

# The Effects of Concentration Gradient of Nitrogen Compounds on the Ammonium-nitrogen and Nitrate-nitrogen Fluxes at Sediment-Water Interface

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## Research Article

**Keywords:** concentration gradient, diffusion flux, nitrogen, sediment-water interface, eutrophication control, hydro-fluctuation belt

**Posted Date:** December 29th, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-1048698/v1>

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# Abstract

The incubation experiments focused on altering concentration gradients of nitrogen between sediment and overlying water to examine the diffusion flux of ammonium-nitrogen ( $\text{NH}_4^+$ ) and nitrate-nitrogen ( $\text{NO}_3^-$ ) at sediment-water interface. In this study, the diffusion flux can be estimated based on calculating the average of the net change rate of nutrient concentrations in the overlying water. For the incubation experiment of different TN concentrations in the sediment, the results showed that the diffusion flux of ammonia at sediment-water interface is  $-52.57\sim 84.57 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , and for nitrate diffusion flux, the changing range during the incubation experiment is  $-110.13\sim 143.25 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ . For the incubation experiment of different nitrogen concentrations in the overlying water, the results of  $\text{NH}_4^+$ -N diffusion flux in L, M, H treatment were 3.37, -4.94, -3.84  $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , respectively. And the average diffusion flux of nitrate in L (0 mg  $\text{NO}_3^-$ -N, 0 mg  $\text{NH}_4^+$ -N), M (0.5 mg  $\text{NO}_3^-$ -N, 1.5 mg  $\text{NH}_4^+$ -N) and H (1 mg  $\text{NO}_3^-$ -N, 2.5 mg  $\text{NH}_4^+$ -N) treatment were 12.30, 10.39 and 7.11  $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ . Results highlighted that concentrations gradient of nutrients were indeed an important factor affecting the diffusion flux at sediment-water interface. In addition, the diffusion of nutrients at sediment-water interface in aquatic ecosystem is not only controlled by concentration gradients, some other factors such as incoming water, hydrodynamics, dissolved oxygen content, sediment structure, biological disturbance, horizontal migration and diffusion of nutrients and turbulent diffusion caused by wind and wave, are equally important.

## 1 Introduction

The continuous exchanges of solutes and particles between the sediment and its overlying water play a critical role in material cycling in the aquatic ecosystem, which affect the biological activity, chemical composition and ecosystem structure as well. In the biogeochemical cycles, there are three main processes should be considered. Firstly, the particulate organic matter in the overlying water is deposited into the sediment layers, which referred to as the depositional process. And then the particulate organic matter is mineralized in the sediment to form soluble intermediates. Lastly, some dissolved chemicals can transfer to the overlying water by diffusion or buried via sedimentation. The global nitrogen cycle has been dramatically changed due to the human activities, some practices such as agricultural fertilization increase the nitrogen level in aquatic ecosystems (Galloway et al.,2004; Li et al.,2021). There are plenty of negative impacts on increasing nitrogen loads such as bottom water hypoxia, nitrogen is a key factor leading to eutrophication, besides, nitrate is known to contribute to aquatic area acidification (Kelly et al.,1990). Phosphorus (P) enrichment is also a cause of eutrophication, many researchers have stated that it should be controlled as well (Paerl et al., 2011).

However, nitrogen biogeochemical cycling is more complicated. Therefore, controlling N is often a more challenging approach when dealing with aquatic ecosystem eutrophication (Queiroz et al.,2020). External nutrients sources are often considered the main cause of eutrophication, thus the primary method of eutrophication control is to mitigate external input, which include sewage discharge, non-point source pollution and fertilizer application, etc. (Liu et al., 2019; Papera et al., 2021). Many studies have shown

that even if external input is greatly controlled, the aquatic ecological environment is not enough to restore to the ideal state as nitrogen will be continuously released from sediments to overlying water (Jeppesen et al., 2005; Yin et al., 2019; Présing et al., 2001).

Different nitrogen reactions are occurred in the sediment, overlying water and the sediment-water interface. Within the sediments, reactive nitrogen deposition as organic N which can produces ammonium ( $\text{NH}_4^+\text{-N}$ ) by mineralization,  $\text{NH}_4^+\text{-N}$  is further converted into nitrate ( $\text{NO}_3^-\text{-N}$ ) by nitrification under aerobic condition. Below the oxycline,  $\text{NO}_3^-\text{-N}$  (via denitrification) and  $\text{NH}_4^+\text{-N}$  (via anammox) are convert to  $\text{N}_2$  in the absence of  $\text{O}_2$ . The dissolved  $\text{NO}_3^-\text{-N}$  and  $\text{NH}_4^+\text{-N}$  also diffused between the sediment and overlying water under the driving force of concentration difference. These reactions control the nitrogen net exchange fluxes across the sediment-water interface, which may alter the availability of nitrogen in the aquatic ecosystem. Controlling the presence of nitrogen in aquatic system is a critical management issue due to the high inputs both from non-point source pollution and inner release, resulting in the problem of eutrophication and hypoxia (Mulholland et al., 2008).

