

Spatial-temporal variation of nitrogen and diffusion flux across the water-sediment interface at the hydro-fluctuation belt of Danjiangkou reservoir in China

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ABSTRACT

Based on overlying water and sediment sample collection from 15 sites during July, September, November 2018 and January 2019 in the hydro-fluctuation belt of Danjiangkou reservoir China, the variation of nitrogen (N) was studied. And the concentrations of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and $\text{NO}_2^-\text{-N}$ in the sediment, pore water and overlying water were determined to evaluate the diffusion flux across the water-sediment interface. The results showed that the lowest sediment N concentration was 36.54 mg/L in July, and the highest one was 145.93 mg/L in November. Spatially, the sediment N concentrations were higher in tidal soil and loam than in sandy soil. According to the diffusion fluxes of NH_4^+ , NO_3^- and NO_2^- , sediments at all sites tend to release N to the overlying water except in the sampling month of November, when the sediment acts as a sink of NO_3^- . The highest release rates of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ were $17.66 \text{ mg m}^{-2}\cdot\text{d}^{-1}$ and $80.15 \text{ mg m}^{-2}\cdot\text{d}^{-1}$, respectively, which are much higher than the release rate of $\text{NO}_2^-\text{-N}$ ($0.29 \text{ mg m}^{-2}\cdot\text{d}^{-1}$). The findings indicate that hydro-fluctuation belt sediment contributes a lot to the nitrogen contents in the overlying water, and internal pollution is a main reason for the water quality deterioration and even eutrophication.

Key words | Danjiangkou reservoir, diffusion flux, hydro-fluctuation belt, nitrogen, sediment

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INTRODUCTION

Eutrophication is one of the greatest concerns in the field of water environment and water ecology. Excess nutrient accumulation (especially nitrogen and phosphorus) is of critical importance in the eutrophication of aquatic ecosystems. Due to eutrophication, problems such as algal blooms, oxygen depletion, decreasing species biodiversity, and aquatic ecosystem deterioration may occur (Smith & Schindler 2009; Chislock *et al.* 2013). Under the influence of human activities, eutrophication and hypoxia of aquatic ecosystems has become a problem of water pollution control worldwide.

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Nitrogen (N) plays a dominant role in the biogeochemical cycle of aquatic ecosystems, and the change of its content and proportion will affect the community structure of aquatic vegetation, the sediment nutrient distribution and energy transformation (Zhao *et al.* 2019). Many rivers and lakes worldwide have changed their trophic status due to large amounts of nitrogen entering the water bodies (Xu *et al.* 2010), and some studies have estimated that anthropogenic N from grey footprints could contribute 32.6 million tons annually to aquatic systems (Mekonnen & Hoekstra 2015). As one of the main limiting factors for eutrophication, N mainly comes from atmospheric deposition, nitrogen fixation and sediment retention, etc. (Holland *et al.* 1999; Herridge *et al.* 2008). On the one hand, sediment can act

as an important retention tank for nitrogen and purify the overlying water. On the other hand, taking agricultural fertilization as an example, only 30–40% of the fertilizer applied to farmland can be absorbed and utilized by crops, and the excess nitrogen accumulated in the sediment is mobilized and released and results in eutrophication of the water body, even groundwater pollution (Luederitz *et al.* 2001). Thus, sediment plays an important role in the eutrophication process as well as restoration and water quality control.

Due to the uneven spatial–temporal distribution of water resources in China, plenty of water conservancy and hydropower projects have been constructed to achieve the optimal allocation of water resources and promote the sustainable development of the social economy. However, water level fluctuation caused by reservoirs for electric power generation, irrigation and flooding control has been a common phenomenon worldwide. Under the long-term periodic fluctuation of water level, a large area of hydro-fluctuation belts has been formed. Hydro-fluctuation belt refers to the interface between terrestrial and aquatic ecosystems formed in the basin of a reservoir due to water level fluctuation caused by hydrologic regulation (Gregory *et al.* 1991). Hydro-fluctuation belts play a critical role in buffering and filtering non-point source pollution, such as reservoir sediments, organic matter, agricultural fertilizer and wastewater. It is the last barrier to ensure the safety of reservoir water quality (Gregory *et al.* 1991; Zhang *et al.* 2012a).

According to the characteristics of hydro-fluctuation belts, a large area of land is in the alternating state of drying–wetting annually, which causes a change in soil physical–chemical characteristics, soil oxidation–reduction state, soil anaerobic–aerobic state and microbial environment (Ma *et al.* 2010; Erakhrumen 2011). However, after inundation, the problem is that nutrients, heavy metals and pesticides accumulated in the sediments are mobilized, released across the water–sediment interface and transported to the overlying water, resulting in water environment deterioration (Ma *et al.* 2008). The change of water quality and sediment properties in hydro-fluctuation belts is closely related to the periodic fluctuation of water level; the highest values of total phosphorus, soluble reactive phosphorus, nitrate and chlorophyll-*a* were found during the minimum water level phase of reservoirs (Geraldés & Boavida 2005).

