumn; however, the dry mass concentration of Si during winter was highest, followed by autumn and then summer and spring. The C/N molar ratio of cultured *S*. *costatum* collected during spring was 56.47, which was much higher than those collected during other seasons. This difference was likely caused by the low N content in cells of cultured *S*. *costatum* in spring. The N/P molar ratio was highest in autumn, followed by summer, winter, and then spring. The seasonal changes in the Si/P and Si/N molar ratios of cultured *S*. *costatum* were similar, with higher values being observed in autumn and spring than summer and winter.

Similar to seawater nutrient concentrations and their structure, the C, N, P, and Si contents and dry mass concentrations of cultured *S*. *costatum* also displayed seasonal differences in JZB. This may indicate that there is a relationship between nutrient assimilation by phytoplankton and the seawater nutrient structure because phytoplankton can retain some life habits (cell shape, nutrients' assimilation) after being cultured (Han et al. 2004). The relative C, N, P, and Si contents of cultured *S*. *costatum* collected during summer and winter were higher, which was consistent with seasons of phytoplankton blooming and high chlorophyll-*a* concentrations in JZB (Wu et al. 2005; Li et al. 2005). The SiO_3–Si concentration in seawater during spring was only 0.66 μmol L^{-1}, which was below the threshold value of the diatom growth (2.0 μmol L^{-1}), and the SiO_3–Si/PO_4–P and SiO_3–Si/DIN molar ratios were far lower than the Redfield value (16 and 1 respectively); therefore, SiO_3-Si was the limiting factor of *S*. *costatum* growth, which was consistent with the low N, P, and Si contents and their percentages in the cells of cultured *S*. *costatum* collected during spring.

Table 9 Dry mass concentrations (mg g^{-1}) and molar ratios of C, N, P, Si of cultures of *S. costatum* collected during different seasons

Month	C	N	P	Si	C/N	N/P	Si/P	Si/N
2 (Shen et al. 2008)	323.3 ± 12.1	93.1 ± 10.2	5.4 ± 1.0	12.7 ± 1.5	4.1	38.0	2.6	0.07
4	284.7 ± 10.3	5.9 ± 3.5	0.46 ± 0.12	1.8 ± 0.87	56.5	28.3	4.2	0.15
8	324.4 ± 14.2	62.9 ± 7.5	3.6 ± 1.2	6.8 ± 2.1	6.0	38.8	2.1	0.05
11	216.8 ± 21.5	31.6 ± 6.9	1.7 ± 0.34	8.7 ± 1.2	8.0	42.4	5.8	0.14

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Nutrient Composition and Biomass of *Coscinodiscus asteromphalus* in Jiaozhou Bay, China

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Abstract The large diatom *Coscinodiscus asteromphalus* was separated from seawater in Jiaozhou Bay using a repeated precipitation method, and then, its nutrient compositions of carbon (C), nitrogen (N), phosphorus (P), and silicon (Si) combined with chlorophyll-a (Chl-*a*) were examined for the first time for a natural population. Results show that the contents of C, N, P, Si, and Chl-*a* in *C. asteromphalus* cells were 35,610.5, 9374.2, 352.4, 1105.5, and 1767.0 pg/cell, respectively, and the corresponding molar ratios of C/N, N/P, Si/P, and Si/N in *C. asteromphalus* cells were 4.5, 66.0, 2.7, and 0.07, respectively, which are different from the Redfield ratio. Additionally, their C/Chl-*a* mass ratio was 23.2. High N/P ratio and low Si/P and Si/N ratios in *C. asteromphalus* cells were consistent with those in particulates of any size and seawater in the bay, reflecting an ecological response of phytoplankton to the nutrient structure of seawater, suggesting Si limitation to phytoplankton growth. The fact that *C. asteromphalus* spread all over the bay mainly in summer and autumn and the fact that Chl-*a* content in *C. asteromphalus* cells could account for a maximum percentage of 78% of those in the water column suggest that the contribution of *C. asteromphalus* to phytoplankton biomass was significant in Jiaozhou Bay.

