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Geochemical characteristics and influence to overlying water of nitrogen in the sediments from Cascade Reservoirs of the Lancang River

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ABSTRACT

In order to reveal the effect of nitrogen forms in sediments on nitrogen cycling in overlying water of reservoirs, the distribution characteristics of total nitrogen and bioavailable nitrogen form was analyzed by chemical sequential extraction method in ten representive sediment samples collected in three cascade canyon reservoirs along Lancang River, China. The factors that influence the release of nitrogen form and its potential risk to the overlying water were discussed. The result indicated that there were abrupt changes in the contents of nitrogen speciations between the upstream and downstream of the cascade dams, and the single reservoir also shown obvious spatial gradient characteristics. The concentrations of total nitrogen (TN) ranged from 829.8 mg/kg to 2013.2 mg/kg and the relative concentrations of different nitrogen form ranked according to the following sequence: the non-transferable N (NT-N, 39.19%~62.36%) > organic matter-sulfide fraction N (OSF-N, 23.79%~44.56%) > ion exchangeable N (IEF-N, 6.57%~12.18%) > carbonate fraction N (CF-N, 2.24%~4.22%) > iron-manganese oxides fraction N (IMOF-N, 1.53%~3.87%). IEF-N, CF-N, IMOF-N and OSF-N were the transferable nitrogen forms. The highest content of transferable nitrogen in the sediments from the front of dam of reservoirs (Xiaowan, Manwan, Dachaoshan) was consistent with the reservoir age and pollution degree. The nitrogen concentration in the overlying water was closely related to the distribution of IEF-N from the sediments. OSF-N was an important source of nitrogen in the overlying water. Moreover, NH_4^+-N was the main component of IEF-N, CF-N and IMOF-N. However, the concentrations of NH_4^+-N were relatively higher in the sediments from the front of dams where water bodies flow slowly, indicating that the coupling relationship between eutrophication risk and the cycle of nitrogen in the sediments.

Keywords: Cascade Reservoirs; sediment; nitrogen speciation; the Lancang River

1 INTRODUCTION

The cycle of nutrient elements (C, N, P, etc.) is the basic material cycle in nature(Cai et al. 2004; Zhang et al. 2018). However, human activities may break the original material cycle process(Boyer et al. 2001; Nga et al. 2016), and then, a series of environmental problems may arise, such as water eutrophication, acid rain, greenhouse effect, etc. As one of the key elements of water eutrophication, the biogeochemical process of nitrogen in water and sediments has always been the focus on attention (Davis et al. 2010; Hampton et al. 2017; Rabouille et al. 2001; Yang et al. 2017). The main forms of nitrogen in lake and reservoir ecosystems are dissolved inorganic nitrogen (NO_3^-, NO_2^-, NH_4^+), dissolved organic nitrogen (amino acids, proteins, urea, humus) and granular organic nitrogen (animal and plant debris, ammonia nitrogen adsorbed on mineral surface), which are multiform coexistence and susceptible to microbial activities (Lü et al. 2005; Nga et al. 2016; Zhu et al. 2011), making the nitrogen cycle of lake and reservoir ecosystems complex and changeable.

Nitrogen inputs in lakes and reservoirs includes biological nitrogen fixation, anthropogenic input, atmospheric dry and wet deposition (Cai et al. 2004; Yang et al. 2019), surface runoff, etc. The transformation process of nitrogen involves mineralization and decomposition of organic matter, assimilation and nitrification; The output of nitrogen includes nitrification and denitrification releasing N_2O, runoff output, plant absorption and utilization (Hampton et al. 2017; Li et al. 2018; Rabouille et al. 2001). These processes are organically combined, and there are complex coupling relationships. After a complex biogeochemical process, some nitrogen-containing substances are released into the atmosphere in the form of gases. In addition, nitrogen in overlying water is absorbed by sediments through adsorption, complexation, flocculation and sedimentation, and becomes an important reservoir of nitrogen in lakes and reservoirs(Greenwood and Research 2010; Plas et al. 2007). Under the coupling effects of physics, chemistry and biology, nitrogen in sediments continuously releases to the overlying water and becomes an internal source of nitrogen in lakes and reservoirs(Wang et al. 2008).

Nitrogen is divided into organic and inorganic forms in sediments, both of which are necessary for the metabolism of phytoplankton, zooplanktons, and micro-organisms (Yang et al. 2017; Zhu et al. 2011). At the same time, there are different physical and chemical properties and influencing factors. The size and distribution characteristics of various forms of nitrogen is closely related to the environment of lakes and reservoirs (Hampton et al. 2017; Liu et al. 2015a). It can be said that nitrogen reflects the changes of water environment of lakes and reservoirs to a certain extent. In recent years, the existing forms of nitrogen in sediments of lakes and reservoirs have been extracted and distinguished by the division methods proposed by Wang et al., 2008. According to this classification method, N in sediments is mainly divided into transferable nitrogen (TFN) and non-transferable form (NTN). NTN mainly enters into mineral lattices or is encapsulated by particulate matter and could not be extracted. At the same time, it can be non-biologically utilized, and its contribution to nutrient cycle is limited. The convertible fractions of nitrogen are the main part of the N cycle. According to the different binding modes, it can be further divided into ion-exchangeable form (IEF-N), carbonate form (CF-N), iron-manganese oxide form (IMOF-N), and organic matter-sulfide form (OSF-N).