Reservoirs act in an indispensable role in water supply and water resources management, and reservoir water quality protection is one of the greatest concerns with the development of urbanization in China (Shi *et al.* 2016). Due to long water residence time, nutrients and mineral elements can accumulate in reservoirs more easily than in running water (Szarek-Gwiazda & Mazurkiewicz-Boroń 2002). To date, some studies have examined the distribution characteristics and load of soil organics and nutrients in the hydro-fluctuation belts, and gradually hydro-fluctuation belts have become a hot topic in the water environment domain. The aim of this study was to study the spatial–temporal distribution of overlying water and sediment and investigate the diffusion process of nitrogen in the reservoir hydro-fluctuation belt, which will provide a theoretical basis for managing the water environment of Danjiangkou reservoir.

MATERIALS AND METHODS

Study area description

Danjiangkou reservoir is one of the world's largest water conservancy and hydropower projects. It is located in Henan province and Hubei province, at the junction of Han River and Dan River (110°47'53"–110°34'47"E, 32°14'10"–32°58'10"N). Danjiangkou reservoir is also the water intake of the North-to-South water transfer middle route project and the largest freshwater lake in Asia. The sub-tropical monsoon climate in Danjiangkou reservoir basin is characterized by four distinctive seasons. The mean annual temperature is 13.7 °C and the mean annual precipitation is 805 mm with around 80% occurring between April and October (Cheng *et al.* 2013). The soil type at the site is classified as yellow-brown soil, based on the Chinese soil classification system (Liu *et al.* 2014).

The crest elevation of Danjiangkou reservoir dam was raised in 2013 in accordance with the North-to-South water transfer project program. The normal water level is gradually being raised to 170 m, the highest water level is 172 m and the dead water level is 160 m. According to the operation mode of the reservoir, the water level of Danjiangkou reservoir runs at about 160 m in the flood season from May to June 21; by August 21, the water level rises to

163.5 m (autumn flood control water level); and after October 1, the water level gradually increases back to normal water level (170 m). There occurs a drop zone with a vertical difference from altitude 160 m to 172 m, and a large number of terrestrial ecosystems have been transformed into riparian ecosystems, forming a hydro-fluctuation belt of over 285.7 km².

Collection and chemical analysis of water and sediment samples

Fifteen field experimental sites were allocated in the hydro-fluctuation belts of Danjiangkou reservoir area and located using a GPS device; locations are shown in Figure 1. According to the soil type, the 15 sampling sites can be categorized into loam, sandy soil and tidal soil (four sites for loam, six for sandy soil and five for tidal soil) (Table 1). Field sampling campaigns were performed in July, September, November 2018 and January 2019, which represented two stages (drying and inundation). Also, the seasonal variation (summer, autumn and winter) could be studied. There was no obvious rain before sampling. Overlying water samples were collected in 500 ml polyethylene bottles by using 60 ml syringes at approximately 10 cm below the water

surface. Water samples were stored at 4 °C in a car refrigerator for further processing and analysis. Additionally, during each sampling campaign, the overlying water temperature, dissolved oxygen (DO, mg·L⁻¹), pH and electrical conductivity (EC, μs·cm⁻¹) were measured simultaneously in situ by a multi-parameter water quality meter (HORIBA, Japan). Calibration of sensors was performed before measurement.

The sediment-water column samples were collected at each plot by a gravity sampler, and the sediment samples were sealed in polyethylene plastic bags and kept at 4 °C for further analysis. The sediment samples were separated into two parts, one part for the measurement of sediment physicochemical properties, which were freeze-dried, homogenized and ground to fine powder for analyzing TN, NH₄⁺-N, NO₃⁻-N and NO₂⁻-N, and the other one for sediment pore-water analysis. Pore water was extracted from bulk sediment by centrifugation at 3,000 rpm for 30 minutes (TDZ4-WS, Shanghai Incorporation) and filtered through 0.45 μm cellulose acetate filters by low pressure vacuum. Pore water could be extracted from greater volumes of sediment more rapidly, especially from sandy sediments.

The index of nutrient elements in the overlying water and sediment of Danjiangkou hydro-fluctuation belt includes

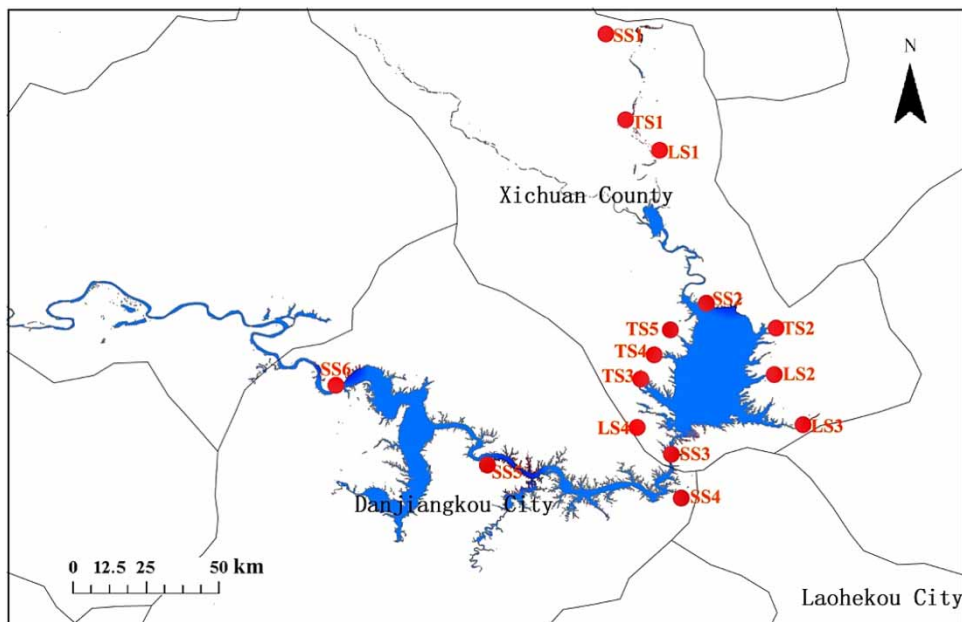


Figure 1 | Location of different sampling sites in hydro-fluctuation belts of Danjiangkou reservoir, China.

