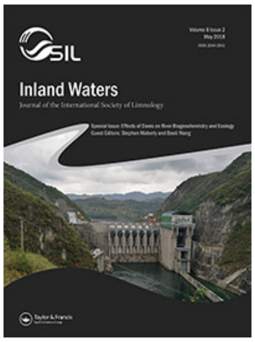

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Sources and key processes controlling particulate organic nitrogen in impounded river–reservoir systems on the Maotiao River, southwest China

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ABSTRACT

The $\delta^{15}N$ of nitrate (NO_3^-) and particulate organic nitrogen (PON) was used to study the sources and fate of nitrogen in the impounded Maotiao River, southwest China. During months when the reservoirs thermally stratified, denitrification was the key process in the hypolimnion in Hongfeng and Baihua reservoirs. Based on the $\delta^{15}N$ of PON and NO_3^-, PON in the epilimnion of reservoirs was dominated by NO_3^- assimilation during stratification. Most $\delta^{15}N$ of PON was higher than that of NO_3^- in the reservoirs in October, indicating that PON in reservoirs was mainly derived from exogenous nitrogen input or denitrification rather than assimilation of NO_3^- in the epilimnion. Relationships between the molar carbon:nitrogen (C:N) ratio and $\delta^{15}N$-PON indicated the main sources of PON in reservoirs were from phytoplankton, produced in inflowing rivers and the reservoir under the joint influence of soil organic matter, denitrification, and exogenous nitrogen inputs. The $\delta^{15}N$ in PON and NO_3^- increased gradually from upstream to downstream, by $8.21 \pm 0.65‰$ and $1.74 \pm 3.66‰$, respectively, suggesting an accumulative effect caused by the downstream waters. Overall, this study provides insight into the nitrogen biogeochemical cycling of river–reservoirs systems using stable nitrogen isotopes and C:N to specify the effects of river impoundment on nitrogen dynamics.

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cascade reservoirs; impounded river; molar C:N; nitrogen isotope; particulate organic nitrogen

Introduction

The nitrogen isotopic composition of particulate organic nitrogen (PON) has been applied to identify the influence of biogeochemical processes, including primary production and nitrogen transformations in aquatic environments (Kendall et al. 2001, Lu et al. 2016, Bardhan et al. 2017). The isotopic composition of PON can also be used to assess the sources and cycling mechanisms of organic matter and to identify microbial processes (Lu et al. 2016). Considerable attention has focused on the utilization of organic nitrogen stable isotopic ratios, in addition to the carbon:nitrogen (C:N) ratio, as natural tracers identifying organic matter provenance in near-shore marine, estuarine, lacustrine, and riverine environments (Maya et al. 2011, Morales et al. 2014, Fadda et al. 2016, Mbaye et al. 2016). In lakes and reservoirs, the isotopic composition of PON is largely governed by isotopic fractionation during uptake by phytoplankton and the isotopic composition of source nutrients. In eutrophic Lake Lugano, the highly depleted ^{15}N of the near-bottom PON indicated the active presence of methanotrophic bacteria during sub-oxic conditions (Lehmann et al. 2004). In the Tillari Reservoir, analysis of $\delta^{15}N$-PON provided insight into the biogeochemistry of reservoirs by establishing the detailed seasonal variation of nitrogen cycling (Bardhan et al. 2017). Seasonal thermal stratification has a major effect on PON dynamics in lakes and reservoirs, especially in July when the stratification is the most intense and in October when stratification starts to break down (Wang et al. 2014, Liu et al. 2017).

China has a large number of natural freshwater lakes as well as man-made reservoirs. Dam construction has obvious major impacts on a river, and a cascade of dams will have an even greater impact. Artificial reservoirs cause changes in hydrology, transparency, and nutrient cycling compared with the original river. As a result, reservoir ecosystems can shift from river-type heterotrophy to lake-type autotrophy. In addition, artificial reservoirs, and hydropower reservoirs in particular, generally release water from the bottom of the reservoir. A water quality discontinuity occurs in the outflowing

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river compared to the inflowing rivers, and changes in nitrogen biogeochemical cycling may also occur, with unknown impacts on the nitrogen species and controlling factors downstream. These changes have not been well documented and are poorly understood.

In this study, 4 reservoirs on the Maotiao River in southwest China were investigated, with the major objectives to (1) understand how PON and nitrogen species are influenced by a series of hydropower dams, (2) assess the effects of these changes on nitrogen cycling, and (3) trace the sources of PON using $\delta^{15}N$ of PON and nitrate (NO_3^-), and the C:N ratio.

Study sites

The Maotiao River, located in the middle of Guizhou province, China, is a southern tributary of the Wujiang River, an important tributary of the Changjiang River (Fig. 1). It has a total length of 180 km, drains a catchment area of 3195 km^2, and has a mean water discharge of 55.9 m^3/s. Karst geology accounts for about 70% of the total drainage area, and water chemistry is controlled by carbonate dissolution under the influence of carbonic and sulfuric acid (Han et al. 2010). The terrain in this area is highly vegetated. The Maotiao River Basin has a subtropical monsoon humid climate, with an annual mean temperature of 13.8 °C and multiyear average annual rainfall of about 1200 mm. Hongfeng reservoir (HFR), Baihua reservoir (BHR), Xiuwen Reservoir (XWR), and Hongyan reservoir (HYR) are situated northwest of Guiyang, the capital of Guizhou province (Fig. 1). These 4 reservoirs are closely connected and were constructed on the mainstream of the Maotiao River in 1959, 1965, 1961, and 1974, respectively. The Maotiao River receives a large number of exogenous nitrogen inputs, including from agricultural and industrial zones, and inputs from fish-culturing in cages within the reservoirs. Currently, HFR and BHR are in a state of eutrophication, which could easily lead to anoxic conditions in their hypoliminia. The main hydrological features of these reservoirs are listed in Table 1.

