

## Response Mechanisms of Nitrate and Ammonium Concentrations to Hydrological Processes in the Hyporheic Zone of Pastoral Riparian Areas: Postprint

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### Abstract

In pastoral and irrigated agricultural areas, substantial amounts of nitrogen-laden livestock excreta and nitrogen fertilizers migrate from soils into surface water and groundwater, constituting the primary source of watershed non-point source pollution. The riparian hyporheic zone represents an effective barrier for mitigating nitrogen pollution loads, and elucidating the transport, transformation, and removal processes of nitrogen within this zone is crucial for watershed nitrogen pollution control. This study selected the upper reach of the Xilin River in a typical grassland pastoral area to conduct continuous monitoring of river water and riparian groundwater levels, ammonium ( $\text{NH}_4$ ) and nitrate ( $\text{NO}_3$ ) concentrations, and relevant environmental factors during the summer flood season. A coupled flow and reactive nitrogen solute transport model for the riparian hyporheic zone was developed using FEFLOW. The model, calibrated against field observations, accurately reproduced the dynamic variations of water levels and the two primary nitrogen species concentrations in the riparian hyporheic zone. The results demonstrate that: (1) The riparian zone exhibits elevated nitrogen pollution risk during the summer flood season, with  $\text{NH}_4$  concentration increasing from  $0.2 \text{ mg} \cdot \text{L}^{-1}$  pre-rainfall to  $7.23 \text{ mg} \cdot \text{L}^{-1}$  post-rainfall, and  $\text{NO}_3$  concentration rising from  $1 \text{ mg} \cdot \text{L}^{-1}$  to  $8.27 \text{ mg} \cdot \text{L}^{-1}$ . (2) Both observed and simulated results reveal that nitrogen dynamics in the hyporheic zone are intimately linked to hydrological processes including rainfall and surface water-groundwater exchange, with  $\text{NH}_4$  and  $\text{NO}_3$  concentrations exhibiting distinct response mechanisms to storm events. (3) During rainfall events, the more mobile  $\text{NO}_3$  infiltrates into the riparian zone from river water and surface sources via leaching, resulting in significant concentration increases. Concurrently, rainfall events intensify river water-groundwater exchange, thereby influencing nitrogen biogeochemical cycling through controlling

nutrient inputs and regulating the variations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations in the riparian hyporheic zone. This study provides preliminary insights into the buffering mechanisms of pastoral riparian zones on nitrogen-related hydrological and biogeochemical processes, offering scientific reference for nitrogen pollution control in pastoral regions.

## Full Text

## Preamble

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### Response Mechanisms of Nitrate and Ammonia Nitrogen Concentrations to Hydrological Processes in the Riparian Hyporheic Zone of Pastoral Areas

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**Abstract:** In pastoral and irrigated agricultural areas, large amounts of nitrogen from livestock manure and chemical fertilizers enter surface water and groundwater from soils, representing the primary source of watershed non-point source pollution. The riparian hyporheic zone serves as an effective barrier for reducing nitrogen pollution loads, and clarifying its role in nitrogen migration, transformation, and removal is critical for controlling watershed nitrogen pollution. This study selected an upper reach of the Xilin River in a typical steppe pastoral area and conducted continuous monitoring of water levels, ammonia ( $\text{NH}_4^+$ -N) and nitrate ( $\text{NO}_3^-$ -N) concentrations, and related environmental factors in river water and riparian groundwater during the summer flood season. Using these high-resolution measurements, a three-dimensional water flow and nitrogen reactive transport model of the riparian hyporheic zone was developed using FEFLOW. The calibrated model accurately reproduced the dynamic variations in water levels and the two primary nitrogen species concentrations in the riparian hyporheic zone. The results indicate: (1) The riparian zone faces high nitrogen pollution risk during the summer flood season, with  $\text{NH}_4^+$ -N concentrations rising from  $0.2 \text{ mg} \cdot \text{L}^{-1}$  before rainfall to  $7.23 \text{ mg} \cdot \text{L}^{-1}$  after rainfall, and  $\text{NO}_3^-$ -N concentrations increasing from  $1 \text{ mg} \cdot \text{L}^{-1}$  to  $8.27 \text{ mg} \cdot \text{L}^{-1}$ . (2) Both measured and simulated results demonstrate that nitrogen dynamics in the hyporheic zone are closely related to hydrological processes such as rainfall and river water-groundwater exchange. (3) During rainfall events, the more mobile  $\text{NO}_3^-$ -N infiltrates the riparian zone from river water and surface infiltra-

