A preliminary study on the distribution characteristics of nutrients (N, P, Si, C) in the Wujiang River Basin*

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Abstract The distribution of nutrients (N, P, Si, C) in the Wujiang River surface water was studied during the high-flow and low-flow periods in 2002. The results showed that nitrate nitrogen (NO_3-N) is the main form of dissolved inorganic nitrogen (DIN) in the Wujiang River Basin. It accounts for about 90% of DIN. The average NO_3-N concentrations in the mainstream are 147.5 μM in the high-flow period and 158.0 μM in the low-flow period, respectively. The average concentrations of total phosphorus (TP) are 6.43 μM in the high-flow period and 4.18 μM in the low-flow period, respectively. Of the various forms of phosphorus, particulate phosphorus (PP) has the highest percentage (62.9%) of TP in the high-flow period. In the low-flow period, however, phosphate is the main form of phosphorus, which accounts for 49% of TP. With the Wujiangdu Reservoir as the boundary, the concentrations of DIN and phosphorus in the upper reaches are different from those in the lower reaches of the Wujiang River. As a whole, the concentrations of DIN and phosphorus are both higher in the low-flow period than in the high-flow period. The spatial and temporal variations of DIN and phosphorus concentrations suggested that DIN and phosphorus come from agricultural and domestic wastewaters and groundwaters and that the Wujiangdu Reservoir has an important impact on the concentrations and distribution of DIN and phosphorus in the Wujiang River. The distribution patterns of dissolved silica (DSi) and dissolved organic carbon (DOC) are similar. Both of them maintain no change in the whole course of the river and their concentrations (with the exception of the reservoir itself) are higher in the high-flow period than in the low-flow period. The average DSi and DOC concentrations in the mainstream are 85.4, 84.6 μM in the high-flow period and 60.8, 53.9 μM in the low-flow period, respectively. The concentrations of nutrients in most of the major tributaries are lower than in the mainstream. This suggested that the contributions of most tributaries are relatively small but importance should be attached to the influence of some individual tributaries such as the Qingshuijiang River and the Weng'an River on the mainstream.

Key words Wujiang River; surface water; nutrient; distribution

1 Introduction

Rivers are the important sources of nutrients to estuaries and coastal zones. Nutrients transported by rivers provide an important material basis for the reproduction of organisms at the river mouths and in the neritic zones. However, in recent years, due to over-transport of nutrients (especially N, P) by rivers, lake and offshore eutrophication has become a serous environmental problem (Justic et al., 1995; Bricker and Stevenson, 1996).

As a result, scientists of various countries have shown great interest in the transport amounts of nutrients in the rivers. For example, the research program on LOICZ Land and Ocean Interactions in the Coast Zone (LOICZ, 1994 – 2000) organized by the International Geosphere-Biosphere Program (IGBP) took the transport of biogenetic elements in the rivers as the first and foremost object of action (Hopkins and Kinder, 1993). In this aspect China has a long way to go, and most of the research work in this aspect is restricted to a rough estimation of the hydrology data obtained by the main hydrological stations at the river mouths and on the rivers in the past. There has been made no systematic and deep-going investigation in this aspect (Zhang et al., 1995).

The water quality of the Wujiang River as the largest tributary on the southern bank of the Yangtze Riv-

ISSN 1000-9426

* This research project was granted jointly by the Key Research Orientation Project under the Knowledge-Innovation Program sponsored by the Chinese Academy of Sciences (KZCX 2-105) and the National Natural Science Foundation of China (Grant No. 40103008).

er has a great influence on the Three-Gorges Reservoir, and in order to develop water power resources of the Wujiang River, a series of hydropower plants are under construction at present time. So, it is of great significance to study nutrients in the Wujiang River Basin. Unfortunately, little has been reported in literature concerning research on nutrients in the Wujiang River Basin (Han Guilin and Liu Congqiang, 2001; Zhang Sheng et al., 2003). In order to understand the influence of anthropological activities on the biogeochemical cycle of biogenetic elements in the Wujiang River and provide the theoretical basis and scientific grounds for the Wujiang River water power resource management and environmental protection, a systematic study was carried out on the nutrients in the whole Wujiang River and its main tributaries during the periods of July 15 – 30 (high-flow period) and December 9 – 25 (low-flow period) of 2002.

