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Zhiliang Shen *Editor*

Studies of the Biogeochemistry of Typical Estuaries and Bays in China

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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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Contents

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

Nutrients and Their Transport in the Changjiang River 3
Zhiliang Shen and Qun Liu

The Relationships of the Nutrients in the Changjiang River Estuary and the Flow of the Changjiang River Water 31
Zhiliang Shen

Budget and Control of Nitrogen in the Changjiang River Catchment and Its Mouth 39
Zhiliang Shen, Qun Liu, Shumei Zhang, Hui Miao and Ping Zhang

Budget and Control of Phosphorus in the Changjiang River Catchment and Its Mouth 61
Zhiliang Shen, Zheng Li and Hui Miao

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 83
Zhiliang Shen, Shuqing Zhou and Shaofeng Pei

Nutrient Dynamics of the Upwelling Area in the Changjiang Estuary 105
Shaofeng Pei, Zhiliang Shen and Edward A. Laws

A New Method for Estimating Fine-Sediment Resuspension Ratios in Estuaries—Takes the Changjiang Estuary as an Example 125
Zhiliang Shen

The Removal of Zinc, Cadmium, Lead, and Copper in the Changjiang Estuary . . . 133
Zhiliang Shen and Mingxing Liu

Distributions and Removals of Nutrients in Seawater and Interstitial Water of the Sediments in the Huanghe River Estuary . . . 143
Zhiliang Shen, Xingjun Liu and Jiaping Lu

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 . . . 159
Mingjiang Zhou, Zhiliang Shen and Rencheng Yu

Long-Term Changes in Nutrient Structure and Its Influences on Phytoplankton Composition in Jiaozhou Bay . . . 175
Zhiliang Shen

Ecological Responses of Phytoplankton to Nutrient Structure of Seawater in Jiaozhou Bay . . . 191
Zhiliang Shen, Qun Liu, Yulin Wu and Yun Yao

Silica Supply and Diatom Blooms in Jiaozhou Bay . . . 209
Zhiliang Shen, Yun Yao and Yulin Wu

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

Particulate Organic Carbon and Its Composition in Jiaozhou Bay . . . 227
Zhiliang Shen, Heming Yang and Qun Liu

Nutrient Compositions of Cultured *Thalassiosira rotula* and *Skeletonema costatum* from Jiaozhou Bay . . . 237
Zhiliang Shen, Yulin Wu, Qun Liu and Yun Yao

Differences in Nutrient Compositions of Cultured Marine Diatoms: Different Sea Areas, Sizes, and Seasons . . . 251
Shengjun Pan, Zhiliang Shen, Wenping Liu, Xiaotian Han, Hui Miao and Haiqing Ma

Nutrient Composition and Biomass of *Coscinodiscus asteromphalus* in Jiaozhou Bay, China . . . 269
Zhiliang Shen, Qian Shi, Shan Zheng and Shengjun Pan

Correction to: Studies of the Biogeochemistry of Typical Estuaries and Bays in China . . . C1
Zhiliang Shen

Index . . . 283

Editor and Contributors

About the Editor

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)

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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 9282×10^8 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

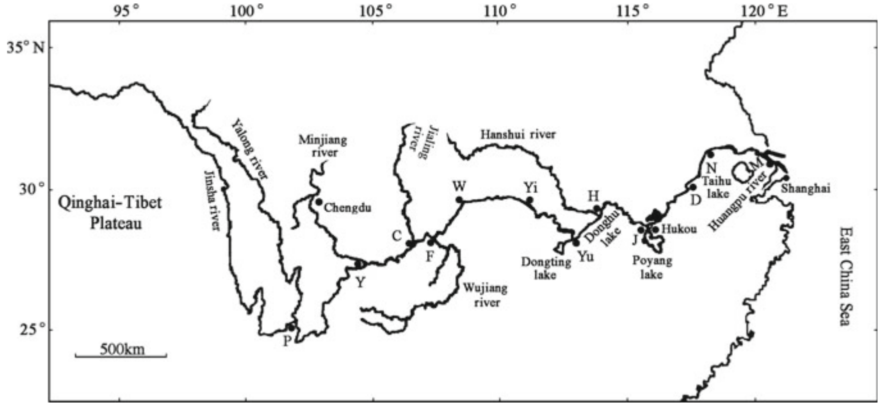

Fig. 1 Investigation stations: *P*, Panzhihua; *Y*, Yibin; *C*, Chongqing; *F*, Fuling; *W*, Wanxian; *Yi*, Yichang; *Yu*, Yueyang; *H*, Hankou; *J*, Jiujiang; *D*, Datong; *N*, Nanjing; *M*, River mouth

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).

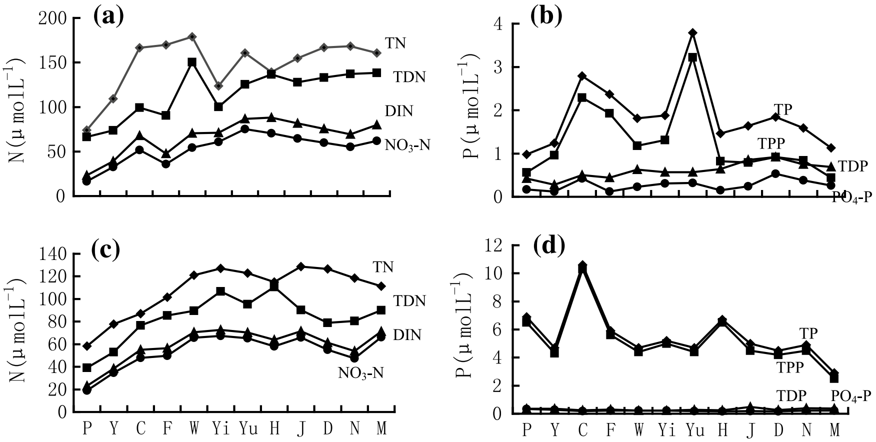

Fig. 2 Distributions and variations of N and P in the Changjiang mainstream in the dry and flood seasons: **a**, **b** dry seasons; **c**, **d** flood seasons. *F, Y, Q, F, W, Yi, Yu, H, J, D, N, M* have the same meaning as Fig. 1

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 (μmol 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