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Seasonal changes of nutrient fluxes in the Upper Changjiang basin: An example of the Longchuanjiang River, China

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SUMMARY

Fluxes of dissolved and particulate nitrogen (N) and phosphorus (P) variables were measured monthly from September 2007 to March 2009 in the upper Longchuanjiang River (Yunnan Province, China) to determine annual loads and seasonal variability. Dissolved N (DN) and particle associated P (PAP) contributed 56% and 99% of the total nitrogen (TN) and total phosphorus (TP) yields of 549 and 608 kg/km^2/yr. Fluxes of particulate N (PN), dissolved P (DP), PAP and TP exhibited great seasonality because they were highly correlated with water discharge. Areal export rates of NH_4^+–N, PN, PAP and TP were higher than in the main channel and most tributaries of the Changjiang River. High particulate loads were contributed to erosion of phosphorus-rich soils during heavily rains in the wet season. Median measured concentrations of TN, NH_4^+–N and TP exceeded the maximum permissible limit for domestic and recreational use in China. High nitrogen and phosphorus concentrations draw attention to the potential for additional nutrient loading to foster the formation of algal blooms in locations where free-flowing river sections are changing into cascades of reservoirs. Importantly, the great seasonality in the data shows necessity of sufficient sampling for determining annual fluxes.

1. Introduction

Stream nitrogen (N) and phosphorus (P) have a variety of natural and anthropogenic sources including chemical weathering (Chalk and Keeney, 1971; Holloway et al., 1998), decomposition of organic material, atmospheric deposition, agricultural chemical fertilizers, and effluents from livestock, domestic and industrial sources (Li et al., 2008, 2009a; Elser et al., 2009). Increases in available forms of N and P as a result of human activity have resulted in worldwide eutrophication in both freshwater and coastal marine ecosystems (Meybeck et al., 1989; Turner et al., 2003; Duan et al., 2007; Conley et al., 2009; Elser et al., 2009), causing hypoxia, harmful algal blooms and losses of fishery production in aquatic ecosystem. Further, the biogeochemical cycles of nutrients have been altered particularly by human population expansion and industrialization (Elser et al., 2009), thus nutrients such as N and P species in fluvial system have increasingly been of great concern.

Riverine N:P ratios receive much attention because the changes in element ratios of nutrients by human activities have been breaking the balance of nutrients and deteriorating the ecosystem (Justic et al., 1995; Howart et al., 1996; Elser et al., 2009). One of the potential impacts is to influence phytoplankton production ratios and associated shifts of phytoplankton species in aquatic ecosystem (Justic et al., 1995; Rabalais et al., 1996). The tributaries and main channel of the Changjiang River are strongly influenced by anthropogenic activities. Over the past 50 years, especially since the 1980s, nutrient (especially N) concentrations and loads increased as high as 4-fold (Duan et al., 2000; Yan et al., 2003), and consequently Changjiang is heavily polluted by nitrogen (Chen et al., 2000; Liu et al., 2003).

Prior research on the Changjiang has focused on steam water geochemistry, levels of nutrients and associated budget and the effects of nutrient loading on aquatic ecosystems (i.e., Zhang, 1996; 1999; Chen et al., 2000; Duan et al., 2000, 2007, 2008; Liu et al., 2003; Shen et al., 2003; Shen and Liu, 2009). While most previous studies were conducted before or during the 1980s and the 1990s, it is urgent to update the nutrient variables in the Changjiang and its tributaries to examine their dynamics and patterns.

Longchuanjiang River, located in the upper stream of the Changjiang, has been experiencing various human activities (Zhu et al., 2007, 2008). They caused the changes in concentrations and fluxes of nutrient and the shifts in their element ratios, which consequently altered the patterns of nutrients in its

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downstream. Moreover, increasing nutrients in the upper Changjiang's tributaries will cause eutrophication in the Three-Gorges Reservoir. Our previous paper reported major element geochemistry and revealed anthropogenic effects on water chemistry (Li et al., 2011). Hereine, we investigate the effects of anthropogenic activities on N and P variables in the Longchuanjiang River. Specifically, we quantify seasonal fluxes of TN, DN, NO_3^-–N, NH_4^+–N, PN, TP, PAP and DP to better understand how they are affected by various human activities, such as land-cover change, dam building, and intensified agricultural activity, that are taking place in the attachment. This study would help water conservation in the Changjiang's headwater and provide updated data in developing regional to global models of nutrient exports from watersheds.

2. Study area

Originating in Nanhua County in southwest China, the Longchuanjiang River joins the lower Jinshajiang, a tributary of the upper Changjiang (Fig. 1). The 231-km river covers an area of 5560 km^2 (24°45′N–26°15′N and 100°56′E–102°02′E). The 1788 km^2 upper catchment (west of Xiaohekou station) above our sampling site has a sub-tropic monsoon climate, characterized by annual mean temperature of 15.6 °C. Annual rainfall depth is 825 mm, with more than 80% occurring in the rainy season from May to October (Lu, 2005). Elevation extends from 700 to 3000 m a.s.l. The area is dominated by purple phosphorus-rich soils (Wang et al., 2008), which is very susceptible to water erosion and weathering. Erosion in the region had accelerated over the past decades because of increased land-use pressures related to population growth and economic incentives that drive development. Activities that directly influence water quality include deforestation (in earlier times), intensified agriculture activity, reservoir building, stone excavation and road construction. In several counties (e.g., Nanhua and Chuxiong), industrial and domestic wastes are discharged directly into the river.