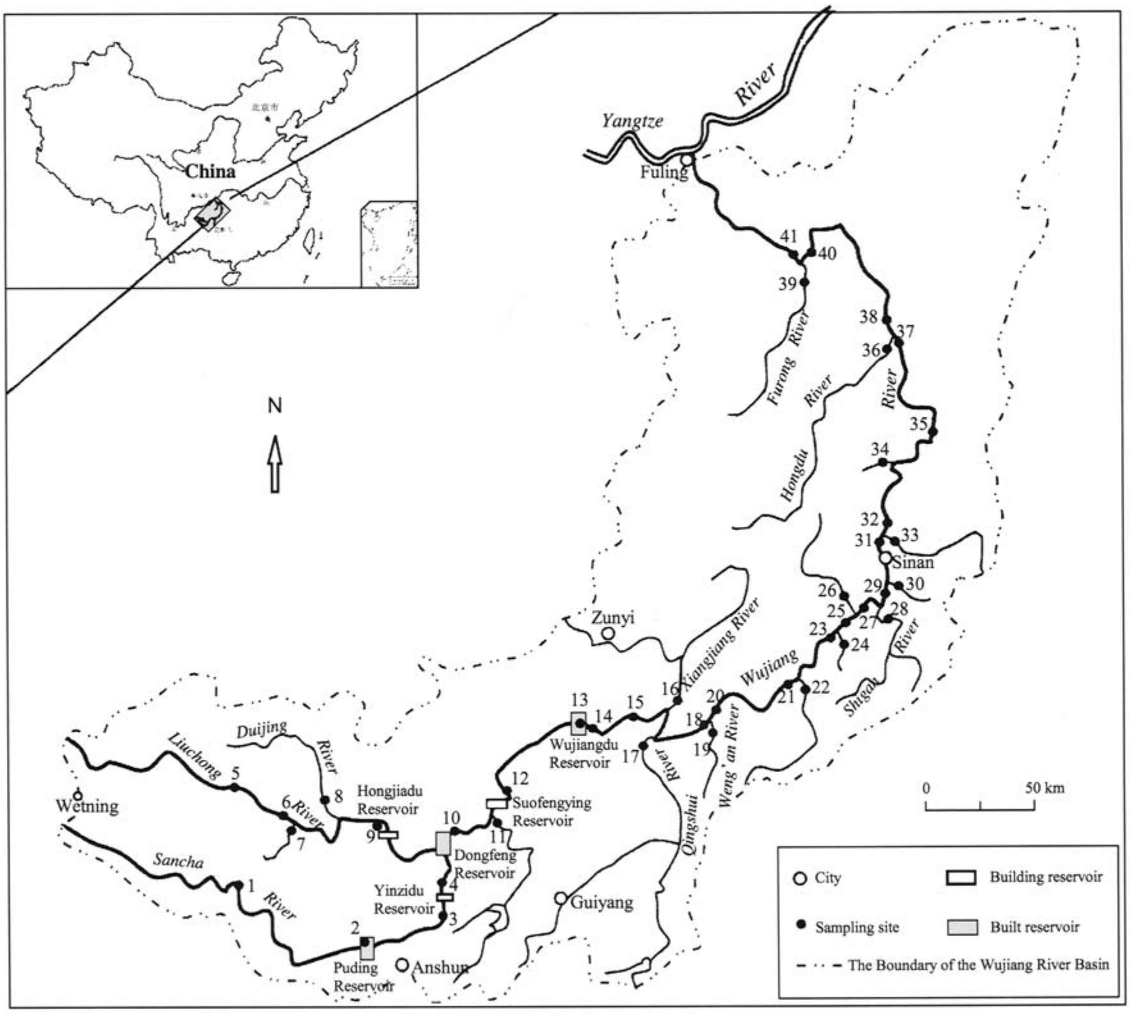

Fig. 1. Sketch map showing the sample localities in the Wujiang River Basin.

2 Sampling and analytical methods

The Wujiang River is the largest tributary on the southern bank of the Upper Yangtze River, and it is also a river with the largest drainage area within the bounds of Guizhou Province. The river originated from Weining, western Guizhou, and its mainstream has a natural head of 2124 m, belonging to a typical mountainous river. The strata in the Wujiang River Basin are dominated by carbonate rocks, which account for about more than 70%. The radial flow is concentrated in the high-flow period from May to October, and accounts for 80% of the total flow. From November to April of the next year is the low-flow period. In this work we took the Liuchong River in the upper researches of the Wujiang River, as a tributary, into consideration and the Sancha River as the mainstream of the Wujiang River.

The Wujiang River is generally shallow and the river gradient is relatively large. So river degradation is violent and water is mixed evenly. In this study we only collected surface water samples (20 cm bellow the water surface). Sample localities are shown in Fig. 1. In accordance with the circumstances or by boating or by paddling, we tried to collect water samples in the central part of the river to avoid water sample contamination. The sample container and 0.45 μm-sized mixed fibre membrane filter were first immersed in 10% HCl solution for 24 hours and then washed three times with distilled water, and finally rinsed three times on the spot with the sample. The brown glass bottle and glass fibre filters were combusted at 450 ℃ for two hour for the measurement of DOC (Waterman GF/F, 0.7 μm). The surface water samples were filtered immediately on the spot, and then poisoned with saturated mercury chloride ($HgCl_2$) to avoid any bacterial development and stored in the dark for later analysis.

