Long-term impacts of reservoir operation on the spatiotemporal variation in nitrogen forms in the post-Three Gorges Dam period (2004–2016)

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Abstract
Nitrogen (N) is an essential nutrient limiting life, and its biochemical cycling and distribution in rivers have been markedly affected by river engineering construction and operation. Here, we comprehensively analyzed the spatiotemporal variations and driving environmental factors of N distributions based on the long-term observations (from 2004 to 2016) of seven stations in the Three Gorges Reservoir (TGR). In the study period, several water quality indexes of the river reach improved, whereas N pollution was severe and tended to be aggravated after the TGR impoundment. The anti-seasonal reservoir operation strongly affected the variations in N forms. The total nitrogen (TN) concentration in the mainstream of the Yangtze River continuously increased, although it was still lower than that in the incoming tributaries (Wu and Jialing rivers). Further analysis showed that this increase occurred probably because of external inputs, including the upstream (76%), non-point (22%), and point source pollution inputs (2%). Additionally, different N forms showed significant seasonal variations; among them, the TN and nitrate nitrogen concentrations were the lowest in the impoundment season (October–February), and the ammonia nitrogen concentrations were the highest in the sluicing season (March–May). Redundancy analysis revealed that the water level and distance to the Three Gorges Dam were significant contributors to N forms distribution. Our findings could provide a basis for managing and predicting the water quality in the Yangtze River.

Keywords
Three Gorges Reservoir · Spatiotemporal variations · Water level · Nitrogen transformation · External input

Introduction
Dams play a significant role in addressing the demand for flood control, power generation, and navigation improvement (Chen et al. 2019; Li et al. 2012; Nilsson et al. 2005). Rivers worldwide have been intensively dammed; more than 70,000 large dams have been constructed, and at least 3700 large dams with a capacity of more than 1 MW have been proposed or are under construction (Maavara et al. 2015; Shi et al. 2020; Zarfl et al. 2015). However, these projects likely disrupt the river continuity and may have adverse consequences on the balance and functional integrity of river systems (Nilsson et al. 2005; Tang et al. 2018; Wang 2020; Yan et al. 2015). After impoundment, dam-affected river reaches would be converted into lakes, and this modified fluvial regime likely increases the water retention time and changes the seasonality of suspended and dissolved material fluxes (Eiriksdottir et al. 2017; Friedl and Wüst 2002; Maeck et al. 2013). Moreover, the biota, especially microorganisms, may be affected by anoxia, sedimentation, and nutrient level variations in reservoir systems (Eiriksdottir et al. 2017; Yan et al. 2015).

Nitrogen (N), an essential component of all living organisms and primary nutrient for biological growth, is strongly related to the water trophic status (Kuypers et al. 2018; Ran et al. 2017; Zheng et al. 2016). The microbial transformation of N is generally described as an orderly cycle that includes six processes, namely, N fixation, nitrification, denitrification, anammox, assimilation, and ammonification. In the aquatic ecosystem, inorganic N conversion, such as nitrification and
denitrification, has been an essential topic for several decades (Boyer et al. 2006b; Zhu et al. 2018). Ammonia can be oxidized to nitrate through nitrification and eventually converted back to dinitrogen through denitrification or anaerobic ammonium oxidation. These alterations of the N oxidation state are controlled primarily by microbial reactions, which can be affected by many factors (Kim et al. 2016; Povilaitis et al. 2012). For instance, nitrification is aerobic, whereas denitrification usually involves anaerobic and heterotrophic bacteria (Kim et al. 2016; Zhu et al. 2018).