3. Methods

3.1. Sampling and chemical analyses

Daily water discharge and monthly precipitation were recorded from January 2007 to March 2009 by the staff of the Xiaohekou discharge gauging station located in the Chuxiong County (Fig. 1). Water samples for chemical analysis were collected during the second week of each month, throughout the 19-month sampling period (September 2007–March 2009). A total of 19 depth-integrated samples were collected in acid-washed 5-l high density polyethylene (HDPE) bottles using the mechanized pulley system that is used to determine the discharge rating curve. Samples were filtered immediately through pre-ashed 0.7-μm pore size Whatman GF/F filters in a plastic tent to avoid contamination. Filtrates were used to determine dissolved nutrient concentrations. Water samples for analysis of TP were not filtered. All water samples were acidified to pH < 2 with high purity HCl, then preserved in clean (marinate for 24 h in 1:10 hydrochloric acid solution beforehand) HDPE bottles in the freezer for prior to analysis.

N and P species were determined using the ultraviolet–visible spectrophotometric method (Grassholf et al., 1983; CSEPB, 2002a). DN was measured with potassium peroxodisulphate oxidation-colorimetry; TP and DP with ammonium molybdophosphate colorimetry, and NH_4^+–N and NO_3^-–N by the Nessler reagent method and UV spectrophotometry, respectively. Particulate nitrogen (PN) was determined using a CHN analyzer. The concentration of TN was determined as the sum of DN and PN; and PAP was calculated as the difference between TP and DP. Detection limits for NO_3^-–N, NH_4^+–N, DN, DP and TP were 0.08 mg/l, 0.02 mg/l, 0.05 mg/l, 0.01 mg/l and 0.01 mg/l,

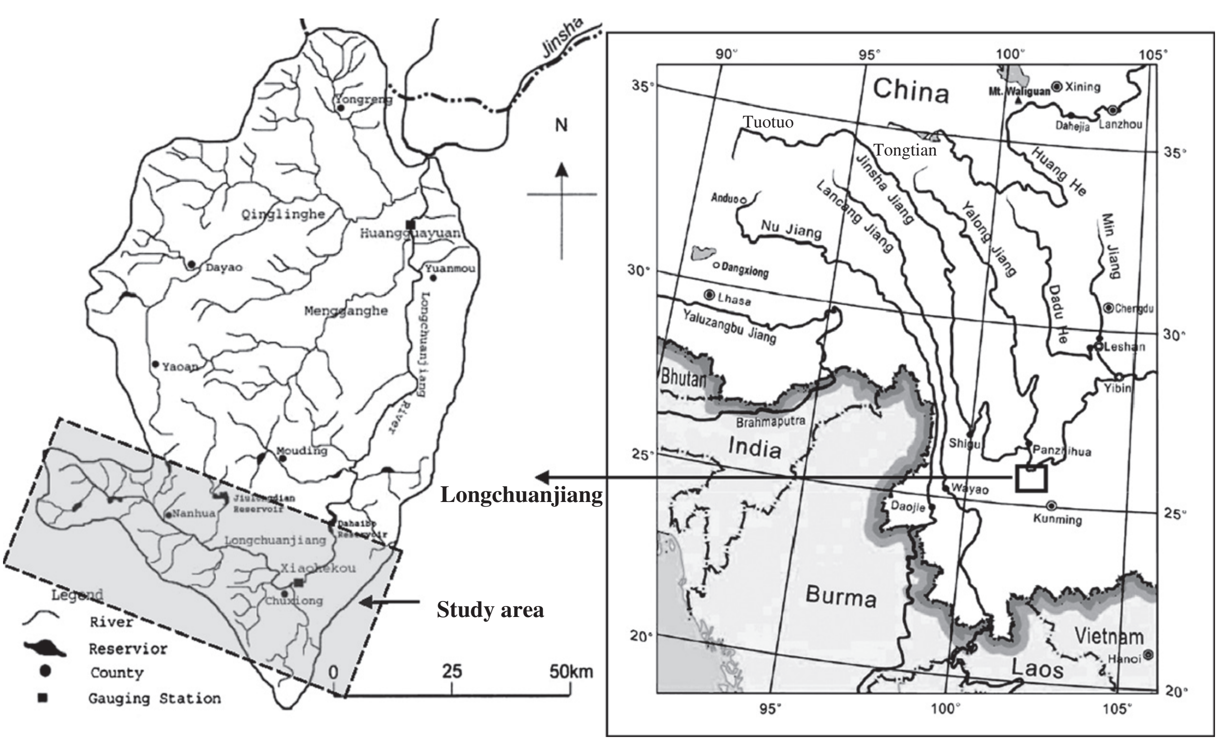

Fig. 1. Map of the Longchuanjiang River with sampling sites and gauge stations, and other Changjiang's tributaries, China.

respectively. Replicates samples were performed for all tests to assure data quality control.