Keywords Nutrient composition · Chlorophyll-*a* · *Coscinodiscus asteromphalus* Jiaozhou Bay

A large number of studies on the nutrient composition of phytoplankton were focused on laboratory-cultivated species (Burkhardt and Riebesell 1997; Marchetti and Harrison 2007; Shen et al. 2008; Baines et al. 2011). However, there might be differences between the cultured phytoplankton species indoors and the natural population, since it is not possible to completely emulate field conditions in the laboratory. The major

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difficulties in measuring the nutrient composition of natural phytoplankton population are how to separate a specific phytoplankton species from seawater and how to isolate a sufficient number of fresh cells. In addition, particles separated from seawater using filtering methods include not only phytoplankton cells but also a part of zooplankton and debris, which probably confound the measurement of nutrient composition for a specific species (Beardall et al. 2001; Segura-Noguera et al. 2012, 2016). Therefore, compared to the well-studied laboratory cultures, nutrient composition of natural phytoplankton population is relatively less studied and poorly known (Sakshaug et al. 1983; Ríos et al. 1998).

The cell volume, fresh weight, and carbon and nitrogen contents of 87 common phytoplankton species in China Seas were calculated by Sun et al. (2000) using the method of phytoplankton biomass estimated from cell volume and plasma volume. Kuninao et al. (2000) determined the carbon, nitrogen, phosphorus, and Chl-*a* contents of *Coscinodiscus wailesii* in natural seawater in the Seto Inland Sea, Japan. Segura-Noguera et al. (2016) analyzed the elemental composition of single natural marine microplankton cells using energy-dispersive X-ray microanalysis method.

Jiaozhou Bay is a semi-enclosed bay situated in the western part of the Shandong Peninsula, China. It is surrounded by Qingdao City (population 7×10^6), with an area of about 390 km^2 and an average water depth of about 7 m. The bay mouth is narrow (about 2.5 km wide) and connects with the South Yellow Sea (Shen, 2001). The large diatom *Coscinodiscus asteromphalus* generally observed in temperate coastal waters is frequently found in Jiaozhou Bay; especially, it becomes dominant at times from summer to autumn. Due to the large volume of *C. asteromphalus*, its biomass is considerable and its contribution to the ecosystem might be noteworthy. Interestingly, the nutrient composition of *C. asteromphalus* has not been examined previously for a natural population, although its Chl-*a*, protein, potassium, and magnesium contents have been determined for laboratory cultures (Werner 1971). In this study, we simultaneously determined the contents of carbon, nitrogen, phosphorus, silicon, and Chl-*a* of natural *C. asteromphalus* collected from Jiaozhou Bay for the first time and studied the ecological response of *C. asteromphalus* to the nutrient structure of seawater and the considerable contribution of *C. asteromphalus* to phytoplankton biomass in Jiaozhou Bay.

1 Materials and Methods

1.1 Field Sampling

Seasonal investigations were carried out in May, August, and November 2009 and February 2010 at station 2 (36° 9.50′ N, 120° 15.00′ E) with a water depth of 6 m and station 3 (36° 09.30′N, 120° 19.80′E) with a water depth of 7 m (Shen et al. 2008) in Jiaozhou Bay. Surface seawater samples were collected using a Niskin sampler. The water samples for nutrients and total inorganic carbon were preserved (with 0.3%

chloroform and 100 μL saturated $HgCl_2$ solution, respectively) in polyethylene bottles and glass bottles, respectively, and stored in a low-temperature icebox (−20 °C) for analyzing at the laboratory later.

Ten phytoplankton samples were collected vertically from bottom to surface layer using a phytoplankton net (0.2 m^2 net mouth area, 167-μm mesh) at station 2 on September 17, 2009, and station 3 on September 1, 2010, respectively. Each phytoplankton sample was collected in 300 mL seawater and stored in a polyethylene bottle for *C. asteromphalus* separation and elemental composition analysis. In addition, six surface water samples were collected and filtered using 0.45-μm Millipore filters for determining chlorophyll-*a*.