NO_3-N was determined by ion chromatography, NH_4-N by Nash reagent colorimetry, and NO_2-N by the N-(1-naphthyl)-ethylenediamine method. PO_4-P was determined by the molybdenum blue method and DSi was determined by the molybdosilicate method, respectively. TP and dissolved total dissolved phosphorus (TDP) were determined by the peroxysulphate digestion followed by PO_4-P determination. For the details of the procedure, refer to the Compiling Committee for Water and Wastewater Monitoring and Analysis Methods under the National Environmental Protection Bureau (2002). Particle phosphorus (PP) is the D-value between TP and TDP. DOC was determined by a High TOC Ⅱ Type (Elementar, Germany) high-temperature catalytic oxidation method, with the precision being ±1%. Water temperature (T), pH, dissolved oxygen (DO) and electrical conductivity (EC) were measured *in-situ* using a portable multi-parameter instrument (pIONneer 65).

3 Results and discussion

3.1 The basic physical and chemical properties of surface water in the Wujiang River Basin

The physicochemical parameters (Table 1) for the water column of the Wujiang River obtained in this study are very close to those reported in 1999 (Han Guilin and Liu Congqiang, 2001). The pH values of river water from the whole Wujiang River Basin are within the range of weak alkalinities, fully demonstrating the influence of carbonate rocks in the karst areas on the river water. Additionally, as can be seen from Table 1, either during the high-flow period or during the low-flow period, the contents of dissolved oxygen (DO) in the surface water of the Wujiang River are very high. This may be due to the great river gradient in the Wujiang River Basin and the strong re-aeration capacities. At the same time, it is also reflected that the Wujiang River water is in a good oxidation state.

Table 1. Physicochemical parameters for Wujiang River water

	T (℃)	pH	DO (mg/L)	EC (μs/cm)
High flow	23.5 ±2.0	8.4 ±0.2	9.4 ±1.1	323 ±38.0
Low flow	12.5 ±3.1	8.5 ±0.2	10.5 ±1.7	424 ±54.2

3.2 The distribution of nitrogen in the surface water of the Wujiang River Basin

In the Wujiang River Basin NO_3-N is the main form of dissolved inorganic nitrogen (DIN), which accounts for about 90% of DIN. During the high-flow period the concentrations of NO_3-N in the mainstream of the Wujiang River varied between 99.3 – 186.1 μM, with an average of 147.5 μM; during the low-flow period, between 122.3 – 203.4 μM, averaging 158.0 μM (Fig. 2a). The values obtained in this study are slightly higher than those obtained in 1999 (Han Guilin and Liu Congqiang, 2001), 2.8 times those of the mainstream of the Yangtze River (Shen Zhiliang et al., 2003).

It is seen from Fig. 2a that during the high-flow period the concentrations of NO_3-N vary only slightly in the whole drainage system, while during the low-flow period the concentrations of NO_3-N tend to increase drastically, followed by a steady trend. The sudden increase of the contents of NO_3-N in the lower reaches of the Wujiangdu Reservoir may be attributed to the following reasons: (1) the impoundment and discharge regulation of the Wujiangdu Reservoir (water flow) make it changed the water quality in the lower reaches; (2) dense population on both banks of the middle and lower reaches of the Wujiang River, more cities and towns located along the lower reaches than along the upper reaches, and better development of agriculture and township enterprises have brought about more serious pollution; and (3) underground runoff supply in the lower reaches of the mainstream of the Wujiang River during the low-flow period is greater than that in the upper reaches (Zhang Mingbo et al., 2003). The contents of NO_3-N in the upper reaches are greater during the high-flow period than during the low-flow period, probably in relation to serious water erosion and soil loss in the upper reaches. And the concentrations of NO_3-N in the lower reaches are lower during the high-flow period than during the low-flow period. This may be ascribed to the influence of point-source pollution and still greater underground runoff supply in the lower reaches. In addition, during the high-flow period, water flow is large and dilution may lead to a decrease in the concentrations of NO_3-N.