Methods

Water sampling on the Maotiao River system was conducted in July and October 2007 in tributaries, mainstream rivers, water columns in reservoirs, and downstream of the dam (Fig. 1). Based on a previous study on these reservoirs, July is when thermal stratification is most intense and October is when destratification begins (Liu et al. 2017). Samples from water columns in the reservoirs were collected at the deepest site, generally 0.4–0.5 km upstream from the dam. Samples downstream of the dams were collected 0.5 m under the

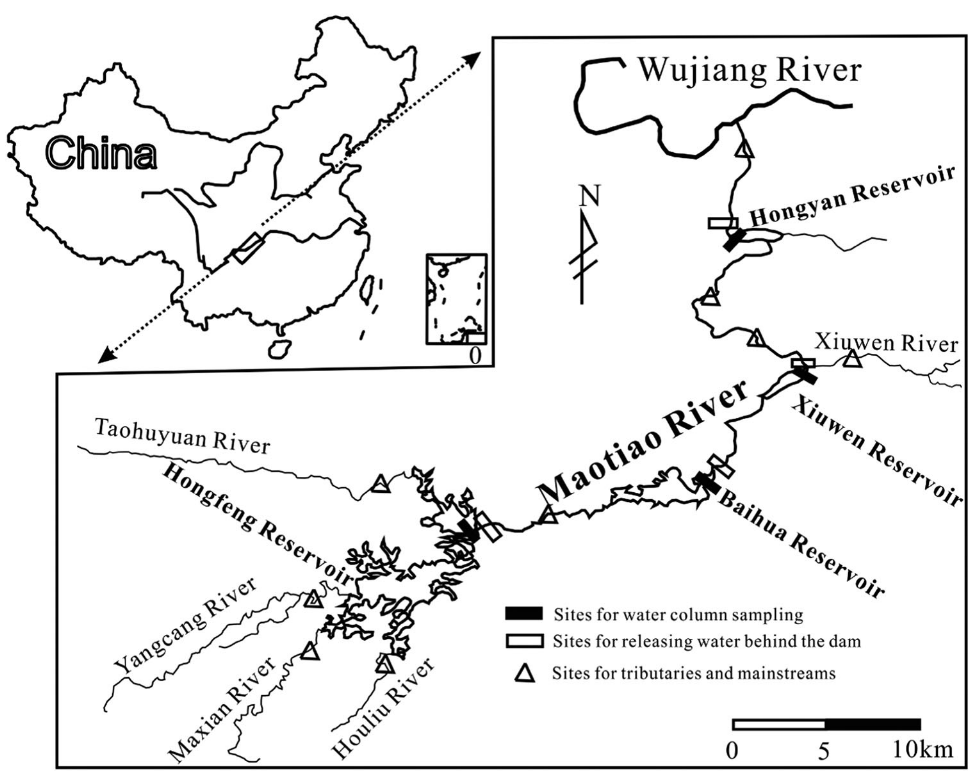

Figure 1. Location of sampling sites along the Maotiao River, China.

Table 1. Hydrological features of the 4 studied reservoirs.

Reservoir	Drainage area (km^2)	Average flow (m^3/s)	Average annual precipitation (mm)	Total volume ($10^8 m^3$)	Height of dam (m)	Residence time (d)	Impounded year
Hongfeng	1596	29	1585	7.53	54	300.5	1959
Baihua	1895	35	1362	2.21	50	73.1	1965
Xiuwen	2145	39	1230	0.114	49	3.4	1961
Hongyan	2792	48	1108	0.304	60	7.3	1974

water surface and samples along the water column at depths of 0.5, 3, 6, 10, 15, and 25 m (not available in July in HFR) in the reservoir using a Niskin bottle. For the tributaries and mainstream, water samples were taken 0.5 m under water surface in the middle of the river.

Water temperature (T), pH, dissolved oxygen (DO), and chlorophyll levels were measured *in situ* using an automated multiparameter monitoring instrument (YSI 6600 v2). A known volume of water was filtered through 0.70 μm precombusted (600 °C) Whatman GF/F filters. Samples for NO_3^- and ammonium (NH_4^+) analysis were acidified by addition of H_2SO_4 (pH < 2), and samples for NO_3^- isotope analysis were acidified with HCl (6N, final pH ≈ 2.5). Both samples were stored at <4 °C in the dark prior to analysis, as were the filter papers subsequently used to analyse the C:N ratio and the nitrogen isotope ratio of PON.