1.2 Sample Treatment and C. asteromphalus *Separation*

Phytoplankton samples collected in situ were filtered through 250-μm mesh to remove larger zooplanktons and other particulate matters. The samples from station 2 were classified under a microscope, and then, they were shaken well and poured into a 500-mL measuring cylinder. Since *C. asteromphalus* cells are big and heavy, they tend to accumulate at the bottom of the measuring cylinder. After subsiding for 20 min, a small sample at bottom was taken and checked under a microscope. If other phytoplankton species besides *C. asteromphalus* were observed in the sample, seawater in the upper layer (over a 100 mL scale from bottom) was removed with a pipette, and then, the remainder 100 mL sample at the bottom was diluted with clear seawater (pre-filtered with 0.45-μm Millipore filter). The process of subsiding–checking–diluting sample was repeated several times to eliminate other phytoplankton species. We checked under a microscope that other phytoplankton species did not exist in the samples. In the experiment, we also found that *C. asteromphalus* was easily absorbed on glass walls, which is helpful for collecting the target cells. Finally, we obtained a set of three samples, and their cell densities were 1000, 848, and 798 cells mL^{-1}, respectively, with an average of 882 cells mL^{-1}, accounting for 93% of the total cell number. Other phytoplankton species were *Coscinodiscus subtilis* and *Coscinodiscus oculus-iridis*. After the accumulated experience, using the method described above, from the rest of the phytoplankton samples, another set of three samples was prepared with an average of *C. asteromphalus* cell density of 1000 cells mL^{-1}, and all cells were *C. asteromphalus* in the samples.

Phytoplankton samples from station 3 were treated using the same method above. Because *C. asteromphalus* cells accounted for 98% of the total cells in samples and the other 2% were *Skeletonema costatum* cells, we easily obtained two sets of six samples, in which the average cell density of *C. asteromphalus* was about 1000 cells mL^{-1}, accounting for 100% of the total cell number.

1.3 Sample Preparation

Nine samples with 3 mL each were collected from every set of *C. asteromphalus* samples obtained above. Three of them for determining C and N contents were filtered with pre-combusted (450 °C, for 6 h) 25-mm-diameter Whatman GF/D glass fiber filters, and the others for determining P and Si (triplicate for each element) were filtered with 25-mm-diameter Millipore filters (0.45 μm). And then, all filters and blank membranes immersed by filtrates were rinsed with deionized water and immediately stored in a low-temperature icebox for further analyses. Additionally, three 5 mL samples were collected from every set of *C. asteromphalus* samples from station 3 and then filtered with 47-mm-diameter Millipore filters (0.45 μm). These filters were immediately stored in a low-temperature icebox as well for determining Chl-*a*.

1.4 Analyses and Calculations

Nutrients in the seawater and P and Si contents of *C. asteromphalus* were determined using a Skalar flow analyzer made in the Netherlands. The determining methods of nutrients of nitrate (NO_3–N), nitrite (NO_2–N), ammonia (NH_4–N), phosphate (PO_4–P), and silicate (SiO_3–Si) refer to Shen et al. (2008). Dissolved inorganic nitrogen (DIN) is equal to the sum of NO_3–N, NO_2–N, and NH_4–N. Total inorganic carbon (TIC) in the seawater was measured using the high-temperature catalytic oxidation method with a total organic carbon analyzer. The samples for determining P content of *C. asteromphalus* were digested referring to Koroleff's (1976) method and measured with the potassium peroxodisulphate oxidation colorimetry (Shen et al. 2008). The samples for determining Si content of *C. asteromphalus* were measured referring to Treguer and Gueneley's (1988) method and then were measured by colorimetry (Shen et al. 2008). C and N contents of *C. asteromphalus* were measured using a model 240C element analyzer (Yang and Liu 1995). Chl-*a* contents were measured using a Turner Designs fluorophotometer.

The contents of C, N, P, and Si in *C. asteromphalus* cells were calculated as:

$$Q = C \cdot F/D \tag{1}$$

where Q is the content of element in cell (pg $cell^{-1}$), C is the molar concentration of element (μmol L^{-1}), F is the conversion coefficient of unit, and D is the cell density in *C. asteromphalus* sample (cell mL^{-1}).

The software of Microsoft Office Excel was used for statistical analyses in this study. The average values and standard deviations of nutrients in the seawater and C, N, P, Si, and Chl-*a* contents in *C. asteromphalus* cell were calculated using the Excel of Microsoft Office. T test was used to estimate the differences of elemental

composition of *C. asteromphalus* between these two set of samples at station 2 and between these samples at stations 2 and 3.

Data used in this section also include the data of phytoplankton cell densities and Chl-*a* contents during 2009 and 2010 from Jiaozhou Bay National Marine Ecosystem Research Station.