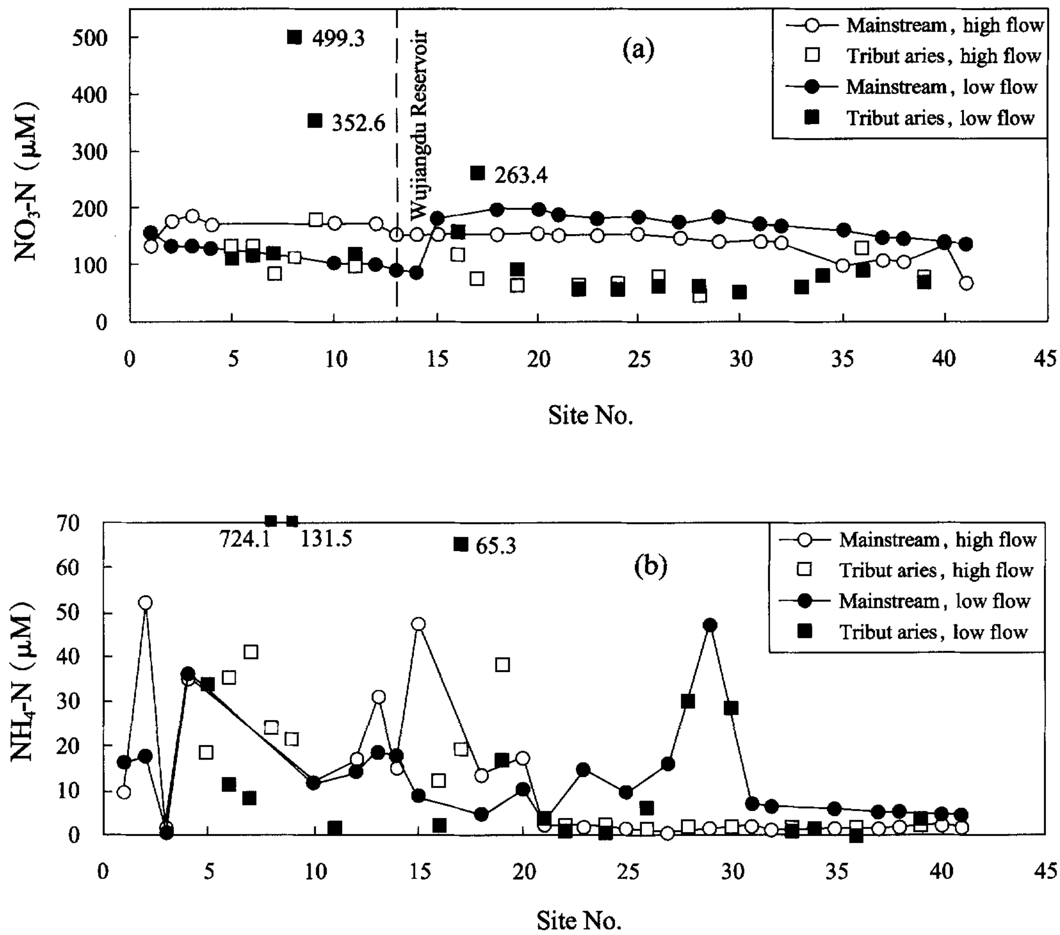

Fig. 2. The distribution of nitrogen in surface water of the Wujiang River Basin. Note: The values reported from sample localities No. 8 and No. 9 are 724.1 μM and 131.5 μM, respectively, during the low-flow period.

During the high-flow period the contents of NH_4-N in the mainstream of the Wujiang River are 0.5 – 52.0 μM, averaging 11.6 μM; during the low-flow period, 1.7 – 157.4 μM, averaging 47.4 μM. In comparison to NO_3-N, the contents of NH_4-N vary very complicatedly along the river course (Fig. 2b), generally high in the upper reaches and low in the lower reaches. This may be attributed to the entry of large quantities of NH_4-N in the non-point sources into the mainstream of the Wujiang River in response to the serious water erosion and soil loss in the upper reaches. In the upper reaches the contents of NH_4-N vary slightly from one season to another while in the lower reaches the seasonal variation trend of NH_4-N is similar to that of NO_3-N, i. e., the contents of NH_4-N are higher during the high-flow period than in the low-flow period. All this provides further evidence that in the lower reaches the influence of point-source pollution and underground runoff supply is dominant. For example, sample localities 28, 29 and 30 in the lower reaches are located at the Jiangkou Village and near the Zhaojia Town, Sinan County and the high contents of NH_4-N in water samples from those localities may be attributed to more serious anthropological pollution.

For the contents of NO_3-N and NH_4-N in water samples from sample localities 8, 9 and 17 in the middle and upper reaches of the Wujiang River during the low-flow period, please refer to Fig. 2. From this figure it can be seen that the concentrations of NO_3-N and NH_4-N in water samples from those localities are far greater than those in the mainstream of the Wujiang River. Of the sample localities, the No. 8 and No. 17 sample localities are located respectively on the tributaries of the Wujiang River—the Duijiang River and the Qingshuijiang River, and these two rivers flow through Dafang County and Guiyang City of Guizhou Province, respectively. It is seen that the two rivers have been more seriously polluted by anthropological activities. Even though the concentrations of NO_3-N and NH_4-N in the two rivers are close to those of the mainstream of the Wujiang River during the high-flow period and the water flow is relatively low, their impact on the water quality of the mainstream of the Wujiang River could not be neglected.

