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Impoundment-induced nitrogen–phosphorus imbalance in cascade reservoirs alleviated by input of anthropogenic nutrients

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ABSTRACT

The ratio of nitrogen to phosphorus (N:P) is an important variable that has a close relationship with the ecological problems of nuisance algal blooms and eutrophication in aquatic environments in terms of nutrient limitation. Reservoirs generally have much higher retention efficiency for P than for N. This inherent dissimilarity in the N and P biogeochemical cycles likely results in N–P stoichiometric imbalance in downstream rivers and reservoirs, consequently causing an increase in the N:P ratio and aggravating P limitation. Here we determined the total N (TN) and total P (TP) concentrations in the cascade reservoirs of the Wujiang River and Lancangjiang River basins. The results show that TN:TP ratios in these 2 basins exhibited a common inverted V-shaped (\wedge) pattern downstream. We found that P is not only retained by reservoirs more efficiently than N but is also replenished at faster rates than N given anthropogenic impacts; consequently, the N–P imbalance caused by these impoundments is alleviated within a short distance downstream because of inputs of anthropogenic nutrients. Our research suggests that construction of cascade reservoirs does not necessarily lead to strict P deficiency and anomalously high N:P ratios downstream.

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cascade reservoirs; Lancangjiang River; N–P imbalance; nutrient retention; TN:TP ratio; Wujiang River


Introduction

Rivers and lakes receive, retain, and export carbon, nitrogen (N), phosphorus (P), and silicon (Si) at disparate rates (Grantz et al. 2014). Recently, many case studies (Humborg et al. 1997, Teodoru and Wehrli 2005, Vanni et al. 2011, Burford et al. 2012, Powers et al. 2013, 2015) and models (Alexander et al. 2008, Harrison et al. 2009) have focused on the differences in retention among N, P, and Si by impoundments, which has potentially profound influences on the ecology, environment, and water quality in downstream waters.

The stoichiometric ratio between N and P (N:P) is one of the most important factors influencing aquatic ecology (Guildford and Hecky 2000, Ptacnik et al. 2010). Human activities and natural processes can alter the balance of N and P cycling in aquatic ecosystems (Yan et al. 2016). With respect to nutrient sources, lake TN:TP ratios often reflect the sources of nutrients (Downing and McCauley 1992). Natural, undisturbed catchments export much less P than N, causing high TN:TP in oligotrophic lakes. Eutrophic lakes generally receive various source of nutrients with lower average TN:TP (Downing and McCauley 1992). Vanni et al. (2011) found that the

rates and ratios at which catchments export nutrients were strongly influenced by land use practices, and that nutrient export in waters from agricultural catchments generally had high TN:TP ratios (140) compared with those from forested and mixed-used catchments (18 and 54, respectively). Nutrient export from urban sewage, agricultural discharges, and animal slurries generally has low a TN:TP ratio (Yan et al. 2016). The modeling results of Alexander et al. (2008) showed that in agricultural sources, corn and soybean cultivation was the largest contributor to catchment N export, but P originated primarily from animal manure on pasture and rangelands. Regarding transport processes of nutrients, Green and Finlay (2010) found that at seasonal time scales, stream water TN:TP ratios were negatively correlated with discharge in semiarid climates and positively correlated with discharge in humid climates, whereas during over-ground storm events, TN:TP ratios decreased with increasing discharge across all catchment types. This information agrees with findings of Correl et al. (1999) that the lowest TN:TP ratios occurred during the largest storms. These observations demonstrate the importance of physical controls of TN:TP ratios in stream waters.

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In addition to sources and transport of nutrients, in-lake biogeochemical processes are another important factor causing N–P stoichiometric imbalance. In general, TN:TP is 2–5 times higher in reservoir output than in catchment input (Cook et al. 2010, Vanni et al. 2011, Grantz et al. 2014), indicating that reservoirs retain P more efficiently than N. Numerous similar studies in other reservoirs (e.g., Alexander et al. 2008, Bosch et al. 2009, Burford et al. 2012) support this finding. Accordingly, P deficiency and the TN:TP ratio would likely increase progressively from stage to stage because of the cumulative effect produced by cascade reservoirs, indicating that the N–P imbalance would be magnified downstream in the lower reaches of a basin. Atmospheric N deposition (Elser et al. 2009) and human-induced N inputs (Peñuelas et al. 2013) can potentially result in additional increases in TN:TP ratios in some areas, aggravating N–P imbalances. Retention of N and P in lakes and reservoirs can decrease nutrient concentrations in waters and therefore might have a positive effect on eutrophication. Interactions between N and P in waters are complex, however, and the removal of N and P are associated with each other (Finlay et al. 2013). Large N–P imbalances resulting from nutrient retention will substantially influence aquatic ecology (Ptacnik et al. 2010) and N removal (Finlay et al. 2013) in the downstream waters of the reservoir. Therefore, understanding sources and transport of both N and P and their complex interactions is needed to develop effective nutrient management plans (Alexander et al. 2008). Previous studies of N and P retention have focused on single systems, and few have provided information for connected rivers and cascade reservoirs. In this study, we examined TN and TP concentrations and the TN:TP stoichiometric ratio in 2 river basins with well-developed cascade hydroelectric dams. The objective of this study was to determine how a cascading reservoir system affects TN:TP ratios. Given the evidence that reservoirs retain P more efficiently than N, we expected that reservoirs would cause the TN:TP ratio to increase progressively down a cascade.

Materials and methods

Study basins and reservoirs

The Wujiang River basin (25°56′–30°01′N, 105°09′–109°2′E) is located in the Guizhou karst plateau of southwestern China (Fig. 1). The catchment is about 700 km long, 120 km wide, and runs from southwest to northeast at an elevation of 700–2400 m a.s.l. Permian and Triassic age limestones and dolomites dominate the bedrock. The catchment is characterized by

well-developed karst landforms, steep-sloped valleys and gorges, and is sparsely vegetated (mainly with shrubs and limited broadleaf and coniferous forests). A subtropical, monsoon climate prevails, with a mean annual temperature of 14 °C and a mean annual precipitation of 1195 mm in the basin.

