Nitrate–Nitrogen Transport in Horizontal Soil Columns of the Yellow River Delta Wetland, China

Horizontal movement of nitrate–nitrogen was simulated in horizontal soil columns from a typical tidal flooding wetland and a short-term flooding wetland of the Yellow River Delta. The primary objectives of this study were to investigate the changes in transport fluxes of nitrate–nitrogen with increasing movement distances and to identify the relationship between transport fluxes of nitrate–nitrogen and water diffusion coefficients. The results showed that the transport fluxes of nitrate–nitrogen were significantly and negatively correlated with movement distances in both wetlands, and decreased exponentially with increasing distances. However, the transport fluxes of nitrate–nitrogen increased exponentially with increasing water diffusion coefficients in both wetlands. The higher transport fluxes of nitrate–nitrogen in surface soils were observed compared to deeper soils, while they were higher in surface soils at the distances near the tracer water head. The findings of this study can contribute to water quality protection by regulating buffer zone width based on the horizontal movement of nitrate–nitrogen.

Keywords: Buffer zone; Eutrophication; Marsh soils; Transport fluxes; Water pollution

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1 Introduction

Nitrogen is one of increasing environmental pollutants, which can cause water pollution and eutrophication of surface waters. As nitrate–nitrogen is less adsorbed by soil colloids and clays and exits in the solute forms in soil solution [1], nitrate–nitrogen can lead to underground water pollution due to vertical movement and leaching [2, 3]. Reddy et al. [4] presented that the nitrate–nitrogen leaching was an important process of nitrogen loss in soil or sediments affecting flooded wetlands. However, Reilly et al. [5] found that nitrate concentration in groundwater of Prado wetland was <1 mg m⁻³ day⁻¹, and nitrate from wetland lost to groundwater was negligible. Therefore, lateral movement might be an important process for nitrate–nitrogen loss in wetland ecosystems.

Bai et al. [6] presented that nitrate–nitrogen can laterally move from riverine soils to adjacent rivers or lakes. Nitrate–nitrogen movement was influenced by soil water content, soil physical properties, and water movement velocity [1]. Bai et al. [7] found that horizontal transport rates of nitrate–nitrogen were mainly controlled by non-saturated water diffusion coefficients. Fustec et al. [8] stated that overwetted soils would turn drier after dam construction, leading to a decrease in the capacity of wetland soils controlling the movement of nitrate–nitrogen from agricultural fields. Additionally, Haag and Kaupenjohann [9] studied landform effects on nitrate–nitrogen movement from agricultural fields to rivers, and they presented that ditch/corridor could greatly improve nitrate movement to waters compared to community ecotone/stagnant area. Groffman et al. [10] also observed that riverine wetlands (a big community ecotone) can obviously inhibit nitrate movement from uplands to rivers. Bai et al. [7] simulated the horizontal movement of nitrate–nitrogen in horizontal soil columns from an inland salinity-alkaline wetland. They presented that nitrate–nitrogen transport fluxes increased with increasing water content and decreased with increasing movement distances. However, little information is available on horizontal transport of nitrate–nitrogen in coastal wetland soils with different flooding frequencies.

Rapid agricultural development in the lower reach of the Yellow River resulted in the eutrophication of the waters of the Yellow River estuary due to a large number of nitrate and phosphorus inputs. Therefore, it is very necessary to study horizontal movement of nitrate–nitrogen in the wetland soils to control the eutrophication of the adjacent waters of rivers using the natural riparian buffer zone. The primary objectives of this study were: (1) to investigate the changes in nitrate–nitrogen transport fluxes with increasing movement distances in salt marsh soils of the Yellow River Delta, China; (2) to identify the relationship between transport fluxes of nitrate–nitrogen and water diffusion coefficients.

