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

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ABSTRACT

Based on overlying water and sediment samples collection from fifteen sites during July, September, November 2018 and January 2019 in hydro-fluctuation belt of Danjiangkou reservoir China – the variation of nitrogen (N) was studied. And the concentrations of NH$_4^+$-N, NO$_3^-$-N and NO$_2^-$-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 concentrations 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 sandy soil. According to diffusion fluxes of NH$_4^+$, NO$_3^-$ and NO$_2^-$, sediments at all sites tend to release N to the overlying water except sampling month of November, where sediment act as a sink of NO$_3^-$. The highest release rates of NH$_4^+$-N and NO$_3^-$-N were 17.66 mg m$^{-2}$·d$^{-1}$ and 80.15 mg m$^{-2}$·d$^{-1}$, respectively, which is much higher than the release rate of NO$_2^-$-N (0.29 mg m$^{-2}$·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 deteriorate even eutrophication.

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

INTRODUCTION

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

Nitrogen (N) play a dominant role in the biogeochemical cycle of aquatic ecosystem, the change of its content and proportion will affect the community structure of aquatic vegetations, the sediment nutrients distribution and energy transformation (Zhao et al. 2019). Many rivers and lakes worldwide have changed the trophic status due to large amount of nitrogen entering the water bodies (Xu et al. 2010), and some studies have estimated that anthropogenic N from grey footprints could contribute to 32.6 million tons annually to aquatic systems (Mekonnen & Hoekstra 2018). As one of the main limiting factors for eutrophication, N mainly comes from atmospheric deposition, nitrogen fixation and sediment retention et al. (Holland et al. 1999; Herridge et al. 2008). On the one hand, sediment can act
as an important retention tank for nitrogen and purified the overlying water. On the other hand, take agricultural fertilization as an example, only 30%–40% of the fertilizer applied to farmland can be absorbed and utilized by crops, the excess nitrogen accumulated in the sediment are mobilized and released and result in eutrophication of the water body, even groundwater pollution (Luederitz et al. 2002). Thus, sediment play an important role in eutrophication process as well as restoration and water quality control.

Due to the uneven spatial-temporal distribution of water resource 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 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 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 alternated state of drying-wetting annually, which has 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 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 minimum water level phase of reservoir (Geraldes & Boavida 2005).

Reservoirs, act as an indispensable role in water supply and water resources management, reservoir water quality protection is one of the most concern with the development of urbanization in China (Shi et al. 2016). Due to long water residence time, nutrients and mineral elements could accumulate in reservoir more easily than in running water (Szarek-Gwiazda & Mazurkiewicz-Boroń 2002). To date, some studies have examined the distribution characteristics and load of soil organic 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.

MATERIAL 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 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 has been raised in 2013 according to 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 operation mode of the reservoir, the water level of Danjiangkou reservoir is running 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 occurred a drop zone with the vertical difference (from altitude 160 m to 172 m), and a large number of terrestrial ecosystems have been transformed into riparian ecosystem, forming a hydro-fluctuation of over 285.7 km².

**Collection and chemical analysis of water and sediment sample**

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 (4 sites for loam, 6 for sandy soil and 5 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 seasonally variation (summer, autumn and winter) can be studied. There was no obvious rain before sampling. Overlying water samples were collected in a 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 process 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, the sediment samples were sealed in polyethylene plastic bags and kept at 4 °C for further analysis. The sediment samples were separated for two parts, one part for the measurement of sediment physio-chemical 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. Porewater 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 overlying water and sediment of Danjiangkou hydro-fluctuation belt includes the following: total nitrogen (TN), ammonium nitrogen...
(NH₄⁺-N), nitrate nitrogen (NO₃⁻-N) and nitrite nitrogen (NO₂⁻-N). The index of nutrient elements in pore water includes NH₄⁺-N, NO₃⁻-N as well as NO₂⁻-N. Analysis methods were as follows. TN were determined by alkaline potassium persulfate digestion-UV spectrophotometry method. After sample filtering by a 0.45-μm cellulose acetate filters, NH₄⁺-N was determined by Nessler’s reagent colorimetric method, NO₃⁻-N was determined by UV spectrophotometry method (the chromogenic agent was phenol disulfonic acid) and NO₂⁻-N was determined by 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, the sediment porosity was calculated as follows:

\[
\varphi = \frac{W_d}{((1 - W)d_w + Wd_s)}
\]

(1)