Therefore, it's significant to recognize the nitrogen exchange process in the sediment-water interface for nitrogen flux control. Reactive nitrogen is released from sediments and maintained in the pore water, in the static aquatic ecosystem, the nitrogen transferred into the overlying water across the sediment-water interface by direct diffusion process under a concentration gradient. Thus, many studies applied Fick's first law to determine the exchange flux between sediment and water interface (Wang et al., 2020; Zhao et al., 2017; Murray et al., 2006; Cheng et al., 2014). According to the Fick's first law, the exchange flux can be estimated based on the concentration difference between sediment (pore water) and overlying water. The rates and magnitudes of fluxes depend on the nitrogen content of sediment and dissolved nitrogen concentrations in overlying water. Despite the importance of these two factors on controlling the rates of N fluxes in the sediment-water ecosystem, there have been no comparisons of influence degree of the two factors on the diffusion flux. By identifying which factor makes the diffusion more efficient, the relevant results have certain significance in the management strategy of controlling internal release.

The aim of this study was to examine and determine how concentration gradient between pore water and surface water influences nitrogen dynamics at sediment-water interface. We hypothesized that concentration gradient is a major factor affecting N migration at sediment-water interface. In this paper, we designed two groups of indoor incubation experiments which were different sediment nitrogen concentrations and different overlying water nitrogen concentration, respectively. We further quantify the diffusion fluxes under these two factors and their migration direction, which defined as either deposit from overlying water into sediment or release from sediment to water. Finally, we relate these findings to their impact on ecosystem processes and some suggestions on controlling internal release were put forward.

## 2 Material And Method

## 2.1 Description of the study sites

The experiments were conducted on three types of sediments with different total nitrogen (TN) and organic matter concentrations in the hydro-fluctuation belt of Danjiangkou reservoir. According to the previous research (Wang et al., 2020), the sediment with highest TN concentration (sample 1) located in Gaozhuang (sandy soil; 32°28'15"N 111°24'10"E), the sediment with median TN concentration (sample 2) located in Zhuyuan village (tidal soil; 33°0'47"N 111°17'37"E) and the sediment with lowest TN concentration (sample 3) located in Nanchengang (loam; 32°26'38"N 111°24'12"E). The top 10 cm sediment cores were sampled in March 2021. Apart from these sediment cores, three extra sediment samples were collected at each site to test sediment properties before the incubation experiment. The collected sediment samples were put in a sealed plastic bag and kept at 4°C for further analysis. Table 1 shows the sediment properties of surface soils (0-10 cm) at the three sampling sites.

Table 1  
physical and chemical properties of surface sediment at each sampling site

Site	Moisture content (%)	Porosity (%)	OM (g/Kg)	TDN (mg/Kg)	DON (mg/Kg)	NH <sub>4</sub> <sup>+</sup> -N (mg/Kg)	NO <sub>3</sub> <sup>-</sup> -N (mg/Kg)	NO <sub>2</sub> <sup>-</sup> -N (mg/Kg)
S1(5)	41	64.8	20.59	156.78	104.41	29.84	22.30	0.23
S2(2)	24	45.6	16.94	151.13	101.39	26.47	23.06	0.21
S3(6)	34	57.7	14.41	133.77	86.58	25.04	21.75	0.40

## 2.2 Incubation experiment design

The experiments were carried out in April 2021 in the laboratory at North China University of Water Resources and Electric Power. The square aquaria were prepared for incubation experiment. The dimension of the aquarium was 15 cm×12 cm×30 cm. The aquaria were filled with 10 cm sediments and the sediments were inundated with 15 cm self-made solution, which was similar to the property of natural river water and the specific compositions were shown in Table 2, the solution was equilibrated by pumping air for 48 hours, the pH, Eh, TDS and conductivity of the solution were 7.07, 72 mv, 0.049 g/L and 0.081 ms/cm, respectively. The pore water sampler (Rhizon SMS-10 cm, 0.15 μm, Female luer lock, Rhizosphere Research Products bv.) was placed 1 cm below the sediment-water interface (Figure 1).

Table 2  
Self-made simulated overlying water constitute and concentrations

Compound	Ca(HCO <sub>3</sub> ) <sub>2</sub>	Mg(HCO <sub>3</sub> ) <sub>2</sub>	NaHCO <sub>3</sub>	KCl	MgSO <sub>4</sub>	MgCl <sub>2</sub>
Concentrations (mg/L)	117.05	35.28	19.36	6.30	16.75	1.61

To explore the effects of different TN concentrations in the sediment on diffusion flux of nitrogen, we selected 3 types of sediment samples (Table 1), the determination of sampling points was based on the

soil type, the land use mode before inundation and the measured value in the hydro-fluctuation belt in Danjiangkou reservoir (Incubation experiment 1). For different nitrogen concentrations in the overlying water simulation, the sediment collected at S1 were added to overlying water with different nitrogen concentrations. Three concentration gradients are proposed to be designed: (1) 0 mg/L ammonia nitrogen, 0 mg/L nitrate nitrogen; (2) 0.5 mg/L ammonia nitrogen, 1.5 mg/L nitrate nitrogen; (3) 1.0 mg/L ammonia nitrogen, 2.5 mg/L nitrate nitrogen (Incubation experiment 2). All incubations were carried out with three replicates per treatment and utilizing distilled water as overlying water was considered as controls. In the expressions, S refers to artificial solutions and D refers to distilled water.

