Nutrients and Their Transport in the Changjiang River



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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 SiO₃-Si was found along the Changjiang River. However, the concentrations of total nitrogen (TN), total dissolved nitrogen, dissolved inorganic nitrogen (DIN), nitrate (NO₃–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 1988).

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, SiO₃-Si, and their molar ratios in the dry and flood seasons, as well as the relations of N, P, and SiO₃-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 km². 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 km². 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 km². 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 km². 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 m³ s⁻¹ or 9282 \times 10⁸ m³ a⁻¹, most of which comes from precipitation. The annual average and annual total of precipitation are 1057 mm and 19,120 \times 10⁸ m³, 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 \times 10⁸ 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

Water systems	Catchment areas (km ²)	Ratios (%)	Length (km)		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

 Table 1
 Characteristics of the Changjiang water system

^aThe runoff and sediment load of main tributaries of the Xiangjiang River, Zishui River, Yuanjiang River, and Lishui River

^bThe 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

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

Table 2 Average concentrations ^ (μ mol L⁻¹) of N in the Changjiang mainstream

^aAverage 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 NO₃-N, DIN, TDN, TN in the dry and flood seasons were found in Panzhihua, being 16.5, 23.2, 66.5, 74.1 μ mol L⁻¹ and 18.9, 23.1, 39.2, 58.4 µmol L⁻¹, respectively. NO₃-N concentration was very close to the level of 14.3 μ mol L⁻¹ previously reported by Wang and Zuo (1986). The variations in DIN and NO3-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 NO₃-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 μ mol 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 NO₃-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. PO₄–P concentration was relatively constant in the mainstream, ranging from 0.12 to 0.53 μ mol L⁻¹ in the dry season and 0.17–0.45 μ mol L⁻¹ in the flood season. TDP concentrations increased gradu-

Tributaries	NO ₃ -N			DIN			NDN			NT		
	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 concentr	ations in Ap	ril-May 195	77 among N	concentratio	ms in the Dc	metinghu La	uke for the a	verage of its	three tributs	aries of the X	Kiangijang R	iver, Zishui

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ally from 0.28 to 0.92 μ mol L⁻¹ from the upper reaches to the lower reaches in the dry season and varied less from 0.22 to 0.49 μ mol 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 μ mol L⁻¹) and TPP $(0.56 \ \mu mol \ L^{-1})$ were found in Panzhihua, while high those were in Chongqing (2.79 and 2.29 μ mol L⁻¹, respectively) and Yueyong (3.79 and 3.22 μ mol L⁻¹, respectively). From Hankou to the mouth, the concentrations of TP and TPP were relatively constant (1.13–1.84 μ mol L⁻¹ for TP and 0.44–0.92 μ mol 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 μ mol 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 ($73 \pm 19\%$ and $85 \pm 18\%$ 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).

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Tributaries	PO4-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	06.0	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	$\begin{array}{c} 0.36 \pm \\ 0.18 \end{array}$	1.25 ± 2.16	$\begin{array}{c} 0.27 \pm \\ 0.10 \end{array}$	$\begin{array}{c} 0.82 \pm \\ 0.55 \end{array}$	1.71 ± 2.31	$\begin{array}{c} 0.31 \pm \\ 0.09 \end{array}$	1.11 ± 0.56	$\begin{array}{c} 0.33 \pm \\ 0.14 \end{array}$	3.63 ± 2.44	$\begin{array}{c} 1.94 \pm \\ 0.64 \end{array}$	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 concer	ntrations i	n April–N	1ay 1997 ;	among the	sir concen	trations in	the Dong	tinghu La	ike for the	average c	of its three	tributarie	s of the X	iangjiang

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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) ^bNot including the Huangpujiang River

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

 $\mbox{Table 5} \ \mbox{ Average concentrations a (μmol L^{-1}) of P and SiO_3-Si in the Changjiang mainstream}$

^aAverage concentrations from Panzhihua to the mouth

2.3 Silicate

The variations of SiO₃–Si concentrations in the mainstream in the dry and flood seasons were not significant, ranging from 175.6 to 201.2 μ mol L⁻¹ and from 128.4 to 162.0 μ mol L⁻¹, respectively. SiO₃–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 SiO₃–Si concentration is not significantly affected by environmental pollution, it would be expected that the SiO₃–Si concentration has a even distribution along the river, not like N and P. SiO₃–Si concentrations in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season in this study. SiO₃–Si concentration in the flood season 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, NO₃-N was the major form in the Changjiang water. The average NO₃–N/DIN ratio in the mainstream (0.79 \pm 0.05 and 0.90 ± 0.04 in the dry and flood seasons, respectively) was higher than that in the tributaries $(0.74 \pm 0.10 \text{ and } 0.84 \pm 0.09 \text{ in the dry and flood seasons, respec$ tively). 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 NH₄–N and NO₂–N to NO₃–N. This result is consistent with literature reports in Changjiang River and its estuary. For example, Fu and Shen (2002) found that the average NO₃–N/DIN ratios were 74 and 95% in the dry and flood seasons, respectively, inside the river mouth. Higher NO₃-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, NH₄-N accounted for 87.7% of DIN in the precipitation in the Changiang 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 \pm 3 and 86 \pm 16% in the mainstream and tributaries, respectively) than that in the dry season (64 ± 15 and $54 \pm 23\%$ 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 Pincluding 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 Changiang 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 μ 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/PO₄–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 SiO₃–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 SiO₃–Si/PO₄–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/PO₄–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 I	nolar ratios of N, P,	Si in the Changjiang	g River				
Seasons		TN/TP	TDN/TDP	DIN/PO4-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