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

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

| Site | Sampling coordinates | Soil type | Land use | Area/km² | 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% |

### Diffusion flux

It’s 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 environments. Generally, nutrients released from sediments and maintained in the pore water first, and then they are transformed and diffused into overlying water under the concentration gradient (Zhao et al. 2017). In the static water, the transport process across the sediment-water interface is dominant 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 NH₄⁺-N, NO₃⁻-N and NO₂⁻-N were determined by Fick’s first law. According to Ullman & Aller (1982), the Fick’s first law can be expressed as follows:

\[
F = \frac{\varphi D_w \partial C}{\partial x}
\]

(2)

where F is the flux of a solute with concentration C at depth x, \( \varphi \) is the sediment porosity on the surface, \( D_w \) is
the ideal diffusion coefficient of nutrients in the infinitely dilute solution. For NH$_4^+$-N, $D_w = 17.6 \times 10^{-6}$ cm$^2$s$^{-1}$; For NO$_3^-$-N, $D_w = 19.0 \times 10^{-6}$ cm$^2$s$^{-1}$; For NO$_2^-$-N, $D_w = 19.1 \times 10^{-6}$ cm$^2$s$^{-1}$. $\theta$ 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 porewater at the depth of 1 cm minus the overlying water in the sediment surface.

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

$$\theta^2 = \phi F_r$$

(3)

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

$$F_r = \frac{1}{\phi^m}$$

(4)

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

RESULTS AND DISCUSSIONS

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 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 day time in summer, the photosynthesis of phytoplankton can increase more DO in the water column. Additionally, since the monitoring time is daytime, with the phytoplankton photosynthesis stopped at night, the DO concentrations will be reduced significantly. However, despite that, the DO concentrations are much higher than water quality criteria (criterion V, 2 mg L$^{-1}$) (GB3838-2002).

Studies have found that some sediment characteristics affects the nutrients diffusion and flux in the water-sediment interface (Murray et al. 2006). It’s significantly 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.

| Site | Period | Overlying water | Sediment |
|------|--------|-----------------|----------|
| 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 | 30.54 | 31.42 |
|      | Nov. 2018 | 19.97 | 13.01 | 8.29 | 37.91 | 15.38 |
|      | Jan. 2019 | 9.79  | 15.80 | 8.16 | 34.58 | 11.97 |
| TS   | Jul. 2018 | 31.28 | 20.90 | 8.05 | 0.63 ± 0.06 | 23.81 | 10.28 |
|      | Sep. 2018 | 28.63 | 11.29 | 8.58 | 35.48 | 11.97 |
|      | Nov. 2018 | 20.12 | 13.45 | 8.48 | 32.39 | 14.24 |
|      | 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 | 32.39 | 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 types 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 ± S.D. (where $n = 4$).
compounds. The temporal variation of NH$_4^+$-N, NO$_3^-$-N and NO$_2^-$-N in the sediment of hydro-fluctuation belt is shown in Figure 3. The highest NO$_2^-$-N concentrations in the sediment was found in July, 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 were used for agriculture during the dry period of reservoir before the water level increases, which lead 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 find in November. The top 5 cm vertical depth of sediment can be considered as an active area for nutrients release and transport by biogeochemical dynamics. The increased NO$_3^-$-N concentrations 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 had a similar trend to nitrate. For the dissolved inorganic N concentrations in the sediment of hydro-fluctuation belt in Danjiangkou reservoir, the lowest concentrations (36.54 mg L$^{-1}$) was in July, while the highest one (145.95 mg L$^{-1}$) was in November, which was 3 times higher than the lowest value.

The spatial variation of different N components in the sediment of hydro-fluctuation belts were shown in Figure 4. The sampling sites were in SS (SS1-SS6), TS (TS1-TS5) and LS (LS1-LS4). The main nitrogen forms which include NH$_4^+$-N, NO$_3^-$-N and NO$_2^-$-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 microorganism made nitrogen accumulation more significant in 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, more non-point N pollutants enter the reservoir rather than deposited in the sediments. Agricultural non-point pollution mainly refers to the pollution caused by soil particles, nitrogen, phosphate, pesticide and other organic or inorganic pollutants entering water. Agricultural land is the

![Figure 2](https://example.com/fig2.png)  
**Figure 2** | The trend of DO concentrations (mg L$^{-1}$) in the overlying water with temperature (°C). (a) The sediment moisture content (%) in SS, TS and LS. (b).  