2 Materials and methods

2.1 Site description

The Yellow River Delta National Nature Reserve is located at the mouth of the Yellow River in Dongying City of Shandong Province, and nearby the south coast of Bohai Bay and the west coast of Laizhou Bay. This area has a mid-latitude temperate monsoonal continental semi-humid climate, with an annual mean temperature
of 12.3°C, the annual radiation of 125.2 kcal cm⁻² and the annual mean sunshine time of 2682 h. Groundwater level is shallow in this delta and easily salinization occurs as it is basically loose rock class pore water with higher salinity. In addition, the Yellow River Delta has Retreat Haiti caused by the counteraction between sea and land, and soil formation time is relatively short. Five soil types were developed in this delta, including yellow brown soil, and lime concretion black soils, fluvo-aquic soil, and saline soil, and paddy soil, of which fluvo-aquic soil and saline soil are the dominate soil types.

2.2 Soil sampling and analysis

Two typical reed wetlands with different flooding frequencies were selected in the study area. One is tidal flooding wetland (permanent flooding zone, 37°43’35” N, 119°12’44” E) and the other is a short-term flooding wetland (less than 1 month flooding/year under the control of water and sediment regulation, 37°45’52” N, 119°09’43” E). Soil samples from 0 to 40-cm depth were randomly collected with three replicates in both typical reed wetlands in January of 2010, and soil profiles were sectioned into 0–10, 10–20, and 20–40 cm. Three replicates at the same soil layer in both wetlands were mixed to gain a composite sample, respectively. One soil core (4.8-cm diameter) was randomly collected from each wetland for the determination of soil bulk densities.

All soil samples were placed in polyethylene bags and brought to the laboratory, and then air-dried at room temperature for more than 3 wk. Each soil was divided into three portions. The first portion was used for soil particle analysis, second portion was sieved through 2-mm sieve and used for simulation experiments, and the third portion was sieved through 0.18-mm sieve and used for determining physico-chemical properties of soils. The physico-chemical properties of the soils in the experiments are listed in Tab. 1.

Soil organic matter (SOM) was determined using Walkley and Black [11] method; soil pH was measured using a pH meter (soil/water, 1:5); soil samples were oven dried at 105°C for 24 h for bulk density determination. Soil particle size analysis was carried out on laser particle size analyzer (S3500, Micotrac, USA).

2.3 Laboratory experiment

This experiment was carried out using water diffusion apparatus with a length of 100 cm and a diameter of 5 cm (Fig. 1). To maintain the same matric potential of soils during the period of nitrate-nitrogen movement, the effects of gravitational potential and pressure potential on water diffusion were avoided by means of the big difference between thickness and length of soil column. The water diffusion instrument contains three components: water chamber (10 cm), which is connected with Mariotte bottle to maintain constant water head; sieving layer (10 cm), which is filled with filter layer and fine quartz to keep water diffusion as the form of laminar low; soil column container (60–80 cm).

Each soil sample was filled in the water diffusion apparatus according to the soil bulk density and was simulated with two replicates and one blank. In the experiment, KNO₃ solution (100 mg NO₃⁻/L) was served as constant water head to simulate nitrate–nitrogen transport and KNO₃ solution was substituted with distilled water in the blank experiment. The experimental time was continuously recorded when the wetting front moved to 0, 5, 8, 11, 14, 17, 20, 23, 26, 29, 32, 35, 38, and 41 cm in the soil columns. The water head was closed after 44 cm of the soil core was wetted, and then soil samples were collected from wetting front in turns at once at these points (at 3-cm intervals) with recorded time. Because water contents near the water head occurred in jumps and might be overestimated, soil samplings were not collected at the distance of 5 cm away from the sieving layer. Each soil sample was divided into three parts: two parts were used for determining nitrate–nitrogen content, while another part was for water content. The soil samples were oven-dried at 105°C for 24 h to constant weight for the determination of water content. Nitrate–nitrogen (NO₃⁻–N) content in these soil samples was determined on Auto-analyzer 3 (AA3, Germany).