Concentrations of NO_3^- and NH_4^+ were measured with an automatic flow analyser (SKALAR Sans Plus Systems, Breda, Netherlands). The frozen filters were rinsed with HCl (6N), KCl (0.1 mol/L), and Millipore water (18.2 MΩ) in sequence to eliminate carbonates and inorganic nitrogen and then freeze dried. The molar C:N ratio (mol/mol) of POM was analysed with an elemental analyser (Elementar Co., Langenselbold, Germany). The concentration of particulate organic carbon (POC) and PON were calculated using the filtered water volume, the POM weight, and the C:N ratio. The NO_3^- isotope of water samples was measured by the ion-exchange method (Silva et al. 2000). Water samples were passed through a column prefilled with anion exchange resin (Dowex 1×8, 200 mesh), and then NO_3^- was eluted from the resin by addition of HCl. The eluant was neutralized by silver oxide (Ag_2O) converting the NO_3^- into $AgNO_3$. The nitrogen isotope ratio of $AgNO_3$ was measured by isotope-ratio mass spectrometry. IAEA-N3 and a KNO_3 working standard were used for calibration. The average NO_3^- adsorption efficiency was >95%, and analytical precision of $\delta^{15}N\text{-}NO_3^-$ in duplicate was 0.4‰. Filters with POM samples were pre-dried (70 °C) and loaded into quartz tubes evacuated with 1 g of copper oxide, and 1 g of copper wire and then sealed in a vacuum line. CO_2 and N_2 were combusted at 900 °C for 1 h in a muffle furnace and then cryogenically purified in the vacuum line. Nitrogen isotopes of PON were determined from the purified gases prepared in the vacuum line by MAT 252. The analytical precision of $\delta^{15}N$-PON in duplicate was 0.3‰.

Statistical analysis was conducted using SPSS Statistics 22.0.0, Grapher 12.0, and Microsoft Excel based on Windows 10. In all analyses where $p < 0.05$, the factor and the relationship tested were considered statistically significant.

Results

Based on the vertical temperature variation, the 4 reservoirs on the Maotiao River were significantly thermally stratified in July but became vertically mixed in October. As reported in our previous studies, thermal stratification was most intense in July and gradually disappeared by October (Liu et al. 2011, 2017); thus, July and October are crucial months for thermal stratification and the nitrogen biogeochemical processes. However, the temperature difference between surface and bottom of the 4 reservoirs varied widely in July. BHR had the greatest temperature difference of 16.69 °C, followed by HYR with 3.56 °C, HFR with 2.69 °C, and XWR with a small difference of 1.43 °C. HYR and XWR had much shorter water residence time and less total volume than BHR and HFR (Table 1), indicating that the rapid exchange of water can reduce the build-up of density differences in the water column. In addition, although HFR had the longest water residence time and largest total volume, the maximum depth was only 15 m in July (Fig. 2). The water columns were destratified in October, apart from BHR, where the temperature at the bottom water was 10.70 °C compared to a surface temperature of 19.24 °C.

Thermal stratification and its influences on water parameters including pH, DO, and chlorophyll *a* (Chl-*a*), were clearly observed in July. The epilimnion in each reservoir was always oxic. The concentration of DO dropped rapidly within the thermocline and became anaerobic in the hypolimnion (depth >10 m) in HFR and BHR, but the hypolimnion was oxic or hypoxic (DO > 81.3 μmol/L) in XWR and HYR. The Chl-*a* concentration and pH were much higher in the epiliminia than the hypoliminia in July. Chl-*a* reached 18.3, 12.7,