In the Guizhou section of the Wujiang River basin, the total human population reaches >23 million, including an urban population of ~6.4 million. Discharges of domestic sewage and chemical fertilizer are important sources of nutrients to receiving waters. In addition, this catchment is well known for the large reserve of high-quality phosphate, and its subsequent mining leads to high export of P into surface waters.

The Lancangjiang River originates in the Tibetan Plateau in southwestern China, flowing southward through Qinghai, Tibet, and Yunnan and then out of China (Fig. 1). After flowing out of China, the river is called the Mekong River and flows through Myanmar, Laos, Thailand, Cambodia, and Vietnam, and finally to the South China Sea. The Lancangjiang River is 2161 km long with a mean annual runoff of $760 \times 10^8 \text{ m}^3$ and a catchment area of $16.7 \times 10^4 \text{ km}^2$ (within China).

The Lancangjiang River basin (93°40′–101°50′E, 21°45′–33°45′N) spans a latitude range of 12° from north to south (Fig. 1c). The Yunnan section of the catchment is characterized by a landscape of steep mountains and deep and narrow gorges. The catchment has variable climatic conditions due to the large differences in longitudinal and elevation. The western Yunnan region along the middle reaches of the Lancangjiang River is subtropical with a mean annual temperature of 12–15 °C and annual precipitation of 1000–2500 mm. The southwestern Yunnan region along the lower reaches of the Lancangjiang River is subtropical to tropical, with a mean annual temperature of 15–22 °C and annual precipitation of 1000–3000 mm. The whole river basin has a southwestern monsoon climate. Precipitation is concentrated from June to August (>60%). Rainstorms occur mostly in July and August, with the most intense rainfall occurring in the middle river reaches.

The Wujiang and Lancangjiang rivers are both important hydropower bases of China. From the upper to lower reaches of the main stream of the Wujiang River, 11 cascade reservoirs have been constructed (Fig. 1b, Table 1): Hongjiadu (HJD), Puding (PD), Yingzidu (YZD), Dongfeng (DF), Suofengying (SFY), Wujiangdu (WJD), Goupitan (GPT), Silin (SL), Shatuo (ST), Pengshui (PS), and Yinpan (YP). In the Yunnan section of the Lancangjiang River, 6 cascade hydropower stations have been constructed from the middle to lower reaches: Gongguoqiao (GGQ), Xiaowan (XW), Manwan (MW), Dachaoshan (DCS),

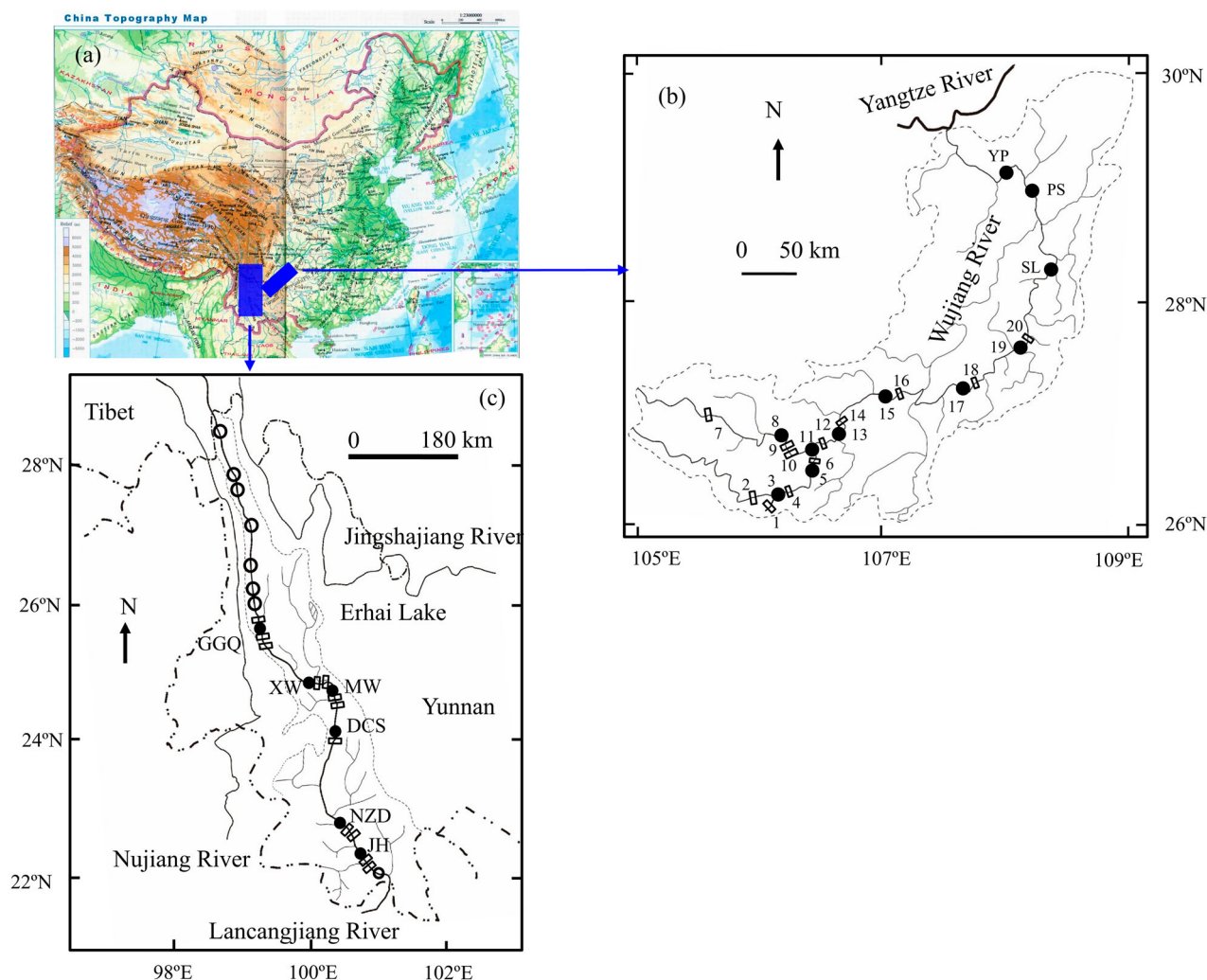


Figure 1. Location of study sites in (a) China, (b) the Wujiang River basin, and (c) the Yunnan section of the Lancangjiang River basin. Broken lines represent basin boundaries, open rectangles denote river sampling sites, open circles denote planned reservoir, and filled circles represent constructed reservoirs. Sampled sites (b) in the Wujiang River basin are labeled with numbers (4 = PD; 5 = YZD; 8 = HJD; 11 = DF; 13 = SFY; 15 = WJD; 17 = GPT; 19 = SL). See Tables 1 and 2 for full names of reservoirs.