![Figure 3](https://example.com/fig3.png)  
**Figure 3** | The temporal variation of different N forms in the sediment of hydro-fluctuation belt in Danjiangkou reservoir.
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 quantity of TN and TP entering Danjiangkou reservoir was about 1508.34 and 158.50 t/a respectively. Nitrogen fertilizer is the main source of fertilizer pollution, 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 2011). During flood season, the quantity of NH$_4^+$-N, TN and TP entering Danjiangkou reservoir account for 50.1%, 50.8% and 47.3% of the total amount of the whole year respectively. Therefore, the overall nitrogen concentrations were higher in TS and LS than SS, and the highest sediment nitrogen concentration were observed in November 2018.

**Temporal and spatial variation of nitrogen in surface water**

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

![Figure 4](https://iwaponline.com/wp-content/uploads/2020/04/f4.jpg)

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

![Figure 5](https://iwaponline.com/wp-content/uploads/2020/04/f5.jpg)

*Figure 5* The main forms of nitrogen were ammonium (NH$_4^+$-N) and nitrate (NO$_3^-$-N), there were no obvious fluctuations in NH$_4^+$-N concentrations observed, and the lowest NH$_4^+$-N concentrations were detected in winter (Nov.

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

![Figure 6](https://iwaponline.com/wp-content/uploads/2020/04/f6.jpg)

*Figure 5* The temporal variation of different N forms in the overlying water of hydro-fluctuation belt in Danjiangkou reservoir.
2019), this can be explained by the lower temperature which lead to the lower microbial degradation of organic nitrogen compounds.

However, the NO$_3$-$N$ concentrations showed a fluctuation over time. The lowest overlying water NO$_3$-$N$ concentrations (1.37 mg L$^{-1}$) observed in Sep. 2018, according to the operation mode of Danjiangkou reservoir, the water level of the hydro-fluctuation belts increase since August and large area of lands are changed to 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$_3$-$N$ concentrations, and the aquatic vegetations in water could absorb the nutrients, all of these combined actions lead to a lower nitrate concentration. After this, NO$_3$-$N$ concentrations increased rapidly and reached to highest concentration (4.59 mg L$^{-1}$) in November, which 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 nutrients fluxes and nitrification. The concentration of NO$_3$-$N$ decreased in January as a result of the lower temperature which not only weaken the activity of nitrifying bacteria but also reduce the nutrients diffusion rates.

The spatial variation of different N components in the overlying water of 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 the spatial variation. However, for the main components, NH$_4$$^+$-$N$ and NO$_3$-$N$, had higher concentrations in TS than SS and LS. The sampling sites for TS were mainly used as agricultural lands, orchard and adjacent to villages. With the water level rising, excess N nutrients accumulated in the agricultural lands are released and result in higher concentrations of the water layer. Moreover, parts of the untreated domestic wastewater discharged into water body, and the lower self-purification capacity in the hydro-fluctuation belt, all of which lead to higher NH$_4$$^+$-$N$ and NO$_3$-$N$ concentrations in water layer (Wei et al. 2009).

Figure 6 | The spatial variation of different N forms in the overlying water of hydro-fluctuation belt in Danjiangkou reservoir.
Diffusion flux of nitrogen across water-sediment interface

As the increasing loads of nitrogen by agricultural fertilizers and non-point pollution, lots of dissolved nitrogen accumulated in the sediment by adsorption and sedimentation which lead to the higher nitrogen concentrations in the surface of sediment (Cheng et al. 2014). According to the Equations (2)–(4), the required the 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 parameter m, Fr and \( \theta^2 \) can be determined, the actual diffusion coefficients of nutrients were 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. 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 except sampling month of November, where both sites were a relative large sink of NO\(_3\) (−14.558 to −10.610 mg m\(^{-2}\)d\(^{-1}\) for SS, −16.971 to −14.020 mg m\(^{-2}\)d\(^{-1}\) for TS and −5.573 to −4.334 mg m\(^{-2}\)d\(^{-1}\) for LS). And it can be found that the release of nitrogen nutrients in Danjiangkou hydro-fluctuation belt are not to be neglected. NH\(_4\)-N and NO\(_3\)-N release rates reach up to 17.66 mg m\(^{-2}\)d\(^{-1}\) and 80.15 mg m\(^{-2}\)d\(^{-1}\), respectively, which is much higher than the release rate of NO\(_2\)-N (0.29 mg m\(^{-2}\)d\(^{-1}\)). The concentration ratio of NH\(_4\)-N and NO\(_3\)-N between pore water and overlying water ranged from 1.43 ~ 2.40 and 1.13 ~ 7.65, respectively. Generally, the sites which had obvious concentration gradients tend to have higher ratios. This indicates that ammonium and nitrate are the main nitrogen pollution in the study area and nitrate have higher diffusion fluxes than ammonium, while nitrite is the intermediate product of nitrification and denitrification, which will not accumulate in terrestrial and aquatic ecosystem for a long time (Burns et al. 1995).

