Response to reviewers' comments on "Evaluating Long-Term Effectiveness of Managed Aquifer Recharge for Groundwater Recovery and Nitrate Mitigation in an Overexploited Aquifer System" by Y. Zhu, Z. Guo, S. Wan, K. Chen, Y. Wang, Z. Zeng, H. Shen, J. Ye, and C. Zheng

Reviewer's comments in black; Response to reviewer's comments in blue; Revisions in the revised manuscript in red.

We would like to thank the editor and the reviewer for their constructive comments, which have helped us improve the presentation of this work. We have revised our manuscript according to the reviewer's comments and have provided below a point-by-point response to the reviewer's comments.

Reviewer #1

1. The paper is interesting and well written, and it is relevant to the water management of a vital area of China: Xiongan New District.
   There are two major issues that require a much more careful analysis, and I hope the authors can revise their paper accordingly. The first is the description of denitrification. In this manuscript, the authors used a two-step reduction to simplify the process. This is OK, but requires a much more careful and detailed analysis to justify its correctness. It is well known that denitrification is a complex process controlled by many factors. So, the authors should carefully justify why such a two-step reduction treatment is acceptable for this site!

   Response:

   Thank you for the detailed review. We agree that denitrification is a complex biogeochemical process involving multiple enzymatic pathways, intermediate products and microbial communities.

   The justification for adopting the two-step simplification ($NO_3^- \rightarrow NO_2^- \rightarrow N_2$) in our regional-scale model is based on the following three reasons:

   (1) The shallow aquifer system in the Xiong'an New Area is characterized by oxidizing conditions (high dissolved oxygen) and a scarcity of organic electron donors (Li et al., 2023). The Michaelis-Menten kinetics employed in our model (Eq. 5 and Table 1) explicitly include dual-Monod terms for electron donor limitation (Acetate as a proxy for DOC) and inhibition terms for dissolved oxygen. The overall denitrification rate is controlled primarily by the availability of the electron donor and the inhibition threshold of oxygen, rather than the transformation rates of intermediate species (like N_2O). Therefore, our model structure is sufficient to capture the "bottleneck" of the reaction at this site.

   (2) The primary objective of this study is to evaluate the long-term, regional-scale (536 km^2) evolution of nitrate mass and the relative contribution of dilution versus reaction. The two-step reduction mechanism effectively conserves the mass balance of Nitrogen and simulates the permanent removal of

nitrate from the aqueous phase. While simplified, this approach is widely accepted in regional-scale Reactive Transport Modeling where computational efficiency is paramount, and parameter uncertainty for multi-step intermediate reactions would be prohibitively high (Guo et al., 2023; Karlović et al., 2022; Jin et al., 2024).

(3) Our results indicate that denitrification contributes only ~9% to the total nitrate reduction, while dilution dominates (~91%). Even if a more complex reaction network were used, the limiting environmental conditions, particularly the low availability of organic carbon and the high concentrations of dissolved oxygen, which collectively suppress denitrification rates. Thus, the current simplification provides a robust, albeit conservative, estimation of the biochemical contribution without over-parameterizing the model.

Revisions have been made in line 112:

"While denitrification involves complex enzymatic pathways, this two-step simplification is adopted based on the specific hydrogeochemical conditions of the study area, which is characterized by oxidizing environments and a scarcity of organic electron donors (Li et al., 2023). Under these conditions, the overall reaction rate is primarily controlled by the availability of electron donors and the inhibition threshold of dissolved oxygen, rather than the transformation rates of intermediate species. Therefore, the kinetic model employed Equation (5), which explicitly includes dual-Monod terms for donor limitation and oxygen inhibition, is sufficient to capture the rate-limiting steps and conserve nitrogen mass balance at the regional scale, while avoiding the excessive parameter uncertainty associated with complex multi-step reaction networks (Guo et al., 2023; Karlović et al., 2022; Jin et al., 2024)."

2. The second issue is related to Eq. 5. The author stated that " For example, according to the redox gradient theory, sulfate reduction may be inhibited by oxygen, nitrate, and trivalent iron dissolved in groundwater. These effects are modeled using an inhibition term in equation (5)". This is not sufficient. I would like the authors to explain what "inhibition term in Eq. (5)" is used and why. In one sentence: more elaboration is needed here!