With a length of over 6000 km, the Yangtze River has hundreds of large dams (higher than 15 m; Li et al. 2017; Ran et al. 2017). Three Gorges Reservoir (TGR), one of the largest hydropower complex projects in the world, has significantly reversed the seasonal changes in natural hydrology; in its operation, the water level is artificially regulated to a low level for the need of hydropower energy or flood control in summer and a high level for stable water supply or navigation in winter (Han et al. 2018). The dam holds water and sediments, and 1.8×10^{12} kg of sediments (retention rate over 80%) was trapped from 2003 to 2013 along the 700-km-long TGR (Yang et al. 2014); the clear water discharge has caused substantial river bed erosion downstream the dam (Xu and Milliman 2009; Yang et al. 2018). The Three Gorges Project also faced severe controversies concerning the environmental and ecological impact of dams; for instance, water eutrophication, along with construction and operation, has become a hot and critical issue (Chai et al. 2009; Gao et al. 2016; Liu et al. 2018; Ran et al. 2017; Zhou et al. 2013). In the TGR basin, nitrate-nitrogen (NO−3-N) and total nitrogen (TN) are identified as vital pollution indices in an assessment based on the Canadian Council of Ministers of the Environment Water Quality Index (Xia et al. 2018). Although the TGR has accounted for 5% of N retention in the Yangtze River basin from land to sea since 2004, the enhanced signals of dissolved inorganic nitrogen (DIN) concentrations in the lower reach of the Yangtze River have also been observed (Sun et al. 2013). The DIN concentration dramatically increased from an average of 37 μmol L\(^{-1}\) in the 1980s to 120 μmol L\(^{-1}\) in the 2000s (Dai et al. 2011). The reservoir operation has implications not only for N transport but also for N transformation in the TGR (Chai et al. 2016; Shi et al. 2020; Wang 2020). For example, frequent artificial floods created by the reservoir operation can reduce the ability of soil to retain nutrients and promote the release of N in sediments via coupled nitrification-denitrification processes (Ye et al. 2019; Yu et al. 2020). Moreover, the level of bacterial activity in generating nitrogenous nutrients was changed in the TGR; the abundance of functional genes involved in the N cycle was higher in backwater sites with dam effect than that in riverine sites without dam effect (Yan et al. 2015). Since the construction of the Three Gorges Dam (TGD), the transport and transfer patterns of N have changed dramatically, and these variations potentially have a sustainable and crucial effect on the N distribution and trophic status in the TGR.

Therefore, the spatiotemporal variations in N and their relationship with environmental factors should be studied to assess the water quality status and impact of TGR operation, especially when the hydrology regime has undergone tremendous changes since TGR impoundment. The influencing mechanisms of the changing hydrological regime on N cycling in the TGR have been revealed through laboratory experiments by artificially increasing hydrostatic pressure, creating an anti-seasonal wet-dry cycle, and prolonging water residence time (Chai et al. 2016; Shi et al. 2020; Yu et al. 2020). However, most studies have preferred short-term investigation because of difficulties in obtaining long-term observed data (Ding et al. 2019; Huang et al. 2014; Luo et al. 2011; Ran et al. 2017). The time variability of N in TGR involves a wide range of scales from days, months, to multi-years because of the coupled effect of natural (precipitation and monsoon) and anthropogenic (regular operation and staged impoundment of TGR) factors; as such, studies based on massive monitoring data are more valuable for assessing the long-term impact of TGR operation on N distribution. Additionally, studies may explore the relationship between environmental factors and different N forms based on long-term monitoring data on water quality and hydrological parameters.

Here, we collected the observed data of 20 parameters, including N concentrations and other hydrology and water quality variables, in seven gaging stations in the TGR basin from 2004 to 2016. The variations of these parameters were determined by significance analysis and Mann–Kendall (MK) test; the correlations between N concentrations and other parameters were tested by Kendall’s Tau and redundancy analysis (RDA). Our study aimed to (i) investigate the long-term effects of TGR operation on the hydrology and water quality, (ii) analyze the N distribution in different temporal stages, and (iii) explore the driving environmental factors of dam-induced spatiotemporal variations in N forms. This study helped enhance the understanding of the relationships between N concentration and damming-induced environmental variations and provide a scientific basis for evaluating nutrient contents and managing the system of damming rivers.

Materials and methods

Study area

The TGR basin (29°16′–31°25′ N, 106°–110°50′ E) spans the Jiangjin District of Chongqing to the Yichang City of Hubei and covers more than 20 county-level administrative regions; of these regions, over 70% are in Chongqing (Fig. 1). With a water surface area of 1084 km\(^2\), the TGR is rich in water...
resources, and nearly 90% of the inflow water in the upper reach of the TGR comes from the Yangtze River (71%), Jialing River (13%), and Wu River (16%; Wang et al. 2015; Zheng et al. 2016).