Nuozhadu (NZD), and Jinghong (JH) (Fig. 1c, Table 2). Eight others in the upper reaches are under construction (Fig. 1c, Table 2). These reservoirs are narrow, deep, and gorge-shaped with various residence times of water (Tables 1, 2).

Sampling

In this study, reservoir water samples were collected with Niskin samplers at different depths in 8 mainstream reservoirs in the upper and middle reaches of the Wujiang River (Fig. 1b) in September 2013, July 2014, June 2015, and January 2016. The vertical intervals for reservoir water samples ranged from 3 to 30 m based on the vertical variation gradients of hydrochemical parameters (e.g., temperature, and pH). Samples from inflowing rivers and outflowing waters were also collected. Sampling in the Lancangjiang River catchment

was performed in the middle-lower reaches in September 2016 because many reservoirs in the upper-middle reaches are under construction (Fig. 1c).

Analysis

Samples for TN and TP measurement were acidified with concentrated sulfuric acid to a pH of <2 and then stored at low temperature. In the laboratory, TN and TP measurements were completed within 2 weeks. TN was measured with an ultraviolet spectrophotometer (UV 9100, Beijing LabTech Instruments Co.) after digestion with potassium persulfate at 120 °C. The lower limit of detection for this method is 0.05 mg L⁻¹ and the upper limit is 4 mg L⁻¹. TP was determined by digestion of whole-water samples followed by the ammonium molybdate spectrophotometric method to measure phosphate (Vanni et al. 2011). This method has a lower limit of

Table 1. Summary characteristics of 8 reservoirs in the upper and middle reaches of the Wujiang River basin.

Reservoir name	Longitude	Latitude	Catchment area (km ²)	Water flow (m ³ s ⁻¹)	Water level (m)	Surface area (km ²)	Volume (×10 ⁸ m ³)	Height of dam (m)	Water residence time (d)	Impounding time (year)
Puding (PD)	105°48.3′	26°22.7′	5871	114	1145	20.6	4.21	75	40.6	1994
Yinzidu (YZD)	106°8.6′	26° 34.5′	6425	152	1088	13.9	5.43	129	41.3	2004
Hongjiadu (HJD)	105°51.6′	26°54.3′	9900	155	1140	80.5	49.25	179	368.8	2004
Dongfeng (DF)	106°9.4′	26°51.2′	18 161	345	970	19.1	8.63	162	28.1	1994
Suofengyin (SFY)	106°22.5′	26°57.6′	21 862	427	835	5.7	1.57	116	4.3	2005
Wujiangdu (WJD)	106°54.4′	26°18.9′	27 790	502	760	47.8	21.40	168	49.3	1979
Goupitan (GPT)	107°37.6′	27°22.8′	43 250	717	630	57.6	55.64	233	89.8	2011
Silin (SL)	108°10.8′	27°47.9′	48 558	849	440	38.4	12.05	117	19.4	2007

detection of 0.01 mg L⁻¹ and an upper limit of 0.6 mg L⁻¹. Dilution was first performed for samples with concentrations of TN and TP that exceeded the upper limits of the analytical methods.

Results

TN and TP concentrations in the cascade reservoirs in the Wujiang River basin

The TN concentrations in the mainstream reservoirs in the Wujiang River basin ranged from 1 to 6 mg L⁻¹ (Fig. 2a–d), with large differences in different reservoirs. As a whole, TN concentrations in the reservoirs in the upper reaches were higher than those in the lower reaches. This trend was clear in the results obtained in September 2013 (Fig. 2a): reservoirs PD, YZD, and HJD, all headwater reservoirs in the upper reaches, had high TN concentrations, followed by reservoirs DF and SFY in the middle reaches, and reservoirs WJD and GPT in the lower reaches. Similar scenarios occurred in July 2014 (Fig. 2b), June 2015 (Fig. 2c), and January 2016 (Fig. 2d). TN concentrations were variable throughout the water column but generally increased with depth. Despite vertical differences in TN concentrations at different times (Fig. 2a–d), the sampling interval-weighted average TN concentrations still displayed similar patterns, that TN concentrations in the upper reservoirs were 1.2–3.1 times higher than those in the lower reservoirs (Fig. 3a).

The lowest concentration of TN in the reservoirs occurred in September 2013 (Fig. 3a). The weighted average TN concentrations ranged from 0.88 to 2.67 mg L⁻¹ in 7 of the reservoirs sampled, with an overall mean of 1.92 mg L⁻¹ (Fig. 3a). By comparison, the weighted average TN concentrations for these reservoirs in July 2014, June 2015, and January 2016 ranged from 3.51 to 4.80, 3.24 to 4.51, and 3.13 to 3.78 mg L⁻¹, respectively, and the overall means were 3.91 (6 reservoirs), 3.85 (7 reservoirs), and 3.49 mg L⁻¹ (7 reservoirs), respectively (Fig. 3a). The peak TN concentration occurred in July 2014, after which TN concentrations

exhibited a descending trend, especially in the upper reservoirs.