## **2.3 Sampling and chemical analysis**

### **2.3.1 Water samples**

During the experiment, water temperature (T), pH, dissolved oxygen (DO) and total dissolved solid (TDS) were measured daily by a portable multi-functional water quality analyzer (HORIBA, Japan) at 10 AM. The surface water was collected at 0d, 3d, 6d, 9d, 12d and 14d by using a 60 ml syringe at 5 cm below the water surface for incubation experiment 1, and the surface water was collected at 0d, 4d, 8d, 12d and 15d for incubation experiment 2. Pore water was taken anaerobically at the same frequency by connecting 50-ml syringe to the rhizon sampler. After each sampling, the aquaria were replenished with 100 ml self-made solution to compensate for the loss of the sampling volume. Besides, water losses by evaporation etc. were compensated with demineralized water adjusted according to water level. For water samples, TN,  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ ,  $\text{NO}_2^-\text{-N}$  and total organic carbon (TOC) were measured.

### **2.3.2 Sediment samples**

Before and after the incubation experiment, amount of sediment samples was collected to compare the changes of each treatment. The sediment samples need pretreatment before analysis which include air-drying, homogenization and grinding. For sediment samples, TDN,  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ ,  $\text{NO}_2^-\text{-N}$  and OM were measured.

### **2.3.3 Analysis methods**

Analysis methods (Wang, 2020) were as follows: TN was determined by the alkaline potassium persulfate digestion-UV spectrophotometry method. Samples for analysis of  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$  and  $\text{NO}_2^-\text{-N}$  were filtered (0.45  $\mu\text{m}$  cellulose acetate filters),  $\text{NH}_4^+\text{-N}$  was determined by Nessler's reagent colorimetric method,  $\text{NO}_3^-\text{-N}$  and  $\text{NO}_2^-\text{-N}$  was determined by a UV spectrophotometry method. For sediment OM measurement, a part of sediment was dried at 100°C for 48h until a constant weight was achieved, the difference between the pre and post weights were regarded as the organic fractions. OM and porosity were measured before and after the incubation experiments. TOC was determined by potassium dichromate- volumetric method.

## **2.4 Diffusion flux estimation**

The nutrients diffusion flux at the sediment-water interface can be estimated based on the average of the net change rate of nutrient concentrations in the overlying water at each sampling interval during incubation experiment, and then normalized by sediment -water interface area. The equations are as follows:

$$F_i = \frac{M(t)}{A \cdot \Delta t} = \frac{V[C(t) - D(t-1)]}{A \cdot \Delta t}$$

3

$$D(t) = \frac{(V - V_0) \cdot C(t) + V_0 \cdot C_0}{V}$$

4

$$\bar{F}_i = \frac{1}{n-1} \sum_{i=1}^{n-1} F_i$$

5

Where  $F_i$  is the exchange flux time  $t$  ( $\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ ),  $M(t)$  is the change of nutrient mass in the overlying water from  $t-1$  to time  $t$  (mg),  $V$  is the volume of overlying water ( $\text{m}^3$ ),  $A$  is the area of sediment-overlying water interface ( $\text{m}^2$ ),  $C(t)$  is the measured concentrations of nutrients in the overlying water at time  $t$  ( $\text{mg} \cdot \text{L}^{-1}$ ),  $D(t)$  is the concentrations of nutrients in the overlying water at time  $t$  when the sampling loss is considered ( $\text{mg} \cdot \text{L}^{-1}$ ),  $V_0$  is the sampling volume of surface water (mL),  $C_0$  is the nutrient concentrations in the initial surface water ( $\text{mg} \cdot \text{L}^{-1}$ ),  $\bar{F}_i$  is the average exchange flux in  $t$  time ( $\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ ),  $n$  is the sampling times. Positive values are indicative of efflux while negative values indicate influx. Since the overlying water needs to be replenished during the incubation experiment, which will affect the initial concentration in the overlying water, thus the results should be corrected by Equation 4.

## 2.5 Quality control and statistical analysis

For all samples, triplicate analyses were measured and the results expressed as the average of these. In the experiment, analytical pure reagent and ultrapure water were used, and the reagent used for standard curve is the standard solution prepared by Jinnong Science and Technology Co., Ltd, Zhengzhou. All statistical were carried out with SPSS for windows.