3.2. Nutrient fluxes estimation

Interpolation and extrapolation were used to calculate annual loads from the monthly measured concentrations and daily river discharge measurements (Webb et al., 1997). Extrapolation was used when reasonable regression equations ($R^2 > 0.5$ with p values < 0.05) could be determined for daily water discharge (independent variable) and nitrogen and phosphorus concentration values (independent variables); e.g., PN, DP, PAP and TP fit this criteria (see below). Interpolation was used for calculations involving TN, DN, NO_3^-–N and NH_4^+–N, required assuming concentrations changed at a constant per-day rate between two measured monthly values (Duan et al., 2000, 2007). Annual fluxes were calculated as the sum of all interpolated/extrapolated daily values. Catchment nutrient areal export rates were obtained by dividing the annual fluxes with the catchment drainage area.

4. Results

4.1. Hydro-climatology

River discharge demonstrated a similar trend with precipitation, with higher flows occurring during May to October/November, and lower values occurring in the low-flow period of then December to March/April dry season (Fig. 2). Precipitation in 2008 (1083 mm) was higher than in 2007 (958 mm); and both years were wetter than the 825 mm mean reported by Lu (2005). Monthly precipitation varied from 0 mm (March and December 2007) to 254 mm (July 2008); and approximately 95% of the total fell between May and November (Fig. 2). The highest daily discharge value (210 m^3/s) was associated with an extreme event occurring in November 2008; and the lowest daily value (0.12 m^3/s) occurred in April of 2008 dry season. Mean discharge for the 2008 low-flow and high-flow periods were 1.6 and 17.4 m^3/s respectively, demonstrating the great seasonality in streamflow (Fig. 2). Sampling months were divided into two regimes that corresponded to the monsoon climate and river runoff: high flow (September and October in 2007, and May through November in 2008) and low flow periods (November in 2007–April in 2008 and December in 2008–March in 2009).

4.2. Monthly variations in nutrients

Concentrations of dissolved N and P variables demonstrated a general dilution effect during the high-flow period, in contrasts to particulate variables, which tended to increase during the same period. Dissolved nitrogen was primarily composed of NO_3^-–N and NH_4^+–N in all but one sample these two exceeded the independent DN determination. Dissolved nitrogen comprised largest part (~86%) of TN signature, and therefore tracked TN seasonality (Fig. 3). In contrast with nitrogen, approximately 95% of TP was PAP, and therefore the concentrations of TP and PAP exhibited similar seasonality patterns (Fig. 3).

Reliable regressions could be developed between discharge and only for four variables: PN ($R^2 = 0.7$, $p < 0.01$), PAP ($R^2 = 0.9$, $p < 0.01$), TP ($R^2 = 0.9$, $p < 0.01$) and DP ($R^2 = 0.6$, $p < 0.01$) (Fig. 4). Because meaningful regression equations could not be determined between discharge and TN, DN, NO_3^-–N and NH_4^+–N, interpolation was used to calculated annual loads for these variables (Fig. 4).

Fluxes of several N and P variables reached maximums during November in the 2008 high-flow period: TN (90 g/s), DN (74 g/s), NO_3^-–N (52 g/s), (NH_4^+–N) 40 g/s, TP (66.1 g/s) and PAP (65.6 g/s) (Appendix a). Peak values for PN (22 g/s) and DP (0.6 g/s) occurred in July and August 2008, respectively (Appendix a). The positive relationship between discharge and particulate concentrations, as well as the great difference between daily flows in the wet versus dry season, resulted in high-flow period fluxes of PN and PAP being 3–4 orders of magnitude higher than those in the low-flow period (Appendix a). Despite the negative relationship between concentration of DP and discharge (Fig. 4), fluxes displayed some seasonality (Appendix b).

The annual load of TN and TP, estimated via interpolation, was an estimated 765 and 541 Mg/yr, which was equivalent to about 428 and 303 kg/km^2/yr (Table 1). Dissolved and particulate N loads were 553 and 212 Mg/yr (310 and 119 kg/km^2/yr); and DP and PAP loads were 8 and 533 Mg/yr (4 and 298 kg/km^2/yr). In comparison, loads for PN, DP, PAP, and TP determined with the extrapolation method were 428, 7, 1080, and 1087 Mg/yr – these values for particulate variables were all nearly twice those determined via interpolation (Table 1).

5. Discussion

5.1. Controls of seasonal variations of nitrogen and phosphorus

The significant seasonality for particulate variables (PN and PAP) was consistent with patterns found in other studies conducted on

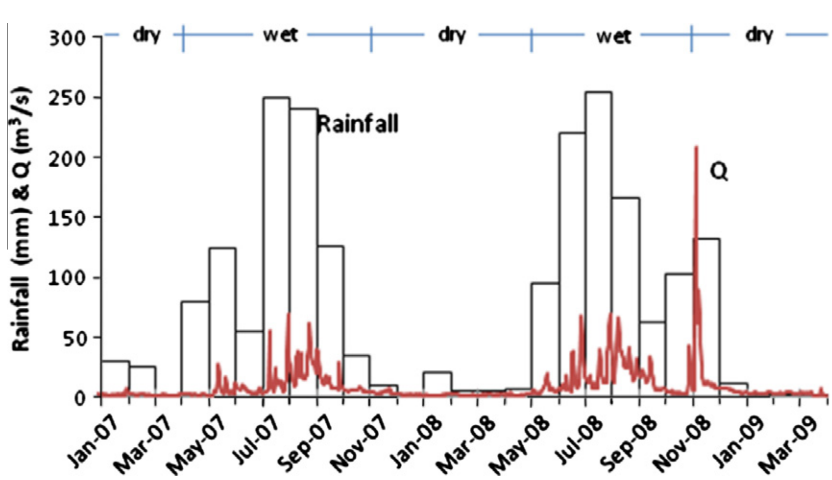

Fig. 2. Hydrological characteristics including daily water discharge (m^3/s) and monthly precipitation (mm) from January 2007 to March 2009 by staff of the Xiaohekou discharge gauging station in the Longchuanjang River, China.