It is well known that the cascade development on large rivers has significantly changed the runoff process and sediment transport of natural rivers (Wei et al. 2009; Wei et al. 2011). Meanwhile, slow-flowing water formed by reservoirs will also have an impact on water quality, which may cause serious eutrophication of water bodies (Greenwood and Research 2010; Plas et al. 2007). Dams constructed by hydropower stations also block sediments in rivers and influence biogeochemical cycling biogenic materials (Fu and He 2007; Liu et al. 2013; Wang et al. 2012). In addition, the fragmented area formed by the reservoir will also pose a threat to landscape ecology, aquatic habitat and fish breeding and migration. The Yunnan section of Lancang-Mekong River is a key basin for hydropower development in southwestern China and one of the thirteen largest hydropower bases in China. The impact of cascade development on ecological environment is one of the focuses of debate in Southeast Asian countries along the lower Mekong River (Laos, Myanmar, Thailand, Cambodia and Vietnam). Most of the existing studies focused on the impact on the construction of Lancang River cascade reservoir on runoff, water quality, water temperature, sediment and other aspects, but few reports on the biogeochemical cycle of biomass represented by C, N, P in cascade reservoirs (Chong et al. 2014; Li et al. 2007; Yang et al. 2014). In recent decades, although there have been many studies on nitrogen cycle in lakes and reservoir sediments, they are limited to single reservoir or lake. Most of the research objects are concentrated on inorganic forms of nitrogen. Few studies have further classified nitrogen according to its existing forms, let alone analyzed its sources and influencing factors (Borics et al. 2014; Wang et al. 2018). In this paper, the N fractions in sediments of typical cascade reservoirs of Lancang River (Xiaowan, Manwan and Dachaoshan) are studied by using the method of fractional leaching and separation, and the relationships between the nitrogen forms and the physical and chemical factors of sediments are discussed. The influencing factors of different forms of nitrogen release and their potential risks to water environment are discussed, which provides a new way to elucidate the nitrogen cycling process in the sediments of cascade reservoirs.

2 MATERIALS AND METHODS

2.1 Study area

The Lancang-Mekong River originates from Guyong-Pudigao creek in Tanggula Mountains of the Qinghai-Tibet Plateau. The two rivers merge into the Lancang River after Qinghai enters Changdu of Tibet. The main stream is about 4500 km. The total length of the river is 2179 km in China. The basin area is about 1648,000 km^2. The annual average runoff is 475 billion m^3, and the natural drop is about 4583m. The whole length of the Yunnan section of Lancang River is 1240 km (Liu et al. 2013). It enters the province from Weixi County, Yunnan Province, and enters Laos from Mengla County. As of 2018, the Yunnan section of Lancang River has built 7-level hydropower stations, which are Gongguoqiao, Xiaowan, Manwan, Dachaoshan, Nuozhadu and Jinghong from top to bottom. Considering the construction time, influence degree and sedimentary condition of cascade reservoirs, Xiaowan (XW), Manwan (MW), and Dachaoshan (DCS) were selected as the research objects in this study. The study area is located at 99°22′E-100°39′E, 23°59′N-25°22′N, and has an elevation of 850-3000m, a large topographic fluctuation, generally high around and low in the middle. Among them, Xiaowan Dam was the "leading hydropower station" in the Lancang River cascade reservoir, while Manwan was the first cascade hydropower station built in the Lancang River. The main features of the three cascade reservoirs are described in table 1. The average annual temperature in the reservoir area is 11-21 °C, and the average annual rainfall in the reservoir area is 1000-1200mm. The dry (November-April) and wet (May-October) seasons are distinct. About 85% of the precipitation is concentrated in the wet season. The region's economy is dominated by agriculture. The main crops are rice, maize, wheat, legumes and other food crops, as well as cash crops such as rape, catching-up, tea and flue-cured tobacco.