Table 1 | Sampling coordinates, soil types and land use of the sampling sites

Site	Sampling coordinates	Soil type	Land use	Area/km ²	Ratio
SS1	111°16'58"E, 33°4'31"N	Sandy soil	Lands for municipal parks	4.81	3%
SS2	111°20'2"E, 32°29'29"N		Dock, tourist area	3.21	2%
SS3	111°18'17"E, 32°21'43"N		River bank under Danjiangkou bridge	1.60	1%
SS4	111°17'36"E, 32°19'53"N		Urban riparian area	8.02	5%
SS5	111°9'1"E, 32°22'15"N		River bank under Tuliang bridge	1.57	1%
SS6	111°1'56"E, 32°25'25"N		River bank under Xijun bridge	1.59	1%
TS1	111°17'37"E, 33°0'47"N	Tidal soil	Shrub and grassland	11.23	7%
TS2	111°24'10"E, 32°28'15"N		Agricultural land	28.89	18%
TS3	111°17'9"E, 32°27'16"N		Agricultural land	19.26	12%
TS4	111°16'29"E, 32°26'33"N		Agricultural land	24.07	15%
TS5	111°15'51"E, 32°24'14"N		Agricultural land	17.65	11%
LS1	111°18'47"E, 32°34'20"N	Loam	Shrub, dock	3.22	2%
LS2	111°24'12"E, 32°26'38"N		Agricultural land	16.05	10%
LS3	111°24'51"E, 32°23'45"N		Floodplain	8.02	5%
LS4	111°18'12"E, 32°27'56"N		Agricultural land	11.21	7%

the following: total nitrogen (TN), ammonium nitrogen ($\text{NH}_4^+\text{-N}$), nitrate nitrogen ($\text{NO}_3^-\text{-N}$) and nitrite nitrogen ($\text{NO}_2^-\text{-N}$). And the index of nutrient elements in pore water includes $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ as well as $\text{NO}_2^-\text{-N}$. Analysis methods were as follows. TN was determined by the alkaline potassium persulfate digestion-UV spectrophotometry method. After sample filtering by 0.45 μm cellulose acetate filters, $\text{NH}_4^+\text{-N}$ was determined by Nessler's reagent colorimetric method, $\text{NO}_3^-\text{-N}$ was determined by a UV spectrophotometry method (the chromogenic agent was phenol disulfonic acid) and $\text{NO}_2^-\text{-N}$ was determined by a UV spectrophotometry method (the chromogenic agent was sulfanilamide and *n*-(1-naphthyl)-ethylenediamine dihydrochloride). Sediment moisture content (W) was determined by a gravimetric method, dried 6 h at 105 °C until a constant weight was reached, and the sediment porosity was calculated as follows:

$$\varphi = \frac{Wd_s}{((1 - W)d_w) + Wd_s} \quad (1)$$

where W is the moisture content, d_s is the sediment average density (2.65 g cm^{-3}) and d_w is the density of the overlying water (1 g cm^{-3}). Three replicates were done for each parameter and from each plot.

Diffusion flux

It is important to recognize the exchange processes of nutrients between the sediments and the overlying water in order to understand the impacts of polluted sediments on the aquatic environment. Generally, nutrients are released from sediments and maintained in the pore water first, and then they are transformed and diffused into the overlying water under a concentration gradient (Zhao et al. 2017). In static water, the transport process across the sediment-water interface is dominated by the direct diffusion process. The diffusion flux can be estimated based on the measured concentration gradient between sediment pore water and overlying water. Positive values are indicative of desorption (efflux) while negative values indicate adsorption (influx). In this study, the diffusion fluxes of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and $\text{NO}_2^-\text{-N}$ were determined by Fick's first law. According to Ullman & Aller (1982), Fick's first law can be expressed as follows:

$$F = \frac{\varphi D_w}{\theta^2} \frac{\partial C}{\partial x} \quad (2)$$

where F is the flux of a solute with concentration C at depth x , φ is the sediment porosity on the surface, and D_w

is the ideal diffusion coefficient of nutrients in the infinitely dilute solution. For $\text{NH}_4^+\text{-N}$, $D_w = 17.6 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$; for $\text{NO}_3^-\text{-N}$, $D_w = 19.0 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$; for $\text{NO}_2^-\text{-N}$, $D_w = 19.1 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$; θ is the tortuosity and $\partial C/\partial x$ is the concentration gradient of chemical species between pore water and overlying water, which was calculated from sediment pore-water at a depth of 1 cm minus the overlying water at the sediment surface.

Tortuosity was estimated from porosity and F_r (formation resistivity factor) (Bear 1972):

$$\theta^2 = \varphi F_r \quad (3)$$

F was estimated by an empirical formula in accordance with Archie (1942):

$$F_r = \frac{1}{\varphi^m} \quad (4)$$

where $\varphi \geq 0.7$, $m = 3$; $\varphi < 0.7$, $m = 2$.