The construction of TGD started in 1994, and the water storage and sedimentation began in 2003. After 2010, a 650-km-long reservoir was formed, with a maximum capacity of approximately 3.93×10¹⁰ m³ (Wang et al. 2015; Wang 2015). As shown in Fig. 2, the water level stepwise raised to a maximum of 175 m during three impoundment periods (period I, June 2003–September 2006; period II, October 2006–September 2009; and period III, October 2009–present). The TGR usually stores clear water in the dry season and discharges muddy water during the flood season to limit sedimentation and create advantages in terms of navigation, flood control, and power generation as much as possible (Ran et al. 2017). Therefore, the operation cycle of the TGR can be divided into three seasons: low water level season (June–September), impounding season (October–February), and sluicing season (March–May).

Data were collected from seven key hydrological stations (Fig. 1) to study the N variation in the TGR over the entire cycle of the operation schedule. Among these stations, the Zhutuo (ZT), Beibei (BB), and Wulong (WL) sites were chosen as the inflow stations of the TGR located in the Yangtze River, the Jialing River, and the Wu River, respectively. In the TGR mainstream, ZT, Cuntan (CT), Qingxichang (QXC), and Wanxian (WX) sites are 756, 604, 479, and 288 km away from the TGD, respectively. The QXC site and its upstream sites are considered the tail region of TGR, while the WX site is the representative site of the middle region. Additionally, the Yichang (YC) site 38 km downstream of TGD represents the outflow control station for a comparative study. The river reaches from the WX to the YC site were converted to a lake with a decreased water velocity and prolonged retention time.

**Data collection, sampling, and analysis**

The water samples were collected and analyzed in accordance with the *Environmental Quality Standards for Surface Water in China* (MEPC 2002). The observed monthly hydrology and water quality data from 2004 to 2016 were gathered from the Changjiang Water Resources Commission. Twenty parameters were included: water level (Z, m), flow rate (Q, m³ s⁻¹), water temperature (WT, °C), flow velocity (U, m s⁻¹), pH, electrical conductance (EC, μS cm⁻¹), oxidation-reduction potential (ORP, mv), fluoride (F⁻, mg L⁻¹), suspended sediment (SS, mg L⁻¹), chloride (Cl⁻, mg L⁻¹), sulfate (SO₂⁻, mg L⁻¹), water hardness (mg L⁻¹), alkalinity (mg L⁻¹), permanganate index (PI, mg L⁻¹), dissolved oxygen (DO, mg L⁻¹), 5-day biochemical dissolved oxygen demand (BOD₅, mg L⁻¹), ammonia nitrogen (NH₄⁺-N, mg L⁻¹), nitrite-nitrogen (NO₂⁻-N, mg L⁻¹), NO₃⁻-N (mg L⁻¹), and TN (mg L⁻¹). Here, the sum of NH₄⁺-N, NO₂⁻-N, and NO₃⁻-N refers to the DIN, and the difference between TN and DIN refers to residue-N, including particulate N and dissolved organic N. At the YC site, several parameters, including flow velocity, F⁻, SO₂⁻, PI, and BOD₅, and observations before 2007 (period I) were unavailable.
One-way ANOVA was performed to explain the significance of variations in N concentrations (NH₄⁺ 4-N, NO⁻ 2-N, NO⁻ 3-N, and TN) in different temporal stages. The mutation points and trends of these variations were determined via the Mann–Kendall (MK) test. The relationships between various N forms and environmental variables were determined through RDA. In RDA, all data were logarithmically transformed to eliminate the influence of extreme values on ordination scores. Kendall’s Tau test was also applied for comparison.

**N input, output, and retention**

Rocks are the major components of the riverbed along the main channel, so the direct groundwater discharge into the TGR can be ignored. Therefore, the total N input of the TGR mainly includes upstream, point source, and non-point source pollution inputs. Given the difficulties in obtaining detailed and comprehensive data, the load of total N input \( L_{in} \) can be estimated based on the mass balance for the TGR as follows:

\[
L_{in} = L_{out}/(1-R_N),
\]

where \( R_N \) is the annual N retained by the reservoir (%), which can be calculated on the basis of the theoretical relationship proposed by Howarth et al. (1996):

\[
R_N = 88.45(H/T)^{-0.3677},
\]

where \( H \) is the mean depth (m) and \( T \) is the water residence time (year) estimated as

\[
T = V/Q,
\]

where \( V \) is the effective reservoir volume (m³), \( L_{out} \) is the load of outflow (YC site), which can be calculated as

\[
L_{out} = C_N \times Q \times t,
\]

where \( C_N \) is the TN concentration (mg L⁻¹) and \( t \) is the elapsed time.