tion under leaching effects, causing significant concentration increases. Simultaneously, rainfall events enhance river water-groundwater exchange, regulating hyporheic zone  $\text{NH}_4^+$ -N concentration changes by controlling nutrient inputs and influencing nitrogen biogeochemical cycling. This study preliminarily reveals the buffering mechanisms of pastoral riparian zones in hydrological and biogeochemical nitrogen processes, providing scientific references for nitrogen pollution control in pastoral areas.

**Keywords:** riparian hyporheic zone; nitrogen transport; hydrological process; groundwater simulation; Xilin River

## Introduction

Nitrogen-induced eutrophication is a globally concerning water environmental issue. Excessive application of synthetic fertilizers in agricultural ecosystems and large discharge of livestock manure from animal husbandry constitute important sources of nitrogen non-point source pollution. Excess nitrogen in the atmosphere, surface water, and soil enters water bodies driven by hydrological processes, causing water environmental pollution. Nitrate ( $\text{NO}_3^-$ -N) and ammonia ( $\text{NH}_4^+$ -N) are the most predominant nitrogen forms in water bodies. The riparian hyporheic zone, as a mixing area of surface water and groundwater, promotes material and energy exchange through water exchange, forming distinct redox gradients and diverse biological communities. It is therefore widely recognized as a hotspot for nutrient transformation, particularly nitrogen cycling. Clarifying the migration, transformation, and sources of these two nitrogen species in the riparian hyporheic zone is key to controlling nitrogen pollution loads.

Research indicates that the summer flood season is a hotspot period for nitrogen transformation, with rainfall-runoff events being the primary driver of watershed nitrogen non-point source pollution that stimulates nitrogen cycling turnover. Related studies have analyzed the dynamic relationship between pollutant concentrations and rainfall/discharge, using hysteresis phenomena to explain nitrogen sources and pathways—whether nitrogen enters rivers rapidly through surface runoff during rising water periods or is discharged from groundwater during falling water periods. However, relying solely on river discharge and nitrogen concentration monitoring with hysteresis analysis is insufficient to accurately identify nitrogen migration and transformation. It is necessary to combine high-frequency monitoring of nitrogen and related environmental factors in the riparian hyporheic zone to further clarify its turnover processes.

Most studies have shown that the riparian hyporheic zone acts as a nitrate sink, where processes such as nitrification, denitrification, and anaerobic ammonium oxidation depend on nitrogen supply, water chemistry characteristics, and hydrological conditions (e.g., flood characteristics, groundwater levels). Currently, researchers have conducted extensive studies on river hyporheic zones near irrigated agricultural areas. For example, Darwiche Criado et al. found that

$\text{NO}_3^-$ -N sources differ between wet and dry seasons and respond differently to hydrological processes. Pan et al. discovered that redox conditions in the hyporheic zone affect nitrogen biogeochemical transformation processes, with denitrification and anaerobic ammonium oxidation intensities showing spatial variation within certain ranges. However, current domestic research on nitrogen migration and transformation patterns in pastoral riparian zones remains insufficient, with most studies focusing only on  $\text{NO}_3^-$ -N migration and transformation under denitrification. Based on this, our study conducted high-frequency monitoring of water levels, water nitrogen concentrations, and related environmental factors during the flood season, and used the simulation software FEFLOW to construct a water flow and nitrogen reactive transport model for the riparian hyporheic zone. The aim was to analyze nitrogen dynamics in the river and riparian hyporheic zone and their response to hydrological processes, explore the sources and transport mechanisms of the two primary nitrogen species in the riparian hyporheic zone, and provide references for riparian zone management and watershed nitrogen pollution control.