2.4 Volumetric water contents and water diffusion coefficients in unsaturated soils

The volumetric soil water contents (θ) could be calculated by the weight of the water contents multiplied by the soil bulk densities [6]. The Boltzmann constant (λ) and water diffusion coefficients could be calculated according to the following Eqs. (1) and (2) [12]:

\[
\lambda = xt^{-1/2}
\]

\[
D(\theta) = \frac{1}{2} \frac{\Delta \lambda}{\Delta \theta} \sum_{\theta_0} ^{\theta} (\lambda \Delta \theta)
\]

![Figure 1. Sketch map for nitrogen movement meter in horizontal soil column.](image)

**Table 1.** Physico-chemical properties of soils in the experiment

<table>
<thead>
<tr>
<th>Sampling sites</th>
<th>Soil layer (cm)</th>
<th>Clay (%)</th>
<th>slit (%)</th>
<th>Sand (%)</th>
<th>Bulk density (g cm⁻³)</th>
<th>Porosity (%)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tidal flooding wetland</td>
<td>0–10</td>
<td>2.76</td>
<td>92.55</td>
<td>4.69</td>
<td>1.07</td>
<td>58.64</td>
<td>9.30</td>
</tr>
<tr>
<td></td>
<td>10–20</td>
<td>4.03</td>
<td>85.61</td>
<td>10.36</td>
<td>1.34</td>
<td>47.73</td>
<td>9.02</td>
</tr>
<tr>
<td></td>
<td>20–40</td>
<td>3.68</td>
<td>81.78</td>
<td>14.54</td>
<td>1.31</td>
<td>50.72</td>
<td>8.93</td>
</tr>
<tr>
<td>Short-term flooding wetland</td>
<td>0–10</td>
<td>0.04</td>
<td>93.30</td>
<td>6.66</td>
<td>1.40</td>
<td>52.04</td>
<td>8.33</td>
</tr>
<tr>
<td></td>
<td>10–20</td>
<td>0.01</td>
<td>64.08</td>
<td>35.92</td>
<td>1.27</td>
<td>47.75</td>
<td>8.52</td>
</tr>
<tr>
<td></td>
<td>20–40</td>
<td>1.87</td>
<td>66.88</td>
<td>31.25</td>
<td>1.40</td>
<td>47.75</td>
<td>8.52</td>
</tr>
</tbody>
</table>
the experiment (min).

Figure 3 shows the relationships between water diffusion coefficients and movement distances in horizontal soil columns from the short-term flooding wetland. This was in agreement with the result reported by Bai et al. [6] in his study of water diffusion in a saline-alkaline wetland of China.

These formulas in the tidal flooding wetland were expressed as forms with the goodness-of-fits of >0.87:

\[ Y_{0.10} = 59.509 \exp(-0.178 x), (R^2 = 0.906, p < 0.01) \]
\[ Y_{10-20} = 324.27 \exp(-0.273 x), (R^2 = 0.875, p < 0.01) \]
\[ Y_{20-40} = 49.858 \exp(-0.206 x), (R^2 = 0.887, p < 0.01) \]

Similarly, the goodness-of-fits of those models in the short-term flooding wetland was >0.84 and the fitting formulas were given:

\[ Y_{0.10} = 5.563 \exp(-0.257 x), (R^2 = 0.922, p < 0.01) \]
\[ Y_{10-20} = 14.599 \exp(-0.202 x), (R^2 = 0.881, p < 0.01) \]
\[ Y_{20-40} = 33.124 \exp(-0.168 x), (R^2 = 0.848, p < 0.01) \]

As for tidal flooding wetland, water diffusion coefficients changed greatly with increasing movement distances at the 10–20 cm soil layer. This was associated with higher clay contents at this layer (4.03%) and lower porosity (47.73%) compared to other layers, as high clay content and lower porosity can impede water movement. Similarly, we can observe the 20–40 cm soil layer with higher clay contents and lower porosity had the highest water diffusion coefficients in short-term flooding wetland. Jouquet et al. [13] also presented that higher clay contents can reduce the number of big holes and capillary pores which are used to transmit water to great degree and gave rise to lower porosity limiting the diffusion of water. Compared to tidal flooding wetland, higher water diffusion coefficients were observed in short-term flooding wetland, which is probably related to lower clay contents and soil pH values in this wetland.