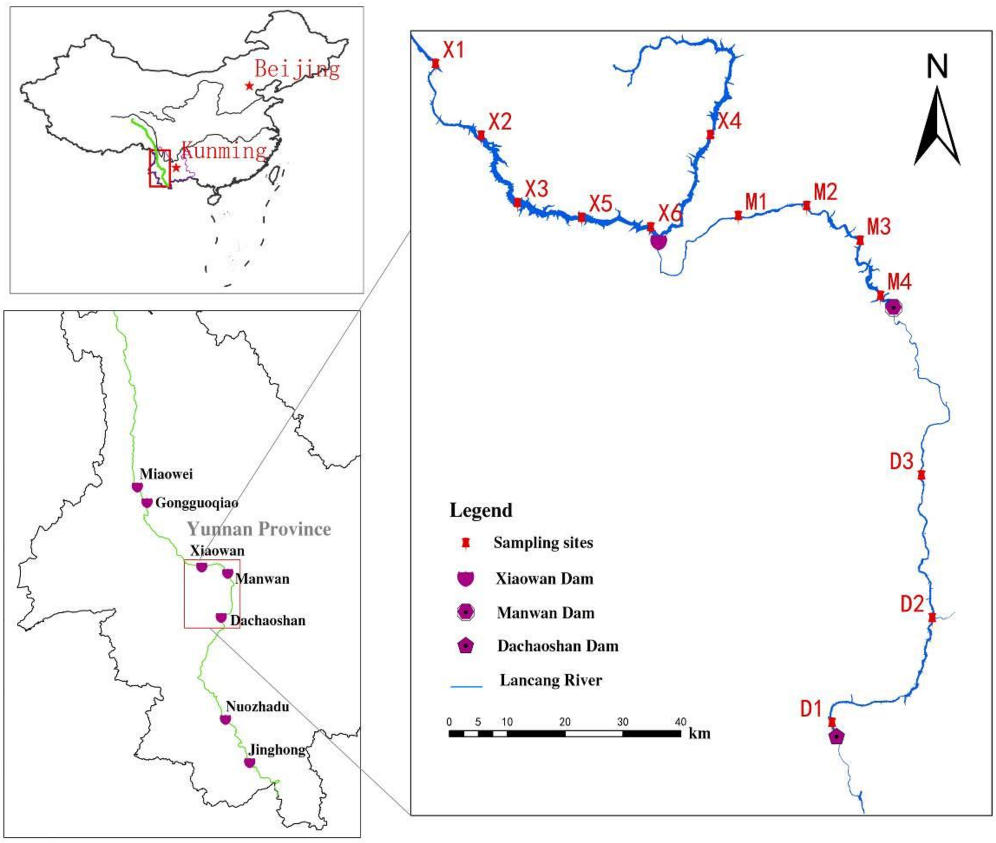

Figure 1. Sediment sampling sites in three cascade reservoirs (Xiaowan, Manwan and Dachaoshan) of

Lancang River

Table 1. The main features of the three cascade reservoirs in the Lancang River

	Xiaowan	Manwan	Dachaoshan
Completed (year)	2012	1993	2003
Average inflow (m^3/s)	1220	1230	1340
Total storage (km^3)	14.56	0.92	0.93
Active storage (km^3)	9.9	0.26	0.37
Full supply level (masl)	1236	994	906
Min. oper. level (masl)	1162	982	860
Net head (m)	248	89	80
Dam height (m)	300	126	110
Plant capacity (MW)	4200	1500	1350
Energy production (GWh)	18540	7870	7090

2.2 Sample collection and chemical analysis

In August, 2018, we collected 13 surface sediment samples (0-8 cm) and overlying water at corresponding sites, each of which involved three sampling zones- riverine, transitional and lacustrine zones in the reservoirs (Fig.1). Surface sediment samples were collected by Peterson dredger, overlying water were collected by2.5L Nisin sampler. The sampling site was located near the center of the river on the vast lake surface. Two to three repetitive samples were collected at each sampling point. After removing the foreign impurities such as gravel, shells, animals and plants, they were fully mixed in a plastic basin and filled with polyethylene sealing belt about 1 kg. The collected water and sediment samples were stored frozen in a portable refrigerator, and transported to the laboratory as soon as possible before being analyzed. Then they were freeze-dried and ground into particles which can pass through a standard 100-mesh nylon sieve for further experiments.

Water temperature (T), dissolved oxygen (DO), electrical conductivity (EC), oxidation reduction potential (ORP) and pH were determined using YSI EXO2 (YSI Inc., Yellow Spirings, OH). Water samples were filtered through pre-combusted 0.45μm mixing fiber Millipore filters (Bandao Industrial Co., Ltd, China), then total nitrogen (TN) concentrations in filtrate were analyzed by a Continuous flow analyzer (SKALAR, San Plus System, Netherlands). Total organic carbon (TOC) content was determined by the TOC-V Total Organic Carbon analyser (Vario TOC Cube, Elementar, Germany).

The sediment grain-size compositions were detected with the laser particle analyser (Microtrac S3500 Inc., USA). Total carbon (TC) and organic carbon (TOC) content were determined by a total organic carbon analyzer (Elementar Liqui TOC II, Frankfurt, Germany). Total nitrogen (TN) of the sediments were determined using elemental analyser (PerkinElmer 2400 CHN Inc., USA). Nitrogen in NH_4^+, NO_3^- and NO_2^- was quantified using a Continuous flow analyzer (SKALAR, San Plus System, Netherlands). Metals- Ca, Fe, Mn and Al were determined by SEPAC method (HJ/T 166-2004) (inductively coupled plasma atomic absorption spectrometry, ICPAES) (SEPAC, 2004).

2.3 Separation of nitrogen Fractions in sediments

According to the previous report (Song et al. 2002), N fractions in sediments were determined using the promoted Ruttenburg's (Ruttenberg and Oceanography 1992)sequential extraction process. Ion-exchangeable form (IEF-N), carbonate-bound form (CB-N), iron-manganese oxide-bound form (IMOBF-N), and iron-manganese oxide form (IMOF-N) were selectively extracted by $MgCl_2$, HAc-NaAc, NaOH and $K_2S_2O_8$ (alkaline), respectively (Table 2). Alkaline potassium persulphate oxidation method was used to determine total nitrogen (TN; APHA, AWWA, and WPCE 1998). The content of NH_4^+-N and NO_3^--N in the supernatant was determined by sodium hypobromide oxidation method and Zn-Cd reduction method respectively, and the content of convertible nitrogen was the sum of the above four nitrogen contents. And the residual-N was determined by the difference between TN and the N fractions extracted above. All samples were analyzed in triplicate, and the results were expressed as the average. Experiments demonstrated high reproducibility of the methods and the experimental error was within 5%.