Table 3 | The parameters of diffusive fluxes across the sediment-water interface (NH\(_4\), NO\(_2\) and NO\(_3\))

| Site | Nutrients | Porosity/% | M   | Fr  | \( \phi^2 \) | \( D_{aw} (10^{-4} \text{cm}^2 \text{s}^{-1}) \) |
|------|-----------|------------|-----|-----|-------------|-----------------|
| SS   | NH\(_4\)   | 0.51 ± 0.08| 2   | 3.84| 1.96        | 17.6             |
|      | NO\(_3\)   |            |     |     |             |                  |
|      | NO\(_2\)   |            |     |     |             |                  |
| TS   | NH\(_4\)   | 0.63 ± 0.06| 2   | 2.52| 1.59        | 17.6             |
|      | NO\(_3\)   |            |     |     |             |                  |
|      | NO\(_2\)   |            |     |     |             |                  |
| LS   | NH\(_4\)   | 0.64 ± 0.08| 2   | 2.44| 1.56        | 17.6             |
|      | NO\(_3\)   |            |     |     |             |                  |
|      | NO\(_2\)   |            |     |     |             |                  |

Table 4 | Diffusive fluxes across the sediment-water interface of NH\(_4\), NO\(_2\) and NO\(_3\)

| Site | Period | NH\(_4\)-N | NO\(_3\)-N | NO\(_2\)-N |
|------|--------|------------|------------|------------|
|      |        | \( \text{dC/dx}/(\text{mg L}^{-1}\text{cm}^{-1}) \) | \( F/\text{(mg m}^{-2}\text{d}^{-1}) \) | \( \text{dC/dx}/(\text{mg L}^{-1}\text{cm}^{-1}) \) | \( F/\text{(mg m}^{-2}\text{d}^{-1}) \) | \( \text{dC/dx}/(\text{mg L}^{-1}\text{cm}^{-1}) \) | \( F/\text{(mg m}^{-2}\text{d}^{-1}) \) |
| 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 | 15.731−17.655 | 0.012 | −5.573 to −4.334 | 0.021 | 0.126−0.162 |
|      | Jan. 2019 | 1.155 | 6.305−8.103 | 0.016 | 39.005−50.150 | 0.017 | 0.101−0.129 |
Fluxes of NO$_3^-$-N varied significantly with sampling period, 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 condition. The oxygen level in water-sediment interface depending mostly on the 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 in water-sediment interface, denitrification process often occurred (Kemp et al. 1997). Additionally, anoxic condition could accelerate the nutrients exchange between sediment and the overlying water. The decreased release rate in January as a consequence of the lower temperature in winter which 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 water body and maintain the growth of hydrophyte and phytoplankton in the Danjiangkou reservoir, this is only one side of the matter. On the other side, the diffusive fluxes of nitrogen shown in Table 4 are quite large that may have a negative effect on water body for a duration, although the nutrients from external sources have been effectively controlled. The internal nutrients mobilization from sediment would be an important cause lead to eutrophication.

CONCLUSIONS

In this study, the physiochemical 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, and the lowest sediment nitrogen concentration (36.54 mg L$^{-1}$) were observed in July, and the highest concentration (145.93 mg L$^{-1}$) was in November, which was 3 times higher than the lowest value. These indicate that water quality deteriorate and eutrophication are more likely to occur in the reservoir in November.

(2) The main nitrogen components in the overlying water is NH$_4^+$-N, NO$_3^-$-N, 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. The agricultural land is the most important type of land use in the hydro-fluctuation belt of Danjinagkou reservoir. The sampling site of TS had higher N concentrations, which indicate that agricultural irrigation was more likely to cause water pollution in hydro-fluctuation belts.