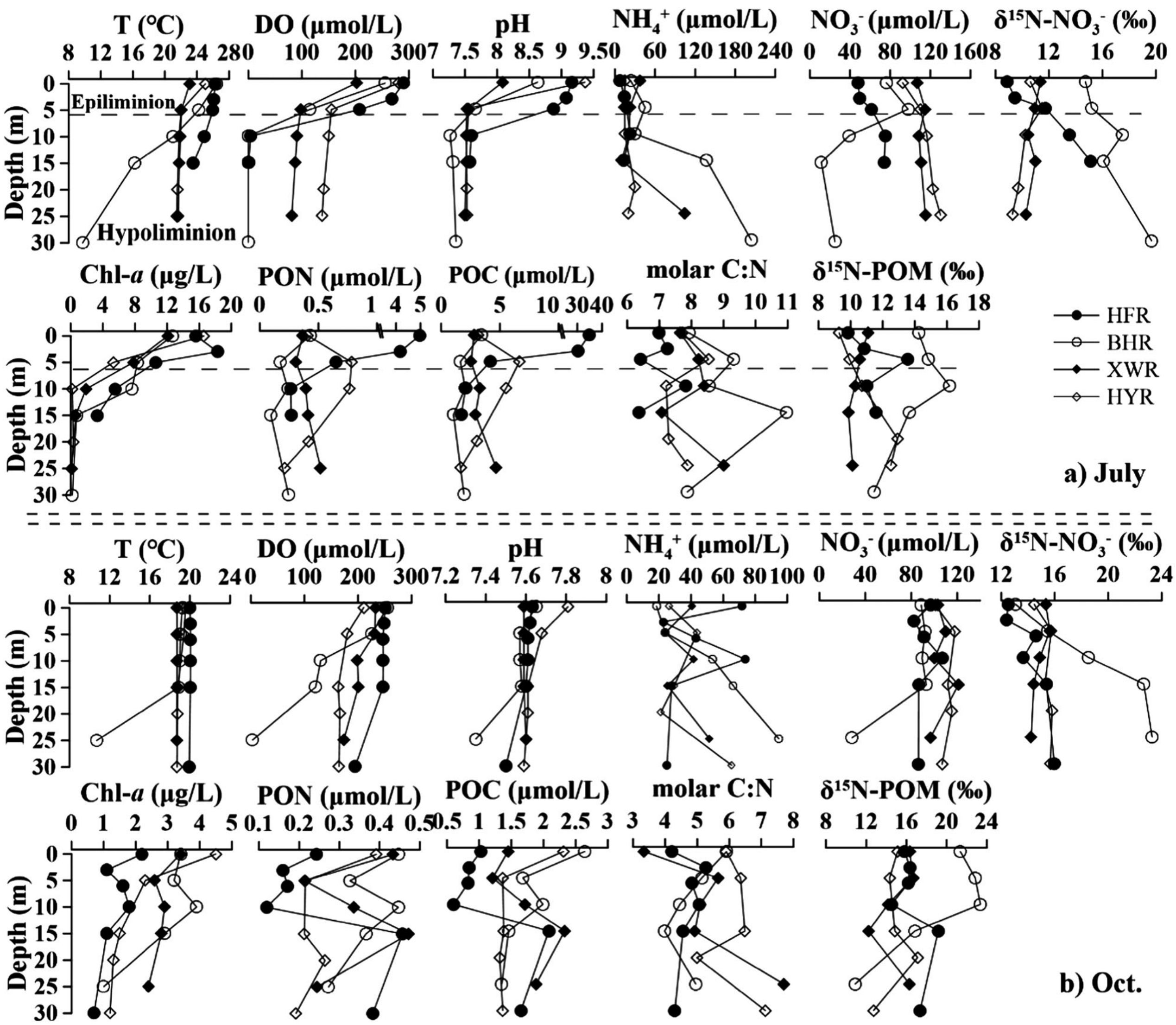

Figure 2. Vertical variation of water parameters, nitrogen species, C:N, and $\delta^{15}N$ in nitrate and POM in (a) July and (b) October. The dashed horizontal line shows the approximate depth of the thermocline in July.

12.1, and 16.6 μg/L in HFR, BHR, XWR, and HYR, respectively, and pH reached 9.16, 8.63, 8.09, and 9.37, respectively, (Fig. 2). Water parameters including T, DO, pH, and Chl-*a* in the epiliminia were much higher in July than in October. In October, pH, DO, and Chl-*a* did not vary with depth. Compared with other reservoirs on the Wujiang River, reservoirs on the Maotiao River had markedly higher epilimnetic Chl-*a* concentrations than reservoirs on the mainstream of the Wujiang River (Liu et al. 2011, 2017), suggesting that the Maotiao River was more eutrophic than the Wujiang River.

As expected, T, pH, and Chl-*a* in reservoirs decreased down the Maotiao River in July (Fig. 3), mainly caused by the release of water from the base of the upstream dam. DO, pH, and Chl-*a* below the dam were similar to values in the hypoliminion of the upstream reservoir because downstream waters were mainly discharged from hypoliminion (Wang et al. 2011, Liu et al. 2017). In the tributaries, DO was 33.1–384.7 μmol/L in July and 148.4–244.4 μmol/L in October, pH was 7.42–8.64 in July and 7.59–8.05 in October, and Chl-*a* was 0.2–6.5 μg/L in July and 0.2–4.3 μg/L in October, following the same seasonal variation pattern as reservoir water.

Epilimnetic NO_3^- concentrations (0–6 m for HFR, 0–5 m for other reservoirs) in reservoirs typically increased with depth in July, from 47.8 to 61.6 μmol/L in HFR, 76.2 to 97.9 μmol/L in BHR, 107.0 to 114.8 μmol/L in XWR, and 92.4 to 110.1 μmol/L in HYR (Fig. 2). NO_3^- concentrations gradually increased or were unchanged with depth below the epilimnion in July in HFR, XWR, and HYR, whereas NO_3^- in BHR was greatly reduced in the anoxic hypoliminon from 39.2 μmol/L at 10 m, to 11.5 μmol/L at 15 m, to 25.4