The TP concentrations in the mainstream reservoirs in the Wujiang River basin were generally <60 µg L⁻¹, except for reservoirs GPT and SL (in the lower reaches), where TP concentrations were relatively high (Fig. 2e–h). The only exception occurred in reservoir PD in July 2014 (Fig. 2f). This particular sampling was performed after a rainstorm, so that high TP concentrations occurred in the headwater reservoir, inflowing water, and outflowing water. The spatial variation in TP concentrations differed greatly among the reservoirs from the upper to lower reaches, exhibiting an approximately U-shaped distribution (Fig. 3b). The TP concentrations decreased downstream in the upper reaches to those in the middle reaches, and increased from the reservoirs in the middle reaches to those in the lower reaches.

TN and TP concentrations in the cascade reservoirs in the Lancangjiang River basin

The TN concentrations in the mainstream reservoirs in the Lancangjiang River basin were low, generally <1.5 mg L⁻¹ (Fig. 4a and d). In the relatively shallow reservoirs MW (40 m) and JH (30 m), TN concentrations increased in the near surface (Fig. 4a), likely due to the addition of N from run-off. By contrast, in the relatively deep reservoirs XW (160 m) and NZD (>200 m), TN concentrations decreased slightly in the surface water.

The TP concentrations in the reservoirs in the Lancangjiang River basin were <60 µg L⁻¹, except in reservoir JH in the lower reaches where the TP concentrations were >60 µg L⁻¹ (Fig. 4b and e). The shallow reservoirs (MW and JH) showed similar vertical patterns of TN, TP, and the molar TN:TP ratio (Fig. 4d–f). The deeper reservoirs (XW and NZD) showed contrasting patterns of TN and TP by depth (Fig. 4a–c). TN and TP displayed reverse patterns of variation at the 2 deeper reservoirs (Fig. 4a–b).

At a catchment scale, TN and TP concentrations varied appreciably along the river from the upper to lower reaches (Fig. 5a–b). From reservoirs GGQ through

Table 2. Summary characteristics of the reservoirs in the Yunan section of the Lancangjiang River ordered from upstream to downstream.

Step of cascade	Reservoir name	Longitude	Latitude	Catchment area (km ²)	Water flow (m ³ s ⁻¹)	Water level (m)	Surface area (km ²)	Volume (×10 ⁸ m ³)	height of dam (m)	Water residence time (d)	Impounding time (year)
1st	Gushui (GS)	98°45.4'	28°36.3'			2265		15.39	242		Under construction
2nd	Wulonglong((WLL)	98°54.6'	27°59.2'	85 900	743	1906		2.72		4.3	Under construction
3rd	Lidi (LD)	99°2.2'	27°49.5'	86 400	763	1818		0.75		1.1	Under construction
4th	Tuoba (TB)	99°4.8'	27°14.1'	88 700	822	1735		10.39	158	14.6	Under construction
5th	Huangdeng (HD)	99°7.7'	26°34.3'	91 900	901	1619		15.49	203	20.0	Under construction
6th	Dahuaqiao (DHQ)	99°8.7'	26° 21.8'	92 600	925	1477		2.62		3.3	Under construction
7th	Miaowei(MiW)	99°8.7'	25°53.1'	93 900	960	1408		6.60	140	8.0	2015
8th	Gongguoqiao (GGQ)	99°19.7'	25°35.5'	97 200	1010	1307		3.16	105	3.6	2011
9th	Xiaowan (XW)	100°8.7'	24°46.4'	113 300	1210	1240	181.1	150.00	295	143.0	2004
10th	Manwan (MW)	100°25.5'	24°40.3'	114 500	1230	994	23.9	9.20	132	8.7	1995
11th	Dachaoshan (DCS)	100°22.0'	24°3.9'	121 000	1330	899		9.40	111	8.2	1997
12th	Nuozhadu (NZD)	100°23.1'	22°40.3'	144 700	1730	812	320.0	217.49	262	145.6	2011
13th	Jinghong (JH)	100°46.3'	22°5.3'	149 100	1830	602	32.8	11.39	108	7.2	2008
14th	Ganlanba (GLB)	100°59.6'	21°51.1'			539	10.5		60		Under construction