Table 2. Extraction procedure used in present work

Step	Sequential extraction method	N fractions
1	1 g Sediments added to 20 ml 1 M $MgCl_2$ at pH = 7, shaken for 2 h at 25℃	IEF–N
2	Residual sample added to 20 ml HAc-NaAc, shaken for 6 h at 25℃	CF-N
3	Residual sample added to 20 ml 0.1 M NaOH, shaken for 17 h at 25℃	IMOF-N
4	Residual sample added to 20 ml 0.24M NaOH, 20g/L $K_2S_2O_8$, shaken for 2 h, sterilization of autoclave for 1 h (115℃)	OSF-N

2.4 Analytical methods

Statistical analyses were conducted using SPSS 22.0. statistical package and Origin 2018. A one-way ANOVA test was performed to identify significant differences among different N fractions and among heavy metals in the sediments. The correlation analysis was carried out by Pearson Correlation to provide a quantitative explanation of the relationship between N fractions and heavy metals.

Besides identification of the simultaneous relationships among N fractions and the influencing factors including overlying water, the metal contents and grain size distribution of the sediments, redundancy analysis undertaken in CANOCO software (version 4.5) also can reveal the relationship between different sampling sites (González et al. 2003). The variables explain the spatial variation of the N fractions in the sediments best with $p < 0.05$ before a forward selection procedure combined with Monte Carlo permutation tests.

3 RESULTS AND DISCUSSION

3.1 General physicochemical properties of overlying water and sediment in the reservoirs

The physical-chemical features and the chemical component contents of overlying water and sediment of the three reservoirs were presented in Table 2. The pH of the three reservoirs water varied from 7.98 to 8.58, which indicated the water in reservoir was slight basic. The changes of pH in overlying water significantly influenced hydroxide, carbonate, and silicate equilibria, and these equilibria could regulate the precipitation and dissolution, the sorption and desorption of phosphorus. Dissolved organic carbon concentrations, measured 0.5m above sediment surface and varied from 2.59 to 3.11 mg/L. The concentrations of TN, NH_4^+-N, NO_3^--N in overlying water exhibited a range of 0.83-1.21, 0.23-0.41 and 0.41-0.61 mg/L, respectively. The grain size composition of sediments has an important influence on the adsorption, resolution and migration of nitrogen nutrients. The main components of the surface sediments of the three cascade reservoirs in the transitional and lacustrine zones are clay and silt, and the content of sand minerals is less. All samples contained a water content of approximately 14%, and total organic carbon contents ranged from 8.86 to 18.91 g/kg, with a mean of 13.19 g/kg.

Xiaowan Reservoir is the leading reservoir in the cascade reach of Lancang River. As a large high dam reservoir with multi-year regulation performance, it has significant impact on the flow change of downstream rivers. However, the effect of Xiaowan on sediment interception and accumulation has not been fully revealed since its operation time is only 8 years. It is worth noting that the X4 sampling site located in the middle reaches of Heihuijiang River which is the largest tributary of Xiaowan Reservoir, has different water quality and sediment indexes, compared with other main stream sampling points. Dali, Eryuan and other cities in the upper reaches of Heihuijiang River are densely populated, and the waters with developed agricultural economic activities have a greater impact on water bodies. Manwan was the first constructed dam in Lancang River and has operated for 26 years, which accelerated the sedimentation in the reservoir and contributed to the high contents of OSF-N in the sediments. Similar to Liu et al. (2015), the average concentration of Ca in Manwan Reservoir was the highest of the three reservoirs. Whereas, the highest values of IMOF-N and TN were found in lacustrine zones. Along Manwan and Dachaoshan Reservoir, there are more farmland than Xiaowan Reservoir, which intensifies the external loading of N and contributes to the increasing contents of TN in the sediments. The average concentration of Al, Fe and Mn increased along the longitudinal direction of the three reservoirs with the maximum values in Dachaoshan Reservoir. Silt/clay speciation was the most abundant speciation in the sediments of three reservoirs and the average percentage increased from 57.64% in Xiaowan Reservoir to 67.01% in Dachaoshan Reservoir. It was reported that the fine-textured speciation has an impact on N sorption because it has the specific surface area to provide the possible sorption sites (Yang et al. 2017). Therefore, it was significant to further study the relationship between grain size speciations and the N fractions.

Table 2. Average contents of physical and chemical properties of overlying water and sediments in three cascade reservoirs