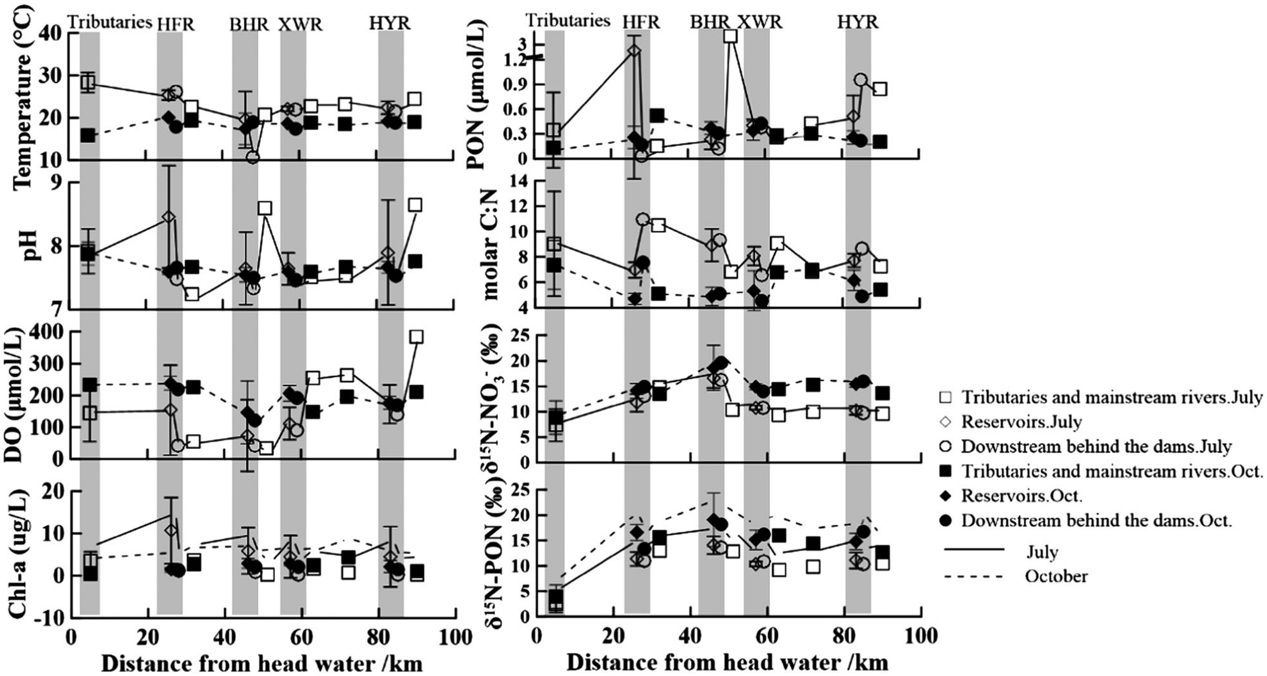

Figure 3. Longitudinal distribution of water parameters, PON, C:N, $\delta^{15}N$ of nitrate, and $\delta^{15}N$ PON.

μmol/L at 20 m. By comparison, NH_4^+ in this water column greatly increased from 29.8 μmol/L at 10 m, to 137.1 μmol/L at 15 m, to 203.9 μmol/L at 20 m. In October, depth profiles of NO_3^- and NH_4^+ in BHR were similar to those in July (Fig. 2). In October in HFR, both NO_3^- and NH_4^+ in the epilimnion (from 3 to 10 m) increased markedly and then decreased with depth to 15 m but displayed little spatial variation in XWR and HYR throughout the water column.

Vertical and seasonal variation in the isotopic composition of NO_3^- was observed in the reservoirs in Maotiao River (Fig. 3). The $\delta^{15}N$ of NO_3^- in HFR, BHR, XWR, and HYR reservoirs averaged 11.74‰, 16.64‰, 10.81‰, and 10.26‰ in the water column in July and 14.09‰, 18.60‰, 14.92‰, and 15.40‰ in October, respectively. The highest values of $\delta^{15}N$ of NO_3^- were found in BHR, reaching 19.68‰ in July and 23.28‰ in October. Coupled to the decreasing NO_3^- and increasing NH_4^+ with depth in BHR, steadily increasing $\delta^{15}N$ of NO_3^- in BHR was observed throughout the water column in both July and October. Similar large vertical distribution patterns of $\delta^{15}N$ of NO_3^- in HFR were also found in July and October. The vertical distribution of the $\delta^{15}N$ of NO_3^- was almost uniform in the water columns of HYR and XWR. Downstream of the dam, the $\delta^{15}N$ of NO_3^- was higher than in upstream surface waters in the reservoir because it was sourced from depth (Fig. 3).

POC and PON had large vertical and seasonal variation in reservoirs on the Maotiao River. The average concentrations of POC and PON in HFR, BHR, XWR, and HYR in July were 14.6, 2.0, 3.3, and 4.0 μmol/L and 2.1, 0.24, 0.40, and 0.52 μmol/L, respectively. The highest concentrations of POC and PON were found in the epiliminion of HFR in July, reaching 34.7 and 4.96 μmol/L, respectively. POC and PON in reservoirs in October were generally lower than in July, except in BHR, where the PON in October had a higher average concentration of 0.37 μmol/L.

The molar C:N ratio varied within a narrow range in water columns of reservoirs on the Maotiao River (Fig. 3) and averaged 7.0, 8.9, 8.1, and 7.7 in HFR, BHR, XWR, HYR in July, decreasing markedly in October to average values of 4.7, 4.9, 5.3, and 6.2 in the 4 reservoirs, respectively. Tributaries and mainstream rivers generally had higher C:N ratios than reservoirs (Fig. 3), especially in inflowing rivers of HFR, where the highest C:N ratio reached 12.6, indicating allochthonous inputs.

The $\delta^{15}N$ of PON exhibited large variation with time and depth in reservoirs (Fig. 2). High $\delta^{15}N$ of PON were observed in reservoirs, with average values of 11.4‰, 14.1‰, 10.4‰, and 11.1‰ in July and 16.6‰, 19.1‰, 15.1‰, and 14.8‰ in October throughout the water column for HFR, BHR, XWR, and HYR, respectively. The higher $\delta^{15}N$ of PON in October when the reservoirs were mixed compared to July when the reservoirs were stratified may reflect the effect of phytoplankton on the PON in reservoirs, which was also indicated by Lehmann et al. (2004). Although the concentration of PON increased in October, a sharp reduction of $\delta^{15}N$ of PON was observed in the hypoliminion of BHR in both months, from 16.2‰ to 11.5‰ in July and from 23.4‰ to 10.9‰ in October, mainly caused by the stable anoxic condition in the hypoliminion of BHR. Longitudinally, reservoirs had higher $\delta^{15}N$ of PON than tributaries and rivers. $\delta^{15}N$ of PON increased significantly along the river in both months (Fig. 3).