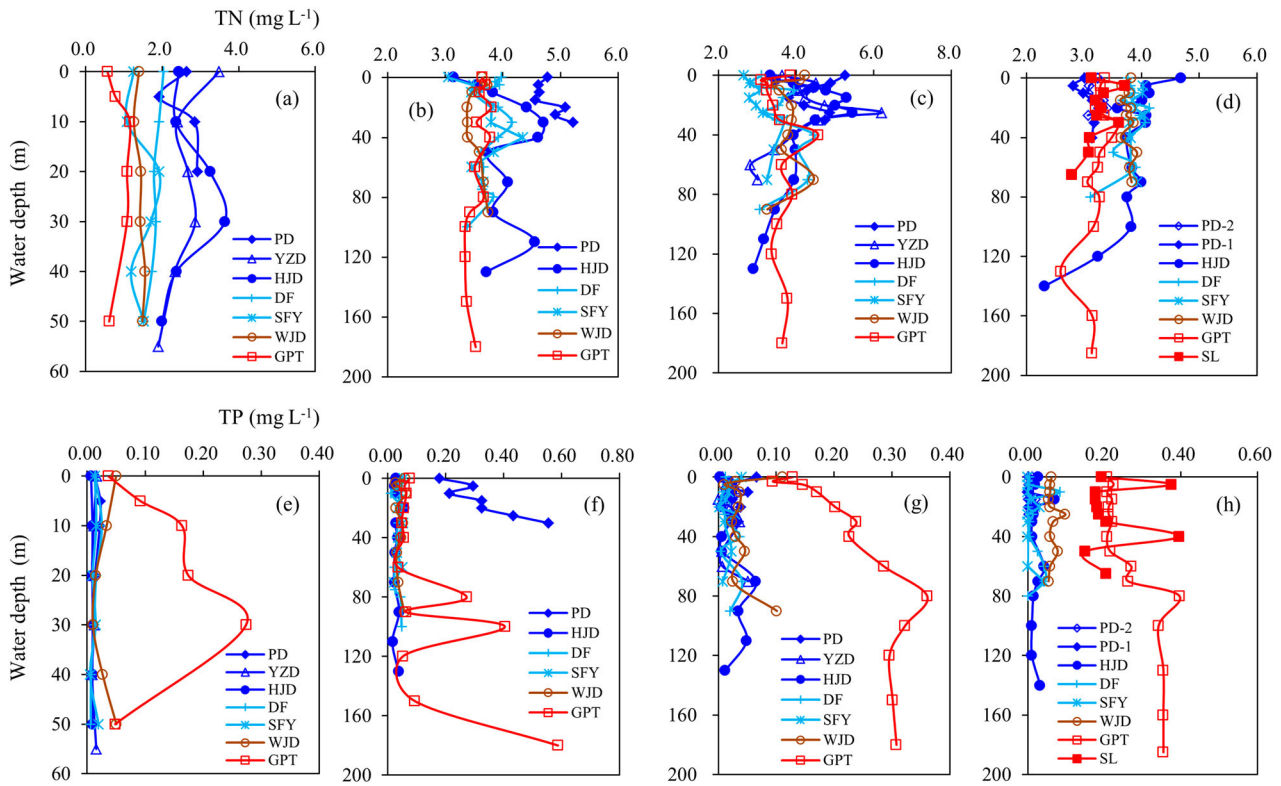


Figure 2. Depth profiles of TN (top) and TP (bottom) concentrations in reservoir water columns of the Wujiang River hydro cascade. Profiles were measured in (a and e) September 2013, (b and f) July 2014, (c and g) June 2015, and (d and h) January 2016. Reservoirs are consistently ordered from upstream (blue) to downstream (red) in all legends. See Table 1 for reservoir names.

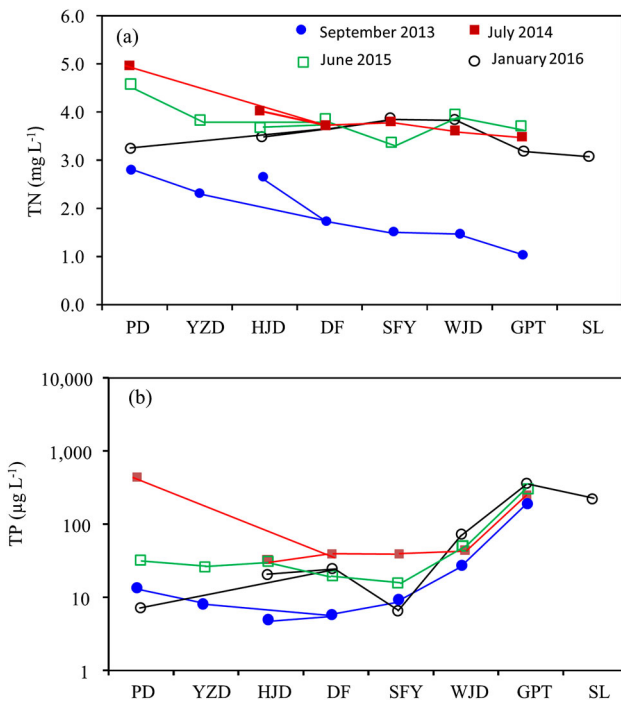


Figure 3. Variations of (a) TN and (b) TP concentrations from the upper to middle reaches of the Wujiang River. Samples were collected in September 2013 (blue filled circles), July 2014 (red filled squares), June 2015 (green open squares), and January 2016 (black open circles). See Table 1 for reservoir names.

reservoirs XW and MW, TN and TP concentrations increased considerably, indicating that N and P inputs increased along the river from the upper to lower reaches. Farther downstream to reservoir NZD, both TN and TP concentration decreased. From reservoir NZD to JH, TN and TP concentrations increased appreciably.

Variations in TN:TP ratio in the cascade reservoirs in two river basins

In reservoirs in both river basins, the TN:TP ratios from the upper to lower reaches commonly exhibited an inverted V-shaped pattern (\wedge) (Fig. 6). On most sampling occasions, the TN:TP ratios first increased downstream from the upper reaches, reached a peak in a reservoir in the middle reaches, and finally decreased in the lower reaches (Fig. 6). The TN:TP ratios in the reservoir in the lower reaches were even lower than that in the headwater reservoir. In the Wujiang River basin, the interannual variations in the TN:TP ratios in the reservoirs in the upper reaches had a large range (25–1230), but the TN:TP ratio ranges for the reservoirs in the lower reaches were much smaller (Fig. 6a). The range of TN:TP ratio was relatively small (25–80)