**Results**

**General variation trend of hydrological and water quality regimes**

Since the operation of the TGR began, the hydrological and water quality regimes have undergone significant temporal and spatial variations. The values of 16 environmental factors (except four N forms) in different impoundment periods and seasons are listed in Tables 1 and 2. The three impoundments dramatically raised the water level and substantially decreased the suspended sediment concentration \( C_{ss} \) and flow velocity in the TGR. Among the seven stations, the WX site suffered the most remarkable effect of TGR operation; that is, the water level rose by 23.8 m, whereas flow velocity and \( C_{ss} \), respectively, dropped by 46.7% and 84% from period I to period III (Table 1). One-way ANOVA revealed that the water temperature and flow rate in all stations exhibited no significant trend (Table s1). The periodic mean pH values were greater than 8.0, and water alkalinity also increased over time. This result indicated that the overlying water in the TGR would remain in a weak alkaline state in the long run. An overall rise in ion concentration level was found during the three periods, with a sharp increase in Cl⁻ and SO₂⁻ 4 and a slight increase in F⁻, EC, and water hardness, especially at the WX site, the closest site to the TGD. The periodic averaged ORP and DO concentrations shared a similar trend; they significantly decreased from period I to period II and slightly increased in period III. During the monitoring period, the F⁻, DO, PI, and BOD₅ concentrations were in the ranges of 0.07–1.05, 5.45–10.95, 0.55–32.59, and 0.20–2.41 mg L⁻¹, respectively. Although the inter-annual variations in these four parameters showed different trends, the F⁻, DO, and BOD₅ concentrations in all the stations reached the requirement of class I standard (MEPC 2002). The PI concentration was lower than the class III standard (6 mg L⁻¹), but it met the class II standard (4 mg L⁻¹), indicating an overall water quality improvement after the TGR impoundment.

Through the anti-seasonal reservoir operation, the water level in the dry season was higher than that in the rainy season (low water level season on June–September). The flow rate, flow velocity, water temperature, and \( C_{ss} \) were the highest in the low water level season because of frequent flooding in summer (Table 2). In addition to pH, ORP, Cl⁻, and BOD₅, other water quality parameters exhibited significant seasonal changes; among them, water hardness, water alkalinity, EC, F⁻, SO₂⁻ 4, and DO were the highest in the impounding season and the lowest in the low water level season (Table 2). WH and WA represent water hardness and alkalinity, respectively.

**Spatial-temporal variation in N in the TGR basin**

Although several water quality indicators have been improved, N pollution in the TGR is severe and aggravated. As shown in Fig. 3, the TN concentration in almost all stations reached or was even worse than the class V standard (>2 mg L⁻¹; MEPC 2002). The TN concentrations significantly increased toward the TGD in the mainstream from 1.57 mg L⁻¹ at the ZT site to 1.86 mg L⁻¹ at the WX site (p<0.01). The DIN is the existing primary form of TN, which mainly consisted of NO⁻ 3-N (80–91%) and some NH₄⁺ 4-N (2–10%) and NO⁻ 2-N (<2%). The percentage of NO⁻ 3-N increased
Periodic variations in hydrologic and water quality parameters in the TGR basin