RESULTS AND DISCUSSION

Physicochemical characteristics of sediments and overlying water

The physical-chemical characteristics in the sediments and the overlying water from the hydro-fluctuation belt of

Danjiangkou reservoir are shown in Table 2. As seen in Figure 2(a), we can find that the DO of the overlying water in SS, TS and LS decreased with the increasing temperature except for the sampling in July, which has the highest DO concentrations at all sites. This may be attributed to the longer daytime in summer, and the photosynthesis of phytoplankton increasing with more DO in the water column. Additionally, since the monitoring time is daytime, when the phytoplankton photosynthesis stops at night, the DO concentrations will be reduced significantly. However, despite that, the DO concentrations are much higher than the water quality criteria (criterion V, 2 mg L^{-1}) (GB3838-2002).

Studies have found that some sediment characteristics affect nutrient diffusion and flux in the water-sediment interface (Murray et al. 2006). It is significant to analyze the sediment characteristics. Sediment moisture content ranged from 23.81% at SS to 62.17% at LS. And the highest moisture contents at all sites were found in September (Figure 2(b)). Because of the long-duration inundation and sufficient contact between the sediment and overlying water, as well as the biogeochemical processes across the sediment-water interfaces, the sediment porosities in SS, TS and LS were fairly accepted.

Temporal and spatial variation of nitrogen in sediment

Many forms of nitrogen exist in sediment, which include $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, $\text{NO}_2^-\text{-N}$ and some small-molecular organic

Table 2 | Physical-chemical characteristics in the sediments and overlying water during July 2018–January 2019

Site	Period	Overlying water			Sediment		
		T (°C)	DO (mg/L)	pH	Porosity	Moisture content (%)	OM (mg/L)
SS	Jul. 2018	29.54	20.61	7.99	0.51 ± 0.08	26.51	21.86
	Sep. 2018	27.95	10.72	8.47		37.91	15.38
	Nov. 2018	19.97	13.01	8.29		34.58	11.97
	Jan. 2019	9.79	15.80	8.16		23.81	10.28
TS	Jul. 2018	31.28	20.90	8.05	0.63 ± 0.06	30.54	31.42
	Sep. 2018	28.63	11.29	8.58		52.39	32.04
	Nov. 2018	20.12	13.45	8.48		38.91	22.84
	Jan. 2019	7.98	16.75	8.17		33.78	14.24
LS	Jul. 2018	31.14	23.26	8.22	0.64 ± 0.08	27.51	25.52
	Sep. 2018	28.20	10.78	8.54		62.17	28.49
	Nov. 2018	19.49	14.64	8.50		32.39	14.73
	Jan. 2019	7.30	17.11	8.14		37.66	19.82

Values are means of the corresponding soil-type samples. Sandy soil (SS) ($n = 6$), tidal soil (TS) ($n = 5$) and loamy (LS) ($n = 4$) were collected from the hydro-fluctuation belt of Danjiangkou reservoir. For porosity, values are means ± SD (where $n = 4$).

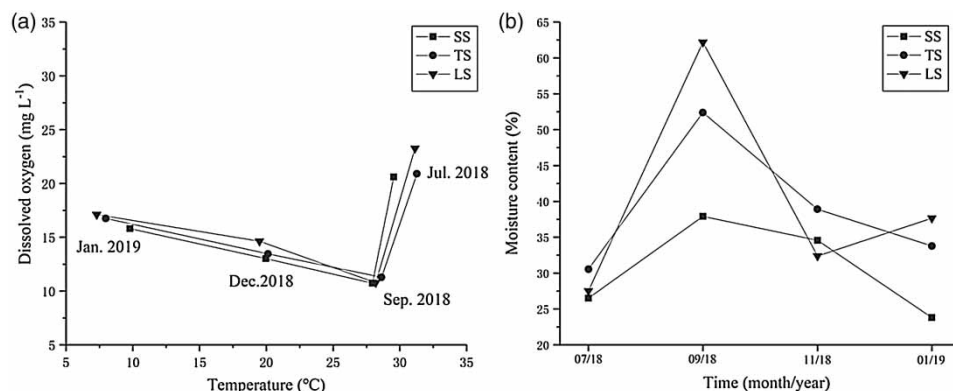


Figure 2 | (a) The trend of DO concentrations (mg L⁻¹) in the overlying water with temperature (°C). (b) The sediment moisture content (%) in SS, TS and LS.

compounds. The temporal variation of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and $\text{NO}_2^-\text{-N}$ in the sediment of the hydro-fluctuation belt is shown in Figure 3. The highest $\text{NO}_2^-\text{-N}$ concentration in the sediment was found in July, when the accumulated amount reached 17.18 mg L^{-1} . The extensive use of chemical fertilizers during agricultural cultivation is undoubtedly an important reason for the accumulation of nitrite in the environment (Zhu & Chen 2002). Large areas of lands are used for agriculture during the dry period of the reservoir before the water level increased, which led to a higher nitrite concentration. After that, the nitrite concentration decreased rapidly and finally stabilized. The nitrate concentrations increased with sampling date and the extreme high value was found in November. The top 5 cm vertical depth of

sediment can be considered as an active area for nutrient release and transport by biogeochemical dynamics. The increased $\text{NO}_3^-\text{-N}$ concentrations were probably due to nitrification enhanced by higher microbial activity, as well as enough organic compounds by long-term agricultural cultivation and increased temperature. The ammonium concentrations were relatively steady, which was a similar trend to nitrate. For the dissolved inorganic N concentrations in the sediment of the hydro-fluctuation belt in Danjiangkou reservoir, the lowest concentration (36.54 mg L^{-1}) was in July, while the highest one (145.93 mg L^{-1}) was in November, which was three times higher than the lowest value.