## 3 Results

### 3.1 Nitrogen concentrations in overlying water and pore water

In different sediment TN concentrations incubation experiment group, the variation range of  $\text{NH}_4^+\text{-N}$  concentration in overlying water is relatively consistent (Table 3). Average concentrations in artificial solution as overlying water ranged from 2.571 to 3.674  $\text{mg}\cdot\text{L}^{-1}$  and in distilled water from 2.625 to 2.796  $\text{mg}\cdot\text{L}^{-1}$ . The concentration of  $\text{NH}_4^+\text{-N}$  in the overlying water was highest in S1 treatment, but there was no significant difference in S2 and S3 treatment. Average  $\text{NO}_3^-$  concentrations in artificial solution ranged from 1.218-1.542  $\text{mg}\cdot\text{L}^{-1}$  whilst those in distilled water ranged from 1.218 to 1.542  $\text{mg}\cdot\text{L}^{-1}$ . The concentration of nitrate in overlying water changed relatively obvious in each treatment. Overall, the concentration of ammonia nitrogen is significantly higher than that of nitrate. No significant interactions were found between artificial solution and distilled water treatment. And for pore water, the  $\text{NH}_4^+\text{-N}$  concentrations were variable. Average concentrations in artificial solution ranged from 2.864 to 7.407  $\text{mg}\cdot\text{L}^{-1}$  and in distilled water from 3.926 to 8.065  $\text{mg}\cdot\text{L}^{-1}$ . When artificial solution as overlying water,  $C(\text{NH}_4^+\text{-N})_{\text{S1}} > C(\text{NH}_4^+\text{-N})_{\text{S2}} > C(\text{NH}_4^+\text{-N})_{\text{S3}}$ . In control group (distilled water as overlying water),  $C(\text{NH}_4^+\text{-N})_{\text{S3}} > C(\text{NH}_4^+\text{-N})_{\text{S2}} > C(\text{NH}_4^+\text{-N})_{\text{S1}}$ . For  $\text{NO}_3^-$  concentrations, there is little difference between overlying water and pore water. Average  $\text{NO}_3^-$  concentrations in artificial solution ranged from 1.053-1.116  $\text{mg}\cdot\text{L}^{-1}$  whilst those in distilled water ranged from 0.994 to 1.137  $\text{mg}\cdot\text{L}^{-1}$ .

In different overlying water N concentrations incubation experiment group, average  $\text{NH}_4^+\text{-N}$  concentration in artificial solution ranged from 2.892 to 2.902  $\text{mg}\cdot\text{L}^{-1}$  and in distilled water ranged from 2.549 to 2.800  $\text{mg}\cdot\text{L}^{-1}$ . According to the concentration ranges of ammonia in L, M, H treatment, no significant difference was found by statistic analysis. However, H treatment indicates additional 1.0  $\text{mg}\cdot\text{L}^{-1}$   $\text{NH}_4^+\text{-N}$  and 2.5  $\text{mg}\cdot\text{L}^{-1}$   $\text{NO}_3^-\text{-N}$  was added to the overlying solution, M referred to 0.5  $\text{mg}\cdot\text{L}^{-1}$   $\text{NH}_4^+\text{-N}$  and 1.5  $\text{mg}\cdot\text{L}^{-1}$   $\text{NO}_3^-\text{-N}$  was added and for L treatment no extra nitrogen compound added to overlying water. The  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  solvent added was not sufficient to affect the nitrogen content in the overlying water, but it can inhibit the diffusion of nitrogen from sediment to water. The more nitrogen added to surface water, the smaller the gradient concentration between sediment and overlying water, and the less ammonia and nitrate released from sediment. For pore water, average  $\text{NH}_4^+\text{-N}$  concentration in L, M, H treatment were 11.726, 6.142, 7.148, respectively. And average  $\text{NO}_3^-\text{-N}$  concentration in L, M, H treatment were 1.529, 2.252, 2.199, respectively. Although the concentrations of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  in each treatment are different, which are relatively small compared with the pore water concentration, and there was little regular effect on them.

Table 3

A summary of ranges and averages of overlying water  $\text{NH}_4^+$  ( $\text{mg}\cdot\text{L}^{-1}$ ) and  $\text{NO}_3^-$  ( $\text{mg}\cdot\text{L}^{-1}$ ) concentrations in different sediment TN concentrations and different overlying water N concentrations incubation experiment groups.

Treatment	Overlying water	$\text{NH}_4^+$ range	Average	$\text{NO}_3^-$ range	Average
S1	Artificial solution	2.248-4.415	3.674	0.375-1.437	1.304
	Distilled water	2.039-3.128	2.676	0.601-1.485	1.374
S2	Artificial solution	2.063-2.835	2.571	0.437-1.330	1.218
	Distilled water	2.065-3.029	2.625	0.414-1.387	1.265
S3	Artificial solution	2.105-3.047	2.702	0.496-1.691	1.542
	Distilled water	2.212-3.704	2.769	0.566-1.624	1.492
L	Artificial solution	2.266-3.443	2.902	0.801-2.405	1.600
	Distilled water	2.139-3.623	2.800	0.892-3.535	1.804
M	Artificial solution	2.182-3.841	3.076	0.896-6.738	2.696
	Distilled water	1.995-2.914	2.549	0.788-1.688	1.414
H	Artificial solution	2.170-3.506	2.892	0.768-2.926	1.685
	Distilled water	2.128-3.215	2.679	0.826-2.029	1.597

Table 4

A summary of ranges and averages of pore water  $\text{NH}_4^+$  ( $\text{mg}\cdot\text{L}^{-1}$ ) and  $\text{NO}_3^-$  ( $\text{mg}\cdot\text{L}^{-1}$ ) concentrations in different sediment TN concentrations and different overlying water N concentrations incubation experiment groups.