Table 1

| Station | Z m | Q m³/s | U m/s | WT °C | pH | EC µS/cm | ORP mv | F⁻ mg/L | SS mg/L | CT mg/L | SO₂⁻ 4 mg/L | WH mg/L | WA mg/L | PI mg/L | DO mg/L | BOD₅ mg/L |
|---------|-----|--------|-------|-------|----|----------|-------|---------|---------|----------|------------|---------|---------|---------|---------|----------|
| WL      |     |        |       |       |    |          |       |         |         |          |            |         |         |         |         |          |
| Period I| 171.96 | 1202.25 | 1.34 | 18.11 | 8.13 | 339.49 | 489.42 | 0.17 | 117.33 | 4.29 | 40.18 | 168.07 | 119.63 | 2.51 | 9.10 | 0.96 |
| Period II | 172.25 | 1411.24 | 1.58 | 17.89 | 8.14 | 354.76 | 434.78 | 0.29 | 22.89 | 3.82 | 49.56 | 182.40 | 120.48 | 1.42 | 8.76 | 0.86 |
| Period III | 175.38 | 1216.07 | 1.39 | 17.93 | 8.10 | 362.16 | 452.25 | 0.36 | 17.61 | 5.47 | 55.95 | 185.65 | 122.73 | 1.48 | 8.80 | 0.84 |
| BB      |     |        |       |       |    |          |       |         |         |          |            |         |         |         |         |          |
| Period I | 180.12 | 3453.08 | 0.89 | 19.27 | 8.24 | 350.71 | 502.82 | 0.23 | 151.19 | 9.13 | 39.83 | 167.01 | 121.26 | 3.18 | 8.29 | 1.24 |
| Period II | 177.40 | 3192.94 | 0.59 | 19.30 | 8.00 | 362.16 | 502.82 | 0.23 | 151.19 | 9.13 | 39.83 | 167.01 | 121.26 | 3.18 | 8.29 | 1.24 |
| Period III | 181.62 | 2954.20 | 0.61 | 19.30 | 8.00 | 362.16 | 502.82 | 0.23 | 151.19 | 9.13 | 39.83 | 167.01 | 121.26 | 3.18 | 8.29 | 1.24 |

Gradually from upstream (80.2% at ZT) to downstream (85.5% at WX) in the mainstream. On a multi-year average, the TN concentration was 2.43 mg L⁻¹ in the Wu River (WL station) and 2.01 mg L⁻¹ in the Jialing River (BB station), indicating relatively higher TN concentrations in tributaries than in the mainstream. Similar to the mainstream of Yangtze River, tributaries dominantly had NO⁻ 3-N, which accounted for 91.0% of TN at the WL station and 81.5% at the BB station. Additionally, the multi-year averaged TN concentration decreased slightly in the outlet (1.83 mg L⁻¹ at the YC station), whereas NO⁻ 3-N took more part of TN form magnitude higher than those of NH⁺ 4-N and NO⁻ 3-N, which the NO⁻ 3-N and TN were the lowest in the impounding season and relatively high in the two other seasons. This event however, the NH⁺ 4-N increased in period III at the BB site compared with that in period I. The staged averaged NO⁻ 3-N and NH⁺ 4-N concentrations at the YC station in period III were higher than those in period II. The concentrations of NO⁻ 2-N in the seven stations were lower, and the varying trend was relatively not evident than those of the other N forms (p>0.05 at the WL and CT sites, p<0.03 at the ZT site, and p<0.02 at the WX site).

The temporal variations in N concentrations displayed dramatic seasonality patterns (Fig. 5). The highest concentration of NH⁺ 4-N was observed in the sluicing season (March–May). The maximum ratio of the NH⁺ 4-N concentrations in this season to those in the other two seasons was approximately 3.8, which occurred at the WX site in 2014. Although extreme differences were found in several years, no clear trend in the seasonal concentrations of NO⁻ 2-N, especially in the tail region (p>0.05 at the ZT, CT, and QXC sites), was detected. The concentrations of NO⁻ 3-N and TN were one order magnitude higher than those of NH⁺ 4-N and NO⁻ 2-N, and ANOVA revealed that their seasonal variations were significant (p<0.03 for NO⁻ 3-N in the QXC site, p=0.04 for TN in the BB site, and p<0.01 in other cases). The concentrations of the NO⁻ 3-N and TN were the lowest in the impounding season and relatively high in the two other seasons.
reoccurred each year at the WX site within the TGR, especially in 2008 when the TN concentration in the low water level season (2.12 mg L\(^{-1}\)) was approximately 1.42 times that in the impounding season (1.50 mg L\(^{-1}\)).