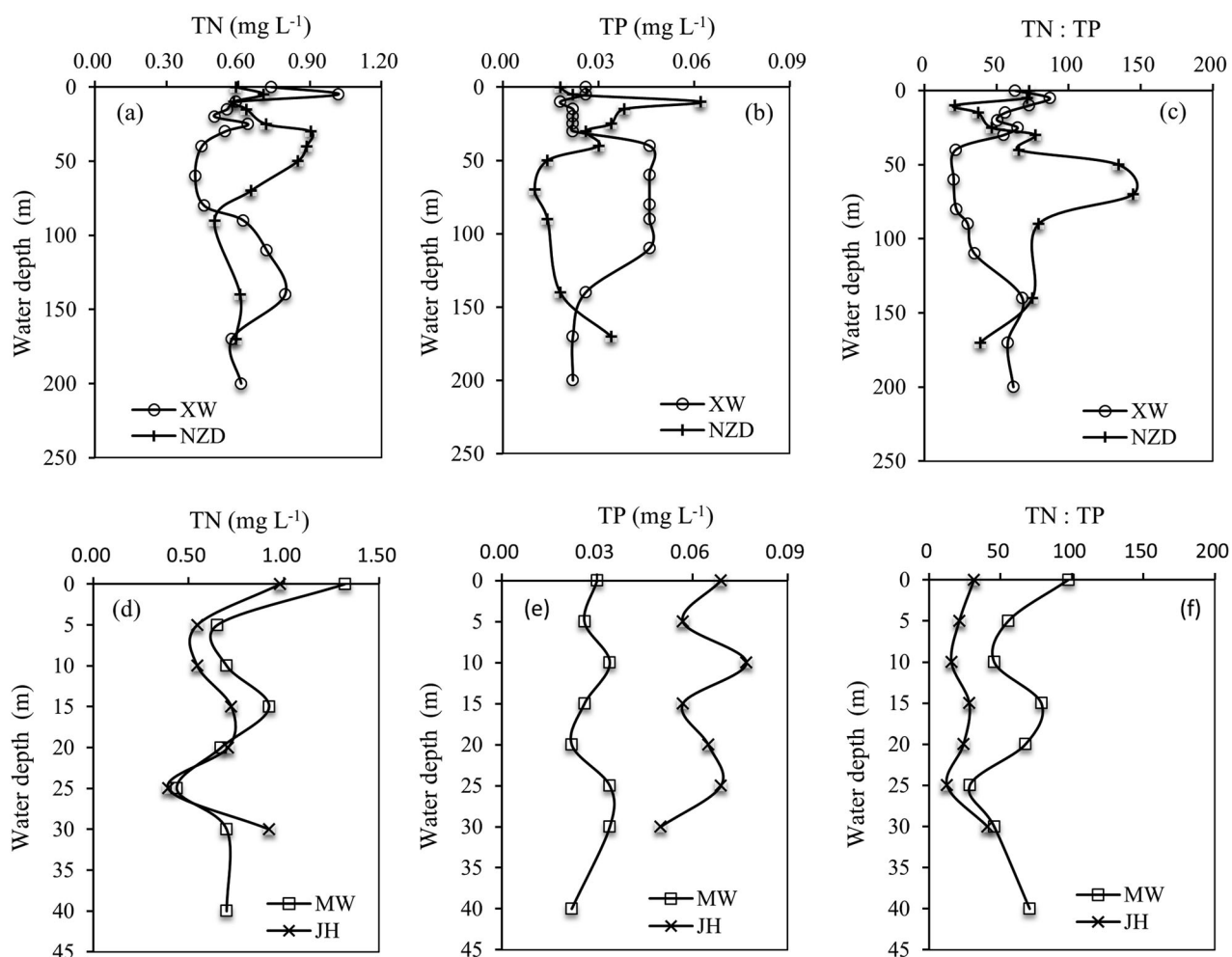


Figure 4. Vertical variation of TN, TP, and the molar TN:TP ratio in the water columns of relatively deep reservoirs XW and NZD (top) and relatively shallow reservoirs MW and JH (bottom) in the Lancangjiang River basin. See Table 2 for reservoir names.

among reservoirs in the Lancangjiang basin (Fig. 6b). From reservoirs XW to NZD in the upper reaches, the TN:TP ratios increased from 40 to 70 and then decreased to 26 in reservoir JH in the lower reaches (Fig. 6b). A comparison suggests that TN:TP ratios differed greatly between the 2 river basins, but they shared a common inverted V-shaped pattern (Fig. 6a–b).

Discussion

Influences of human activities and natural factors on N and P inputs in river basins

Anthropogenic activities are the main factors controlling the inputs of N and P into the 2 studied river basins. The high concentrations of TN in the Wujiang River basin are spatially consistent with the high population density in this area. The population density in the Wujiang River basin ranges from 300 to 400 people per square kilometer, the highest in the Guizhou Province (Zhang et al. 2013). A similar situation occurs in the

Lancangjiang River basin. The TN and TP concentrations increased sharply in reservoirs XW and MW and then decreased slightly in reservoir NZD reservoir (Fig. 5), which corresponds with the spatial population distribution in the Lancangjiang River basin. The population density in some subcatchments (e.g., Erhai Lake catchment) in the middle reaches of the Lancangjiang River basin reached the highest value of 300–400 people per square kilometer (Xu et al. 2003, You et al. 2014). The increase in TN and TP concentrations in reservoir JH (Fig. 5) were also attributed to nutrient inputs from human activities. In the lower reaches of the Lancangjiang River basin, which has a high urbanization rate and per capita gross domestic product (Huang and Yang 2015), most of the population is concentrated in small towns along tributaries. Domestic sewage and chemical fertilizers used in agricultural fields are the main sources of nutrients exported into these waters. As a result, P is the primary pollutant degrading water quality in this region (Chen 1999).

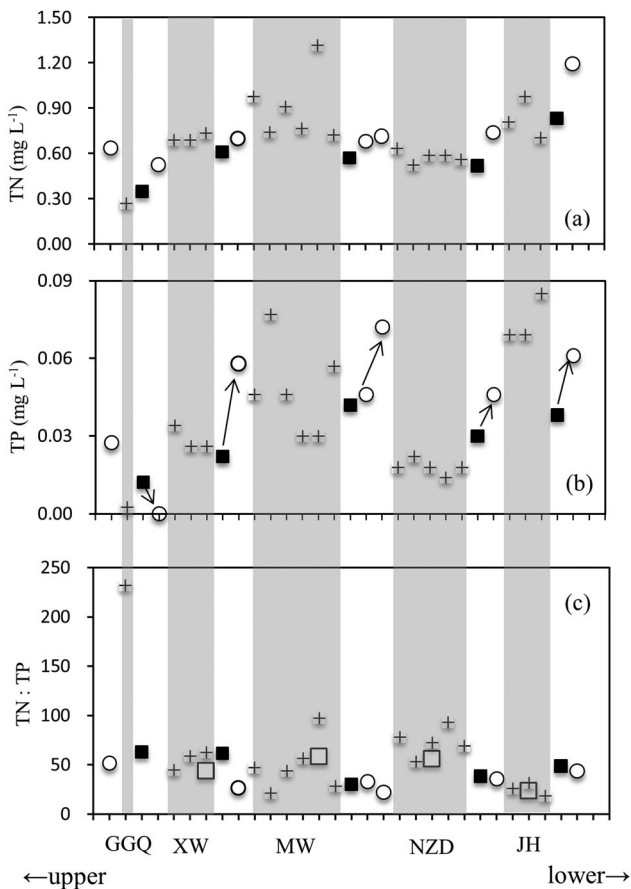


Figure 5. Variation in concentrations of (a) TN, (b) TP, and (c) the molar TN:TP ratio from the middle to lower reaches of the Lancangjiang River basin. Crosses denote reservoir surface waters, open circles denote river waters, filled squares denote water samples from out of dam turbines, and open squares denote vertically weighted averages for reservoirs. Arrows highlight the changes of TN and TP concentrations downstream from the outflow to river waters. Note that the sampling sites of reservoirs are not spaced evenly. TN and TP concentrations and longitude and latitude of all sites are listed in Supplementary Table 1. See Table 2 for reservoir names.