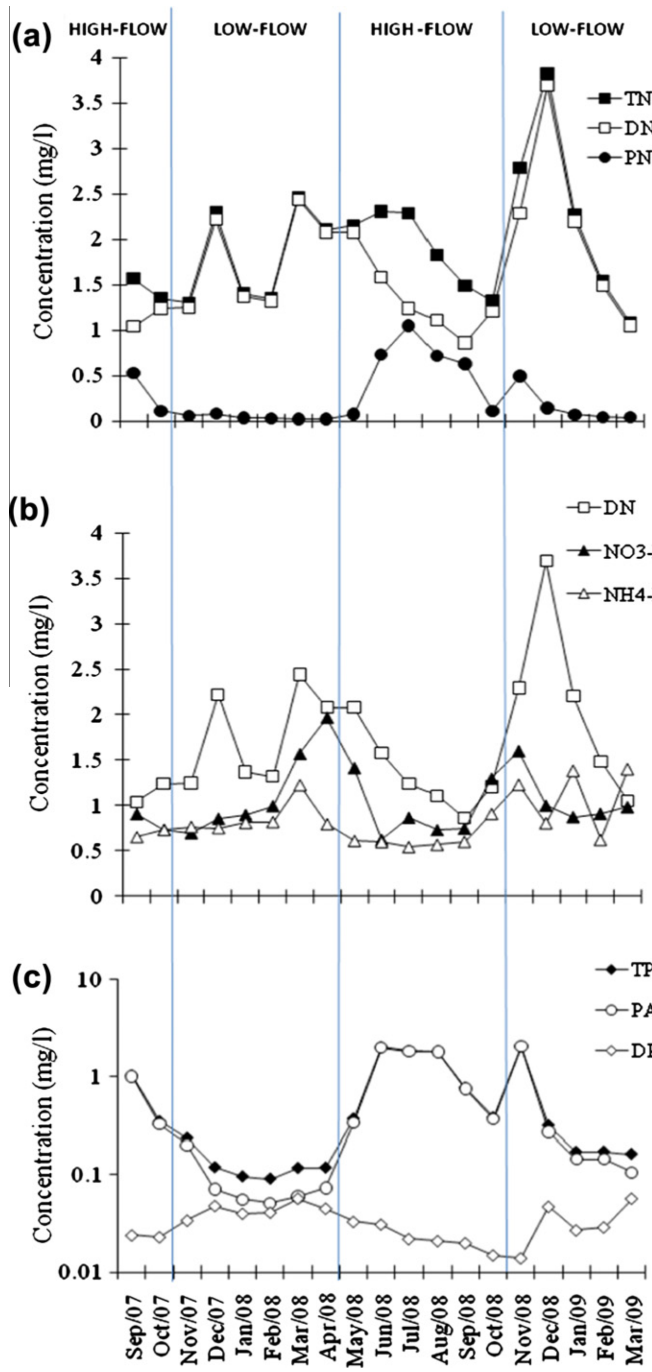

Fig. 3. Seasonal variability in nutrients of the Longchuanjiang River, China: (a) TN, DN and PN (b) DN, NO_3^-–N and NH_4^+–N, (c) TP, PAP and DP (*Y*-axis is mg N/L for (a) and (b), and mg P/L for (b)). The averaged concentration of PN, DP, PAP and TP showed significant differences between high and low flow periods by analysis of variance (least significant difference, LSD test, $p < 0.01$).

Changjiang River (Figs. 3 and 4) (Liu et al., 2003; Shen and Liu, 2009). Great seasonality was probably the result of substantial soil erosion and runoff water entering the river from various sources during the wet season, which was supported by their strong associations with total suspended solid (Fig. 5). The concentration of PAP, the major form of P in the turbid Longchuanjiang River, was more positively associated with water discharge than PN(Fig. 4), which was due to phosphorous-rich purple soils in the catchment (in general in Southwestern China) (Wang et al., 2008). However, DP displayed markedly higher concentration in the low flow period ($p < 0.01$ by ANOVA) as a result of diluted effects of precipitation (Fig. 4) and sorption by suspended matter in the high flow period (Fig. 5) (Baturin, 1978; Berge et al., 1997).