## 1.1 Study Area Overview

The study area is located in the Xilin Gol Grassland in eastern Inner Mongolia Plateau, situated in the transition zone from the semi-humid meadow steppe region in eastern China to the semi-arid typical steppe region in the northwest [Figure 1: see original paper]. The Xilin River is the mother river of the Xilin Gol Grassland, with a total length of 268 km, flowing from southeast to northwest. The Xilin River basin covers an area of 10,542 km<sup>2</sup>, with annual precipitation of 400 mm. The maximum precipitation occurs in the summer flood season from June to August, and the multi-year average evaporation is 1900 mm. Groundwater is primarily unconfined water in loose rocks with strong water yield. The upper phreatic aquifer is dominated by fine sand from the Holocene. The Xilin Gol Grassland is an important pasture in northern China.

## 1.2 In-situ Monitoring Experiment

During the summer flood season of 2021, field monitoring experiments were conducted at an upper reach of the Xilin River near the Inner Mongolia Grassland Ecosystem Research Station of the Chinese Academy of Sciences. The monitoring period was from June 1 to August 31, 2021. The studied river section has a total length of 180 m, with an average width of 8.5 m. The monitoring period included two major rainfall events of 64 mm and 47 mm. Total rainfall during the monitoring period was 180 mm. The riparian groundwater depth was 0.3–0.7 m, and the river water depth was 0.5–1.1 m.

A total of 9 monitoring wells were installed in the river channel and riparian zone [Figure 2: see original paper]. Three monitoring wells (C1–C3) were placed in the river channel at intervals of 5–7 m. Three wells each were installed on the left bank (1L–3L) and right bank (1R–3R) of the river channel at distances

of 10–15 m from the river. The riparian monitoring pipes extended 7–10 m below the ground surface, while the river channel monitoring pipes extended 10–15 cm below the riverbed surface. Pipes with a diameter of 50 mm were used as groundwater monitoring wells, with holes drilled uniformly at 10–15 cm intervals and wrapped with 50-mesh nylon mesh to prevent clogging by silt.

Before monitoring, the topography of the study area was measured using a total station. During the monitoring period, groundwater levels and river water levels were monitored daily using water level gauges and staff gauges. River flow velocity was measured using a current meter and converted to discharge based on river width. A portable water quality analyzer (Multi 3630 IDS SET G) was used every 5–7 days to monitor water temperature, dissolved oxygen (DO), and other water quality parameters in river water and groundwater. River water and groundwater samples were collected in 100 mL brown bottles, stored in a cool and dark place to prevent biogeochemical transformation. The collected water samples were filtered in the laboratory through 0.4  $\mu$ m membrane filters. According to the measurement methods recommended by the Ministry of Ecology and Environment, a Vario TOC analyzer was used to determine dissolved organic carbon (DOC), and a UV spectrophotometer (SHIMADZU UV-2600) was used to determine inorganic nitrogen.  $\text{NH}_4^+$ -N was measured using the Nessler's reagent spectrophotometric method, and  $\text{NO}_3^-$ -N was measured using the UV spectrophotometric method.

### 1.3 Construction of Riparian Hyporheic Zone Water Flow and Solute Transport Model

The riparian hyporheic zone in the study area is recharged by precipitation and river infiltration. The exchange between river water and groundwater depends on the hydraulic gradient between river and groundwater levels and the permeability of sediments. Livestock manure from grazing cattle is the primary nitrogen source in the study area, where nitrification, denitrification, and other reactions may occur under the combined action of hydrological and biogeochemical processes. This study established a three-dimensional water flow and nitrogen reactive transport numerical model for the riparian hyporheic zone of the studied river section based on FEFLOW. The model was used to simulate groundwater levels and nitrogen concentrations during the summer flood season of 2021 based on water flow processes and nitrogen transformation processes in the hyporheic zone.

The model has a length of 180 m and a width of 50 m, discretized using triangular finite element meshes with refinement in the river channel area. The model was set up based on measured surface elevation, with 5 vertical layers, each consisting of 12,000 cells. The system automatically generated 92 simulation time steps, totaling 92 days.