Hydrology is also an important factor influencing influx of nutrients into these waters, (P in particular). P retention in lakes is generally considered a function of areal hydraulic loading rates and hydraulic residence times (e.g., Cook et al. 2010). Hydrological mechanisms are responsible in part for the variations of P concentration in the cascade reservoirs of both river basins. For example, sampling in the Wujiang River basin in July 2014 was conducted after a rainstorm, and as a result of increased erosion caused by the storm, TP concentrations in the headwater reservoir (PD) and the inflow and outflow were 2 orders of magnitude higher than those at other times (Fig. 3b). By comparison, the difference in TN concentration at different sampling times was much smaller (Fig. 3a). A similar scenario existed in the Lancangjiang River basin where the TP concentrations in

samples from reservoir JH collected after a rainstorm were twice those in other reservoirs (Fig. 4e). By comparison, TN concentration differences between reservoirs JH and MW were smaller (Figs 4d–e and 5a–b), indicating that rainstorms have less influence on TN export than on P export. This result agrees with observations reported by Correl et al. (1999) and Green and Finley (2010) that TN:TP ratios declined with discharge during storms. Because the landscape in the 2 river basins consists primarily of steep mountains and deep valleys, especially in the Lancangjiang River basin where the rainstorm frequency is high (Li et al. 2002), the influence of hydrodynamic conditions on catchment export of P is considerable. Ba et al. (2015) found that TP concentrations in reservoirs MW and DCS in 2008 were $<40 \mu\text{g L}^{-1}$ in the nonflood season, but ranged from 70 to $130 \mu\text{g L}^{-1}$ in the flood season from June to August. By contrast, TN concentrations did not display the same seasonal pattern (Ba et al. 2015). These results demonstrate the significant influence of extreme rainstorms on catchment export of P. In addition to these external factors that affect nutrient inputs, in-lake biogeochemical processes influence variation of TN and TP concentrations in the reservoirs. The low concentrations of TN and TP in the surface waters are hypothetically attributed to assimilation, and increases in deep waters are due to subsequent sinking of phytoplankton particles.

Retention of N and P by cascade reservoirs

Reservoirs retain P more efficiently than N (e.g., Burford et al. 2012), and therefore cascade reservoirs may amplify the impoundment-induced N–P imbalances. P retention in reservoirs is a function of hydraulic residence times (Cook et al. 2010). In the Wujiang River basin, the construction of 11 cascade reservoirs has strongly influenced most of the river course, resulting in substantially increased water residence times in the entire basin. N and P transport has become evidently decoupled. Variations in TN and TP concentrations were asynchronous along the river from the upper to lower reaches (Fig. 3a–b). By comparison, relatively long river distances exist between connected cascade reservoirs in the middle–lower reaches of the Lancangjiang River, and TN and TP concentrations exhibited consistent trends (Fig. 5a–b).

The difference in retention efficiencies of N and P is an important factor causing stoichiometric imbalance between N and P in the cascade reservoirs. The estimated retention efficiencies calculated from mass balance show that the retention efficiencies of P in the reservoirs are far higher than those of N. Zhu (2005) found that the retention efficiencies of P and N in reservoir DF in 2005 were 54.7% and 13.5%, respectively. Xiang et al. (2016)

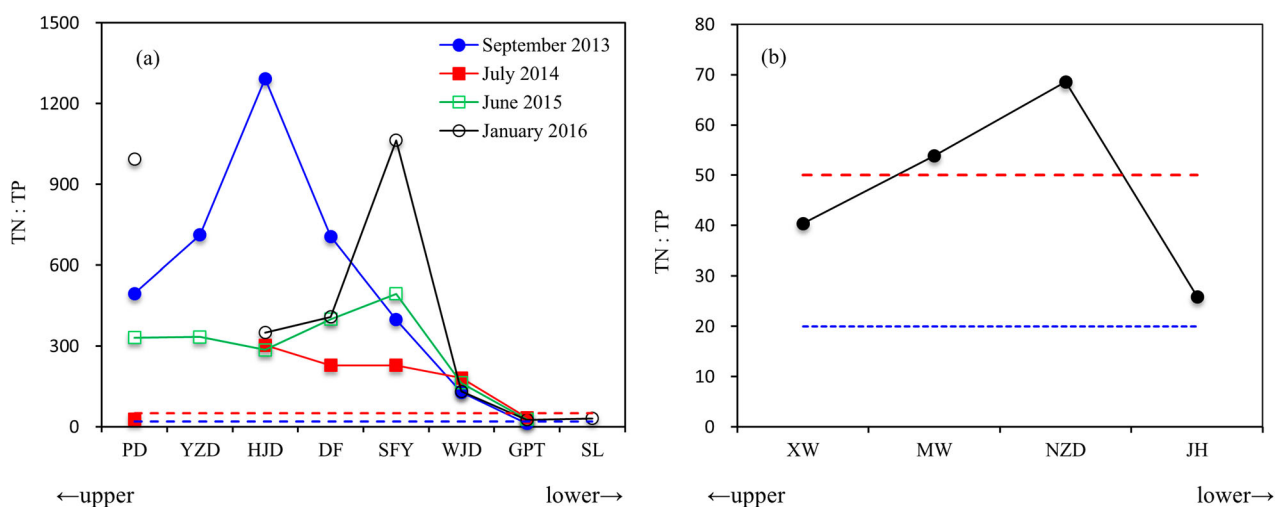


Figure 6. Variation in the molar TN:TP ratio in the cascade reservoirs of (a) the Wujiang River basin and (b) Lancangjiang River basin. Dotted lines represent a TN:TP of 50 (red) and 20 (blue), corresponding to the thresholds for P vs. N limitation respectively (see Ptacnik et al. 2010). See Tables 1 and 2 for reservoir names.