Acid rain and agricultural diffuses in the Changjiang basin are believed to elevate river nitrogen concentrations, particularly in the wet season (Chen et al., 2000; Bao et al., 2006; Li et al., 2009b). Our results, however, showed decreases in dissolved variables such as NO_3^-–N, NH_4^+–N in the high-flow period that likely related to a precipitation dilution effect (Fig. 3; Shen and Liu, 2009). Shen et al. (2003) reported that NH_4^+–N accounted for approximately 88% of dissolved inorganic nitrogen in the precipitation in the Changjiang River basin. With this in mind, large differences in NO_3^-–N/NH_4^+–N ratio between the high and low flow periods could occur if NO_3^-–N did not occur. Our results however demonstrated small variability in the ratio (1.33 versus 1.17) between the high and low flow period, respectively, indicating a mix of input sources throughout the year (e.g., precipitation, agricultural non-point pollutants, and residential sewages) (Chen et al., 2000), rather than a single important anthropogenic source, such as agricultural runoff.

5.2. Environmental status of the Longchuanjiang River

Nitrogen and phosphorus concentrations in the Longchuanjiang River were higher than environmental quality standards for domestic and recreational use in China (GB3838-2002; CSEPB, 2002b, see Appendix Table). While high values could be harmful to humans, such as infant methaemoglobinaemia and stomach cancer by intake of excessive nutrients via food chain (Murphy, 1991), an immediate environmental concern is the effect of eutrophication on aquatic organisms. For example, the interaction of additional nutrient loading and ongoing development of a hydropower electricity facility could result in eutrophication in the areas where free-flowing river is changing into artificial reservoirs.

N:P stoichiometry would help to determine the potential limiting element for phytoplankton growth. The observed high DN:DP element ratios (median = 113, varying from 41 to 362; based on the measured concentrations) indicated that the biological activity could be limited by phosphorus. For example, Hu et al. (1990) claimed that P limited phytoplankton production in the Changjiang Estuary when N:P exceeded 30 (cf. Liu et al., 2003; Duan et al., 2008; Shen and Liu, 2009). However, optimal N:P ratios vary from about 8–45, depending on the ecological conditions (Kahlert, 1998; Klausmeier et al., 2004), only one sample in our considered period fell in this range and thus biological activity was strongly P limited but much more severe during autumn flood (November 2008; Appendix c) in the Longchuanjiang River.

5.3. Comparison with the Changjiang River and tributaries

The annual concentration of PAP was by far the highest observed in various tributaries in the Changjiang River (Table 2). All other variables were within the ranges of reported values, but concentrations of NO_3^-–N, PN, and TP were in the top 2. Both dissolved N and TN were also at the high end of the range. All dissolved concentrations were lower than those reported for the polluted Tuojiang River (Table 2). Concentrations of DN and DP were both similar to those in the Fujiang, Minjiang, Jialingjiang, Xiangjiang, and Hanjiang Rivers (Table 2). Nitrate concentrations were similar to that of the Minjiang and Hanjian Rivers. These three variables were also comparable to annual concentrations reported for the Chiangjiang River by Liu et al. (2003; Table 2). In comparison, NH_4^+–N was high, second only to that in the Tuojiang River (Table 2).

Similar to the Changjiang system (i.e., Liu et al., 2003; Shen et al., 2003; Shen and Liu, 2009), the export fluxes of various forms of nutrients in the Longchuanjiang were mainly controlled by river water flow (Appendices a and b). The areal export rates of TN, DN,

Table 1
Nutrient transported by the upper Longchuanjiang River, China (2008 considered due to samples largely taken in this year).

	TN	DN	NH_4^+–N	NO_3^-–N	PN	DP	PAP	TP
Annual ($\times10^3$ kg/yr)[a]	765	553	264	357	212	8	533	541
Annual ($\times10^3$ kg/yr)[b]					428	7	1080	1087
Areal export rate (kg/km^2/yr)	548.9	309.5	147.7	199.7	239.4	3.9	604.0	607.9

nd means the calculation could not be determined because of the poor relationship between the variables and stream discharge.
[a] Determined via interpolation method.
[b] Determined via extrapolation method.

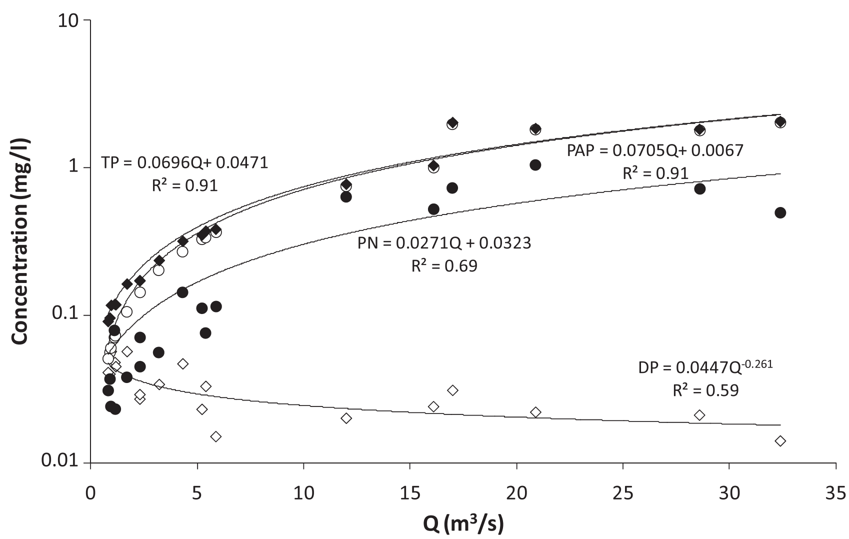

Fig. 4. Scatter plots between nutrients and water discharge in the Longchuanjiang River, China ($p < 0.01$) (other variables showing poor relations with water discharge are not listed).

