

Modeling Nitrogen Cycling in the Hyporheic Zones: A Comparison of First-Order and Monod-Type Kinetics

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Introduction

- Nitrogen transformations in hyporheic zones control nutrient retention and removal, but their reaction pathways are difficult to quantify because hydrological and biogeochemical conditions vary strongly in space and time.

Question:

How to unravel nitrogen transformation dynamics in hyporheic zone?

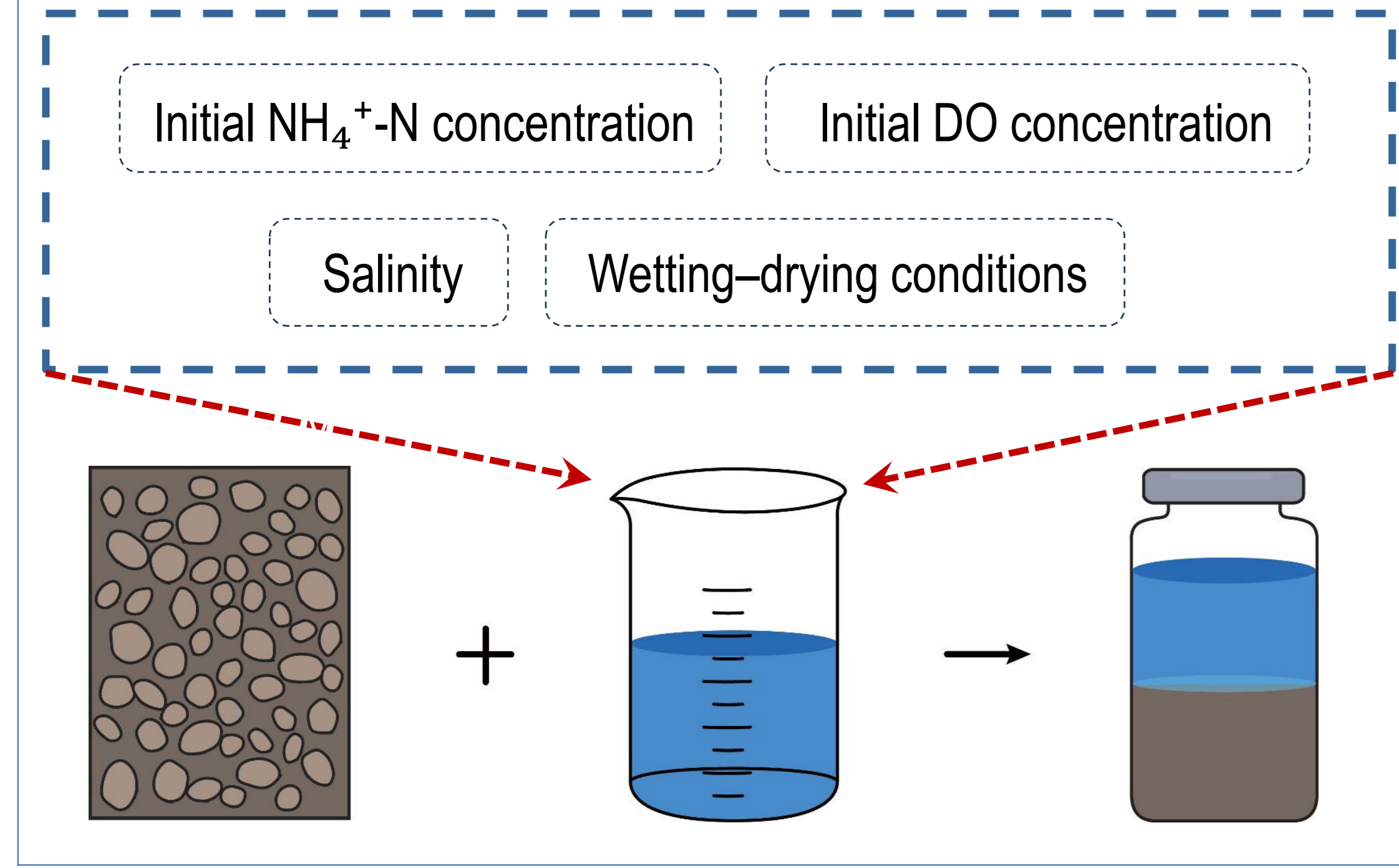
Our Solution:

Microcosm experiments → Kinetic model development → Dominant pathway and parameter identification

Methods

- Experiment:** Soil–water microcosm experiments were conducted to investigate nitrogen transformation dynamics under controlled hyporheic zone conditions. Water samples were collected at 14 time points between 0 and 384 h, and analyzed for aqueous NH_4^+ -N, NO_3^- -N, NO_2^- -N, and DOC concentrations.

Figure 1: Microcosm experiments



- Simulation:** Four kinetic models were developed based on Monod-type and first-order kinetic formulations, with or without explicit environmental regulation terms (Table 1). Model performance and applicability were systematically evaluated by comparing their fitting accuracy and ability to reproduce aqueous NH_4^+ -N, NO_2^- -N, and NO_3^- -N dynamics.

Monod-type kinetic equation and environmental regulation terms

The Monod substrate limitation term:

$$M(C_i, K) = \frac{C_i}{K + C_i}$$

The oxygen inhibition term:

$$I(DO, K_i) = \frac{K_i}{K_i + DO}$$

The effective dissolved oxygen concentration:

$$DO_{eff} = f_{DO} \cdot DO$$

The microbial activation term:

$$X_j(t) = N_0 + \frac{N_{ox,j} - N_0}{1 + e^{k_j(t_c - t)}}$$

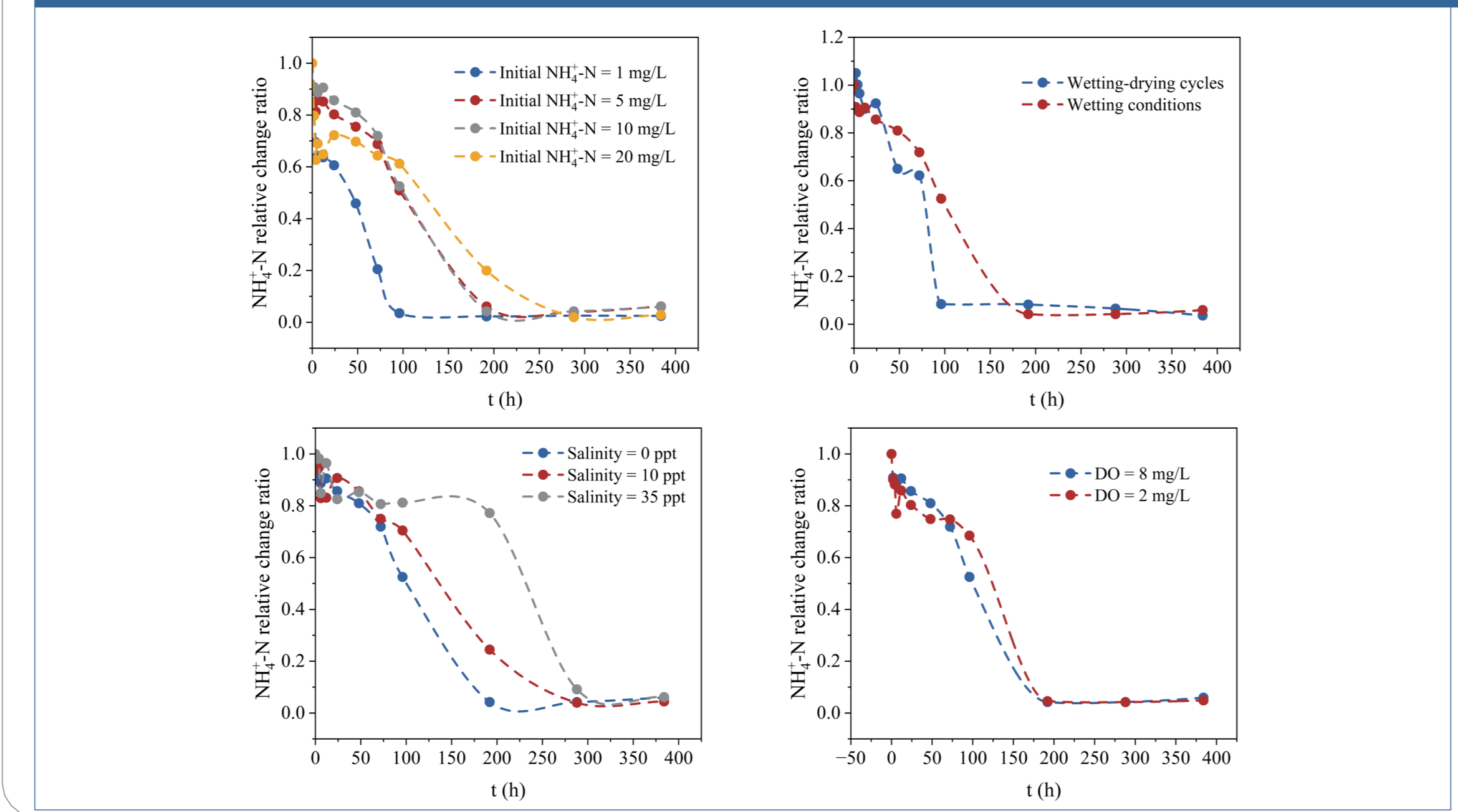
Table 1 Model description

Model	Nitrogen kinetics	Environmental factor
M1	Monod-type	Monod-type
M2	First-order	Monod-type
M3	First-order	First-order
M4	First-order	Removed

Results

- Initial nitrogen substrate concentration controlled the timing and rate of nitrogen transformation.
- High salinity strongly inhibited nitrogen transformation, while DO mainly regulated early-stage reaction rates.
- Wetting–drying cycles accelerated nitrogen transformation compared with continuously wet conditions.

Figure 2: Relative changes in ammonia nitrogen based on microcosm experiments



- The Multi-Monod model (M1) better described NH_4^+ -N depletion and transient NO_3^- -N/ NO_2^- -N accumulation compared with first-order kinetics.