The water flow in the riparian hyporheic zone uses the unsteady flow equation for unconfined aquifers:

$$\frac{\partial}{\partial x} \left( K_{xx} h \frac{\partial H}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_{yy} h \frac{\partial H}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_{zz} h \frac{\partial H}{\partial z} \right) + w = \mu \frac{\partial h}{\partial t}$$

where  $K_{xx}$ ,  $K_{yy}$ , and  $K_{zz}$  are hydraulic conductivities along the x, y, and z coordinate axes ( $\text{m} \cdot \text{d}^{-1}$ ), assuming the coordinate axes align with the principal directions of hydraulic conductivity;  $H$  is the groundwater level (m);  $h$  is the thickness of the unconfined aquifer (m);  $t$  is time (d);  $w$  is the source-sink term ( $\text{d}^{-1}$ ); and  $\mu$  is the specific yield.

The solute reactive transport model uses the advection-dispersion equation:

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) - \nabla \cdot (vc) + R_c$$

where  $c$  is the solute concentration in water ( $\text{mg} \cdot \text{L}^{-1}$ );  $t$  is time (d);  $D$  is the hydrodynamic dispersion coefficient ( $\text{m}^2 \cdot \text{d}^{-1}$ );  $v$  is the average groundwater flow velocity ( $\text{m} \cdot \text{d}^{-1}$ );  $\nabla c$  is the concentration gradient; and  $R_c$  is the solute source-sink term.

The hydrodynamic dispersion coefficient  $D$  is calculated as:

$$D = \alpha v + D_m$$

where  $\alpha$  is the dispersivity (m), divided into longitudinal ( $\alpha_L$ ) and transverse ( $\alpha_T$ ) components, and  $D_m$  is the molecular diffusion coefficient ( $\text{m}^2 \cdot \text{d}^{-1}$ ), assumed to be independent of solute concentration.

Considering that  $\text{NO}_3^-$ -N is highly mobile and susceptible to leaching and denitrification, while  $\text{NH}_4^+$ -N is less mobile and prone to adsorption and nitrification, the primary source of  $\text{NH}_4^+$ -N is mineralization of organic nitrogen. The study area has abundant organic nitrogen sources, and at the riparian zone scale, migration limitation due to  $\text{NH}_4^+$ -N adsorption is not considered. Given that the Xilin River upper reaches have rich soil humus and studies have shown abundant microbial species involved in nitrogen transformation in riparian zones, particularly active during summer with suitable temperatures, this study considers that microbial growth and death processes are not the main factors affecting nitrogen transformation in the hyporheic zone. Microorganisms are treated as having sufficient and stable sources in the model, without considering their growth and death processes.

First-order reaction kinetics are used to describe the source-sink terms as follows:

For  $\text{NO}_3^-$ -N:

$$R_c^{\text{NO}_3} = N_{leach} - K_{\text{NO}_3} C_{\text{NO}_3}$$

For  $\text{NH}_4^+$ -N:

$$R_c^{\text{NH}_4} = N_{min} - K_{\text{NH}_4} C_{\text{NH}_4}$$

where  $N_{leach}$  is the  $\text{NO}_3^-$ -N concentration leached from soil into groundwater ( $\text{mg} \cdot \text{L}^{-1}$ );  $K_{\text{NO}_3}$  is the decay coefficient for  $\text{NO}_3^-$ -N concentration reduction due to various reactions such as denitrification ( $\text{d}^{-1}$ );  $C_{\text{NO}_3}$  is the  $\text{NO}_3^-$ -N concentration ( $\text{mg} \cdot \text{L}^{-1}$ );  $N_{min}$  is the  $\text{NH}_4^+$ -N concentration from organic nitrogen mineralization ( $\text{mg} \cdot \text{L}^{-1}$ ); and  $K_{\text{NH}_4}$  is the decay coefficient for  $\text{NH}_4^+$ -N concentration reduction due to processes such as adsorption and nitrification ( $\text{d}^{-1}$ ).

River locations within the study area were set as first-type (Dirichlet) boundaries, with river stages determined based on daily monitoring data. Precipitation was treated as a source-sink term, with infiltration coefficients calculated as empirical values based on regional vadose zone conditions. According to previous research results, the lateral hyporheic exchange boundary of the studied river section is located 10–15 m from the river channel, where exchange between riparian groundwater and the river is very weak, thus set as zero-flux boundaries. The left and right boundaries may have groundwater inflow or outflow and were set as flux boundaries. The vertical hyporheic exchange boundary is located 10–15 cm below the riverbed surface, with the model bottom set as a zero-flux boundary as there is essentially no vertical exchange. River water  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N concentrations were set as constant concentration boundary conditions using the river module, while concentrations at other boundaries were zero-flux boundaries.