(3) According the 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 sampling month of November, where both sites were a relatively large sink of NO$_3^-$-N. NH$_4^+$-N and NO$_3^-$-N, the release rates reach up to 17.66 mg m$^{-2}$ d$^{-1}$ and 80.15 mg m$^{-2}$ d$^{-1}$, respectively, which is much higher than the release rate of NO$_2^-$-N (0.29 mg m$^{-2}$ d$^{-1}$). The sediment of hydro-fluctuation belt contributes a lot to the nitrogen contents 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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REFERENCES

Archie, G. E. 1942 The electrical resistivity log as an aid in determining some reservoir characteristics. Transactions of the American Institute of Mining, Metallurgical, and Petroleum Engineers 146, 54–62. doi: 10.2118/942054-G.

Bear, J. 1972 Dynamics of fluids in porous media. Engineering Geology 7 (2), 174–175. doi: 10.1016/0013-7952(72)90047-1.

Burns, L. C., Stevens, R. J. & Laughlin, R. J. 1995 Determination of the simultaneous production and consumption of soil nitrite using 15N. Soil Biology and Biochemistry 27 (6), 839–844. doi: 10.1016/0038-0717(94)00219-q.

Cheng, X. L., Yang, Y. H., Li, M., Dou, X. L. & Zhang, Q. F. 2015 The impact of agricultural land use changes on soil organic carbon dynamics in the Danjiangkou Reservoir area of China. Plant and Soil 366 (1-2), 415–424. doi: 10.1007/s11104-012-1446-6.

Cheng, X. J., Zeng, Y. X., Guo, Z. R. & Zhu, L. S. 2014 Diffusion of nitrogen and phosphorus across the sediment-water interface and in seawater at aquaculture areas of Daya Bay, China. International Journal of Environmental Research and Public Health 11 (2), 1557–1572. doi: 10.3390/ijerph110201557.

Chislock, M. F., Doster, E., Zitomer, R. A. & Wilson, A. E. 2005 Eutrophication: causes, consequences, and controls in aquatic ecosystems. Nature Education Knowledge 4 (4), 10.

Erakhrumen, A. A. 2011 Research advances in bioremediation of soils and groundwater using plant-Based systems: a case for enlarging and updating information and knowledge in environmental pollution management in developing countries. Environmental Pollution 20, 143–166. doi: 10.1007/978-94-007-1914-9_6.

Geraldes, A. M. & Boavida, M. J. 2005 Seasonal water level fluctuations: implications for reservoir limnology and management. Lakes & Reservoirs Research & Management 10 (1), 59–69. doi: 10.1111/j.1440-1770.2005.00257.x.

Gregory, S. V., Swanson, S. J., McKee, W. A. & Cummins, K. W. 1991 An ecosystem perspective of riparian zones. Bioscience 41 (8), 540–551. doi: 10.2307/1311607.

Herridge, D. F., Peoples, M. B. & Boddey, R. M. 2008 Global inputs of biological nitrogen fixation in agricultural systems. Plant and Soil 311 (1-2), 1–18. doi: 10.1007/s11104-008-9668-3.

Holland, E. A., Dentener, F. J., Braswell, B. H. & Sulzman, J. M. 1999 Contemporary and pre-industrial global reactive nitrogen budgets. Biogeochemistry 46 (1/3), 7–43. doi: 10.1007/bf01005752.

Kemp, W. M., Smith, E. M., Marvin-Dipasquale, M. & Boynton, W. R. 1997 Organic carbon balance and net ecosystem metabolism in Chesapeake Bay. Marine Ecology Progress 150 (1), 229–248. doi: 10.3354/meps150229.

Liu, R. H., Kang, Y. H., Zhang, C. & Pei, L. 2014 Chemical fertilizer pollution control using drip fertigation for conservation of water quality in Danjiangkou Reservoir. Nutrient Cycling in Agroecosystems 98 (3), 295–307. doi: 10.1007/s10705-014-9612-2.

Luaderitz, V., Eckert, E., Lange-Weber, M., Lange, A. & Gersberg, R. M. 2002 Nutrient removal efficiency and resource economics of vertical flow and horizontal flow constructed wetlands. Ecological Engineering 18 (2), 157–171. doi: 10.1016/s0925-8574(01)00075-1.

Ma, L. M., Zhang, M., Teng, Y. H. & Zhao, J. F. 2008 Characteristics of phosphorus release from soil in periodic alternately waterlogged and drained environments at WFZ of the three gorges reservoir. Environmental Science 29 (4), 1035–1039. (In Chinese).