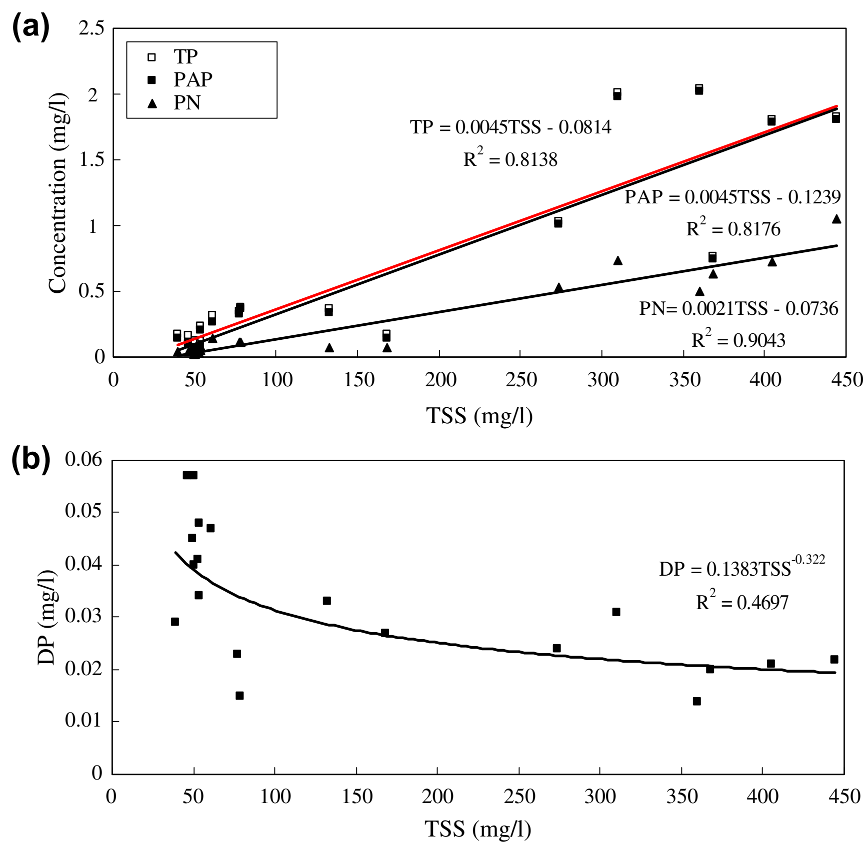

Fig. 5. Co-variations between the concentrations of (a) TP, PAP and PN, (b) DP and total suspended solid (TSS; *not provided*) in the Longchuanjiang River, China ($p < 0.01$).

Table 2
Comparison of the annual mean nitrogen and phosphorus concentrations in the upper Longchuanjiang River with other tributaries of the Changjiang Ricer and other Rivers, China (unit in μg/l).

Tributaries	NO_3^-–N	NH_4^+–N	DN	TN	PN	DP	PAP	TP	Reference
Longchuanjiang	1037	835	1672	1935	263	33	609	642	This study
Yalongjiang	182	10	259	281	22	10	3	13	Shen and Liu (2009)
Daduhe	426	231	1000	1018	18	10	9	19	Liu et al. (2003)
Minjiang	1060	64	1463	1473	10	38	9	47	Shen and Liu (2009)
Tuojiang	5656	2394	10,332	10,345	13	716	37	756	Liu et al. (2003)
Fujiang	1296	392	2005	2911	906	37	43	81	Liu et al. (2003)
Jialingjiang	682	147	1067	1077	10	39	7	46	Shen and Liu (2009)
Wujiang	1287	11	1779	1856	77	214	16	230	Liu et al. (2003)
Xiangjiang	777	150	1166	1417	251	26	16	42	Liu et al. (2003)
Hanjiang	1036	92	1443	1466	22	29	11	41	Shen and Liu (2009)
Ganjiang	559	48	791	900	109	17	15	32	Liu et al. (2003)
Changjiang	984	52	1190			43			Liu et al. (2003)
Changjiang (Datong)	805	136							Shen and Liu (2009)
Huanghe (Lijin)	1420	644							Shen and Liu (2009)
Zhujiang (Gaonu)	658	17							Duan and Zhang (1999)

Table 3
The areal export rates (kg/km^2/yr) of N and P species in the Longchuanjiang River and tributaries in the Changjiang River, China.