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^a Average ratios from Panzhihua to the mouth ^bNot 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/PO₄–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 μ mol L⁻¹ in average) 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 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 NO₃-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 SiO₃-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 NO₃–N, NH₄–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** NO₃-N = 40.46 + 1.402 Q, r^2 = 0.304, p < 0.10; **c** NH₄-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). SiO₃–Si in the Changjiang River mainly came from natural weathering and erosion of silicate minerals, and there was no correlation between SiO₃–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** NO₃–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 $(65,828 \text{ t a}^{-1})$ 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 SiO₃-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 NH₄-N, NO₃-N, PO₄-P, SiO₃-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 NO₃–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 m³ s⁻¹, respectively, at the Datong hydrological station), with the data from the dry and flood seasons in this study (average annual runoff was $39.325 \text{ m}^3 \text{ s}^{-1}$ at the Datong station). Data shows that from the early 1980s to the late 1990s, the average concentration of NO₃-N in the mainstream increased by 0.7 times (from 31.1 to 53.4 μ 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 μ mol L⁻¹). In Fig. 6, it could be seen that the increase of NO₃-N concentration becomes more evident from the upper reaches to the mouth (about 2.7 μ mol L⁻¹ in Panzhihua, but 40.3 μ mol L⁻¹ at the mouth) from the early 1980s to the late 1990s. NO₃-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 NO₃–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. PO₄-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 $0.22 \,\mu$ mol 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 μ mol 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 μ mol L⁻¹ for PO₄–P and 4.1 μ mol L⁻¹ for TP in Datong and Hankou, respectively. Table 7 displays the concentrations of N, P, and SiO₃–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 $31.9 \,\mu$ mol L⁻¹ during 1962–1963 (Liu et al. 1983), 41.8 µmol L⁻¹ during 1979–1981 (Zhang et al. 1984), and 64.8 μ mol 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 μ mol L⁻¹, respectively. Modern agricultural activities using N fertilizers have a major impact on global atmospheric pollution. About 85% of NH₃, 81% of N₂O, 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 NH₃ 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 NO₃-N/PO₄-P in the early 1960s was 30-40 at the Changjiang mouth (Gu et al. 1981). During the annual investigations at the Changijang mouth from August 1985 to July 1986, the molar ratios of NO₃-N/PO₄-P and DIN/PO₄-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/PO₄-P ratio and decreases in SiO₃-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 / INULTIENTS	s concentrations (µmoi		me large woi	rid nvers					
Rivers	Periods	NO ₃ –N	NO ₂ –N	NH4-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					<i>T.T</i>	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)

Table 7 Nutrients concentrations (μ mol L⁻¹) in some large world rivers

^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:

$$F = \Sigma C \cdot Q \cdot f$$

where *F* is average annual transport fluxes (kg s⁻¹) of N, P, and Si, ΣC 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 SiO₃–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 SiO₃-Si entering the Changjiang River. Statistics indicate that there were clear positive linear correlationships between the transport fluxes of various N, P, and SiO₃–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 SiO₃-Si in the tributaries to the export fluxes of the Changjiang mouth were from 37.0 to 73.6%, with the highest for SiO₃-Si and the lowest for PO₄-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 m³ s⁻¹ in 1998 and accounted for 75.4% of exported runoff of the Changjiang mouth, which was very close to the ratio of SiO₃-S flux from the tributaries to the mainstream in the export fluxes of the Changjiang mouth, suggesting that SiO₃-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 NO₃-N, PO₄-P, and SiO₃-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 NO₃–N, NO₂–N, NH₄–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 PO₄–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 Changiang River mouth. Compared to results in 1985-1986 (Shen et al. 1992), the export fluxes of NO₃–N, DIN and PO₄–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 NO₃-N in this study was consistent with the result $(149.9 \times 10^4 \text{ t a}^{-1})$ derived from the data of monthly investigations at the Datong hydrological station in 1998 (Liu et al. 2002). The areal yield of NO₃-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 PO₄–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 $21.8 \text{ kg a}^{-1} \text{ km}^{-2}$ (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 NO₃–N was much higher than that of the Amazon River, but the export flux of PO₄–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
NH4–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
PO4-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 Ann	ual fluxes and	areal yields of	nutrients of th	e tributaries						
Tributaries	Fluxes	NO ₃ -N	NO ₂ -N	NH4–N	DIN	TON	NI	PO4-P	TP	SiO ₃ –Si
Yalongjiang	$10^4 { m t a^{-1}}$	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
	$\rm kg~a^{-1}~\rm km^{-2}$	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
	$\rm kg~a^{-1}~km^{-2}$	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	$\rm kg~a^{-1}~km^{-2}$	564.7	10.97	142.4	718.5	6.169	1410.4	7.673	58.46	3908.1

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Fluxes	NO ₃ –N	NO ₂ –N	NH ₄ -N	DIN	TON	TN	PO ₄ –P	ТР
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
$\begin{array}{c} 1985 - 1986^a \\ (10^4 \ t \ a^{-1}) \end{array}$	63.6	0.38	24.9	88.8			1.4	

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

^aEstimating 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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