Figure 3: Model fitting results for inorganic nitrogen species

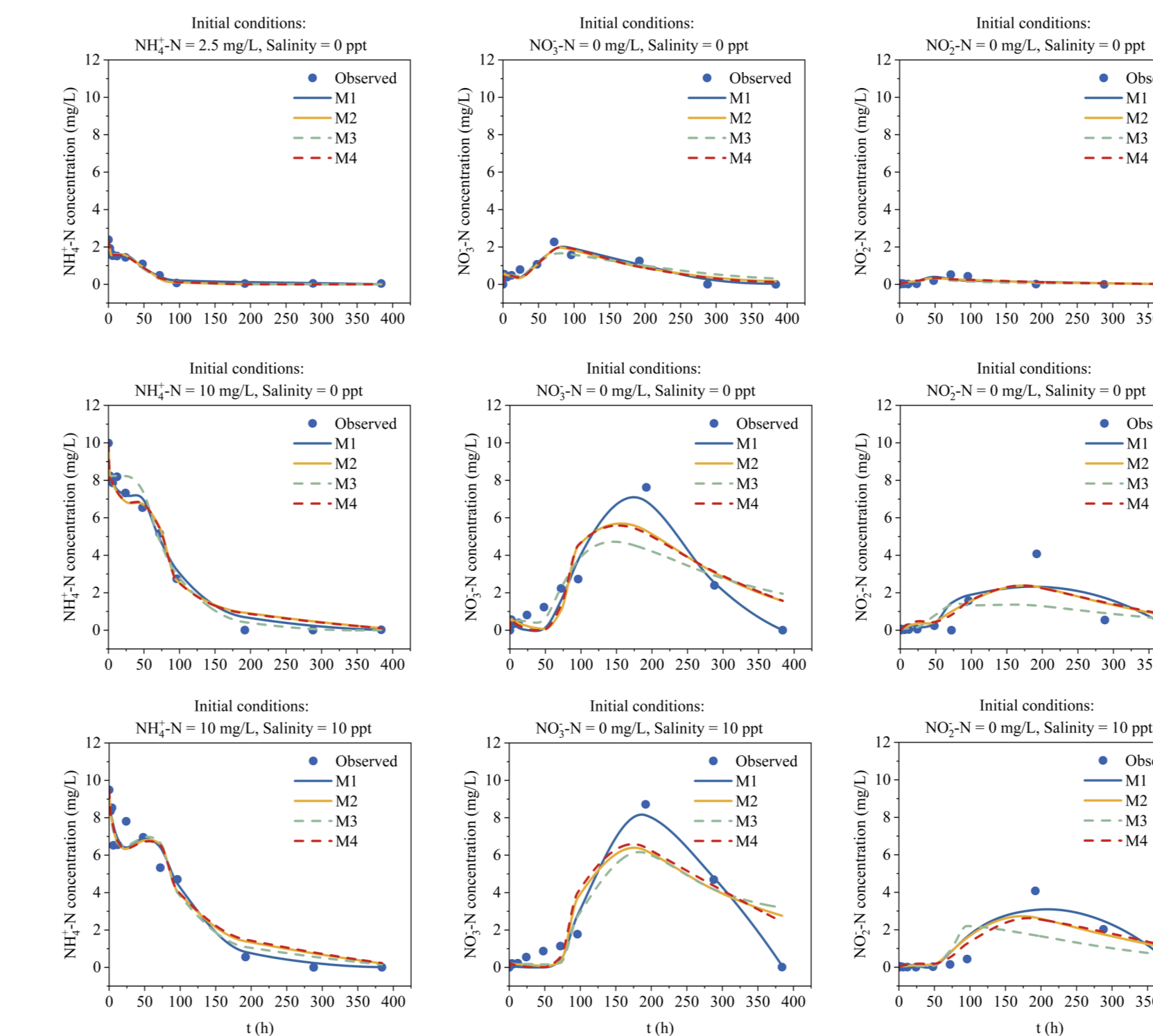
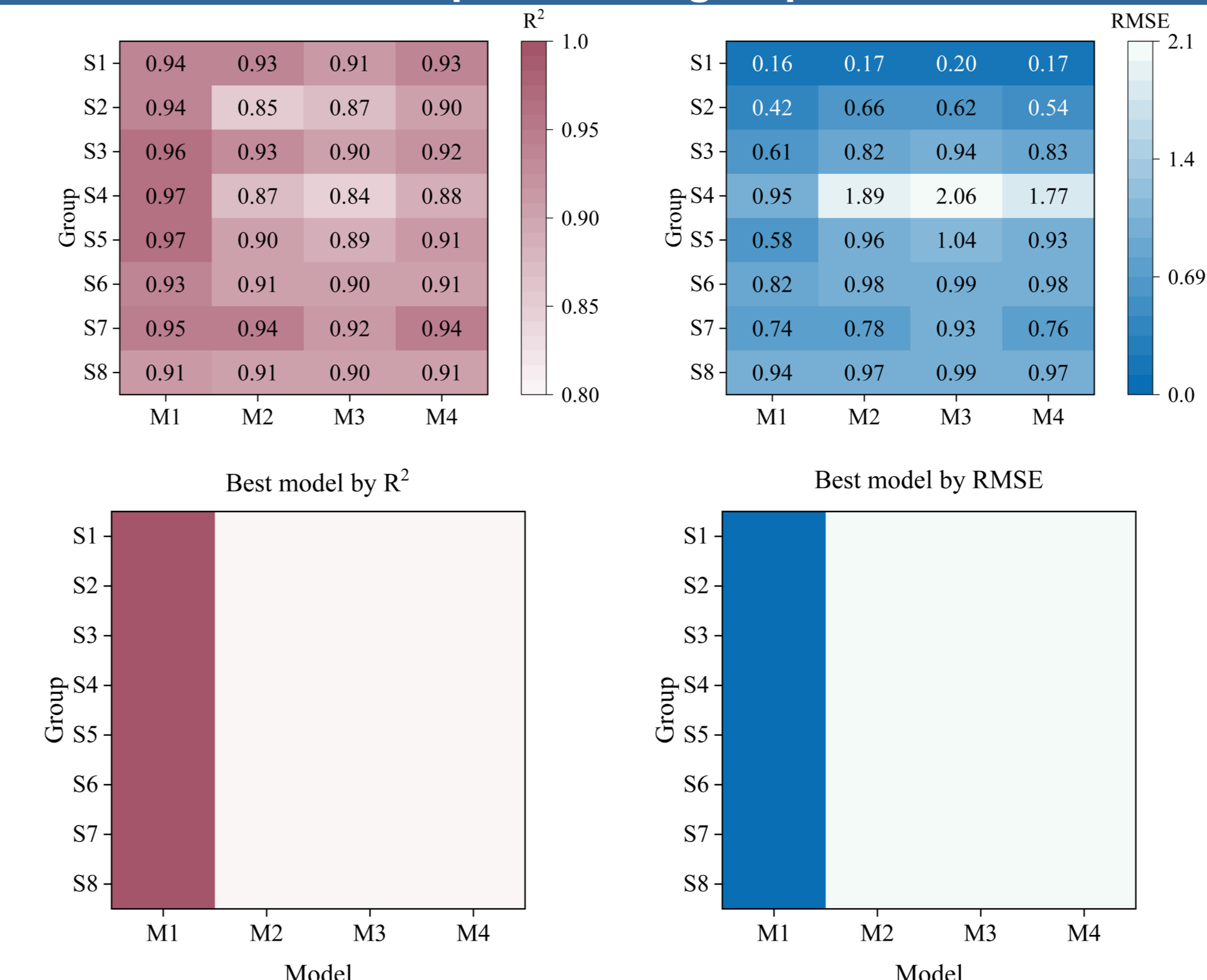