Treatment	Overlying water	$\text{NH}_4^+$ range	Average	$\text{NO}_3^-$ range	Average
S1	Artificial solution	3.501-9.526	7.407	0.518-1.636	1.053
	Distilled water	2.569-5.174	3.926	0.484-1.635	1.061
S2	Artificial solution	2.436-4.222	3.343	0.419-1.614	1.087
	Distilled water	3.979-5.987	5.257	0.399-1.552	0.994
S3	Artificial solution	2.371-3.269	2.864	0.539-2.023	1.116
	Distilled water	2.572-11.655	8.065	0.516-1.801	1.137
L	Artificial solution	7.083-12.750	11.061	0.907-2.021	1.483
	Distilled water	11.105-13.477	12.391	1.007-2.145	1.574
M	Artificial solution	3.656-5.801	4.789	1.179-6.449	2.869
	Distilled water	5.052-9.479	7.494	1.146-2.486	1.635
H	Artificial solution	8.378-10.738	9.716	1.147-2.255	1.683
	Distilled water	3.279-5.884	4.580	1.140-6.504	2.715

### 3.2 Effects of different sediment TN concentrations on diffusion flux of nitrogen at sediment-water interface

Sediment-water interface is the most significant place for material exchange between the bottom of aquatic ecosystem and overlying water. Under the solo or synergistic effects of various physical, chemical and biological processes such as concentration gradients, microbial metabolism and benthic fauna disturbance, dissolved particles can migrate between sediment pore water and overlying water through sediment-water interface. Therefore, sediment usually play a role of "source" or "sink" for nutrients and pollutants migration.

The diffusion fluxes of TN at sediment-water interface from different sampling sites are shown in Fig. 1, the diffusion fluxes of TN gradually increase with incubation time. At the beginning of the experiment the sediment act as the accumulation sinks of nitrogen and then transformed into release source. The average diffusion flux of TN at sampling points S1, S2 and S3 were 72.45, 66.35 and 66.30  $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , respectively. During the incubation experiment, TN is released from sediment to the overlying water, and the higher TN concentration in the sediment, the greater the diffusion flux was shown.

Across the entire incubation experiment, both ammonia and nitrate showed deposition and release process, and there was no regular pattern in magnitude and direction amongst the treatments. The diffusion flux of ammonia at sediment-water interface is  $-52.57\sim 84.57 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , and for nitrate diffusion flux, the changing range during the incubation experiment is  $-110.13\sim 143.25 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , the results indicated that the diffusion flux of nitrate was slightly larger than ammonia (Fig. 2-3). This can be explained by the aerobic condition in the overlying water, in which the dissolved oxygen concentration is  $6.93\sim 10.81 \text{ mg}\cdot\text{L}^{-1}$ , the  $\text{NH}_4^+\text{-N}$  was transformed into  $\text{NO}_3^-\text{-N}$  by nitrification process. Thus, there was an increase in  $\text{NO}_3^-\text{-N}$  concentrations, and its diffusion flux also increased. In the early stage of the incubation experiment,  $\text{NH}_4^+\text{-N}$  dominated the exchange process at sediment-water interface. While in the late stage of the experiment, the exchange process of  $\text{NO}_3^-\text{-N}$  was relatively significant. The average diffusion flux of ammonia at sediment-water interface in S1, S2 and S3 were 16.19, 15.63 and  $12.85 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , respectively, and the nitrate average diffusion flux were 3.08, 7.73 and  $-1.71 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ . The previous analysis showed that the diffusion flux of  $\text{NO}_3^-\text{-N}$  was slightly greater than that of  $\text{NH}_4^+\text{-N}$ , however, the results of average diffusion flux was just the opposite, the average diffusion flux of  $\text{NO}_3^-\text{-N}$  was less than that of  $\text{NH}_4^+\text{-N}$ , indicating that the migration direction of  $\text{NO}_3^-\text{-N}$  at sediment-water interface varied frequently, the accumulation process counteracts the release process.

### 3.3 Effects of different overlying water ammonia and nitrate concentrations on diffusion flux of nitrogen at sediment-water interface

The diffusion process of nutrients at sediment-water interface is determined by the concentration gradients of particles between pore water and surface water. When the nitrogen concentrations ( $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$  etc.) in the overlying water changes, it will inevitably lead to the changes of nitrogen concentration difference between sediment and overlying water, which will affect both the magnitude of diffusion and direction of migration.