		TN	DN	NH_4^+–N	NO_3^-–N	PN	DP	PAP	TP	References
Loungchuanjiang		548.9	309.5	147.7	199.7	239.4	3.9	604.0	607.9	This Study
Changjiang	Min	31.8	13.9	3.5	4.9	11.9	5.6	1.1	6.5	Liu et al. (2003)
	Max	774.2	697.2	51.1	595.0	511.0	26.4	8.7	32.2	
	Mean	505.4	467.6	20.0	379.4	37.2	15.8	4.7	22.9	
Changjiang		1575.0	963.4	160.9	795.1	611.6[a]	12.6	57.7	70.3	Shen and Liu (2009)
Yalongjiang		140.7	123.9	5.6	84.3	16.8	4.7	2.3	7.1	Liu et al. (2003)
		431.2	157.3	40.0	115.1	273.9[a]	3.9	52.1[a]	56.0	Shen and Liu (2009)
Minjiang		998.3	991.9	44.1	718.2	6.4	25.5	6.1	31.6	Liu et al. (2003)
		1070.8	522.6	76.3	437.4	548.2[a]	5.7	66.9[a]	72.6	Shen and Liu (2009)
Tuojiang		5302.6	5299.0	1012.2	3064.6	3.6	372.9	6.1	379.0	Liu et al. (2003)
Jialingjiang		898.4	893.5	101.1	582.4	4.9	21.2	3.3	24.5	Liu et al. (2003)
		1188.1	587.4	97.6	479.6	600.7[a]	3.8	50.4[a]	54.2	Shen and Liu (2009)
Wujiang		848.7	751.6	4.0	560.0	97.0	49.2	17.5	66.7	Liu et al. (2003)
		1618.7	748.2	59.5	685.5	870.5[a]	5.7	79.7[a]	85.4	Shen and Liu (2009)
Xiangjiang		1134.8	934.6	119.8	623.0	200.2	20.8	12.3	33.2	Liu et al. (2003)
Hanjiang		571.2	559.3	21.7	400.4	11.9	14.6	4.6	19.2	Liu et al. (2003)
		803.9	424.7	144.8	272.1	379.2[a]	4.8	17.4[a]	22.2	Shen and Liu (2009)
Ganjiang		707.4	618.5	9.5	457.8	88.9	13.6	12.2	25.9	Liu et al. (2003)

[a] Value was calculated in this paper as the residual of reported data in the original work. Liu et al., 2003, data from one cruise in April–May, 1997. Shen and Liu, 2009, data from two cruises in November 1997 and October 1998 (DN was replaced by DIN, while DP by DIP).

NO_3^-–N and DP in the Longchuanjiang River were much lower than in Changjiang's tributaries. The data however showed that the Longchujiang River was an important source of PAP and NH_4^+–N to the Changjiang River (Table 3). By comparison, NH_4^+–N (148 kg/km^2/yr) was 7-fold higher that the Changjiang in normal non-flood year (20 kg/km^2/yr; 1997) and 1.5 times that during 1986–1988 (105 kg/km^2/yr; Zhang, 1996). NH_4^+–N was comparable to the measurements in the disaster flood year (161 kg/km^2/yr in the 1998 flood year) (Table 3), which was possibly related to the especially heavy autumn flood in 2008 (Fig. 2) and sewage

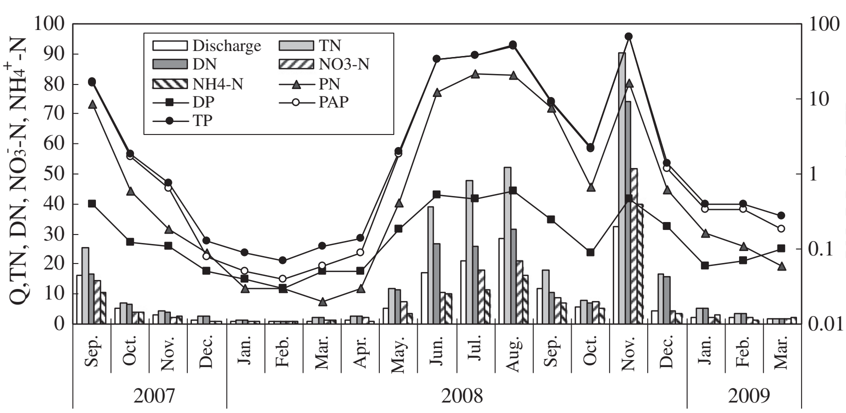

Fig. a. Instantaneous water discharge and nutrient fluxes in the Longchuanjiang River, China (discharge in m^3/s, fluxes in g/s; all the N and P species fluxes showed strong correlations with water discharge ($R^2 > 0.8$, $p < 0.01$)).

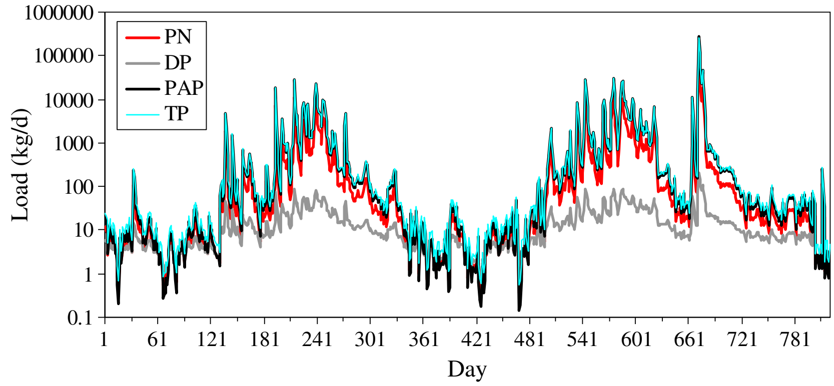

Fig. b. Daily fluxes of nutrient variables using extrapolation in the upper Longchuajiang River, China (*X*-axis from January 2007 to March 2009).