The spatial variations of different N components in the sediment of the hydro-fluctuation belts are shown in Figure 4. The sampling sites were in SS (SS1–SS6), TS (TS1–TS5) and LS (LS1–LS4). The main nitrogen forms of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and $\text{NO}_2^-\text{-N}$ had higher concentrations in TS and LS than SS. This can be explained by the different types of land use (Table 1). The sampling sites of TS and LS are mainly used for agricultural cultivation (73%), floodplain (5%) and wasteland covered by shrub (9%). Thus, the long-term agricultural cultivation and nitrogen fixing by microorganisms made nitrogen accumulation more significant at these sites. And the sampling sites of SS, which had lower nitrogen concentrations probably due to the artificial river bank, could intercept and retain less nitrogen, with more non-point N pollutants entering the reservoir rather than being deposited in the sediments. Agricultural non-point pollution mainly refers to the pollution caused by soil particles, nitrogen, phosphate, pesticides and other organic or inorganic pollutants entering the water. Agricultural land

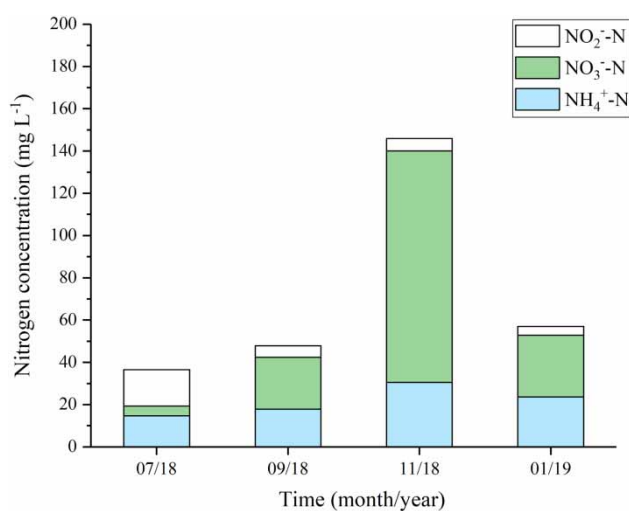


Figure 3 | The temporal variation of different N forms in the sediment of the hydro-fluctuation belt in Danjiangkou reservoir.

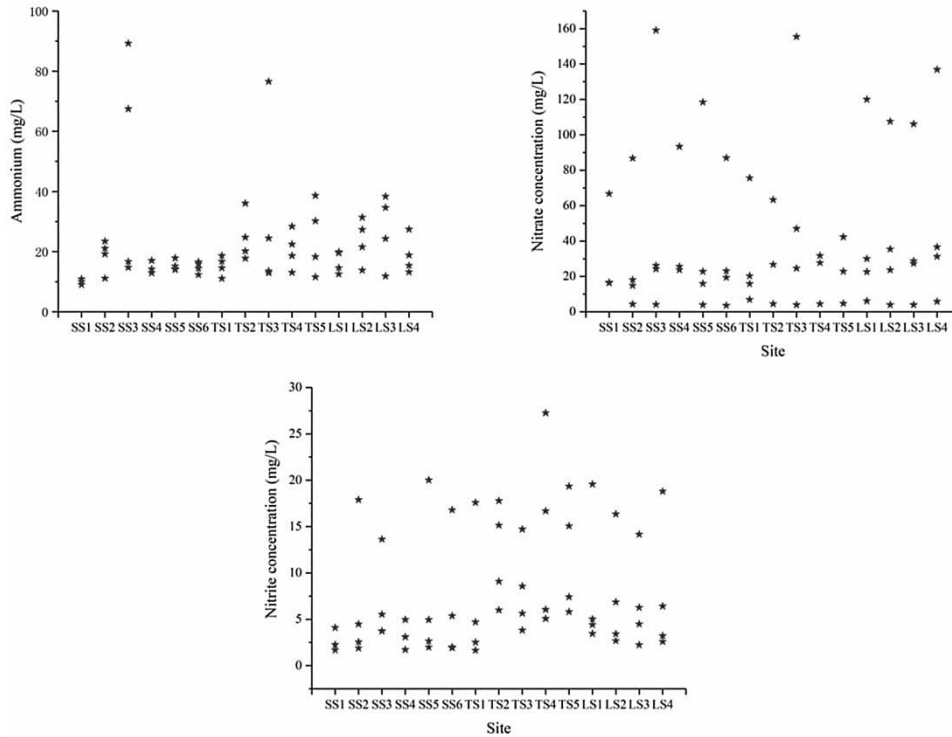


Figure 4 | The spatial variation of different N forms in the sediment of the hydro-fluctuation belts in Danjiangkou reservoir.

is the most important land use mode in the hydro-fluctuation belt of Danjiangkou reservoir (Table 1), the pollution load in agricultural land and bare land are much higher. In recent years, the quantities of TN and TP entering Danjiangkou reservoir were about 1,508.34 and 158.50 t/a respectively. Nitrogen fertilizer is the main source of fertilizer pollution, and the amount of lost nitrogen caused by surface runoff and field drainage accounted for 13.6–16.6% of total fertilizer used for farming (Whipple & Hunter 1977). During the flood season, the quantities of $\text{NH}_4^+\text{-N}$, TN and TP entering Danjiangkou reservoir account for 50.1%, 50.8% and 47.3% of the total amount for the whole year respectively. Therefore, the overall nitrogen concentrations were higher in TS and LS than SS, and the highest sediment nitrogen concentration was observed in November 2018.