Discussion

During the period of thermal stratification, the upper oxic epilimnion had sufficient NH_4^+ and DO to create an environment conducive to nitrification. Nitrification will produce NO_3^- depleted in ^{15}N, and although $\delta^{15}N$-NO_3^- increased in the upper layers (depth <5 m), nitrification cannot explain all the NO_3^- present in the studied reservoirs, except in XWR (Fig. 2). Reservoirs on the Maotiao River had lower concentrations of POC and PON than those in the Tillari Reservoir (Bardhan et al. 2017) apart from the similar, extremely high POC and PON concentration in HFR in July. These high concentrations were also found in other reservoirs, probably due to the algae bloom in the surface water (Ogrinc et al. 2008). Phytoplankton preferentially take up NO_3^- containing the light isotope ^{14}N leaving residual NO_3^- enriched with ^{15}N (Casciotti et al. 2002). In July, Chl-*a* concentrations were high in the epilimnia of the 4 reservoirs, and so the high $\delta^{15}N$-NO_3^- values probably resulted from assimilation in upper water layer. In addition, inflowing rivers with high NO_3^- concentration and isotopic composition will also increase the $\delta^{15}N$-NO_3^- value in reservoirs. Of 4 inflowing rivers to HFR, the Taohuyuan River, which receives sewage from industrial activities in its tributaries, had the highest NO_3^- input and $\delta^{15}N$-NO_3^- and is considered an important external nitrogen input source to the reservoirs on Maotiao River (Xiao and Liu 2006).

Higher $\delta^{15}N$-NO_3^- values were observed in the anoxic hypolimnion in HFR and BHR than in the oxic eplimnion. Comparatively high values of $\delta^{15}N$ of NO_3^- (27.6‰) were also observed in recent studies in the water column of BHR (Yue et al. 2018 [this issue]) and in other eutrophic reservoirs worldwide (Ogrinc et al. 2008, Bardhan et al. 2017). The anoxic hypolimnia of HFR and BHR were characterized by high NH_4^+ and low NO_3^- concentrations, which may indicate that denitrification typically takes place in the hypolimnion in BHR and HFR. During denitrification, microbial degradation of abundant organic matter (OM) preferred to use NO_3^- as an oxidant, which decreased NO_3^- concentrations from 39.2 to 11.5 μmol/L in the hypolimnion in BHR, whereas the NO_3^- decreased only slightly in hypolimnion of HFR, mainly because HFR was shallow (only 15 m; Fig. 2). Because DO concentrations were high in the whole water column in both July and October, denitrification in the hypoliminion of XWR and HYR was not observable. Indeed, no significant stratification and anoxic water layers appeared in the hypolimnion of XWR and HYR, mainly because of the short water residence time (3.4 and 7.3 d, respectively).

The $\delta^{15}N$ of PON in lakes and reservoirs is closely related to NO_3^- uptake (Bardhan et al. 2017). Generally, if NO_3^- assimilation is the major nitrogen process in lakes or reservoirs, $\delta^{15}N$-PON should be less than or equal to that of NO_3^- (Fogel and Cifuentes 1993). The N-isotope enrichment factor ε for NO_3^- uptake by diatoms can be readily estimated from the difference in $\delta^{15}N$ values between the source NO_3^- and the product particulate nitrogen (PON; Lehmann et al. 2004). We estimated an ε of +0.99‰ to +1.37‰ in HFR, −0.50‰ to −0.38‰ in BHR, −0.40‰ to −0.27‰ in XWR, and −1.55‰ to −1.35‰ in HYR (Fig. 4). In July, the $\delta^{15}N$ of PON of surface water in reservoirs, except for HFR, was always lower than that of NO_3^- (Fig. 4), suggesting that NO_3^- assimilation was the major process transforming nitrogen in the epilimnion. This apparent N-isotope fractionation in July in reservoirs is consistent with results from Lake Baldegg and Lake Lugano, which revealed ε values for phytoplankton NO_3^- assimilation between −1.9‰ and −2.7‰ (Teranes and Bernasconi 2000, Lehmann et al. 2004). Although $\delta^{15}N$-NO_3^- was lower than that in PON in HFR (ε of nearly +1‰), high Chl-*a* (up to 18.3 μg/L) in the epilimnion will result in nitrate assimilation being the dominant process. As noted previously, in July the depth of HFR is only 15 m, and therefore ^{15}N-enriched NO_3^- in the bottom water could probably become entrained into the upper layer to some extent. October ε values were mostly much higher than those in July (Fig. 4), suggesting that nitrate assimilation was not the key process and PON

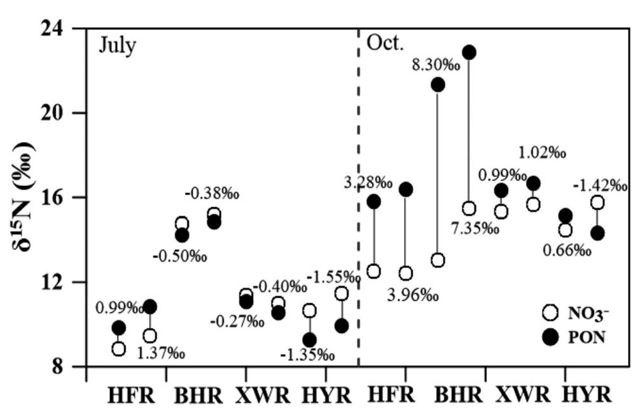

Figure 4. $\delta^{15}N$ of dissolved nitrate and PON in epilimnion (0–5 m). The value of the difference in $\delta^{15}N$ between PON minus nitrate is shown.

was probably influenced by other external nitrogen sources or diffusion of denitrified NO_3^- from the hypolimnion. Similar findings have also been observed in nonthermal stratification periods in Lake Kinneret (Hadas et al. 2009).