### Influence of environmental variables on N distribution

The correlation structures between the N forms (NH\(_4\)-N, NO\(_2\)-N, NO\(_3\)-N, and TN) and other environmental variables in the mainstream sites (ZT, CT, QXC, and WX sites) of the TGR from 2004 to 2016 were achieved through RDA. N forms were response variables, and other 11 parameters, including distance to the TGD, four hydrological parameters (Z, U, Q, and C\(_{so}\)), and six water quality parameters (DO, PI, pH, BOD\(_5\), WT, and F\(^-\)) mentioned in MEPC (2002), were explanatory variables. As presented in the ordination biplot (Fig. 6), the water level and distance to the TGD were vital contributors to the variations in N concentrations. This result indicated that the operation of the TGR might significantly affect the N distribution. The flow velocity (U) is also strongly correlated with the N forms. The higher WT might correspond to an increase in NO\(_2\)-N, NO\(_3\)-N, and TN concentrations and decreased NH\(_4\)-N concentrations. As critical environmental factors in the N cycle, pH and DO could alter the existing N forms, but the observed N concentrations were affected by the aggregate environmental conditions over time. Although there was no direct effect on N transformation, the other water quality parameters had significant correlations with the N forms in the mainstream of the TGR. In particular, F\(^-\) concentration had a strong correlation to N forms, while PI and BOD\(_5\) were also obviously related to NH\(_4\)-N and NO\(_2\)-N concentrations. Similar results were also supported by Kendall’s Tau tests. The corresponding coefficients of N forms and environmental factors are listed in Table s2.

### Discussion

#### N input in the TGR basin

After the impoundment of the TGR, the water quality in the tail and the middle region demonstrated an improvement. For instance, the periodic concentrations of PI and BOD\(_5\)
gradually decreased, but N pollution may be a severe problem in the future. Although no significant annual and periodic variations in the tail region of the TGR were observed, the MK test results (Fig. s1) revealed that the TN concentration in the WX site increased after the impoundment, especially after the 175 m impoundment operation in 2010. Among the observation sites in the mainstream of Yangtze River, the WX station closest to the dam showed the highest TN concentration and was most severely affected by the reservoir operation. As one of the important economic centers in the TGR, the water quality status of the WX site is also closely related to the industrial, agricultural, and population development of the TGR.

The increasing trend of TN concentrations may be related to external N input from the TGR basin. The total N input listed in Table 1 was obtained based on the export load and retention rate (Eq. (1)). The detailed information can be found...
in Table s3. Among the N inputs, upstream, point, and non-point source pollution inputs accounted for about 76%, 2%, and 22% from 2007 to 2016, respectively. Similar to the N output calculation, the upstream input that included three incoming rivers was related to the flow rate and TN concentrations (Eq. (4)). Despite the observable seasonal and annual variations, the TN concentrations in the three incoming rivers were insignificant in the periodic variations (Table s1). Conversely, the improvement of the industrial wastewater treatment technology caused an evident reduction of sewage discharge, but domestic sewage discharge showed a sustained increase because of the high urbanization rate (MEPC 2017). According to the emission standard of the sewage treatment plant (TN ≤ 15 mg L\(^{-1}\)), the point source N input, including N in the domestic and industrial wastewater, was estimated to range from \(1.34 \times 10^7\) to \(2.02 \times 10^7\) kg from 2004 to 2016, with an average of \(1.55 \times 10^7\) kg (Table 3).