Temporal and spatial variation of nitrogen in surface water

Temporal variation of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and $\text{NO}_2^-\text{-N}$ in the overlying water of the Danjiangkou reservoir is shown in

Figure 5. The main forms of nitrogen were ammonium ($\text{NH}_4^+\text{-N}$) and nitrate ($\text{NO}_3^-\text{-N}$), there were no obvious fluctuations in $\text{NH}_4^+\text{-N}$ concentration observed, and the lowest $\text{NH}_4^+\text{-N}$ concentration was detected in winter (November

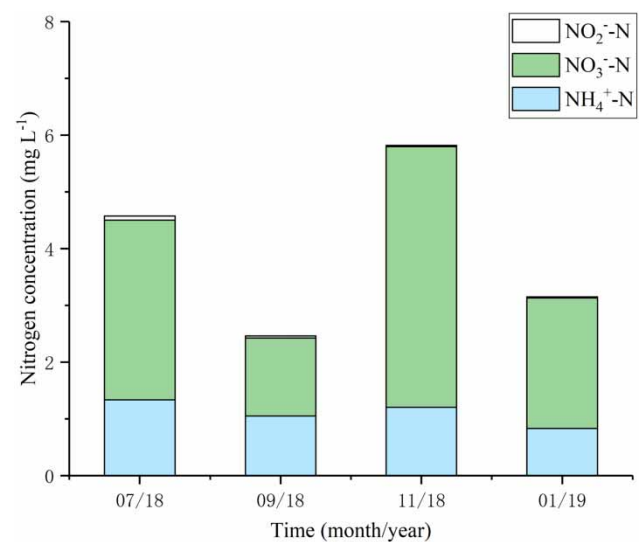


Figure 5 | The temporal variation of different N forms in the overlying water of the hydro-fluctuation belt in Danjiangkou reservoir.

2019), which can be explained by the lower temperature leading to the lower microbial degradation of organic nitrogen compounds.

However, the NO_3^- -N concentration showed a fluctuation over time. The lowest overlying water NO_3^- -N concentration (1.37 mg L^{-1}) was observed in September 2018, and according to the operation mode of Danjiangkou reservoir, the water level of the hydro-fluctuation belts increased from August and large areas of land were changed to a submerged condition. Additionally, the study region has a sub-tropical monsoon climate with most rainfall in summer. Thus, the higher water level and heavy rainfall may dilute the NO_3^- -N concentration, and the aquatic vegetation in the water could absorb the nutrients, all of these combined actions leading to a lower nitrate concentration. After this, NO_3^- -N concentration increased rapidly and reached the highest concentration (4.59 mg L^{-1}) in November, which was probably due to long-time inundation of the sediments and a portion of NO_3^- -N release from the sediments due to the combined processes of nutrient fluxes and

nitrification. The concentration of NO_3^- -N decreased in January as a result of the lower temperature, which not only weakened the activity of nitrifying bacteria but also reduced the nutrient diffusion rates.

The spatial variation of different N components in the overlying water of the hydro-fluctuation belt was also studied (Figure 6). The sampling plots were in SS (SS1–SS6), TS (TS1–TS5) and LS (LS1–LS4). There was no significant difference in TN concentrations with spatial variation. However, the main components, NH_4^+ -N and NO_3^- -N, had higher concentrations in TS than in SS and LS. The sampling sites for TS were mainly used as agricultural lands and orchards and were adjacent to villages. With the water level rising, excess N nutrients accumulated in the agricultural lands were released and resulted in higher concentrations of the water layer. Moreover, parts of the untreated domestic wastewater discharged into the water body, and there was lower self-purification capacity in the hydro-fluctuation belt, all of which led to higher NH_4^+ -N and NO_3^- -N concentrations in the water layer (Wei *et al.* 2009).