		Xiaowan		Manwan		Dachaoshan	
	Parameter	Average	S. D.	Average	S. D.	Average	S. D.
overlying water characteristics	pH	8.31	0.20	8.38	0.10	8.36	0.18
	DO (mg/L)	7.23	0.25	7.40	0.26	6.90	0.20
	ORP (mV)	176.33	10.17	161.25	7.50	152.00	4.00
	EC (μs.cm^{-1})	296.00	7.24	323.25	16.38	298.67	13.65
	TN (mg/L)	1.02	0.12	0.96	0.12	1.04	0.13
	NH_4^+-N (mg/L)	0.31	0.06	0.30	0.05	0.31	0.04
	NO_3^--N (mg/L)	0.52	0.06	0.50	0.07	0.55	0.04
	DOC (mg/L)	2.90	0.17	2.84	0.16	2.76	0.16
Sediment characteristics	bulk density (g.cm^{-3})	0.90	0.15	0.90	0.15	0.93	0.18
	Water content (%)	24.12	8.72	20.53	8.84	22.27	12.16
	Sand (%)	25.02	14.43	30.86	17.46	29.30	19.37
	Silt (%)	27.21	5.85	27.17	7.76	28.30	7.58
	Clay (%)	47.78	9.92	41.97	10.79	33.73	1.30
	TN (mg/kg)	1345.45	450.03	1306.85	438.28	1299.43	442.75
	NH_4^-N (mg/kg)	169.45	28.59	148.01	18.78	156.46	19.99
	NO_3^-N (mg/kg)	47.01	12.41	40.11	8.37	41.05	8.48
	Al×10^4 (mg/kg)	4.43	0.61	5.98	0.67	6.77	0.39
	Ca×10^3 (mg/kg)	2.65	1.51	22.83	0.98	4.41	0.27
	Fe×10^4 (mg/kg)	3.15	0.73	3.44	1.00	3.95	1.05
	Mn×10^3 (mg/kg)	0.37	0.08	0.64	0.12	0.81	0.10

3.2 The longitudinal gradient variation of N Fractions in Sediments of the three cascade reservoirs

Figure 2 shows the longitudinal distribution characteristics of the IEF-N, CF-N, IMOF-N, OSF-N, NTN and TN contents in the sediments. Overall, the TN content in sediments in different zones of reservoir shown similar characteristics and ranked from low to high as follows: lacustrine zones > transitional zones > riverine zones, which is mainly related to the interception of dams, the retention time of reservoir water and the accumulation of sediments in different zones (Chen et al. 2015; Wei et al. 2009). For example, in the upper reaches of riverine zones, because of the shallow water depth, high flow velocity and high proportion of sand in sediments, N pollutants are not easy to flocculate and settle (Bruand and Tessier 2010). After entering the transitional and lacustrine zones, the increase of water depth and the slowdown of flow velocity make the nitrogen nutrients carried by the upper reaches continuously collect and accumulate. The sediments in this area are mainly clay, while IEF-N is easy to adsorb on the surface of clay, which leads to the increase of IEF-N content in sediments in this area. At present, although Erhai lake supplies water to Xiaowan reservoir via Heihuijiang River, the large quantities of agricultural drainage and the relatively high content of TN in the water during the earlier study (the highest reaches 1.9 $mg \cdot L^{-1}$) causes the TN content in sediments in X4 to be relatively high (Liu et al. 2015b; Ni and Wang 2015). Previous studies have shown that lake sediments are considered to be seriously polluted when their total nitrogen content exceeds 1000$mg \cdot kg^{-1}$ (Wang et al. 2008). Therefore, the sediments in the lacustrine zones of all the three reservoirs may be considered seriously polluted by N as a result of the reservoir age and water retention time (Bruand and Tessier 2010). The longitudinal variation trends of the content of IEFN, IMOF-N and OSF-N were essentially the same as the results for TN (gradually increasing from riverine to lacustrine zones). However, the content of CF-N did not show a clear longitudinal variation trend in Dachaoshan reservoir and it even began to decrease and then increased (Figure 2). CF-N is mainly carbonate-bound in sediments, partly bound in clay minerals, and easily released (Biver et al. 2011), then participates in the N cycle of the sediments. Its production and distribution are closely related to the content of carbonate and pH value. Carbonates are widely distributed in the Lancang River basin, and the alkaline water body (pH 7.5 and 8.5) makes the carbonates easy to deposit at the sediment-water interface.

Figure 3 shows the proportions of various N fractions in the TN of the reservoir sediments. In three reservoirs, IMOF-N was the minimum N fractions. IMOF-N includes NaOH leachable fixed nitrogen and Fe/Mn/Al oxide bound nitrogen in clay minerals, which are easily released into water when the pH of sediment-water interface increases and the redox potential decreases (Biver et al. 2011; Wang et al. 2009). The sharp decrease of redox potential at the sediment-water interface caused by the accumulation of phytoplankton residues in lacustrine zones may contribute to the release of IMOF-N (Wang et al. 2015). OSF-N is mainly organic bound nitrogen in sediments, and is the main component of bioavailable nitrogen in reservoir sediments. Organic nitrogen in sediments can include proteins, peptides, amino acids, amino sugars, nucleic acids and other related pigments, humus and so on. It is an important reservoir of nitrogen source in reservoir water. It is mainly interpreted and released in water through physical and chemical processes and microbial activities. And OSF-N accounted for the largest part of N fractions in Xiaowan, Manwan and Dachaoshan Reservoir, which accounted for 68.27%, 65.94% and 69.47% of transferable N respectively. The results show that the abundant organic matter in sediments corresponds to high microbial biomass and activity, and is closely related to NH_4^+-N in interstitial water. This means that the decomposition and release of OSF-N by microorganisms and other environmental conditions is an important source of nitrogen in water (Pisarek and Grata 2013; Rees et al. 2010). The different fractions of nitrogen in the sediments of three cascade reservoirs are affected by the interaction of sediment properties and overlying water. Overall, the proportions of various N fractions in the TN contained in the sediments of the study areas rank as follows: NTN > OSF-N > IEF-N > CF-N > IMOF-N.