Another important cause of N increase in TGR might be non-point source pollution, which was obtained by subtracting the upstream and point source pollution input from the total TN input in this study. Therefore, the non-point source pollution may be overestimated because of the incomplete statistics of point source pollution and upstream input; for example, some micro-enterprise discharges may not be included in monitoring and sewage treatment. However, non-point source pollution that has attracted more attention plays a vital role in the cumulative increase in TN (Alexander et al. 2002; Ma et al. 2011). In addition to natural N fixation through natural vegetation and atmospheric lightning, drastically increased human activities have strongly influenced N loads in the TGR basin (Boyer et al. 2006a; Chen et al. 2016; Galloway et al. 2008; Xv et al. 2020). With expanding population and agricultural activity, chemical fertilizers have been excessively utilized in China, and approximately 53.2% were N fertilizers in the TGR basin from 2004 to 2016 (NBSC 2017). The massive use of N fertilizer has become a crucial N source, accounting for more than 50% of the net anthropogenic regional N input (NANI), followed by atmospheric N deposition, feed N input, and crop fixation (Ding et al. 2020; Xv et al. 2020). According to data from hundreds of observational sites, the average N wet deposition over China increased by nearly 25% from the 1990s to the 2000s (Jia et al. 2015). A similar increasing trend also occurred in the TGR basin, where atmospheric N deposition increased by 22% from 2006 to 2016 (Ding et al. 2020). This variation could be attributed to the exponential increase in energy consumption and industrial waste gas (CBS 2017), identified as potential sources of atmospheric N deposition (Wang et al. 2018). Moreover, crops have been increasing since the 2006 drought, and the use of feed N has increased with the exponentially growing population and economy in Chongqing (CBS 2017). Under rainfall and irrigation actions, considerable non-point source N likely enters the water column through surface runoff, subsurface flow, farmland drainage, seepage (Gao et al. 2016), and frequent flooding caused by reservoir operation aggravates the loss of N.

### Table 3 N input, output, and retention rate in the TGR.

| Year | Input Total (10^7 kg) | Upstream Point source pollution (10^7 kg) | Point source pollution (10^7 kg) | Non-point source pollution (10^7 kg) | Output (10^7 kg) | Retention rate (%) |
|------|----------------------|----------------------------------------|---------------------------------|-------------------------------------|-----------------|-------------------|
| 2004 | NA 68.66             | 1.59                                   | NA                              | NA                                  | NA              | NA                |
| 2005 | NA 1.47              | NA                                     | NA                              | NA                                  | NA              | NA                |
| 2006 | NA NA                | 1.55                                   | NA                              | NA                                  | NA              | NA                |
| 2007 | 77.59 62.08         | 14.3                                   | 14.08                           | 71.28                               | 8.13            |
| 2008 | 76.34 67.64         | 1.73                                   | 6.97                            | 70.01                               | 8.29            |
| 2009 | 73.08 70.90         | 1.66                                   | 0.52                            | 66.77                               | 8.63            |
| 2010 | 74.60 60.65         | 1.40                                   | 12.55                           | 67.94                               | 8.92            |
| 2011 | 58.70 47.33         | 1.35                                   | 10.02                           | 53.14                               | 9.48            |
| 2012 | NA 76.69            | 1.36                                   | NA                              | NA                                  | NA              | NA                |
| 2013 | 77.18 58.81         | 1.47                                   | 16.90                           | 70.10                               | 9.17            |
| 2014 | 97.64 43.02         | 1.51                                   | 53.11                           | 89.36                               | 8.48            |
| 2015 | 83.07 63.43         | 1.54                                   | 18.11                           | 75.49                               | 9.13            |
| 2016 | 94.74 54.16         | 2.02                                   | 38.56                           | 86.85                               | 8.33            |
| mean | 79.22 61.22         | 1.55                                   | 18.98                           | 72.33                               | 8.73            |

NA means data are not available
Possible impacts of reservoir operation on N transformation in the central of TGR

Reservoir operation resulted in dramatic hydrologic variations, such as water level, flow velocity, and $C_{ss}$, which were more substantial in the middle region (WX site) than in the tail region of TGR. Moreover, almost all periodic and seasonal variations of N forms were significant in the WX site. Hence, the impact of reservoir operation on the N variations in the central of TGR could not be ignored.

For a long time, the concentration of $NH_4^+$-N decreased significantly when other N forms increased in the WX site (Fig. 4). Furthermore, most of the abrupt changes in annual N concentrations were detected shortly after the periodic impoundments, according to the results of MK mutation tests (Fig. s1). During the three impoundments, the water area of the TGR basin, which was about 2.53 times at 175 m (1084 km$^2$) than at 135 m (428 km$^2$), increased as the water level rose, leading to a sharp increase in the water-sediment interface (Wang et al. 2020). This increased interface area would provide larger places for N cycling and facilitate the entry of N to the waterbody.