3 Results and discussion

3.1 Water diffusion coefficients in horizontal soil columns

Figures 2 and 3 show the relationships between water diffusion coefficients and movement distances in horizontal soil columns from tidal flooding wetland and short-term flooding wetland, respectively. Water diffusion coefficients increased exponentially with increasing movement distances at all soil layers of both wetlands. This was in agreement with the result reported by Bai et al. [6] in his study of water diffusion in a saline-alkaline wetland of China. These formulas in the tidal flooding wetland were expressed as forms with the goodness-of-fits of >0.87:

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3.2 Nitrate–nitrogen transport rates in horizontal soil columns

Figure 4 shows the changes of NO\textsubscript{3}–N transport rates with increasing movement distances in horizontal soil columns from the tidal flooding wetland. Nitrate–nitrogen transport rates at each soil layer decreased exponentially with increasing movement distances. The goodness-of-fits of these equations reached >0.92. The fitting formulas were expressed as follows:

\[ Y_{0.10} = 3.190 \exp(-0.085 x), (R^2 = 0.928, p < 0.01) \]
\[ Y_{10-20} = 13.513 \exp(-0.189 x), (R^2 = 0.979, p < 0.01) \]
\[ Y_{20-40} = 10.884 \exp(-0.080 x), (R^2 = 0.921, p < 0.01) \]

The changes of NO\textsubscript{3}–N transport rates with increasing movement distances in horizontal soil columns from the short-term
flooding wetland are shown in Fig. 5. Similarly, NO$_3^-$—N transport rates at each soil layer decreased exponentially with increasing movement distances. The goodness-of-fits of these equations reached $>0.89$. The fitting formulas were expressed as follows:

\begin{align*}
Y_{0-10} & = 4.298 \exp(-0.060 \times x), (R^2 = 0.8995, \ p < 0.01) \\
Y_{10-20} & = 12.652 \exp(-0.067 \times x), (R^2 = 0.9198, \ p < 0.01) \\
Y_{20-40} & = 13.351 \exp(-0.070 \times x), (R^2 = 0.9502, \ p < 0.01)
\end{align*}

Sun et al. [14] also observed the exponential increase in nitrate–nitrogen with increasing distances in their studies of freshwater wetland soils.

The highest transport rate of NO$_3^-$—N occurred from 0 to 8 cm for each soil layer in both two types of wetlands, and sequentially showed a rapid decrease from 8 to 18 cm in tidal flooding wetland, and from 8 to 20 cm in the short-term flooding wetland. However, the transport rate kept constant and nearly approached to zero from 18 to 20 cm to 41 cm. This could be explained by the fact that NO$_3^-$ diffusion was controlled by concentration gradient, water potential gradient, and soil matric potential [15]. Nitrate diffusion was greatly impacted by concentration gradient and water potential gradient at the distance from 0 to 18 cm or 20 cm, while soil matric potential became the dominate factor after exceeding 18 or 20 cm in both wetlands. Bai et al. [7] presented that although soil matric has water holding and adsorption capacity, nitrate–nitrogen concentration decreased due to the mutual exclusion from negative charges.