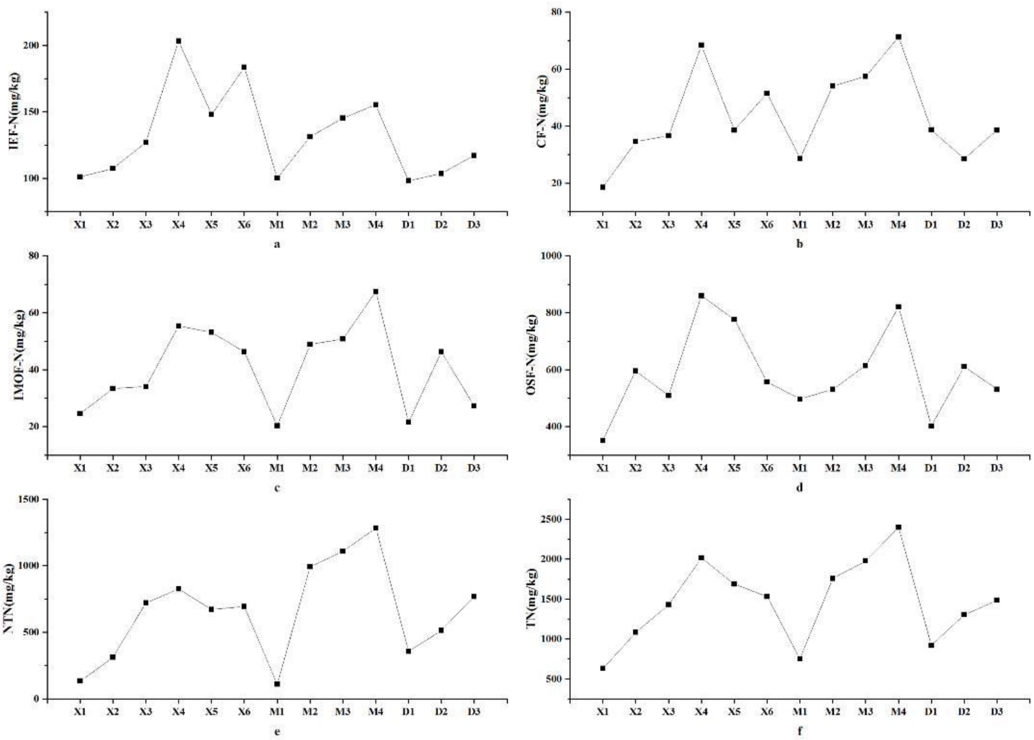

Figure 2. Contents of different N fractions and TN in the sediments of three cascade reservoirs

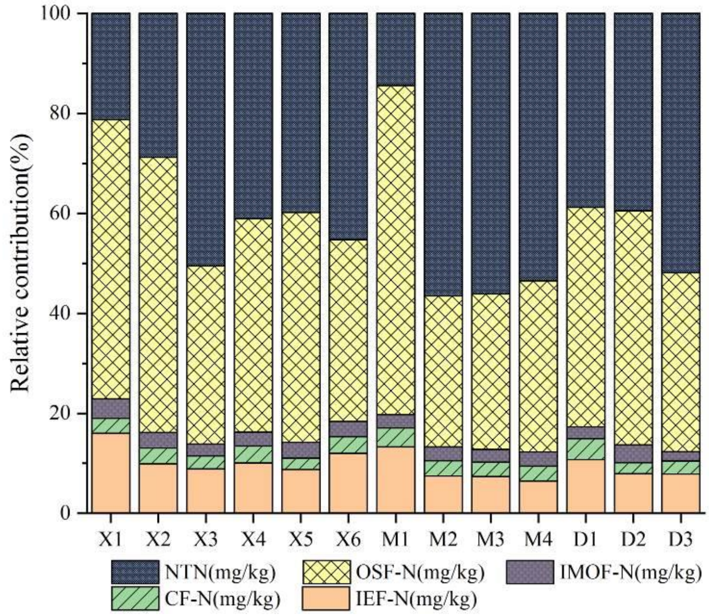

Figure 3. Relative contribution of different N fractions to TN in the sediments

3.3 Geochemical characteristics and influence to overlying water of nitrogen in the sediments

In order to further explore the geochemical behavior of nitrogen speciation in sediments and its impact on water environment, the correlation of nitrogen speciation in reservoir sediments was analyzed by SPSS 22.0 (Table 3) and principal component analysis (Table 4). The results showed that IEF-N, CF-N and IMOF-N were significantly correlated, which indicated that the sources and release processes of inorganic nitrogen were closely related. OSF-N has no significant correlation with other nitrogen forms, indicating that the geochemical behavior of inorganic nitrogen and organic nitrogen are two relatively independent processes (Biver et al. 2011; Wang et al. 2015). In addition, non-transferable form (NTN) was not significantly correlated with various forms of nitrogen. Compared with bioavailable nitrogen, NTN is relatively stable buried in sediments and difficult to release (Wang et al. 2009). The geochemical behavior of NTN is significantly different from that of bioavailable nitrogen.