From the analysis of the correlations between NO_3-N and NH_4-N in the Wujiang River Basin during the low-flow and high-flow periods, it has been found that during the high-flow period both chemical species show a poor correlation ($R = 0.26$, $p < 0.05$, $n = 41$), while during the low-flow period both chemical species show a remarkable positive linear correlation ($R = 0.76$, $p = 0.01$, $n = 41$). This result is in consistency with the result of research on the correlation between NO_3-N and NH_4-N in water samples from the Yangtze River (Shen Zhiliang et al., 2003). High water temperature in summer is favorable to the oxidation of organic nitrogen and further oxidation of NH_4-N, and therefore there exists a weak correlation between NO_3-N and NH_4-N. During the low-flow period both species show a remarkable positive correlation, indicating that both of them stemmed from the same source.

Nitrite nitrogen (NO_2-N) accounts for a small portion of DIN in the whole river basin. During the high-flow period NO_2-N accounts only for 0.94% of DIN; during the low-flow period it accounts for 1.33% of DIN. Their distributions are very complicated (the diagrams are omitted here).

3.3 The distribution of phosphorus in surface water of the Wujiang River Basin

The concentrations of TP are 0.6 – 17.5 μM, averaging 6.4 μM during the high-flow period in the mainstream of the Wujiang River; 0.6 – 9.0 μM, averaging 4.2 μM during the low-flow period. In comparison to the Yangtze River and its other tributaries (Zhang et al., 1999; Duan Shuiwang, 2000), the Wujiang River has very high P contents. In the Wujiang River Basin the main form of phosphorus during the high-flow period is particle phosphorus (PP), which accounts for 74% of the total phosphorus (TP), while dissolved phosphate (PO_4-P), accounting only for 14% of TP; during the low-flow period PP accounts for 27% of TP and PO_4-P accounts for 49% of TP. TP generally shows a trend of increasing from the upper to the lower reaches of the Wujiang River, and during the high-flow period the concentrations of TP are slightly higher than those during the low-flow period (Fig. 3a). Under natural conditions P is derived predominantly from the products of erosion and weathering of rocks and soils in the Wujiang River Basin. Within the river basin the total amount of transported P is controlled by hydrodynamic conditions, of which a considerable amount is transported in the form of "suspended particle phosphorus". This is determined by the properties of phosphorus. When hydrodynamic force is large enough, the total amount of transported P within the river basin may be extremely high.

During the high-flow period, PP is the main form of occurrence in the Wujiang River Basin. The contents of PP in the mainstream are 0.03 – 16.40 μM with an average of 4.80 μM; during the low-flow period, 0.03 – 8.02 μM, averaging 1.12 μM. The distribution characteristics of PP in the Wujiang River Basin are shown in Fig. 3b. During the low-flow period, the concentrations of PP maintain constant in the whole mainstream and varied over an extremely small range. During the high-flow period, PP varies synchronously with TP along the river course, showing a trend of increasing from the upper to the lower reaches. Along the upper reaches of the mainstream of the Wujiang River there exist three water reservoirs (Fig. 1) and these reservoirs are highly capable of scavenging the particles. From the No. 1 sample locality through the Puding Reservoir to the No. 3 sample locality, for example, the concentrations of PP decreased by 95%. This may be the cause of the relatively low concentrations of PP in the upper reaches. The high concentrations of PP in the lower reaches may be ascribed to the following factors: (1) the intensification of hydrodynamic force plus flood discharge over the Wujiangdu Reservoir made the bottom sediments disturbed, thus leading to the re-suspension of surface-layer sediments; and (2) along the mainstream of the Wujiang River coal mining activities on a small scale and further reservoir construction activities would exert some influence on the PP concentrations in the river water. Additionally, the high concentrations of PP may be related to the extensive exposure of phosphorite strata in large amounts in the Wujiang River Basin. For example, the No. 19 sample locality is located on the Weng' an River, which winds its way through the largest phosphorus mining district (the Wengfu Phosphorus Mine) in Asia. In the Nos. 33 and 35 sample localities along the river, the high contents of PP seem to be related to coal mining activities nearby.