Response:

Thank you for the detailed review.We apologize for the confusion caused by using "sulfate reduction"as a general example in the original text, which obscured the specific application to our nitrate model. In the revised manuscript, we will clarify that for the denitrification process modeled in this study, the "inhibition term" (*I*) in Equation (5) specifically refers to Oxygen Inhibition. As shown in Table 1 of our manuscript, the specific mathematical form used is:

$$I = \frac{K_{I,O_2}}{K_{I,O_2}+[O_2]}$$

The reason for using this specific inhibition term is based on the thermodynamic hierarchy of electron acceptors (Appelo and Postma, 2005). In groundwater systems, facultative anaerobes preferentially utilize Dissolved Oxygen (DO) over Nitrate as an electron acceptor because aerobic respiration provides a higher energy yield. Therefore, denitrification is strictly an anaerobic process that only occurs when

DO concentrations drop below a threshold. This inhibition term acts as a switch: high concentrations of DO will drive the term toward zero, effectively shutting down the denitrification reaction rate (R) in Equation (5) until hypoxic conditions are established.

We have rewritten the description following Equation (5) to remove the irrelevant example of sulfate reduction and explicitly state that oxygen is the sole inhibitor considered for the nitrate reduction pathway in this study.

Revisions have been made in line 117:

$$R = \mu_{max} \frac{C_{ED}}{C_{ED}+K_{ED}} \frac{C_{TEA}}{C_{TEA}+K_{TEA}} \frac{K_I}{K_I+C_I}$$

"Regarding the final term in Equation (5), it represents the inhibited effect controlled by thermodynamically more favorable electron acceptors. In the context of denitrification modeled here, the process is strictly anaerobic and is inhibited by dissolved oxygen (Appelo and Postma, 2005). Therefore, C_I represents the concentration of dissolved oxygen. This term functions as a kinetic switch, reducing the reaction rate (R) effectively to zero when dissolved oxygen concentrations are high, reflecting the preferential utilization of oxygen over nitrate by facultative anaerobes."

3. L60, there should be a question mark "?" after the two questions mentioned there.

   Response:

   We have added a question mark in the revised manuscript.

   Revisions have been made in line 60:

   "1) How does MAR affect groundwater recovery in a severely depleted aquifer system? 2) How do heterogeneity and biogeochemical reactions interact with MAR to control the spatiotemporal evolution of nitrate concentrations in groundwater?"

4. L65, when NCP is mentioned for the first time, the full name of NCP must be provided.

   Response:

   Thank you for the detailed review. In our manuscript, the full name of NCP (North China Plain) is already provided at line 34 when it first appears.

Appelo, C. A. J. and Postma, D.: Geochemistry, groundwater and pollution. 2nd, Ed. Balkema, Rotterdam, 2005.

Guo, Z., Chen, K., Yi, S., and Zheng, C.: Response of groundwater quality to river-aquifer interactions during managed aquifer recharge: A reactive transport modeling analysis, Journal of Hydrology, 616, https://doi.org/10.1016/j.jhydrol.2022.128847, 2023.

Jin, Z., Tang, S., Yuan, L., Xu, Z., Chen, D., Liu, Z., Meng, X., Shen, Z., and Chen, L.: Areal artificial recharge has changed the interactions between surface water and groundwater, Journal of Hydrology, 637, 131318, https://doi.org/10.1016/j.jhydrol.2024.131318, 2024.

Karlović, I., Posavec, K., Larva, O., and Marković, T.: Numerical groundwater flow and nitrate transport assessment in alluvial aquifer of Varaždin region, NW Croatia, Journal of Hydrology: Regional Studies, 41, 101084, https://doi.org/10.1016/j.ejrh.2022.101084, 2022.

Li, N., Lyu, H., Xu, G., Chi, G., and Su, X.: Hydrogeochemical changes during artificial groundwater well recharge, Science of The Total Environment, 900, 165778, https://doi.org/10.1016/j.scitotenv.2023.165778, 2023.