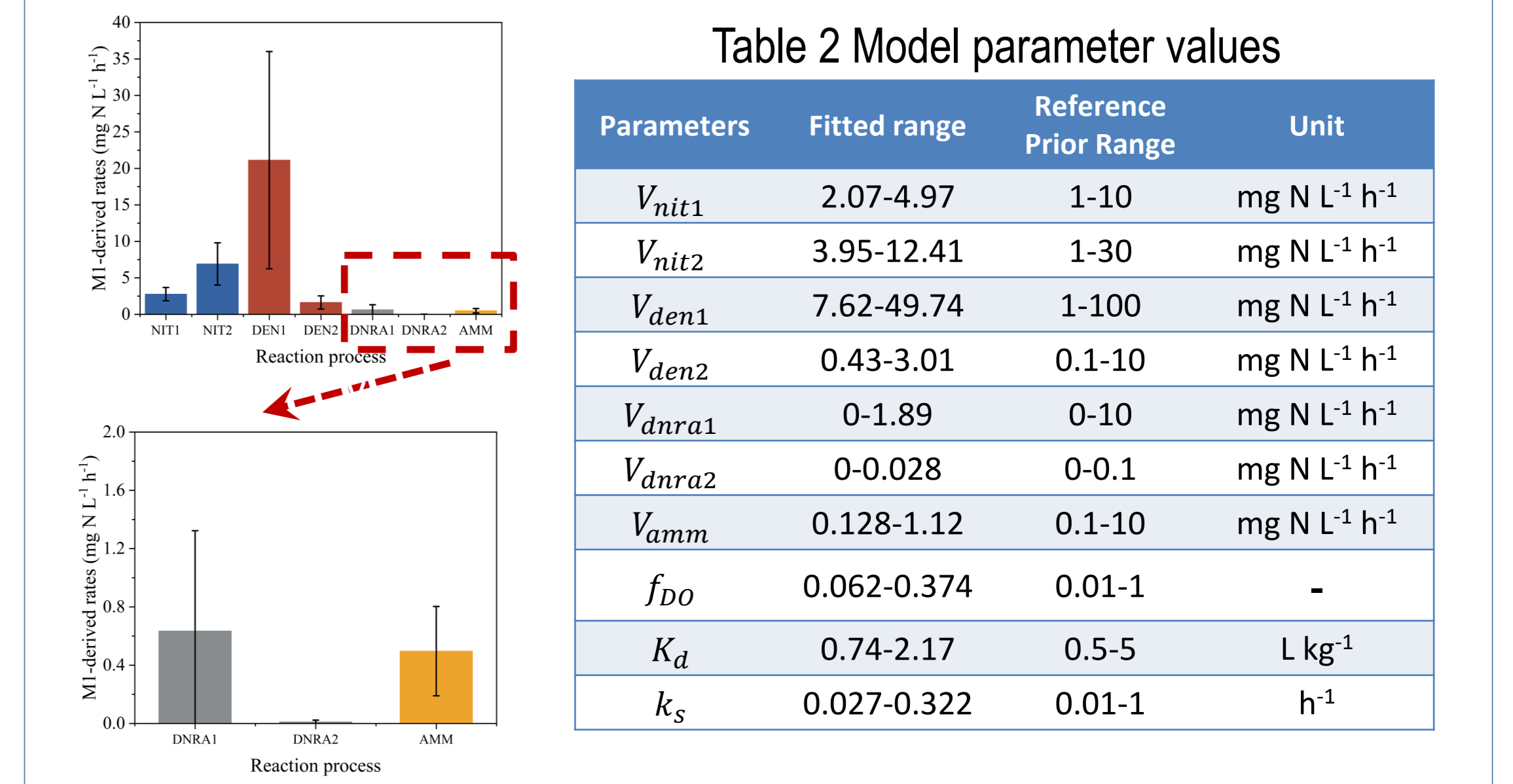