The diffusion flux of TN at sediment-water interface under different overlying water are shown in Figure 4. The diffusion flux of TN between sediment and overlying water reached equilibrium at 10th day of the incubation experiment. For L treatment ( $0 \text{ mg } \text{NO}_3^-\text{-N}$ ,  $0 \text{ mg } \text{NH}_4^+\text{-N}$ ), the sediment acted as the accumulation sink for TN in the overlying water at first and then transformed into release source. However, for M ( $0.5 \text{ mg } \text{NO}_3^-\text{-N}$ ,  $1.5 \text{ mg } \text{NH}_4^+\text{-N}$ ) and H ( $1 \text{ mg } \text{NO}_3^-\text{-N}$ ,  $2.5 \text{ mg } \text{NH}_4^+\text{-N}$ ) treatment, which were opposite to L treatment, the sediment served as the release source of TN and turned into accumulation sink. The diffusion flux of TN in L, M and H treatment were 16.27, 18.68 and  $13.52 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , respectively. The diffusion flux of TN did not express the regular variation with the increase of ammonia and nitrate concentration in the overlying water.

The diffusion flux of ammonia at sediment-water interface decreased first and then increased among all treatments, finally achieving the transformation from source to sink (Fig. 5). The calculated results of  $\text{NH}_4^+\text{-N}$  diffusion flux in L, M, H treatment were 3.37,  $-4.94$ ,  $-3.84 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , respectively. In L treatment,

the concentrations of  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N were relatively low in overlying water,  $\text{NH}_4^+$ -N was released from sediment to surface water. When the concentrations of  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N were higher (M and H treatment), it was absorbed by sediment.

The diffusion flux of nitrate at sediment-water interface was transformed from release source to accumulation sink, and the average diffusion flux in L, M and H treatment were 12.30, 10.39 and 7.11  $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , and the  $\text{NO}_3^-$ -N was released from the sediment in all treatments. The results showed that the diffusion flux of nitrate gradually decreased with the increase of  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N concentrations in the overlying water, and finally reached equilibrium between release and accumulation (Fig. 6). On the whole, the diffusion flux of nitrate was numerically greater than that of ammonia, which can be explained by the strong absorption of ammonia by sediment. According to the data of DO concentrations (8.98-11.69  $\text{mg}\cdot\text{L}^{-1}$ ) in the overlying water, it was found that the aquatic system was in an aerobic state during the incubation experiment. The ammonia was further nitrated, thus the nitrate concentration in the overlying water was significantly higher than that of ammonia, resulting in the greater diffusion flux of nitrate.

The diffusion flux of dissolved inorganic nitrogen (DIN) was obtained by summing the fluxes of  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N, and the average diffusion flux of DIN in L, M, H treatment were 15.77, 5.52 and 3.39  $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , respectively. The release rate dominated the process of nitrogen release from sediment to water (Diamond et al., 1990), and the migration of dissolved nitrogen from pore water to sediment and then into surface water was determined by the concentration gradient between the two medias. Since there was no extra  $\text{NH}_4^+$ -N and  $\text{NO}_3^-$ -N in the overlying water in L treatment, the higher concentration gradient was the main reason for the significant release of DIN from sediment. Therefore, the concentration gradients of DIN between pore water and surface water were affected by controlling the concentration of inorganic nitrogen in the overlying water, resulting in the change of source-sink relationship and TDN diffusion flux at sediment-water interface.

## 4 Discussion

Results from this study indicate that concentrations gradients of particles were indeed an important factor affecting the diffusion flux at sediment-water interface, including deposition or release rates from sediments and diffusion direction during our incubation experiment. In our study, we set up two schemes to alter the N concentration gradient. The first scheme is to change the nitrogen concentrations in the sediment, the other one is to adjust the ammonia and nitrate concentrations in the overlying water. Berelson found that the production of endogenous of N and P nutrients accounts for more than 50% of exogenous nutrients in the study of nutrients biogeochemical cycling in Port Phillip Bay, Australia (Berelson et al., 1998). The nutrients flux from the sediment is mainly caused by the concentration gradients between pore water at sediment surface and overlying water, which directly showed the importance of sediment pore water for nutrients release. Additionally, as a critical sink for nutrients, the quantity of nutrients in the sediment could directly affect the quality of the surrounding environment as

well as the survival, composition of benthos to a certain degree. Obviously, the content of nutrients in the sediment is quite important for the supply or supplement of nutrients to overlying water. Sediment is a “holding place” for nutrients such as N and P, the nutrients can be released into overlying water when the concentration gradients of nutrients are positive.

Sediment is a significant place for nutrients accumulation and intermittent regeneration. It can be seen from the results in Fig. 1 that the diffusion fluxes of TN were positive except at the beginning of the experiment, indicating that sediment is one of the important input sources of nitrogen. Since the diffusion flux of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  is affected by the relative rate of nitrification and denitrification, additionally, aerobic-anaerobic environment occurs alternatively and high activity of organic matter at sediment-water interface, resulting in the strong oxidation-reduction reactions including nitrification and denitrification. The generated  $\text{NH}_4^+\text{-N}$  is difficult to be fully absorbed by microorganisms and  $\text{NH}_4^+\text{-N}$  cannot be completely transformed to  $\text{NO}_3^-\text{-N}$  under anaerobic condition, thus the diffusion flux of  $\text{NH}_4^+\text{-N}$  is relatively high (Fig. 2).