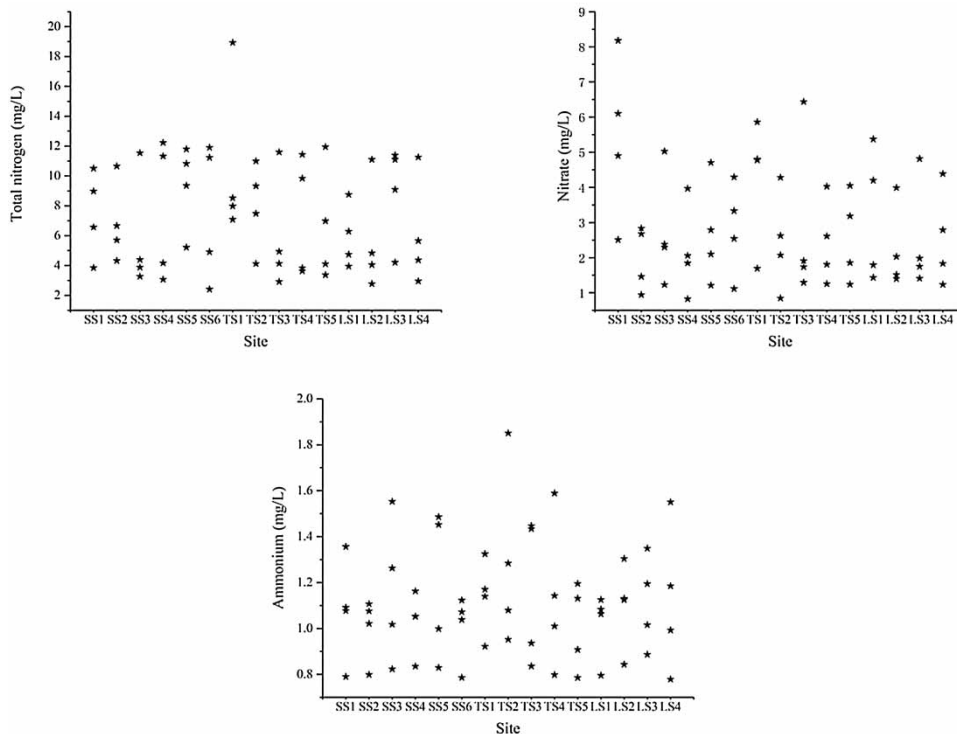


Figure 6 | The spatial variation of different N forms in the overlying water of the hydro-fluctuation belt in Danjiangkou reservoir.

Diffusion flux of nitrogen across water-sediment interface

With the increasing loads of nitrogen from agricultural fertilizers and non-point pollution, lots of dissolved nitrogen accumulates in the sediment by adsorption and sedimentation, which leads to higher nitrogen concentrations in the surface of the sediment (Cheng et al. 2014). According to Equations (2)–(4), the required parameters for diffusive fluxes across the sediment-water interface calculation are shown in Table 3. The top surface area is an active zone for the sediments; the average porosities for three sites were: 51% for SS, 63% for TS and 64% for LS, which are less than 70%, thus the parameters m , F_r and θ^2 can be determined, and the actual diffusion coefficients of nutrients acquired.

Sediment-water interface nitrogen dynamics and fluxes which include transformation (ammonification, nitrification

and denitrification), net movement into sediments (adsorption) and release into overlying water (desorption) via physical and biogeochemical processes are influenced by a wide range of factors. The hydro-fluctuation belt, due to its drying-rewetting regime and microorganism activity, is a place of intense accumulation and recycling of nutrients. The concentration ratio between sediment pore water and overlying water can reflect the releasing of internal pollutants due to the close relationship (Zhao et al. 2017). Based on the calculated diffusive fluxes across the sediment-water interface of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and $\text{NO}_2^-\text{-N}$ (Table 4), sediments at all sites were sources of nitrogen nutrients to the overlying water except in the sampling month of November, when both sites were a relatively large sink of NO_3^- (-14.558 to -10.610 $\text{mg m}^{-2}\cdot\text{d}^{-1}$ for SS, -16.971 to -14.020 $\text{mg m}^{-2}\cdot\text{d}^{-1}$ for TS and -5.573 to -4.334 $\text{mg m}^{-2}\cdot\text{d}^{-1}$ for LS). And it can be found that the release of nitrogen nutrients in the Danjiangkou hydro-fluctuation belt is not to be neglected. $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ release rates reach up to 17.66 $\text{mg m}^{-2}\cdot\text{d}^{-1}$ and 80.15 $\text{mg m}^{-2}\cdot\text{d}^{-1}$, respectively, which is much higher than the release rate of $\text{NO}_2^-\text{-N}$ (0.29 $\text{mg m}^{-2}\cdot\text{d}^{-1}$). The concentration ratios of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ between pore water and overlying water were in the ranges 1.43–2.40 and 1.13–7.65, respectively. Generally, the sites which had obvious concentration gradients tended to have higher ratios. This indicates that ammonium and nitrate are the main nitrogen pollution in the study area and nitrate has higher diffusion flux than ammonium, while nitrite is the intermediate product of nitrification and denitrification, which will not accumulate in terrestrial and aquatic ecosystems for a long time (Burns et al. 1995).

Table 3 | The parameters of diffusive fluxes across the sediment-water interface (NH_4^+ , NO_3^- and NO_2^-)

Site	Nutrients	Porosity/%	M	F_r	θ^2	$D_w/ (10^{-6} \text{ cm}^2 \text{ s}^{-1})$
SS	NH_4^+	0.51 ± 0.08	2	3.84	1.96	17.6
	NO_3^-					19.0
	NO_2^-					19.1
TS	NH_4^+	0.63 ± 0.06	2	2.52	1.59	17.6
	NO_3^-					19.0
	NO_2^-					19.1
LS	NH_4^+	0.64 ± 0.08	2	2.44	1.56	17.6
	NO_3^-					19.0
	NO_2^-					19.1

Table 4 | Diffusive fluxes across the sediment-water interface of NH_4^+ , NO_3^- and NO_2^-