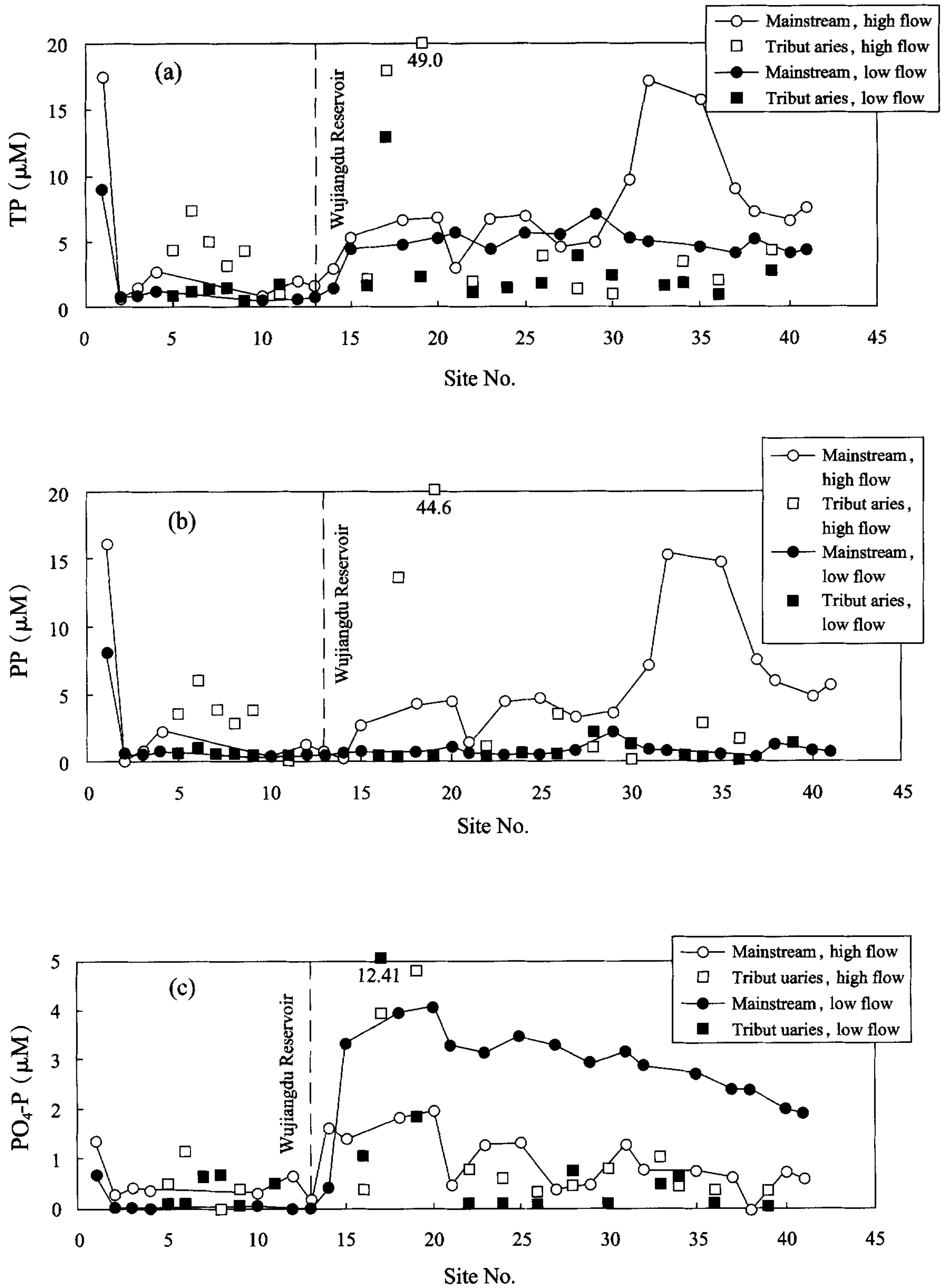

Fig. 3. The distribution of phosphorus in surface water of the Wujiang River Basin.

The concentrations of dissolved phosphate (PO_4-P) in the mainstream of the Wujiang River varied within the range of 0.19 - 1.97 μM with an average of 0.88 μM during the high-flow period; 0.02 - 4.05 μM, with an average of 2.07 μM during the low-flow period. Variations along the river course (Fig. 3c) are similar to those of NO_3-N and NH_4-N. In the upper reaches the concentrations of PO_4-P are slightly higher during the high-flow period than during the low-flow period; in the middle and lower reaches they are higher during the low-flow period than during the high-flow period. Owing to particle adsorption during the high-flow period, the concentrations of PO_4-P are relatively low; during the low-flow period, due to the reduction of particle material, dissolved phosphorus (DP) tends to increase in the water column. Re-production of phosphorus in bottom water and surface sediments of the reservoir tend to increase. Phosphorus in the bottom water and surface sediments of the reservoir may also be one of the reasons of why the contents of PO_4-P in the lower reaches are high (water discharge is generally implemented at the bottom of the reservoir). This needs to be further explored, as well. Moreover, it may be related to the extensive exposure of phosphorite strata in the Wujiang River Basin. Take the No. 19 sample locality for example. During the high-flow period the highest value of PO_4-P (4.78 μM) is produced in the Wujiang River. Meanwhile, the No. 17 sample locality at the Qingshuijiang River which flows through Guiyang City has the highest PO_4-P value (12.41 μM) during the low-flow period, indicating industrial wastewater and urban domestic wastewater would exert some influence on the concentrations of phosphorus in the mainstream of the Wujiang River.