Table 3. Correlation matrix between N fractions in the sediments from the three cascade reservoirs

	IEF-N	CF-N	IMOF-N	OSF-N	NTN
IEF-N	1				
CF-N	0.793**	1			
IMOF-N	0.785**	0.764*	1		
OSF-N	0.464	0.359	0.404	1	
NTN	0.328	0.220	0.556*	0.434	1

* $p < 0.05$, ** $p < 0.01$, n=13

Principal component analysis of nitrogen forms in sediments shows that the cumulative contribution rate of the first three principal components is about 71.73%, which reflects most of the data (Table 3). The contribution rate of the first principal component is about 37.9%. IEF-N, CF-N and IMOF-N have larger loads and have the same change direction. Combined with correlation analysis, it is further shown that IEF-N, CF-N and IMOF-N are similar in their sources. In addition, their effects on water environment are mainly controlled by the changes of N-related factors in overlying water, such as TN, NH_4^+-N and NO_3^--N. NTN is the second principal component with a larger load. As a non-bioavailable and non-transferable N, this component may reflect the influence of burial on the geochemical behavior of nitrogen forms in sediments. On the contrary, the loads of IEF-N, CF-N, IMOF-N and OSF-N imply a greater risk of release of bioavailable nitrogen. The third component is IMOF-N, which mainly reflects the effect of microorganisms on nitrogen morphology in sediments. It mainly reflects the accumulation of IMOF-N in sediments caused by phytoplankton residues and the decomposition and release of IMOF-N by microorganisms. In addition, combined with the first component, the source of IMOF-N also extends the input of the riparian ecosystem of the reservoir, and its decomposition is also affected by physical and chemical factors (Wang et al. 2015). Therefore, the geochemical process of IMOF-N is complex, and the biogeochemical process of organic nitrogen in reservoir sediments and its impact on water environment need to be further studied.

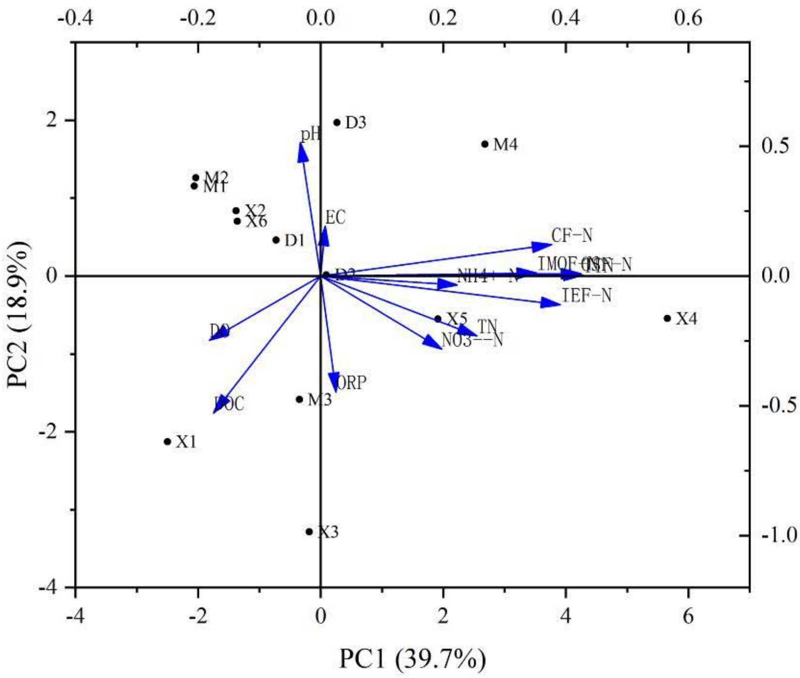

Figure 4. PCA results for N fractions and overlying water in the three cascade reservoirs

Studies also showed the amount of N released from sediments had a close relation with IEF-N, CF-N and IMOF-N (Wang et al., 2008). IEF-N is the main participant of nitrogen cycle in the reservoirs. NH_4^+-N and

NO_3^--N in IEF-N are controlled by different factors, among which NH_4^+-N is positively correlated with organic matter content, while NO_3^--N is correlated with water content in sediments. IEF-N is a weakly bound nitrogen in sediments, which is easy to release, and the rate of migration and transformation at the sediment-water interface is the most significant. The content of IEF-N in sediments of lacustrine zones is 1.3-1.8 times that of other areas, and the TN level in overlying water is 1.4-1.7 times that of other areas, which indicates that IEF-N in sediments of lacustrine zones may contribute significantly to the high nitrogen level of water body (Scholz 2011).

In addition, NH_4^+-N is the main component of IEF-N, CF-N and IMOF-N, followed by NO_3^--N, and NO_2^--N is mostly below the detection limit (Figure 4). NH_4^+-N is the most potential threat to the nitrogen nutrition level in the overlying water. NH_4^+-N is the first inorganic form absorbed and utilized by phytoplankton. During the period of reservoir turnover, sediments are disturbed by temperature and hydrodynamics. The release of NH_4^+-N may promote the growth of phytoplankton. Wang et al. (2009) found that NH_4^+-N in IEF-N has a good positive correlation with organic carbon and sulfide, and NO_3^--N is closely related to allochthonous input. X4 is a sediment sampling site in the upper reaches of Heihuijiang River, a branch of Xiaowan Reservoir, which should have higher NH_4^+-N due to the influence of urban pollution discharge in the upper reaches. However, the content of NH_4^+-N in IEF-N of X4 sediment is not high, but close to that of NO_3^--N. On the one hand, the density of phytoplankton in X4 area is high, the demand for NH_4^+-N is high, and the light intensity at the sediment-water interface is weak, while the process of NO_3^--N absorption into organic nitrogen is slow; on the other hand, NO_3^--N in IEF-N of X4 sediment may be related to a large number of exogenous inputs. At the same time, the natural air-drying pretreatment of samples and the process of sealed refrigeration may also have some influence on the results. Most of NH_4^+-N still exists in CF-N and IMOF-N, probably because NH_4^+-N is similar to K^+, which can be temporarily fixed in minerals and released or converted to other forms of nitrogen under appropriate conditions (Zhu et al. 2011). The mechanism of their existence, migration and transformation is complex. The continuous chemical extraction enriches the morphological and geochemical characteristics of nitrogen in reservoir sediments, but the results inevitably deviate from the real situation of the existing forms of nitrogen in sediments. Therefore, more advanced analytical methods, such as XRD and SEM (Hoesen and Arriaza 2011; Minkina et al. 2018; Nizoli and Health 2012; Pignotti et al. 2018), can be used to further characterize and explore the nitrogen biogeochemical cycle and its impact on reservoir water quality.