There were obvious differences between NO$_3^-$—N transport rates of three soil layers in each wetland. The highest transport rate of nitrate was observed at the 20–40 cm soil layer, followed by the order 0–10 cm>10–20 cm in tidal flooding wetland. However, the lowest transport rate of NO$_3^-$—N occurred at the 0–10 cm soil layer and similar transport rates of nitrate were observed in both deeper soil layers. Bai et al. [7, 16] also observed higher NO$_3^-$—N transport rates in deeper soil layers than in upper soil layers in an inland salt marsh. This was probably related to soil properties of different soil layers. Lower soil pH values and higher sand contents at the 20–40 cm soil layer were observed, contributing to NO$_3^-$ transport in tidal flooding wetland. However, higher NO$_3^-$—N transport rate was observed in surface soil (0–10 cm) compared to the 10–20 cm soil layer, which was associated with higher soil bulk density and lower porosity at the 10–20 cm soil layer (Tab. 1). As for the short-term flooding wetland, much higher sand contents in deeper soils than surface soils improved the NO$_3^-$—N transport rate.

### 3.3 Effects of water diffusion coefficients on NO$_3^-$—N transport in horizontal soil columns

Figures 6 and 7 show relationships between NO$_3^-$—N transport rates and water diffusion rates in horizontal soil columns from tidal flooding wetland and short-term flooding wetland, respectively. Nitrate–nitrogen transport rates increased exponentially with increasing water diffusion coefficients at all soil layers of both wetlands. These formulas in the tidal flooding wetland were expressed as forms with the goodness-of-fits of $>0.85$:

\begin{align*}
Y_{0-10} & = 0.273 \exp(6.950 \times x), (R^2 = 0.900, \ p < 0.01) \\
Y_{10-20} & = 0.031 \exp(3.956 \times x), (R^2 = 0.906, \ p < 0.01) \\
Y_{20-40} & = 0.690 \exp(0.574 \times x), (R^2 = 0.962, \ p < 0.01)
\end{align*}

Similarly, the goodness-of-fits of those formulas in the short-term flooding wetland were $>0.77$ and the fitting formulas were given:

\begin{align*}
Y_{0-10} & = 0.545 \exp(0.007 \times x), (R^2 = 0.860, \ p < 0.01)
\end{align*}
This suggested that NO\textsubscript{3}--N transport rates were closely linked to water diffusion coefficients. This was consistent with the results reported by Sun et al. [14]. Yang and Lei [12] also found horizontal water diffusion coefficients. This was consistent with the results and higher NO\textsubscript{3}--N transport rates are the most rapid in surface soils (0–10 cm), followed by the 10–20 cm soil layer, while much slower in the 20–40 cm soils in both wetlands. Compared to tidal flooding wetland, NO\textsubscript{3}--N transport rate is much slower with increasing water diffusion coefficients in the short-term flooding wetland. After the water diffusion coefficient in the surface soils exceeded 1.0 in the short-term flooding wetland (0.1 in the tidal flooding wetland), NO\textsubscript{3}--N transport rates increased rapidly. As for deeper soils, when water diffusion coefficients exceeded 1.2 (10-20 cm) or 1.99 (20-40 cm) in the short-term flooding wetland [higher than those (0.52 for 10–20 cm and 1.67 for 20–40 cm) in the tidal flooding wetland], we can only observe a rapid increase in NO\textsubscript{3}--N transport rates.

4 Concluding remarks
We simulated the movement of NO\textsubscript{3}--N in the horizontal soil columns in the laboratory. Nitrate transport rates showed a consistent and exponential decrease with increasing movement distances in both wetlands with different flooding frequencies and higher NO\textsubscript{3}--N transport rates were observed in deeper soils. Meanwhile, they increased exponentially with increasing water diffusion coefficients, and NO\textsubscript{3}--N transport rapidly in surface soils under the same water diffusion coefficients. Compared to tidal flooding wetland, short-term flooding wetlands had higher risk of nitrate movement to the adjacent water, because NO\textsubscript{3}--N transport rates are higher in this wetland with lower soil pH and higher sand contents. However, further studies on the effects of soil salt and pH on nitrate movement are still needed to identify the key factor influencing nitrate movement. The findings of this study can provide scientific guidance for wetland management practices and water quality protection of rivers or lakes and contribute to identifying buffer zone width in the coastal region.

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