3.4 The distribution of Si in surface water of the Wujiang River Basin

The average value of dissolved silica (DSi) in the mainstream of the Wujiang River is 85.4 μM, varying from 78.7 to 108.2 μM during the high-flow period; 60.8 μM, varying from 50.2 to 95.4 μM during the low-flow period. The contents of dissolved silica in the Wujiang River are obviously lower than the average value of 216.8 μM for global rivers (Meybeck, 1982), and also lower than the contents of DSi in the Yangtze River (at Datong or Hekou) (Duan Shuiwang, 2000).

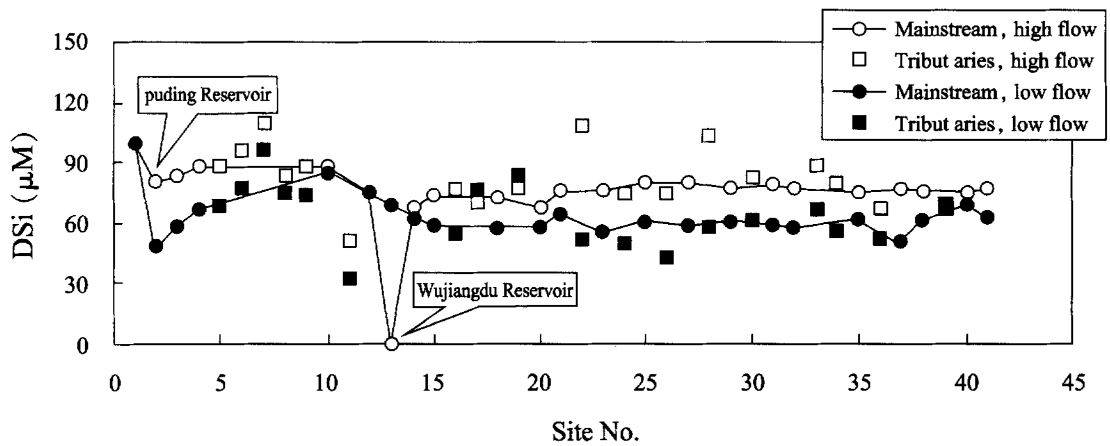

Fig. 4. The distribution of dissolved silica in surface water of the Wujiang River Basin.

Seasonal variation trend of DSi along the course of the Wujiang River is shown in Fig. 4. With the exception that during the high-flow period the contents of DSi in the Wujiangdu Reservoir decrease drastically, they are relatively stable in the whole river basin, with a small magnitude of variation. As for its seasonal variations, the contents of DSi are higher during the high-flow period than during the low-flow period. This demonstrates that DSi in the Wujiang River Basin stemmed predominantly from weathering of rocks and soils, almost without having been affected by anthropological activities. On the other hand, it is also indicated that there exit differences in weathering extent between non-karst areas and the Wujiang River Basin. Weathering in the Wujiang River Basin is still stronger than in non-karst areas. Studies have shown that the chemical erosion rates are far greater than the physical erosion rates in the karst areas of Guizhou Province (Bai Zhanguo and Wan Guojiang, 1998). Due to strong hydrodynamic force during the high-flow period, the products of weathering will be brought into the river by runoff. This may be the reasonable explanation of why the contents of DSi in the river during the high-flow period are higher than during the low-flow period. As viewed from the tributaries of the Wujiang River Basin, the concentrations of DSi are close to those of the mainstream, indicating a similar origin. It can be seen from Fig. 4 that during the high-flow period the contents of DSi tend to decrease when river water flows into the reservoir (especially the Wujiangdu Reservoir). This may be related to the biological processes in the reservoir.

3.5 The distribution of dissolved organic matter (DOC) in surface water of the Wujiang River Basin

Dissolved organic carbon (DOC) is the principal part of carbon flux in many rivers, and it is derived from terrestrial leaching-erosion-dissolution of the river basin and organic metabolism of aquatic ecosystems themselves. The average value of DOC is 84.6 μM, varying within the range of 54.1 – 247.6 μM during the high-flow period; the average value of DOC is 53.9 μM, varying within the range of 31.7 – 77.8 μM during the low-flow period. Obviously, the concentrations of DOC in the mainstream of the Wujiang River are relatively low, below the lower limit of the average level for global rivers (the concentrations of DOC in natural rivers throughout the world are 83 – 1600 μM). In comparison to the mainstream of the Yangtze River (Duan Shuiwang, 2000), the average value of DOC in the Wujiang River accounts for 12% of the average value of DOC in the mainstream of the Yangtze River. This may be related to the landform features of the karst area where the Wujiang River Basin is located. Great losses of soil nutrients will lead to the reduction of organic matter in soils, thereafter resulting in the lower contents of organic matter via leaching than those in non-karst areas.