2 Contents of C, N, P, Si, and Chl-*a* in *C. asteromphalus* Cells

The measured contents of C, N, P, Si, and Chl-*a* in *C. asteromphalus* cells in Jiaozhou Bay seawater are shown in Table 1. Contents of C and N in cells were higher at station 3 than at station 2, but for P, there was an inverse relationship. There are no significant differences in the elemental composition of *C. asteromphalus* between these two set of samples at station 2 (Table 1), as suggested by the results of t test with P values greater than 0.05 (0.724, 0.753, 0.549, and 0.892 for C, N, P, and Si, respectively). No significant differences in the C and N compositions are observed between stations 2 and 3 (Table 1), as suggested by the P values of 0.095 and 0.245 in the t test, but extreme significant difference in the P composition is found since the P value is 1.87×10^{-6} in the t test, much lower than 0.01. Since the two sets of samples at station 2 were collected on the same day, the difference in elemental composition of *C. asteromphalus* is not apparent. However, samples at stations 2 and 3 were collected from different locations and in different years and probably affected by different environmental conditions; thus, the difference in elemental composition of *C. asteromphalus* is more significant, particularly the difference in P.

Comparing with the elemental contents estimated by Sun et al. (2000) via cell volume, the C contents of *C. asteromphalus* in our study were closed to or in the range of those reported values, and the N contents were higher than those reported values. As shown in Table 1, the average contents of C, N, and P in *C. asteromphalus* cells only account for 15, 23, and 5% of those in *C. wailesii* cells, respectively (Kuninao et al. 2000). However, C, N, and P contents of *C. wailesii* reported by different literature varied in a large range. For example, previously reported C and N contents of cultured *C. wailesii* ranged from 146,500 to 213,000 and from 26,628 to 33,285 pg cell^{-1}, respectively (Moal et al. 1987), or 6600 and 930 pg cell^{-1}, respectively (Bienfang and Harrison 1984). Such significant difference in C and N contents of a same phytoplankton species might be related to their growth conditions (Strickland 1960; Parsons et al. 1984; Brzezinski 1985). Chl-*a* contents of *C. wailesii* were 3670 and 6600 pg cell^{-1} for samples collected in January 1995 and in January 1998, respectively (Kuninao et al. 2000), being 2.1 and 3.7 times of those of *C. asteromphalus*. The differences in the contents of C, N, P, Si, and Chl-*a* between *C. asteromphalus* and *C. wailesii* might be associated with their cell sizes. The cell diameter of *C. asteromphalus* measured in this study was 150.0 ± 4.76 μm ($n = 4$), being about half of 293 ± 19.7 μm of *C. wailesii* cell (Kuninao et al. 2000). The

Table 1 Contents of C, N, P, Si and Chl-*a* (pg cell^{-1}) in *Coscinodiscus asteromphalus* cell in Jiaozhou Bay

Stations	Data	*Coscinodiscus*	C	N	P	Si	Chl-*a*
2	September 17, 2009	*C. asteromphalus* (93%)	30,939.8 ± 2853.4	8163.3 ± 683.4	462.1 ± 28.0	1099.9 ± 103.7	
2	September 17, 2009	*C. asteromphalus* (100%)	29,355.6 ± 3903.3	8433.3 ± 1039.2	440.0 ± 48.0	1110 ± 81.1	
3	September 1, 2010	*C. asteromphalus* (100%)	41,073.3 ± 11,216.8	10,450.0 ± 3327.3	253.7 ± 28.0		1767.0 ± 481.7
	Averages		35,610.5	9374.2	352.4	1105.5	
		C. asteromphalus	32,229.7–92,003.0[a]	5147.9[b]			
		Coscinodiscus wailesii [c]	244,000 ± 20,200	41,100 ± 3730	7490 ± 400		6600 ± 700

[a]Estimated by Sun et al. (2000) using the formulas of Mullin et al. (1966), Strathmann (1967), Eppley et al. (1970), and Taguchi (1976)
[b]Estimated by Sun et al. (2000) using the formula of Taguchi (1976)
[c]Kuninao et al. (2000)

cell volumes of *C. asteromphalus* and *C. wailesii* were 7,516,623 (Sun et al. 2000) and 15,100,000 μm^3 (Kuninao et al. 2000), respectively. A carbon–volume linear regression relationship for *C. wailesii* cells with other phytoplankton was set up (Kuninao et al. 2000). We find that the carbon content of *C. asteromphalus* in this study roughly fits the regression line. Experiment results of Werner (1971) showed that the cell valve diameters of cultured *C. asteromphalus* varied from 200 to 75 μm, while their Chl-*a* contents per cell declined from 700 to 280 pg correspondingly, suggesting that Chl-*a* contents declined with the decreasing of cell diameters. It is also observed that Chl-*a* contents of cultured *C. asteromphalus* cells were far smaller than those of samples collected from Jiaozhou Bay.