Similar to $\delta^{15}N$-NO_3^-, high values of $\delta^{15}N$-PON were also found in reservoirs on the Maotiao River in both sampling months. Comparatively heavy $\delta^{15}N$ of PON were also reported in other reservoirs and lakes, such as Lake Lugano and Tillari Reservoir (Lehmann et al. 2004, Bardhan et al. 2017). In July, high $\delta^{15}N$-PON values may result from the algal blooms in the upper layers. In eutrophic HFR and BHR, the dominant phytoplankton were Cyanophyta and Chlorophyta (Wang et al. 2013), and $\delta^{15}N$ of phytoplankton as high as 13.9‰ was reported in the lakes (Vuorio et al. 2006). In addition, in July, NH_4^+ accumulated in the deep layer of the hypolimnion, supplied from the sediment and continuing degradation of OM derived from sinking phytoplankton. Nitrification or assimilation in the oxic epilimnion would result in NH_4^+ enriched in ^{15}N. Hence, a corresponding 15–30% jump in $\delta^{15}N$-PON would occur because of high $\delta^{15}N$-NH_4^+ assimilation (Hadas et al. 2009). In October, $\delta^{15}N$ in PON was much higher than that in NO_3^- in the whole water column of the 4 reservoirs, indicating that the isotopic composition of PON may be due to denitrification or derive from other nitrogen sources (Fig. 2). Similar seasonal variation was also found in Lake Lugano and contributed to the ^{15}N-enriched OM originating from an adjacent water treatment plant (Lehmann et al. 2004). Indeed, riverine NO_3^- input from Taohuyuan River has been the main external nitrogen source to HFR since 1999 (Xiao and Liu 2006). Although the industrial sewage and effluent discharge caused the NO_3^- concentration to be as high as 158.7 μmol/L, the $\delta^{15}N$-PON in river water was only 0.53‰ in October, implying that riverine NO_3^- input could not be the main cause of the high $\delta^{15}N$-PON. Notably high $\delta^{15}N$-PON values in autumn–winter have been reported from other lakes and reservoirs (Teranes and Bernasconi 2000, Lehmann et al. 2004, Bardhan et al. 2017), but the causes are still not well known.

To apportion the OM source contributions to rivers and reservoirs in the Maotiao River, the isotopic characteristics of potential OM sources must be identified, including those from aquatic plants (e.g., phytoplankton and macrophytes), terrestrial plants (C3 and C4), soil OM, effluent detritus, chemical fertilizer, and other sources.

The variation in ranges of $\delta^{15}N$-PON and C:N values for the potential PON sources in Maotiao River (Table 2) indicate that terrestrial plants are an important OM source, divided into C3 and C4 plants. $\delta^{15}N$-PON ranges from −4.1‰ to −2.5‰ in C3 plants and from −0.2‰ to 6.6‰ in C4 plants, whereas the C:N ratio varies from 14 to 31 and 15 to 50 in C3 and C4 plants, respectively (Ogrinc et al. 2008, Xiao and Liu 2010, Lu et al. 2016). Xiao and Liu (2010) observed the C and N cycling and sources in riverine sediment and analyzed the organic nitrogen isotopic composition and C:N ratio in Nanming River in Guizhou, China, documenting the end members for riverine nitrogen isotopic composition. The reported nitrogen isotopic composition of different sources were used in this study because of the similar geographic location and features (Xiao and Liu 2010). Liu et al. (2006) also conducted a study on groundwater in Guiyang city in Guizhou and characterized the nitrogen isotopic composition of effluent discharge and livestock waste as end members (Liu et al. 2006). In addition, Ogrinc et al. (2008) and Vuorio et al. (2006) reported the nitrogen isotopic composition and C:N ratio of phytoplankton to range widely from −15‰ to 20‰ for $\delta^{15}N$-PON and 4 to 8 for the molar C:N ratio.

The origin of PON in rivers and reservoirs can be identified by comparing the $\delta^{15}N$-PON and the C:N ratio (Ogrinc et al. 2008, Xiao and Liu 2010, Lu et al. 2016). The relationship between the $\delta^{15}N$-PON and the C:N ratio showed that most of the POM in reservoirs was mainly linked to phytoplankton (Fig. 5), but livestock waste and effluent discharge also played a role in some reservoirs. PON in river waters, especially in inflowing rivers waters, was mainly derived from soil OM. Although the chosen end members already explained most of the samples, the cause of the high $\delta^{15}N$-PON in reservoirs has not been clearly identified. From our analysis on the nitrogen mechanism, we inferred that the high $\delta^{15}N$-PON was from external nitrogen denitrification.

Table 2. Nitrogen isotopic and elemental compositions of potential sources of POM.

Nitrogen sources	$\delta^{15}N$ signature (‰)	C:N	References
Soil organic matter	5.7 ± 2.0	8 to >25	Liu et al. 2006
Effluent detritus	8.5 ± 1.1	5–8	Xiao and Liu 2010
Chemical fertilizers	0 ± 1.4	0.5–1	Liu et al. 2006
Organic fertilizers	2–30		Kendall et al. 2007
Livestock waste	7.0 ± 3.2	6–16	Liu et al. 2006
Phytoplankton	−15–20	4–8	Ogrinc et al. 2008, Vuorio et al. 2006, Xiao and Liu 2010
Terrestrial C3 plants	−4.1–2.53	14–31	Lu et al. 2016, Ogrinc et al. 2008, Xiao and Liu 2010
Terrestrial C4 plants	−0.21–6.63	15–50	Lu et al. 2016, Ogrinc et al. 2008, Xiao and Liu, 2010