The variation trend of DOC along the river course in the Wujiang River Basin is similar to that of DSi, and in the whole river basin the contents of DOC generally keep constant (Fig. 5). As for their seasonal variation, the contents of DOC are higher during the high-flow period than during the low-flow period. This may be ascribed to the stronger erosion during the high-flow period, leading to the intensification of leaching and output of organic matter in soils, though its seasonal variation is not so remarkable as compared to some other high-nutrient rivers. All this implies that DOC in the Wujiang River may have been derived chiefly from organic matter in terrestrial soils in the river basin, and the metabolism of organic matter in aquatic ecosystems themselves in the river has made a relatively small contribution to DOC in the river. In addition, the variation trend of DOC is similar to that of DSi; the former's concentrations in the upper reaches are very close to those in the lower reaches, showing a slight variation. This indicates that DOC and DSi were both derived from a similar source. From Fig. 5 it can be seen that during the high-flow period, the contents of DOC would increase suddenly when the river flows into the reservoir. This may be related to the influence of biological processes in the water reservoir.

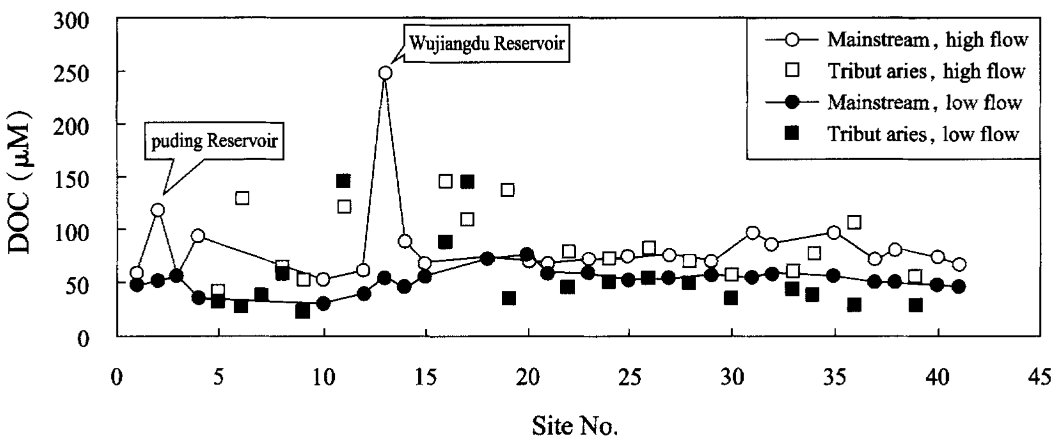

Fig. 5. The distribution of dissolved organic carbon in surface water of the Wujiang River Basin.

4 Conclusive remarks

NO_3-N is the main form of DIN, and dissolved inorganic nitrogen in the Wujiang River Basin is present mainly in the form of NO_3-N, and latter's distribution represents the distribution of DIN. NO_3-N, NH_4-N and PO_4-P were derived predominantly from agricultural non-point-source pollution and domestic wastewaters. Their distributions in the river basin reflect, to some extent, the influence of anthropological activities on water quality. The distributions of NO_3-N and PO_4-P reflect that their concentrations are higher in the middle and lower reaches than in the upper reaches. Their seasonal variation trend is similar to that of NH_4-N, reflecting that their concentrations are higher during the low-flow period than during the high-flow period. All this indicates that the lower reaches of the river starting from the Wujiangdu Reservoir have probably been more seriously polluted by anthropological activities than the upper reaches. This may be ascribed to the fact that the underground runoff supply is much greater in the lower reaches of the Wujiang River than in the upper reaches. Meanwhile, the reservoir may influence the transport of nutrients in the river. As viewed from the distribution of nutrients in the tributaries, it was found that the contents of nutrients in most of the tributaries in the middle and lower reaches of the Wujiang River are lower than those of the mainstream, indicating that the input of nutrients from the tributaries into the mainstream is of small contribution. However, the influence of some individual tributaries (i. e., the Qingshuijiang River, the Weng'an River) on the mainstream should not be neglected.

The rules of distribution of DSi and DOC in the Wujiang River Basin are very similar to each other (with the exception of the reservoir), and in the whole river basin their contents are very constant, indicating that both DSi and DOC are probably similar in source, i. e., DOC may have been derived largely from organic matter in terrestrial soils of the river basin. Additionally, both of them are below the lower limit of global average values, fully demonstrating the features of karst areas of Guizhou Province.

During the high-flow period the drastic decrease of DSi and the sudden increase of DOC in concentrations within the reservoir may be related to biogeochemical processes within the reservoir, which needs to be further studied.

Acknowledgements Sincere thanks are due to Dr. Li Siliang for his assistance in sampling and Mr. An Ning and Mr. Zhou Jingye for their laboratory analysis.

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