The spatial distribution of groundwater levels and solute concentrations on June 1 was used as the initial condition, and the model was calibrated based on measured water levels and solute concentrations during the monitoring period. The pumping method was used to measure the hydraulic conductivity of riverbed and riparian zone sediments. Model parameters are shown in Table 1.

To verify model accuracy, Root Mean Square Error (RMSE) and Coefficient of Determination ( $R^2$ ) were used as evaluation indicators:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - y_m)^2}$$

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - y_m)^2}{\sum_{i=1}^n (y_i - \bar{y})^2}$$

where  $y_i$  is the measured value;  $\bar{y}$  is the mean of measured values;  $y_m$  is the model simulated value; and  $i = 1, 2, \dots, n$ , where  $n$  is the number of data points.

#### 1.4 Model Parameter Sensitivity Analysis

Based on the characteristics of pollutant solute transport simulated by the model, parameters affecting riparian hyporheic zone solute transport were selected for sensitivity analysis. The parameters included: longitudinal dispersiv-

ity  $\alpha_L$ , transverse dispersivity  $\alpha_T$ , molecular diffusion coefficient  $D_m$ , first-order reaction constant  $K_{NO_3}$ , and first-order reaction constant  $K_{NH_4}$ . Local sensitivity analysis was used to evaluate the impact of individual parameter changes on model output without considering parameter coupling. When analyzing sensitivity for one parameter, other parameters were held constant while the parameter value was increased or decreased by 10%, and the resulting changes in simulated concentrations relative to the calibrated model (baseline scenario) were recorded.

## 2.1 Hydrodynamic Processes

Two major rainfall events occurred during the monitoring period: 64 mm from July 20–22 and 47 mm from August 18–19. Influenced by rainfall, river water levels and riparian groundwater levels fluctuated frequently during the monitoring period, showing similar trends but with different magnitudes of change.

From June 1–20, both river and groundwater levels rose slightly. Without significant precipitation in the monitoring area, this was likely caused by upstream inflow. During the continuous rainfall from July 20–22, groundwater levels reached the first major peak of the monitoring period, rising nearly 0.30 m. River water level also rose 0.45 m, slightly higher than groundwater level. After the rainfall ended, water levels recovered to pre-rainfall levels. During the August 18–19 rainfall period, water levels remained relatively stable with only minor increases.

The simulated water level fluctuations matched the actual process well [Figure 3: see original paper]. The simulated and measured groundwater levels showed good agreement, with RMSE between 0.04–0.07 m and  $R^2$  between 0.57–0.85. Simulated values showed slight deviations from measured values, possibly due to differences in riparian infiltration capacity during different rainfall intensities, resulting in slightly different groundwater level rises.

Frequent water level fluctuations during the monitoring period caused changes in the hydraulic gradient between river water and riparian groundwater. Without rainfall, the hydraulic gradient was a small negative value, indicating a weak trend of groundwater discharging to the river [Figure 4: see original paper]. When rainfall occurred, river water level rose more significantly than riparian groundwater level, causing the hydraulic gradient to reverse and indicating river water infiltration recharging groundwater. On July 22, the hydraulic gradient reached the maximum value of the monitoring period at 0.20 m, causing river water and groundwater levels to rise by 0.27 m and 0.30 m, respectively. After the rainfall ended, river water level decreased rapidly to pre-rainfall levels, the hydraulic gradient became negative, and approached zero.

Simulation results show that the model can accurately describe groundwater level dynamics and the exchange process between river water and groundwater under rainfall influence.