The results from Fig. 3 indicated the diffusion flux of  $\text{NO}_3^-\text{-N}$  varied greatly, since the whole incubation experiment was completed under still water conditions, which had little disturbance on sediment. In the decomposition process, the organic matter consumes large amount of dissolved oxygen and reducibility of sediment is enhanced, which affects the nitrification and denitrification process, thus vary the distribution and diffusion of nitrate. The low DO state inhibits the nitrification reaction, and nitrate was consumed during denitrification process, resulting in the lower  $\text{NO}_3^-\text{-N}$  concentration in the sediment than that in the overlying water. In this case, sediment act as the sink for  $\text{NO}_3^-\text{-N}$ . As the intermediate product of nitrification and denitrification, the concentration of  $\text{NO}_2^-\text{-N}$  is low and unstable, thus the significance of its diffusion flux is undefined (Hall et al., 1996).

In the incubation experiment of different overlying water nitrogen concentration, the concentrations of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  in the overlying water had little relationship with corresponding diffusion flux at sediment-water interface, and the correlation is quite low. However, this does not mean that the nutrient concentration in the overlying water has little effects on its diffusion flux. It only shows that when the nutrients concentration of sediment is much higher than that of overlying water, the nutrient concentration in the overlying water is not the decisive factor. The reason for this phenomenon may be that the migration of nitrogen at sediment-water interface is not only controlled by concentration gradient, but also related to other factors such as dissolved oxygen content, sediment structure and horizontal migration and diffusion of nutrients.

## 5 Conclusions

This study sought to determine whether concentration gradients could affect diffusion flux of ammonia and nitrate at sediment-water interface. Results highlighted that concentrations gradient of nutrients were indeed an important factor affecting the diffusion flux at sediment-water interface. With the increase of

TN concentration in the sediment, the diffusion flux increases accordingly. The diffusion flux of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  is affected by the relative rate of nitrification and denitrification, therefore, alternative aerobic-anaerobic environment at sediment-water interface led to sediment act as the sink or source for nutrients at different cases. In addition, the diffusion of nutrients at sediment-water interface in aquatic ecosystem is not only controlled by concentration gradients, some other factors such as incoming water, hydrodynamics, dissolved oxygen content, sediment structure, biological disturbance, horizontal migration and diffusion of nutrients and turbulent diffusion caused by wind and wave, are equally important.

## Declarations

### Ethics approval and consent to participate

Not applicable

### Consent for publication

Not applicable

### Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

### Competing interests

The authors declare that they have no competing interests.

### Funding

This research was financially supported by the National Science Foundation of China [Grant No.51679089]; the Innovation Foundation of North China University of Water Resources and Electric Power for PhD Graduates.

### Authors' Contributions

Conceptualization, H.W. and Y.P.H; Sampling, H.W and Q.W.; Incubation experiment, H.W.; Sample Measurement, H.W.; Writing-original draft, H.W.; All authors contributed to the drafting and approval of the manuscript for submission.

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## Figures

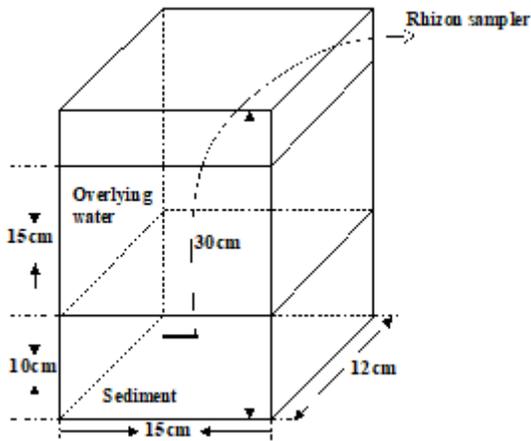


Figure 1

Schematic diagram of aquarium simulation experimental device

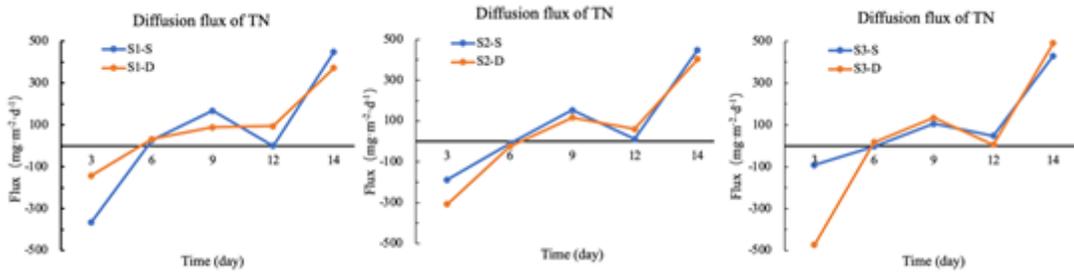
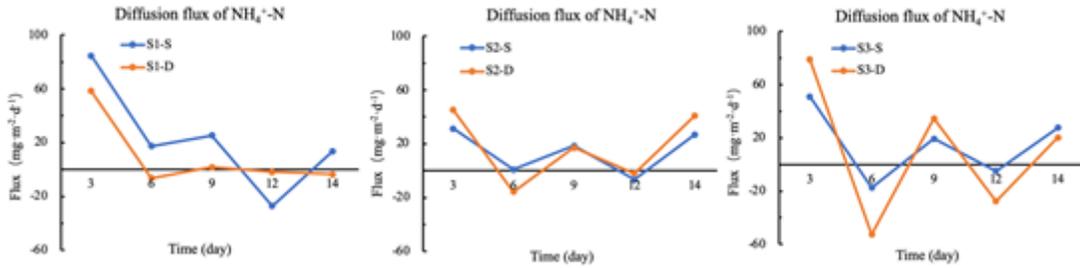