Site	Period	$\text{NH}_4^+\text{-N}$		$\text{NO}_3^-\text{-N}$		$\text{NO}_2^-\text{-N}$	
		$dC/dx/(\text{mg L}^{-1}\cdot\text{cm}^{-1})$	$F/(\text{mg m}^{-2}\cdot\text{d}^{-1})$	$dC/dx/(\text{mg L}^{-1}\cdot\text{cm}^{-1})$	$F/(\text{mg m}^{-2}\cdot\text{d}^{-1})$	$dC/dx/(\text{mg L}^{-1}\cdot\text{cm}^{-1})$	$F/(\text{mg m}^{-2}\cdot\text{d}^{-1})$
SS	Sep. 2018	0.447	1.490–2.045	0.187	0.673–0.923	0.005	0.019–0.026
	Nov. 2018	0.115	0.385–0.528	–2.946	–14.558 to –10.610	0.031	0.114–0.156
	Jan. 2019	0.486	1.620–2.223	16.219	58.144–80.146	0.059	0.212–0.291
TS	Sep. 2018	0.709	3.865–4.679	5.771	33.965–41.115	0.119	0.705–0.853
	Nov. 2018	1.551	8.455–10.235	–2.382	–16.971 to –14.020	0.012	0.071–0.086
	Jan. 2019	0.638	3.478–4.211	6.023	35.445–42.908	0.016	0.095–0.115
LS	Sep. 2018	0.958	5.230–6.725	0.119	31.373–40.337	0.137	0.813–1.045
	Nov. 2018	2.516	13.731–17.655	0.012	–5.573 to –4.334	0.021	0.126–0.162
	Jan. 2019	1.155	6.303–8.103	0.016	39.005–50.150	0.017	0.101–0.129

Fluxes of NO_3^- -N varied significantly with sampling period, and NO_3^- -N diffusive fluxes strongly decreased at all sites by denitrification. The NH_4^+ -N effluxes at all sites indicated sediment organic matter mineralization and reduction of NO_3^- -N, while the increased value measured from September to November except at SS could be the consequence of denitrification supported by anaerobic conditions. The oxygen level at the water-sediment interface depending mostly on organic matter accumulation and dissolved oxygen in the overlying water. The high rate of microbial processes and the long-time sediment inundation usually lead to an anaerobic condition at the water-sediment interface, and a denitrification process often occurs (Kemp *et al.* 1997). Additionally, anoxic conditions could accelerate the nutrient exchange between sediment and overlying water. The decreased release rate in January as a consequence of the lower temperature in winter will not only reduce the microbial reactions but also retard the rate of molecular diffusion.

As a result, sediments seemed to be a significant source of inorganic nitrogen nutrients for the overlying water in autumn and winter despite the low temperature suggesting low mineralization rates and bacterial and benthic microalgae N utilization rates. Sediments in the hydro-fluctuation belt provide the nutrients to the water body and maintain the growth of hydrophytes and phytoplankton in the Danjiangkou reservoir, but this is only one side of the matter. On the other side, the diffusive fluxes of nitrogen shown in Table 4 are quite large and may have a negative effect on the water body for a duration, although the nutrients from external sources have been effectively controlled. The internal nutrient mobilization from sediment would be an important factor leading to eutrophication.

CONCLUSIONS

In this study, the physicochemical characteristics of the sediment and the overlying water in the hydro-fluctuation belt of Danjiangkou reservoir were determined, the spatial-temporal variation of nitrogen in the sediment and surface water were studied, and the diffusive fluxes of nitrogen nutrients across the sediment-water interface were calculated.

- (1) Due to the high concentration of NO_3^- -N and NH_4^+ -N in the sediment, the hydro-fluctuation belt sediment of

Danjiangkou reservoir has become a potential source of inner pollution. The lowest sediment nitrogen concentration (36.54 mg L^{-1}) was observed in July, and the highest concentration (145.93 mg L^{-1}) was in November, which was three times higher than the lowest value. These indicate that water quality deterioration and eutrophication are more likely to occur in the reservoir in November.

- (2) The main nitrogen components in the overlying water are NH_4^+ -N and NO_3^- -N, while the concentration of NO_2^- -N can be neglected. The concentrations of NH_4^+ -N were relatively steady, while the NO_3^- -N concentrations varied significantly over time. Agriculture is the most important type of land use in the hydro-fluctuation belt of Danjiangkou reservoir. The sampling site of TS had higher N concentrations, which indicates that agricultural irrigation was more likely to cause water pollution in hydro-fluctuation belts.
- (3) In accordance with Fick's first law, the diffusive fluxes of NH_4^+ -N, NO_3^- -N and NO_2^- -N across the sediment-water interface were calculated. Sediments at all sites were sources of nitrogen nutrients to the overlying water except in the sampling month of November, when both sites were a relatively large sink of NO_3^- -N. For NH_4^+ -N and NO_3^- -N, the release rates reach up to $17.66 \text{ mg m}^{-2} \cdot \text{d}^{-1}$ and $80.15 \text{ mg m}^{-2} \cdot \text{d}^{-1}$, respectively, which is much higher than the release rate of NO_2^- -N ($0.29 \text{ mg m}^{-2} \cdot \text{d}^{-1}$). The sediment of the hydro-fluctuation belt contributes a lot to the nitrogen content in the overlying water.

AUTHOR CONTRIBUTIONS

Conceptualization, H.W. and Y.P.H.; Sampling, H.W. and L.D.P.; Sample Measurement, L.D.P.; Writing – original draft, H.W. All authors contributed to the drafting and approval of the manuscript for submission.

DISCLOSURE STATEMENT

The authors declare that they have no competing interests.

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