## 2.2 Nitrogen Concentration Changes

During the monitoring period, river water  $\text{NO}_3^-$ -N concentration ranged from 1.27–5.36  $\text{mg} \cdot \text{L}^{-1}$ , while riparian groundwater  $\text{NO}_3^-$ -N concentration ranged from 0.29–8.27  $\text{mg} \cdot \text{L}^{-1}$ . River water and groundwater  $\text{NO}_3^-$ -N concentrations showed similar trends with varying degrees of fluctuation, both peaking on July 23 and August 20. Except at location 1L, river water concentrations were slightly lower than groundwater concentrations [Figure 5: see original paper]. After the 64 mm storm on July 20–22, the average  $\text{NO}_3^-$ -N concentration in riparian monitoring wells increased from 2.28  $\text{mg} \cdot \text{L}^{-1}$  before rainfall to 8.27  $\text{mg} \cdot \text{L}^{-1}$ , then decreased to 0.93  $\text{mg} \cdot \text{L}^{-1}$ . Solute simulation results show that the model accurately depicted  $\text{NO}_3^-$ -N concentration trends in riparian groundwater, with good agreement between simulated and measured results (RMSE: 0.66–0.98  $\text{mg} \cdot \text{L}^{-1}$ ,  $R^2$ : 0.64–0.89). The model slightly underestimated  $\text{NO}_3^-$ -N concentration peaks at some monitoring wells while overestimating them at others, possibly due to spatial variations in nitrogen pollution load inputs across the riparian zone.

River water  $\text{NH}_4^+$ -N concentration ranged from 0.20–1.53  $\text{mg} \cdot \text{L}^{-1}$ , while riparian groundwater  $\text{NH}_4^+$ -N concentration ranged from 0.15–7.23  $\text{mg} \cdot \text{L}^{-1}$ . Compared to  $\text{NO}_3^-$ -N dynamics, river water  $\text{NH}_4^+$ -N concentration remained at low levels with a relatively flat trend, mainly because  $\text{NH}_4^+$ -N in river water is transformed to  $\text{NO}_3^-$ -N through nitrification.  $\text{NH}_4^+$ -N concentration in different monitoring wells showed distinct characteristics. Groundwater  $\text{NH}_4^+$ -N concentration increased significantly and peaked (2.70–7.23  $\text{mg} \cdot \text{L}^{-1}$ ) during the continuous rainfall on July 20–22. After the rainfall ended,  $\text{NH}_4^+$ -N concentration slowly decreased to the minimum value of the monitoring period (0.20–0.87  $\text{mg} \cdot \text{L}^{-1}$ ). There was a slight upward trend in groundwater  $\text{NH}_4^+$ -N concentration after the August 18–19 rainfall (1.48–2.29  $\text{mg} \cdot \text{L}^{-1}$ ). Simulated concentration trends generally matched measured results (RMSE: 0.61–0.74  $\text{mg} \cdot \text{L}^{-1}$ ,  $R^2$ : 0.61–0.70). Simulated concentrations were lower than measured values at some monitoring wells, possibly due to localized high-concentration nitrogen pollutant discharge caused by grazing activities.

Sensitivity analysis results show that when longitudinal dispersivity  $\alpha_L$ , transverse dispersivity  $\alpha_T$ , and molecular diffusion coefficient  $D_m$  were increased or decreased by 10%, the maximum concentration change was only 0.067  $\text{mg} \cdot \text{L}^{-1}$ , indicating low parameter sensitivity. In contrast, reaction parameters showed higher sensitivity. When the  $\text{NO}_3^-$ -N decay coefficient  $K_{\text{NO}_3}$  increased by 10%, the peak concentration decreased by 2.64  $\text{mg} \cdot \text{L}^{-1}$ ; when the  $\text{NH}_4^+$ -N decay coefficient  $K_{\text{NH}_4}$  increased by 10%, the peak concentration decreased by 1.13  $\text{mg} \cdot \text{L}^{-1}$ . Even with a 50% parameter change, the result variation remained less than 0.001  $\text{mg} \cdot \text{L}^{-1}$ . This demonstrates that reaction parameters significantly influence model results, indicating that biogeochemical reactions in the riparian zone play a crucial role in nitrogen fate.