The molar ratios of C, N, P, and Si and the mass ratios of C to Chl-*a* in *C. asteromphalus* cells in Jiaozhou Bay seawater are shown in Table 2. Due to high contents of C and relatively high contents of N but low P contents in *C. asteromphalus* cells at station 3, C/N and N/P molar ratios at station 3 were higher than those at station 2. Comparatively, the C/N molar ratios of *C. asteromphalus* were less than the values estimated by cell volume in the study of Sun et al. (2000) (Table 2). Although the contents of C, N, and P in *C. asteromphalus* cells were less than those in *C. wailesii* cells, C/N ratios of *C. asteromphalus* were lower than those of *C. wailesii* and N/P molar ratios were obviously higher than those of *C. wailesii*, probably because *C. asteromphalus* cells have relative high N contents and low P contents. The C/Chl-*a* mass ratios in *C. asteromphalus* cells were less than those in *C. wailesii* cells as well (Table 2). Since *C. asteromphalus* cells have relatively high contents of C and N, but relatively low contents of Si and P, the C/N/Si/P molar ratio of *C. asteromphalus* measured in this study was 295.5:66.0:2.7:1, suggesting that the ratios of C/P and N/P were higher than the classic Redfield ratio of 106:16:16:1 (Redfield et al. 1963; Brzezinski 1985). It is well known that such variation in elemental ratios principally depends on the growth condition of phytoplankton (Parsons et al. 1984).

3 Comparing Nutrient Composition of *C. asteromphalus* with Nutrient Structure of Seawater

The annual average concentrations and molar ratios of nutrients at stations 2 and 3 in Jiaozhou Bay seawater are shown in Tables 3 and 4, respectively. The C/N/Si/P molar ratios of seawater at stations 2 and 3 were 6031.8:42.4:6.5:1 and 3392.3:58.0:7.7:1, respectively, which significantly deviate from the Redfield ratio of 106:16:16:1. The C/N and N/P ratios were much higher than the Redfield ratio, and the Si/P and Si/N ratios were much lower than the Redfield ratio, showing relatively high C and N concentrations but low Si and P concentrations in the seawater. Such high N/P but low Si/P and Si/N ratios in the seawater were consistent with those in *C. asteromphalus* cells and also consistent with those in all sized groups of particulates found in Jiaozhou Bay with high N/P (24.7–64.6) ratio and low Si/P (4.4–10.8) and Si/N (0.06–0.20) ratios (Shen et al. 2006). Strickland (1960) pointed out that (a) the

Table 2 Molar ratios of C, N, P, and Si, and mass ratios of C to Chl-*a* in *Coscinodiscus asteromphalus* cells in Jiaozhou Bay

Stations	Data	*Coscinodiscus*	C/N	N/P	Si/P	Si/N	C/P	C/Chl-*a*
2	September 17, 2009	*C. asteromphalus* (93%)	4.4	39.1	2.6	0.07	173.0	
2	September 17, 2009	*C. asteromphalus* (100%)	4.1	42.4	2.8	0.07	172.4	
3	September 1, 2010	*C. asteromphalus* (100%)	4.6	91.2			418.2	23.2
	Averages		4.5	66.0	2.7	0.07	295.5	
		C. asteromphalus[a]	7.3–20.9					
		Coscinodiscus wailesii[b]	6.9	12.2				37.0

[a]Estimated by Sun et al. (2000) using the formulas of Mullin et al. (1966), Strathmann (1967), Eppley et al. (1970), and Taguchi (1976)
[b] Kuninao et al. (2000)

Table 3 Concentrations of nutrients ($\mu mol\ L^{-1}$) and Chl-*a* ($\mu g\ L^{-1}$) in surface seawater at stations 2 and 3 in Jiaozhou Bay