The distribution and release of CF-N in the sediments is typically determined by the carbonate and organic matter contents (Table 4). CF-N was only positively correlated with the content of silt and bulk density in sediments. IMOF-N mainly refers to N combined by Fe-hydroxides and Mn compounds in the sediments. Previous studies have shown that high dissolved oxygen, high acidity and alkalinity, low bacterial activity and total organic carbon will reduce the release of IMOF-N (Wang et al. 2008). However, due to the competitive adsorption of organic matter with iron/manganese oxides in surface sediments, high total organic carbon will lead to low IMOF-N. In this study, IMOF-N was not significantly correlated with the content of Al+Mn in sediments (Wang et al. 2009; Yang et al. 2017). This might be caused by the obstruction of clay and ooze, which weakens the release of IMOF-N in the lacustrine zones of sediments. The distribution of OSF-N is related to factors of different grain size fractions, and Eh. The smaller the grain size and the lower the Eh, the higher the OSF-N content. In this study, OSF-N was significantly positively correlated with TOC and silt contents in sediments, which is in accordance with the findings of Lü et al. and Wang et al. Other studies have shown that Fe, Mn and Al oxides in sediments can improve bioavailability of N by reducing the efficiency of nitrogen fixation by CEC (Wang et al. 2008). In fact, the content of overlying water and sediment properties is only a small part of the many factors affecting the distribution of N fractions and the distribution of N fractions in different reservoirs is a result of the synthetic action of the various factors.

Table 4. Correlation between different fractions of N and environmental factors in overlying water and sediments

		IEF-N	CF-N	IMOF-N	OSF-N	TTN
overlying water	pH	-0.065	0.055	-0.146	-0.066	-0.066
	DO	-0.171	-0.201	-0.368	-0.430	-0.399
	ORP	0.251	-0.068	0.222	0.097	0.115
	EC	-0.181	0.228	0.296	0.053	0.053
	TN	0.565*	0.437	0.147	0.459*	0.467*
	NH_4^+-N	0.566*	0.375	0.139	0.369	0.391
	NO_3^--N	0.353	0.200	0.105	0.318	0.314
	DOC	-0.235	-0.476*	-0.147	-0.319	-0.320
sediments	bulk density	0.681*	0.744**	0.710**	0.847**	0.844**
	Water content	0.693**	0.752**	0.709**	0.844**	0.842**
	Sand	-0.636*	-0.619*	-0.680**	-0.771**	-0.768**
	Silt	0.738**	0.724**	0.729**	0.846**	0.849**
	Clay	-0.773**	-0.186	0.711**	0.651*	-0.071
	TOC	0.773**	0.801**	0.756**	0.903**	0.905**
	NH_4^+-N	0.892**	0.567*	0.660*	0.874**	0.875**
	NO_3^--N	0.818**	0.633*	0.501*	0.711**	0.730**
	Al	-0.217	0.234	0.179	0.181	0.145
	Ca	0.463	0.401	0.313	0.608*	0.583*
	Fe	0.402	0.619*	0.607*	0.713**	0.691*
	Mn	-0.156	0.157	-0.007	0.105	0.076

* $p < 0.05$, ** $p < 0.01$, n=13

4. CONCLUSION

The construction of Xiaowan, Manwan and Dachaoshan hydroelectric dams in Yunnan section of Lancang River has significantly changed the characteristics of N fractions in reservoir sediments. The proportions of various N fractions in TN in sediments of reservoirs ranked as follows: NTN > OSF-N > IEF-N > CF-N > IMOF-N. For Lancangjiang Reservoir, the potential threats of bio-available nitrogen include IEF-N, WAEF-N, SAEF-N and SOEFN. Among them, IEF-N is closely related to the level of nitrogen nutrition and eutrophication in overlying water, and SOEF-N is an important source of nitrogen in overlying water.

As shown by the correlation analysis results, IEF-N, IMOF-N, OSF-N, TT-N and TN were significantly positively correlated with the contents of TOC, clay and silt but were significantly negatively correlated with the contents of sand. For the sediments of Lancangjiang river cascade reservoirs, the potential bioavailability of endogenous nitrogen is relatively high, which has great potential ecological risk. While controlling the input of exogenous nitrogen pollution, more attention should be paid to the release of bioavailable nitrogen in sediments and its impact on water environment.

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