### 2.3 Changes in Related Water Environmental Indicators

During the monitoring period, river water pH ranged from 7.52–7.81, and riparian groundwater pH ranged from 7.78–8.31, both being weakly alkaline. River water DOC concentration was 8.01–47.3  $\text{mg} \cdot \text{L}^{-1}$ , while riparian monitoring wells showed DOC concentration peaks of 1.83–29.72  $\text{mg} \cdot \text{L}^{-1}$ . Riparian monitoring well DOC concentration increased from  $7.74 \pm 0.34 \text{mg} \cdot \text{L}^{-1}$  before precipitation to 17.27–29.72  $\text{mg} \cdot \text{L}^{-1}$ , then decreased to the minimum value of 1.21–25.18  $\text{mg} \cdot \text{L}^{-1}$  on August 21–25 after rainfall ended [Figure 7: see original paper]. River water DO concentration was  $7.74 \pm 0.34 \text{mg} \cdot \text{L}^{-1}$ , providing favorable conditions for microbial aerobic respiration. Riparian groundwater DO concentration ranged from 0.2–1.7  $\text{mg} \cdot \text{L}^{-1}$ , indicating an anoxic environment with a dynamic process similar to DOC, also reaching maximum values on July 23.

## 3 Discussion

### 3.1 Nitrogen Pollution Risk in Riparian Zones During Summer Flood Season

From an annual timescale perspective, peak nitrogen concentrations in riparian hyporheic zones during the summer flood season ( $\text{NO}_3^-$ -N: 8.27  $\text{mg} \cdot \text{L}^{-1}$ ,  $\text{NH}_4^+$ -N: 7.23  $\text{mg} \cdot \text{L}^{-1}$ ) were higher than pre-flood season concentrations ( $\text{NO}_3^-$ -N: 5.07  $\text{mg} \cdot \text{L}^{-1}$ ,  $\text{NH}_4^+$ -N: 4.67  $\text{mg} \cdot \text{L}^{-1}$ ) and post-flood season concentrations ( $\text{NO}_3^-$ -N: 2.54  $\text{mg} \cdot \text{L}^{-1}$ ,  $\text{NH}_4^+$ -N: 2.56  $\text{mg} \cdot \text{L}^{-1}$ ). This is mainly because annual precipitation in the study area is low and concentrated in the summer flood season. Large amounts of nitrogen accumulated in surface soil and the hyporheic zone enter water bodies under rainfall scouring, causing significant increases in river water  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N concentrations. This indicates that the summer flood season is a critical period with high nitrogen pollution risk in pastoral riparian zones and a key timeframe for nitrogen pollution load control. Although dissimilatory nitrate reduction to ammonium (DNRA) could be an important mechanism for  $\text{NH}_4^+$ -N production, the groundwater  $\text{NH}_4^+$ -N increase in this study was accompanied by DO elevation rather than a highly reduced environment, suggesting DNRA is not the main factor for  $\text{NH}_4^+$ -N production.

### 3.2 Migration and Transformation of $\text{NO}_3^-$ -N and $\text{NH}_4^+$ -N in Riparian Hyporheic Zones

Experimental and simulation results demonstrate that hydrological processes dominate nitrogen concentration changes in riparian hyporheic zones and rivers, but the mechanisms controlling  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N migration and transformation differ. Although the July 20–22 rainfall was substantial, it did not significantly increase the hydraulic gradient, with most monitoring wells showing negative gradients indicating groundwater recharge to the river, and  $\text{NO}_3^-$ -N concentration only increased slightly. When rainfall ended, the hydraulic gradient fluctuated near zero, indicating weak river water-groundwater exchange. This

lack of  $\text{NO}_3^-$ -N input into the riparian hyporheic zone is unfavorable for mineralization, and  $\text{NH}_4^+$ -N concentration also decreased slowly. This shows that rainfall events regulate  $\text{NH}_4^+$ -N concentration changes in riparian hyporheic zones by altering river water-groundwater exchange and controlling nutrient inputs.