Stations	PO_4–P	SiO_3–Si	NO_3–N	NO_2–N	NH_3–N	DIN	TIC	Chl-*a*
2	0.34 ± 0.09	2.2 ± 1.9	5.5 ± 3.2	0.80 ± 0.35	8.1 ± 3.0	14.4 ± 3.9	2050.8 ± 86.0	0.87
3	0.64 ± 0.16	4.9 ± 3.3	11.5 ± 7.1	1.5 ± 0.44	24.1 ± 7.2	37.1 ± 14.4	2171.1 ± 150.0	1.97

Table 4 Nutrient molar ratios in surface seawater at stations 2 and 3 in Jiaozhou Bay

Stations	C/N	N/P	Si/P	Si/N	C/P
2	142.4	42.4	6.5	0.15	6031.8
3	58.5	58.0	7.7	0.13	3392.3

contents of cellular N and P were considerably influenced by the concentrations of these elements in the surrounding medium, (b) Si content was dependent not only on the amount of Si available in the medium but also on the growth rate of cells and on the type of cell wall constructed by each individual species, and (c) the C content must, therefore, also depend on the physiological condition of cells. It is certain that due to *C. asteromphalus* growth for a long term in Jiaozhou Bay, its nutrient composition was influenced by the nutrient concentrations and molar ratios of seawater. Accordingly, the high N but low Si contents in *C. asteromphalus* cells were an ecological response to specific nutrient structure of seawater (Shen 2001; Shen et al. 2006). In other words, the long-term replete N and relatively deplete Si and P in Jiaozhou Bay, especially the low Si concentration, low Si/N and Si/P ratios of 2.4 ± 1.1 $\mu mol\ L^{-1}$, 0.20 ± 0.19 and 7.5 ± 2.0, respectively, during 1983 and 1986 (Shen 2001), of 2.0 ± 1.9 $\mu mol\ L^{-1}$, 0.19 ± 0.15 and 7.6 ± 8.9, respectively, during 1991 and 1998 (Shen 2001), and of 6.2 ± 4.8 $\mu mol\ L^{-1}$, 0.30 ± 0.24 and 10.1 ± 6.8, respectively, during 1999 and 2006 (Shen 2014, unpublished), resulted in high N and low Si contents in phytoplankton cells. Experimental data (Shen et al. 2008) showed that nutrient structure of cultured phytoplankton collected from Jiaozhou Bay had not been completely changed. Laboratory-cultivated *Thalassiosira rotula* and *S. costatum* from Jiaozhou Bay maintained their high N/P ratios of 31.4 and 38.0, respectively; low Si/P ratios of 0.44 and 2.0, respectively; and low Si/N ratios of 0.01 and 0.05, respectively (Shen et al. 2008). Similar nutrient structures for both phytoplankton and seawater indicate the limitation of Si to phytoplankton growth in Jiaozhou Bay.

4 Distribution of *C. asteromphalus* and Its Contribution to Phytoplankton Biomass in Jiaozhou Bay

Investigation data show that *C. asteromphalus* was not observed from January to July in both 2009 and 2010 in Jiaozhou Bay but observed apparently in August, October, and November of 2009 and from August to December in 2010 with extensive cover-

age over the whole bay. Temporal variations in cell densities and Chl-*a* contents of *C. asteromphalus* at stations 2 and 3 are shown in Figs. 1 and 2. It can be seen that *C. asteromphalus* appeared mainly in summer and autumn in the bay. At station 2, the maximum and secondary cell densities and Chl-*a* contents of *C. asteromphalus* were 1287.5 cells L^{-1} and 2.28 μg L^{-1}, respectively, in September 2010, and 666.7 cells L^{-1} and 1.18 μg L^{-1}, respectively, in August 2009. During these periods, *C. asteromphalus* became dominant and accounted for 60.9 and 80.6% of the total number of phytoplankton cells, respectively. In contrast, at station 3, the maximum and secondary cell densities and Chl-*a* contents of *C. asteromphalus* were 924.0 cells L^{-1} and 1.63 μg L^{-1}, respectively, in August 2009, and 212.0 cells L^{-1} and 0.37 μg L^{-1}, respectively, in October 2009. During the former period, *C. asteromphalus* was dominant and accounted for 78.8% of the total number of phytoplankton cells.

In history, phytoplankton abundance was expressed as cell numbers. However, cell size varied in a large range among various phytoplankton species so that species that relatively unimportant numerically may be very important with biomass. Hence, abundance based on a numerical census tends to overestimate small cells and underestimate the contribution of large cells. Only the biomass can represent the energy distribution in ecosystem more precisely (Sun et al. 2000).