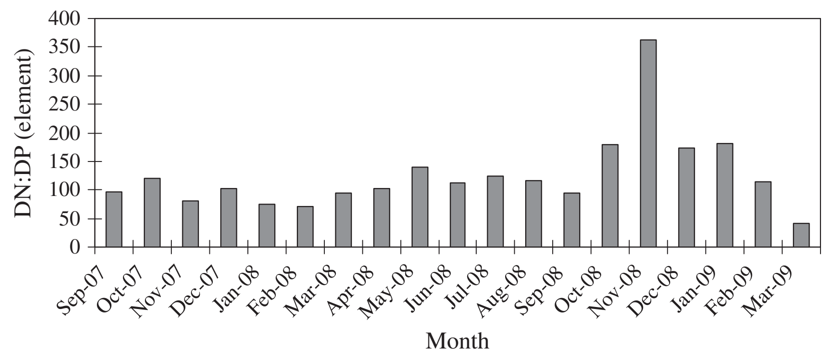

Fig. c. Seasonal element variability in DN:DP in the Longchuanjiang River, China.

discharges from adjacent Chuxiong county in the upper catchment. However, the areal export rate of NO_3^-–N was generally smaller than the average in the Changjiang (Table 3; 420 kg/km^2/yr during 1980–1981) (Edmond et al., 1985), and only comparable to 237 kg/km^2/yr during 1985–1988 (Zhang, 1999). Similarly, the areal export rate of DP in the Longchuanjiang River (3.9 kg/km^2/yr) was substantially lower than the values previously reported on the Changjiang River (9 kg/km^2/yr, Zhang, 1996; 12.6 kg/km^2/yr, Shen and Liu, 2009; 15.8 kg/km^2/yr, Liu et al., 2003; 21.1 kg/km^2/yr, Edmond et al., 1985).

5.4. Data quality

For the variables strongly associated with water discharge the extrapolation method yielded nearly a twofold higher estimate of annual fluxes than interpolation method (Table 1). Of concern is that most estimates of nutrient fluxes on large rivers in the area are based on only a limited number of samples, thus assumption of a constant nutrient concentration in a long time was needed (i.e., Duan et al., 2000, 2008; Shen et al., 2003; Shen and Liu, 2009). Inadequate sampling may be one reason for the great disparity in annual nutrient export estimates for the Changjiang River and tributaries (Table 3). Moreover, many studies have collected samples from a stationary depth (i.e., not depth integrated, often from a water depth of 50 cm) and from one single point, often in the centerline of the river. Such sampling was probably not accurate for estimating particulate concentrations because of vertical distribution of suspended sediment. These methodological errors could also produce, in part, substantial errors in the calculation of PN and PAP yields (Table 3). These potential flaws in previous sampling methodology which was driven by convenience and budget restrictions need to be recognized. Thus, there is an urgent need for new sampling programs to include high-temporal-resolution measurements (daily) in the estimation of annual loads of dissolved and particulate constituents.

6. Conclusion

Dissolved N and particle-associated P were the major forms of nitrogen and phosphorus in the Longchuanjiang River. Particulate nitrogen and phosphorus loads showed remarkable seasonality because of the high correlations between measured concentrations and stream discharge. In contrast, dissolved N and P variables displayed less seasonality. Annual TN and TP loads were 981 and 1087 Mg/yr, which is equivalent to about 549 and 608 kg/km^2/yr, indicating the importance of the Longchuanjiang River as a potential source N and P entering the Changjiang River, for which estimated yields are 141–5303 kg/km^2/yr and 7–85 kg/km^2/yr, respectively. The concentrations of TN, NH_4^+–N and TP were much higher in the Longchuanjiang River than in the Changjiang River and its tributaries, and the high element ratios of DN:DP suggested potential P limitation for phytoplankton growth, which was similar to the Changjiang River. Furthermore, they exceeded the limits for use for domestic or recreational purposes by Chinese standards. The relatively high P and N loads portend the potential for algal bloom formation in sections of the river now changing into cascades of reservoirs, as a result of development hydroelectric facilities. Better estimates of annual loads/fluxes N and P variables could have been improved with more frequent sampling-for example, daily instead of monthly, particularly for particulate variables and/or during the high-flow period. Finally, our difficulties in obtaining accurate estimates call to question the accurateness of the estimates of most other sampling programs in the region.

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Appendix A

See Figs. a–c and Table A1.

Table A1
Maximum limits for several grades of water usage in China (GB3838-2002; CSEPB, 2002b). Median measured NH_4^+–N, TN, and TP concentrations (*n* = 19) were 0.77, 1.8, and 0.32, respectively.

Variables	Grade I	Grade II	Grade III	Grade IV	Grade V
NH_4^+–N (mg/l)	0.15	0.5	1	1.5	2
TN (mg/l)	0.2	0.5	1	1.5	2
TP (mg/l)	0.02	0.1	0.2	0.3	0.4

Grade I: Clean water from headwater and national conservation area that can be used for domestic purposes after simple disinfecting, for recreational purposes and irrigation.
Grade II: Fairly clean water that can be used as domestic water after treatment, for recreational purposes, for fish farming etc, and the area is strictly protected.
Grade III: Water also can be used for domestic, recreational purposes after suitable treatment.
Grade IV: Polluted water which can only be used as industrial water after treatment.
Grade V: Heavily polluted water that should not be used at all.

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