$\text{NO}_3^-$ -N concentration showed a small increase followed by a decrease after continuous low-intensity rainfall events, possibly due to  $\text{NO}_3^-$ -N accumulation in the surface soil layer that was leached out. During the falling water period, concentration decreased slowly. Additionally, increased  $\text{NH}_4^+$ -N concentration in the riparian zone provided conditions for nitrification, leading to some  $\text{NO}_3^-$ -N production. After the storm event on July 20–22, riparian hyporheic zone  $\text{NO}_3^-$ -N concentration increased sharply to the maximum value of the monitoring period [Figure 5: see original paper], mainly because heavy rainfall scouring caused accumulated  $\text{NO}_3^-$ -N in the upper soil layer to be leached out. Some entered river water with surface runoff, while another portion infiltrated directly into riparian groundwater from the ground surface. Due to the high mobility of  $\text{NO}_3^-$ -N, rainfall scouring is the main factor controlling  $\text{NO}_3^-$ -N in riparian zones, with rainfall intensity determining the strength of scouring and the intensity of river water recharging groundwater.

### 3.3 Source-Sink Effects of Pastoral Riparian Zones on Nitrogen

Throughout the monitoring period, river water  $\text{NH}_4^+$ -N concentration was lower than riparian groundwater concentration. Under the influence of continuous rainfall on July 20–22, both river water and riparian hyporheic zone  $\text{NH}_4^+$ -N concentrations gradually increased and peaked on July 23. At this time, river water infiltration recharging riparian groundwater was dominant, with the hydraulic gradient between river water and groundwater being positive. The frequent precipitation events during the summer flood season caused substantial increases in nitrogen concentrations in river water and groundwater, mainly due to large nitrogen load inputs from grazing. Research indicates that 70–90% of nitrogen ingested by animals is returned to pastures through feces and urine. The study area is dominated by cattle grazing, which has higher nitrogen leaching losses than other livestock. Additionally, the study area has sandy soils with large pores and strong permeability, making it easier for  $\text{NO}_3^-$ -N to leach into groundwater.

Throughout the monitoring period, the riparian hyporheic zone showed alternating  $\text{NH}_4^+$ -N production and removal [Figure 8a: see original paper]. According to formula (8), the riparian hyporheic zone showed  $\text{NH}_4^+$ -N production on July 23 (after heavy rain) and August 19 (after light rain), acting as a source of river nitrogen. After light rain on August 19,  $\text{NH}_4^+$ -N production on the left bank (1L–3L) was more significant than on the right bank (1R–3R). During non-rainfall periods, the riparian hyporheic zone primarily showed  $\text{NH}_4^+$ -N removal, with removal rates of 21–25%, acting as a sink for river nitrogen. This may be because as  $\text{NH}_4^+$ -N is consumed during the falling water period, the

riparian hyporheic zone generally tends toward an anaerobic environment ( $\text{DO} < 2 \text{ mg} \cdot \text{L}^{-1}$ ), favoring denitrification. According to variance analysis results ( $P = 0.25 > 0.05$ ),  $\text{NH}_4^+$ -N removal effects on the left and right banks were not significantly different [Figure 8b: see original paper].

The riparian hyporheic zone showed  $\text{NO}_3^-$ -N removal throughout the monitoring period, with removal rates of 18–36%. Therefore, protecting riparian zone biodiversity and preventing soil erosion are effective approaches for nitrogen reduction in pastoral areas. Additionally, grazing not only changes soil structure but also affects microbial processes influencing nitrogen transformation and removal, increasing leaching risks. Thus, strengthening grazing management is also necessary for controlling non-point source pollution.

## 4 Conclusion

Based on flood season monitoring of water levels,  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N concentrations, and related environmental factors in a typical steppe river and its riparian zone, this study established a water flow and nitrogen solute transport model for the riparian hyporheic zone. The model effectively simulated water level and nitrogen concentration dynamics and can serve as a reliable tool for estimating nitrogen pollution loads in riparian zones. During the summer flood season, the Xilin River riparian hyporheic zone faces high nitrogen pollution risk, with the fate of different nitrogen species closely related to hydrological processes such as rainfall and river water-groundwater exchange. The highly mobile  $\text{NO}_3^-$ -N infiltrates the riparian zone from river water and ground surface under leaching effects during rainfall. Simultaneously, rainfall events enhance river water-groundwater exchange, regulating nitrogen concentrations in the riparian hyporheic zone by controlling nutrient inputs and influencing nitrogen biogeochemical cycling. The buffering function of riparian zones can be optimized through grazing management and riparian zone management to reduce nitrogen leaching risks in pastoral areas.

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