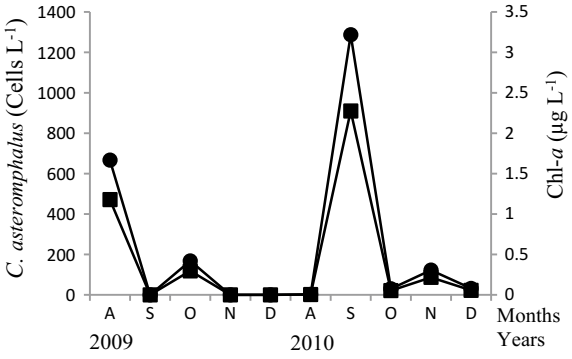

Fig. 1 Temporal variations in cell density and Chl-*a* content of *Coscinodiscus asteromphalus* at station 2: black circle cell density; black square Chl-*a* content

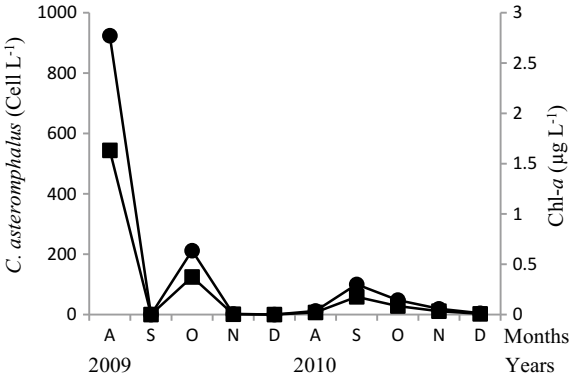

Fig. 2 Temporal variations in cell densities and Chl-*a* contents of *Coscinodiscus asteromphalus* at station 3: black circle cell density; black square Chl-*a* content

Previous studies showed that phytoplankton biomass increased with the increasing of phytoplankton volume (Mullin et al. 1966; Strathmann 1967; Eppley 1970; Taguchi 1976; Kuninao et al. 2000; Sun et al. 2000). In this study, Chl-*a* content in large-cell *C. asteromphalus* was so high (Table 1), possibly showing that the contribution of *C. asteromphalus* to phytoplankton biomass in Jiaozhou Bay was significant. According to the ratios of Chl-*a* contents in *C. asteromphalus* cells (Chl-*a*-a) to those in the water column (Chl-*a*-w) at all stations in Jiaozhou Bay (Shen et al. 2008) from August to December in 2009 and 2010, the contribution of *C. asteromphalus* to the total phytoplankton biomass in Jiaozhou Bay could be estimated (see Fig. 3). Since *C. asteromphalus* was not observed from January to July in 2009 and 2010, its biomass was equal to zero. The maximum contribution of *C. asteromphalus* was 78% of the total Chl-*a* content in the water column in September 2010 in Jiaozhou Bay. Moreover, the contributions were 56% in August 2009, 49% in October 2009, and 43% in September 2010, etc. The annual average contributions were 11.8 and 15.1%, respectively, in 2009 and 2010, suggesting that the contribution of *C. asteromphalus* to phytoplankton biomass was significant particularly in summer and autumn in Jiaozhou Bay. In comparison, the maximum contribution of *C. asteromphalus* to phytoplankton biomass in Jiaozhou Bay is higher than that of *C. wailesii* in the Seto Inland Sea, Japan (67%) (Kuninao et al. 2000). However, different from *C. asteromphalus*, the contribution of *C. wailesii* was mainly in late winter (Kuninao et al. 2000), suggesting that these two kinds of *Coscinodiscus* might have different adaptation to water temperature.

The study of Segura-Noguera et al. (2016) indicated that the masses of C, N, P, etc., in diatoms were not a constant fraction of cell volume but rather decrease with increasing cell volume. Thus, small cells had higher elemental content per unit volume than large cells. Comparing with the small diatom cells directly collected from sea by Segura-Noguera et al. (2016), the contents per unit volume of C, N, P, and Si in large cell of *C. asteromphalus* were 4.7, 1.2, 0.05, and 0.15 fg μm^{-3}, respectively, which are obviously less than these in small cells of *Chaetoceros* spp., *Pseudo-nitzschia* sp., *Rhizosolenia* sp., and *Thalassiosira* spp. Their contents per unit volume of C, N, P, and Si were 2.2–89.5, 2.5–20.8, 0.2–1.5, and 2.3–42.8 fg μm^{-3}, respectively, in *Chaetoceros* spp. cell; 27.3, 10.3, 0.4, and 10.2 fg μm^{-3}, respec-