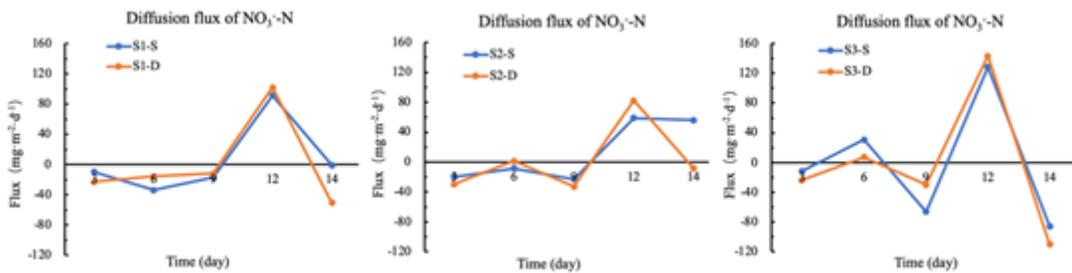
Figure 2

The variation of diffusion flux of TDN at sediment-water interface under different sediment TN concentrations



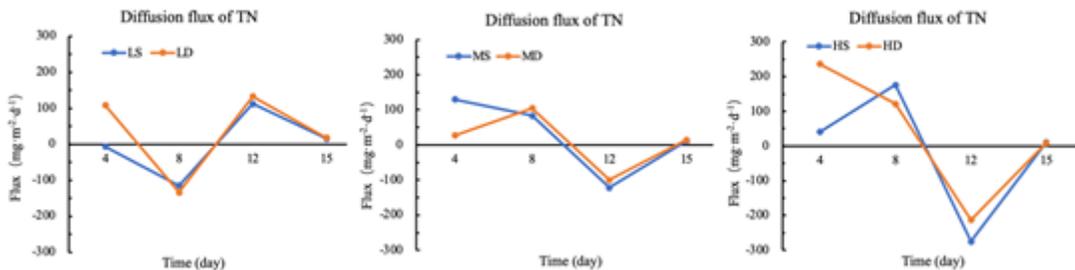
**Figure 3**

The variation of diffusion flux of ammonia at sediment-water interface under different TN sediment concentrations



**Figure 4**

The variation of diffusion flux of nitrate at sediment-water interface under different TN sediment concentrations



**Figure 5**

The variation of diffusion flux of TN at sediment-water interface in L, M, H treatment.

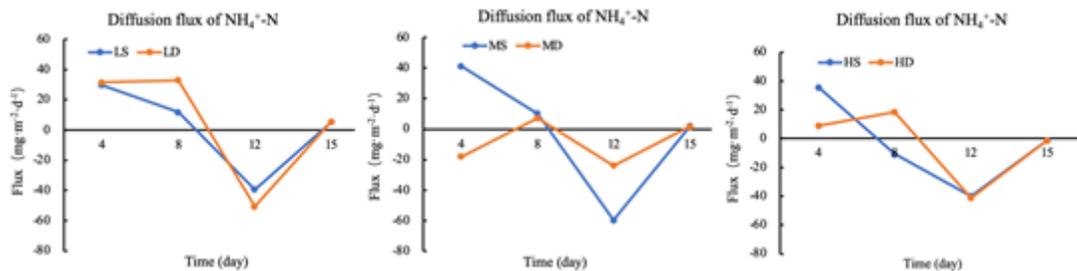


Figure 6

The variation of diffusion flux of  $\text{NH}_4^+\text{-N}$  at sediment-water interface in L, M, H treatment.

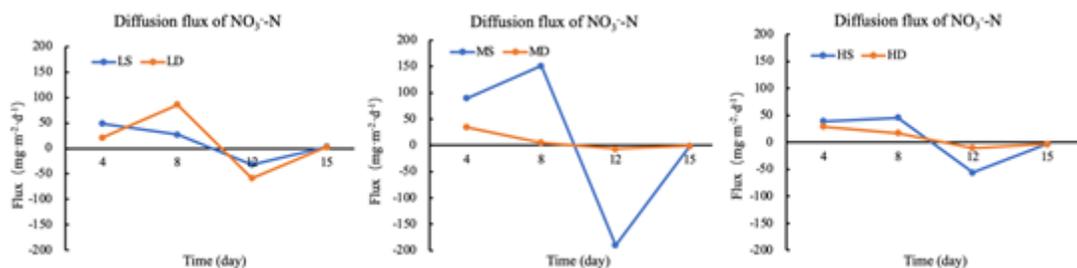


Figure 7

The variation of diffusion flux of  $\text{NO}_3^-\text{-N}$  at sediment-water interface in L, M, H treatment.