Figure 4: Model performance comparison across experimental groups



- Models with environmental regulation terms showed more robust fitting performance, with generally higher R^2 and lower RMSE, indicating the importance of environmental controls on nitrogen transformation rates and pathways.

Figure 5: M1-derived maximum reaction rates and dominant nitrogen transformation pathways in the hyporheic zone, based on microcosm experiments



- The M1-derived reaction rates indicate that nitrate reduction through the first denitrification step (DEN1) was the dominant nitrogen transformation process, followed by nitrite oxidation (NIT2).
- Parameter priors were derived from fitted values and expanded by one order of magnitude for reactive modeling (Table 2).

Conclusions and application

- Nitrification–denitrification jointly controlled nitrogen transformation, with denitrification playing a dominant role even in the shallow hyporheic zone.
- The Multi-Monod model provided the best explanation of nitrogen transformation by explicitly representing both substrate limitation and environmental regulation.

References

- Xing, J., Cai, Y., Zhou, N., Xian, Y., Jiang, S., Zhou, Y., Huang, A., & Yi, D. (2025). Numerical simulation of hyporheic exchange and analysis of driving mechanisms in the tidal Jingzi River, China. *Hydrogeology Journal*, 33(8), 2163-2179.
- Ceresa, L., Guadagnini, A., Rodríguez-Escales, P., Riva, M., Sanchez-Vila, X., & Porta, G. M. (2023). On multi-model assessment of complex degradation paths: The fate of diclofenac and its transformation products. *Water Resources Research*, 59(1), e2022WR033183.

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