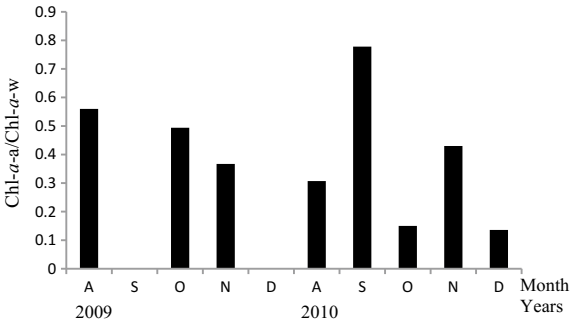

Fig. 3 Temporal variations in mean Chl-*a*-a/Chl-*a*-w content ratios in Jiaozhou Bay: Chl-*a*-a Chl-*a* contents in *Coscinodiscus asteromphalus* cells; Chl-*a*-w Chl-*a* contents in the water column

tively, in *Pseudo-nitzschia* sp. cell; 8.8, 3.9, 0.2, and 3.6 fg μm^{-3}, respectively, in *Rhizosolenia* sp. cell; and 28.6–35.2, 22.5–27.6, 0.7–1.3, and 60.1–141.6 fg m^{-3}, respectively, in *Thalassiosira* spp. cell. Although the elemental contents per unit volume in small cells are higher than those in large cell, however, the volume of *C. asteromphalus* cell is much bigger than that of small diatoms cells; therefore, yielded C by each *C. asteromphalus* cell (Table 1) is far more than that by each small diatom cell, which is consistent with the results in this section.

To sum up, previous studies on nutrient composition of phytoplankton have concentrated mainly on laboratory-cultivated species in the world. Major nutrient elements of C, N, and P have been extensively studied, but a few works involve Si. However, nutrient composition of natural phytoplankton population is rarely reported. The remarkable difficulties in measuring nutrient compositions of natural population are how to separate single phytoplankton species from seawater and how to isolate a sufficient number of phytoplankton cells for examinations. In this study, *C. asteromphalus* cells were separated from Jiaozhou Bay seawater using repeated precipitation method and the contents of carbon, nitrogen, phosphorus, silicon, and chlorophyll-*a* in *C. asteromphalus* cells were measured simultaneously for the first time in this section. However, repeated precipitation method is inapplicable for small-cell phytoplankton. This question is now overcome with the use of single-cell methods (e.g., SXRF: Twining et al. 2003—Anal. Chem. 75: 3806–3816 [https://doi.org/10.1021/ac034227z]; XRMA: Segura-Noguera et al. 2012).

The high N/P ratio and low Si/P and Si/N ratios in *C. asteromphalus* cells were consistent with those in all sized groups of particulates and seawater, reflecting an ecological response of phytoplankton to nutrient structure of seawater and Si limitation to phytoplankton growth in Jiaozhou Bay. As an index of phytoplankton biomass, Chl-*a* contents in *C. asteromphalus* cells were estimated to be 0–78% of the total Chl-*a* in the water column in Jiaozhou Bay, mainly in summer and autumn, suggesting that the contribution of *C. asteromphalus* to the phytoplankton community was significant. This study provides an efficient method of separating the large-cell diatom from natural seawater and subsequently measuring its nutrient compositions, which are meaningful and informative for estimating primary production, determining nutrient limitation, and studying ecological dynamics.

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Correction to: Studies of the Biogeochemistry of Typical Estuaries and Bays in China

Zhiliang Shen

Correction to:
Z. Shen (ed.), *Studies of the Biogeochemistry of Typical Estuaries and Bays in China*,
Springer Earth System Sciences,
https://doi.org/10.1007/978-3-662-58169-8

The book was inadvertently published with an incorrect affiliation "Institute of Oceanology, Chinese Academy of Sciences, Qingdao, China", whereas it should be "Center for Ocean Mega-Science, Chinese Academy of Sciences, Institute of Oceanology, Chinese Academy of Sciences, Qingdao, China". The changes have been updated in the book.

The updated version of the book can be found at
https://doi.org/10.1007/978-3-662-58169-8

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