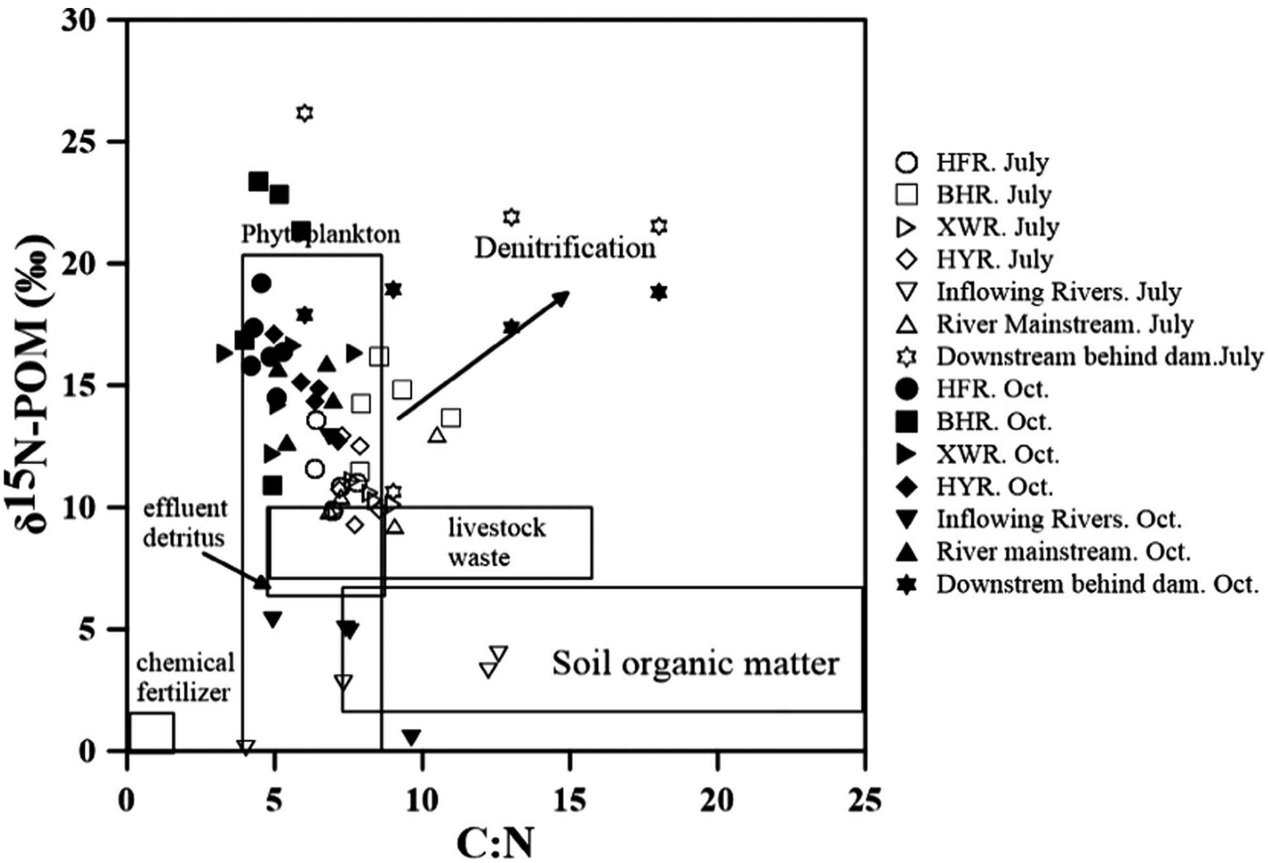

Figure 5. Relationship between $\delta^{15}N$ of PON and molar C:N ratios.

Cascade dam development effects on nutrient biogeochemical cycling have been emphasized in recent years (Ock and Takemon 2014, Wang et al. 2014). In a continuous cascade-developed river, the hydrochemistry of the downstream reservoir could be significantly influenced by upstream reservoirs. For better power generation, water is usually discharged from the bottom of the dam and thus from the hypolimnion with low temperature, pH, DO, and Chl-*a* and high $\delta^{15}N$ of PON and NO_3^- (Fig. 2), potentially affecting the next reservoir. Consequently, the PON and NO_3^- with high $\delta^{15}N$ will be transported to the downstream reservoir and affect its nitrogen isotope composition. In general, $\delta^{15}N$ values of both PON and NO_3^- increased gradually from upstream to downstream by $8.21 \pm 0.65‰$ for $\delta^{15}N$-PON and $1.74 \pm 3.66‰$ for $\delta^{15}N$-NO_3^-, suggesting an accumulative effect on nitrogen isotopic composition by the downstream waters, especially in the cascade development of impounded rivers.

Conclusion

Cascading reservoirs on a river critically affect PON production and transportation. The PON in river–reservoir systems was closely connected to the nitrogen dynamics and biogeochemical processes in reservoirs. Knowledge of the origin and variation in the PON in the reservoirs will be valuable in assessing the nitrogen biogeochemical cycling in cascade developed river. In this study, because of the high eutrophication in the HFR and BHR, PON in the reservoir had a high $\delta^{15}N$, which still has no reasonable explanation for October values. July and October are distinctive months, encompassing extremes from the most intense stratification to water mixing, and the comparison of PON between the 2 periods simplified the seasonal trends of nitrogen dynamics. Using this approach, we found that PON formation and the influence of NO_3^- on PON differed among reservoirs. Additionally, we provided information relating to the sources of organic matter.

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