Additionally, along with the increase of water level difference, the seasonal difference of N concentrations in flood and dry seasons was aggravated in the middle region of TGR during three staged impoundments. As shown in Fig. 7, $NH_4^+$-N and NO$^-_2$-N concentrations were relatively lower in the low water level season than in the impoundment season during period I, but opposite trends appeared during periods II and III; the ratios of NO$^-_3$-N in low water level season and impounding season increased in the WX site.

In each reservoir operation cycle, the water level is regulated to a low level in the rainy season of the Yangtze River (May–October), which reverses the natural hydrology process. Therefore, variations in N forms, which are susceptible to environmental factors, may be altered by large water level fluctuations (145–175 m) and the corresponding dramatic environmental changes caused by reservoir operation. The strong impact of water level variations was also demonstrated by the result of RDA (Fig. 6).

In a low water level season, a water level fluctuation zone (WLFZ) along the reservoir becomes exposed; in the WLFZ, carbon and N contents in soil are high because of the continuous accumulation of organic matter (Wang et al. 2020; Ye et al. 2011). Although the water velocity and $C_{wr}$ in the low water level were lower than those before TGP, they were still about one order of magnitude higher than those in the impoundment period in the WX site. The faster water velocity could strengthen the disturbance to the bottom of the river and promote the ammonification of organic N with oxygen replenishment in the water-sediment surface (Yu et al., 2019). On the other hand, a strong hydrodynamic disturbance would facilitate the suspension of sediments, while the nitrification rate enhances as $C_{wr}$ increases (Wang et al. 2010). The SS is possibly an anoxic/low-oxygen microsite, so coupled nitrification-denitrification may occur in the water column (Xia et al. 2017), and nitrate produced through nitrification at SS can be converted into dinitrogen gas ($N_2$) through denitrification. This N loss enhancement is approximately 25–120% caused by 1 g L$^{-1}$ SS in the Yangtze River (Xia et al. 2017).

When the water level remains high (impoundment season), the dilution effect might make an outstanding contribution to reducing N concentrations because of the dramatically increased storage capacity from $1.71 \times 10^9$ to $3.93 \times 10^9$ m$^3$, comparing to the relatively insignificant variations in N input in the short term. In addition, the reduced water velocity could weaken the entry of N into the water body and prolong the residence time of water in the TGR (Shi et al. 2020). For example, in the reach from the ZT to the WX site, the water residence time increased from 2.69 days in the low water level season to 30.27 days in the impoundment season in 2016. The observably extended water residence time accelerates N removal from a waterbody (Keys et al. 2019; Saunders and Kalff 2001; Tong et al. 2019).

The reservoir operation has regulated the water level and resulted in dramatic environmental variations. However, further developments about the possible impacts of reservoir operation on N variations are still needed to help improve the predictions and management of the water quality in the Yangtze River.

**Conclusion**

In this study, data on 20 hydrological and water quality parameters of seven gaging stations in the TGR basin were collected from 2004 to 2016. The operation of the TGR significantly changed the hydrological regime of natural rivers, improving the water level while decreasing the $C_{ss}$ and water velocity. The impoundment
reduced the PI and BOD$_5$ concentrations, but the TN concentration still met or was even worse than the class V standard of China. The multi-year averaged TN concentration increased along the mainstream of the Yangtze River, but it was still lower than that in the incoming Wu River (2.43 mg/L) and Jialing River (2.01 mg/L). No evident trend was found in the periodic TN concentrations except at the WX and YC sites, whereas other DIN forms markedly changed. The anti-seasonal reservoir operation significantly caused the seasonal variations in different N forms. External input and internal transformation contribute to these variations in N distribution. The continuous long-term increase in the TN concentrations of the TGR was the integrated result of the upstream, non-point, and point source pollution inputs, which accounted for 76%, 22%, and 2%, respectively. In terms of internal transformation, the RDA results revealed that the water level regulated by the anti-seasonal reservoir operation and distance to the TGD had the highest correlations with the variations in N forms.

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### Availability of data and materials
All the data and materials in the manuscript are available upon request.

### Author contribution
Bei Nie: Conceptualization, formal analysis, visualization, writing - original draft preparation
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### Declarations

#### Ethics approval and consent to participate
All the authors have read and approved the manuscript and consented to participation.

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All the authors have consented to publication.

#### Competing interests
The authors declare no competing interests.

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