Ma, L. M., Rena, D., Zhang, M. & Zhao, J. F. 2010 Phosphorus fractions and soil release in alternately waterlogged and drained environments at the water-fluctuation-zone of the Three Gorges Reservoir. Journal of Food Agriculture & Environment 8 (5), 1329–1335. doi: 10.1021/jf100778f.

Mekonnen, M. M. & Hoekstra, A. Y. 2015 Global grey water footprint and water pollution levels related to anthropogenic nitrogen loads to fresh water. Environmental Science & Technology 49 (21), 12860–12868. doi: 10.1021/acs.est.5b03191.

Murray, L. G., Mudge, S. M., Newton, A. & Icely, J. D. 2006 The effect of benthic sediments on dissolved nutrient concentrations and fluxes. Biogeochemistry 81 (2), 159–178. doi: 10.1007/s10533-006-9034-6.

Shi, D. M., Wang, W. L., Jiang, G. Y., Peng, X. D., Yu, Y. L., Li, Y. X. & Ding, W. B. 2016 Effects of disturbed landforms on the soil water retention function during urbanization process in the Three Gorges Reservoir Region, China. CATENA 144, 84–93. doi: 10.1016/j.catena.2016.04.010.

Smith, V. H. & Schindler, D. W. 2005 Eutrophication science: where do we go from here? Trends in Ecology & Evolution 24 (4), 201–207. doi: 10.1016/j.tree.2008.11.009.

Szarek-Gwiazda, E. & Mazurkiewicz-Boroń, G. 2002 Deposition of copper in the eutrophic, submontane dobczyce dam reservoir (Southern Poland) – role of speciation. Water Air and Soil Pollution 140 (1-4), 203–218. doi: 10.1023/a:1020139716502.

Ullman, W. J. & Aller, R. C. 1982 Diffusion coefficients in near-shore marine sediments. Limnology and Oceanography 27 (3), 552–556. doi: 10.4319/lo.1982.27.3.0552.

Urmeneta, J., Alcoha, Ő., Razquín, E., Tarroja, E., Navarrete, A. & Guerrero, R. 1998 Oxygenic photosynthesis and respiratory
activity in microbial mats of the Ebro Delta, Spain, by oxygen exchange method. *Current Microbiology* **37** (3), 151–155. doi:10.1007/s002849900355.

Wei, G. L., Yang, Z. F., Cui, B. S., Li, B., Chen, H., Bai, J. H. & Dong, S. K. 2009 Impact of dam construction on water quality and water self-purification capacity of the Lancang River, China. *Water Resources Management* **23** (9), 1763–1780. doi:10.1007/s11269-008-9351-8.

Whipple, W. & Hunter, J. V. 1977 Nonpoint sources and planning for water pollution control. *Water Pollution Control Federation* **49** (1), 15–23. doi:10.2307/25039214.

Xu, H., Paerl, H. W., Qin, B. Q., Zhu, G. W. & Gaoa, G. 2010 Nitrogen and phosphorus inputs control phytoplankton growth in eutrophic Lake Taihu, China. *Limnology and Oceanography* **55** (1), 420–432. doi:10.4319/lo.2010.55.1.0420.

Zhang, B., Guo, J. S., Fang, F., Li, Z. & Fu, C. 2012a Concentration of nutrients in the soil in water-level-fluctuating zone of Three Gorges Reservoir. *Ecohydrology & Hydrobiology* **12** (2), 105–114. doi:10.2478/v10104-012-0008-0.

Zhao, S. N., Shi, X. H., Li, C. Y., Zhang, S., Sun, B., Wu, Y. & Zhao, S. X. 2017 Diffusion flux of phosphorus nutrients at the sediment–water interface of the Ulansuhai Lake in northern China. *Water Science and Technology* **75** (6), 1455–1465. doi:10.2166/wst.2017.017.

Zhao, C. S., Shao, N. F., Yang, S. T., Ren, H., Ge, Y. R., Zhang, Z. S., Feng, P. & Liu, W. L. 2019 Quantitative assessment of the effects of human activities on phytoplankton communities in lakes and reservoirs. *Science of the Total Environment* **665**, 213–225. doi:10.1016/j.scitotenv.2019.02.117.

Zhu, Z. L. & Chen, D. L. 2002 Nitrogen fertilizer use in China – contributions to food production, impacts on the environment and best management strategies. *Nutrient Cycling in Agroecosystems* **65** (2-3), 117–127. doi:10.1023/a:1021107026067.

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