estimated that the retention efficiencies of P and N in reservoir DF were 24.4% and 20%, respectively, in 2013 and 80.5% and 10.9%, respectively, in 2014. In reservoir PD, retention efficiencies of P and N in 2014 were 49.4% and 7%, respectively (Xiang et al. 2016). In the Wujiang River basin, the decreases in TN concentrations between 2 adjacent connected reservoirs ranged from 2% to 13% in different sampling years (Fig. 3a), basically consistent with the retention efficiency of N in the Three Gorges reservoir (2–7%) reported by Zhang and Zhang (2003).

The biogeochemical processes that lead to more efficient P retention than N retention in the cascade reservoirs are related to hydrological, chemical, and physical conditions of the reservoirs and characteristics of N and P. Some 80% of the TP exported from the Wujiang River basin is particulate P (Liu et al. 2009), so P is easily retained by reservoirs due to particle settling. In addition, the mainstream reservoirs in the Wujiang River basin have strong hydraulic flow, and therefore the bottom of the hypolimnion is not anaerobic. In aerobic environments, P tends to be adsorbed by oxidized particles and becomes trapped in sediments. Total inorganic P in the sediments of reservoir DF accounts for as much as 81.9% of TP (Yin et al. 2010), thus supporting this scenario. In contrast to P, the high concentration of dissolved oxygen in the bottom (Xiang et al. 2016) hinders denitrification, thus reducing N removal. The similarly high hydraulic flow in Lancangjiang River suggests that similar mechanisms are responsible for the higher retention efficiency of P than that of N. Retention might alter the proportions of bioavailable forms of nutrient. In Wujiang River, dissolved inorganic nitrogen (NO_3^- and NH_4^+) accounts for >90%

of TN (Song et al. 2014), indicating that N in the river has high bioavailability. Particulate phosphorus (PP) was the main P species (>75%) in the Wujiang River before 2008 (Cao et al. 2008); however the proportion of PP has decreased to 27%, and the amount of dissolved phosphorus (DP) has exceeded PP in recent years (Song et al. 2014), likely due to the construct of reservoirs that could retain PP at a higher efficiency than DP, which is more bioavailable.

Main factors regulating TN:TP ratios in these reservoirs

The differences in retention rates of N and P in these reservoirs and in replenishment of N and P from various sources regulate TN:TP ratios in both the Wujiang and Lancangjiang river basins. The differences in retention efficiencies of N and P lead to TN:TP ratios increasing in the upper reaches, and the input of anthropogenic nutrients lead to decreasing ratios in the lower reaches, so that the TN:TP ratios exhibit an inverted V-shaped pattern in the whole basin (Fig. 6). Basin hydrology is largely responsible for the wide range of TN:TP ratios in the upper reaches in different years. Combined with reservoir operation, which influences the hydraulics, basin hydrology controls the TN:TP ratio peaks occurring in each reservoir at different sampling times (Fig. 6a). Reservoirs and rivers process N and P in disparate ways and at different rates, thus the construction of a reservoir alters the transport of N and P and N:P ratios. Alexander et al. (2008) found that the in-stream removal rate for TN was 1.4 times greater than that for TP, whereas the reservoir TN removal coefficient was more

than an order of magnitude lower than that for TP. This finding partly explains the differences in TN:TP ratios between river water and reservoir water (Fig. 5c).

Replenishment of N and P can considerably alter TN:TP ratios. Yan et al. (2016) found that on a global scale, P accumulates faster than N in freshwater ecosystems under anthropogenic impacts. To some extent, this finding agrees with previous work, as well as with our observations in the Wujiang and Lancangjiang river basins, that nutrient inputs from anthropogenic sources generally have lower N:P ratios. Anthropogenic activities, including agriculture, industry and urbanization, are generally more intense in lower than in upper reaches of a catchment. Under anthropogenic impacts, catchment export of P occurs more rapidly than N, causing the decline in TN:TP ratios in lower reaches. In particular, P mineral mining and the P chemical industry led to increased P input and sharp decreases in TN:TP ratios in reservoirs WJD, GPT, and SL in the lower reaches of the Wujiang River basin (Figs 3b, 6a). A similar scenario exists in catchments without P mining. For example, in the Lancangjiang River basin, TP concentrations downstream from dam outflows to river waters increased at faster rates than TN concentration (Fig. 5a–b). TP increased about 10-fold (Fig. 5b), whereas TN concentrations doubled (Fig. 5a) in reservoir JH and its outflow compared with concentrations in reservoir NZD. As a result, although differences in retention of N and P by reservoirs increased the TN:TP ratios by 2–5 times, input of anthropogenic nutrients caused the ratios to decrease. We could conclude that P is not only retained more efficiently by reservoirs but is also replenished at a faster rate than N. The N–P imbalance by impoundments may be alleviated over a short distance because of inputs of anthropogenic nutrients. Therefore, construction of cascade reservoirs would not necessarily result in strict P deficiency and anomalously high N:P downstream, despite the cumulative effect.

Conclusions

In the Wujiang and Lancangjiang river basins, anthropogenic activities and natural processes regulate catchment export of N and P into receiving waters. The cascade of reservoirs retain P more efficiently than N, leading to an N–P imbalance and TN:TP ratios that increase by 2–5 times. Intense anthropogenic activities in the lower reaches of the 2 basins result in the replenishment and accumulation of P at faster rates than that of N, causing the TN:TP ratios to decrease to low values. We conclude that the construction of cascade reservoirs will not necessarily cause strict P deficiency and anomalously high N:P in the downstream waters over long distances.

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