

Effects of nitrogen management practices on groundwater nitrate leaching risk and dissolved black carbon remediation performance: a scenario-based analysis

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Abstract. Groundwater nitrate pollution is characterized by high mobility, long-term accumulation, and delayed recovery. Surface nitrogen application influences groundwater leaching risk by altering the amount, timing, and release pattern of NO_3^- -N entering the subsurface. To examine nitrate migration and transformation under different nitrogen management practices and to evaluate the remediation effect of dissolved black carbon (DBC), a one-dimensional saturated vertical simulation was conducted under scenarios of total nitrogen input, application frequency, and release rate. Three representative scenarios, namely conventional nitrogen input, 40% nitrogen reduction, and slow-release nitrogen input, were further compared with and without DBC. The results showed that cumulative bottom NO_3^- -N leaching increased with increasing total nitrogen input, whereas higher application frequency and slow-release input reduced leaching risk. In addition, DBC reduced cumulative bottom NO_3^- -N leaching, increased denitrification removal, and promoted a clearer decline in bottom NO_3^- -N concentration during the later stage of the simulation. Overall, nitrogen management optimization is fundamental for groundwater nitrate risk control, whereas DBC is better considered a supplementary remediation measure under optimized nitrogen management.

1 Introduction

Groundwater nitrate pollution is characterized by high mobility, long-term accumulation, and delayed recovery, and has become a prominent environmental risk in agricultural areas [1–4]. After surface nitrogen enters the subsurface, it undergoes infiltration, migration, and transformation before being expressed as nitrate accumulation and leaching at the lower boundary of the groundwater profile [2,5]. Therefore, groundwater nitrate risk is controlled not only by the total nitrogen input, but also by the way nitrogen is introduced into the subsurface, including its application frequency and release pattern [5–7]. Adjusting these nitrogen management practices may therefore alter the downward migration and bottom leaching of NO_3^- -N and, in turn, affect groundwater nitrate risk.

Dissolved black carbon (DBC) has redox activity and may promote nitrate reduction by participating in electron transfer processes [8,9]. However, its remediation effect may vary under different nitrogen input conditions. At present, nitrogen management and DBC remediation are more often considered separately, whereas their combined effects on groundwater nitrate behavior remain insufficiently understood. In this study, a one-dimensional saturated vertical simulation was conducted to compare groundwater NO_3^- -N leaching under three types of

nitrogen management practices, namely total nitrogen input, application frequency, and release rate. Representative scenarios were further selected to compare cumulative bottom NO_3^- -N leaching and denitrification removal with and without DBC. The aim was to distinguish the relative roles of nitrogen input control and supplementary DBC remediation in groundwater nitrate risk mitigation.

In this framework, total nitrogen input, application frequency, and release rate were considered together because they represent different but complementary dimensions of nitrogen management. Total input mainly controls the overall nitrate load entering the subsurface, whereas application frequency and release rate further affect the temporal distribution of nitrate infiltration and the persistence of nitrate exposure along the groundwater profile. Therefore, comparing these three types of management practices helps clarify not only whether nitrate leaching risk can be reduced, but also through which input-control pathway the reduction is achieved.

2 Materials and methods

A one-dimensional fully saturated vertical reactive-transport simulation was conducted to analyze NO_3^- -N migration and transformation in groundwater under

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different nitrogen management practices and to evaluate the remediation effect of dissolved black carbon (DBC). The model was implemented in COMSOL Multiphysics 6.3 using the Darcy's Law and Transport of Diluted Species in Porous Media interfaces. The model domain was 5 m deep, with the upper boundary defined as $z = 0$ m and the lower boundary as $z = -5$ m, and only vertical transport was considered. Spatial discretization was achieved using a free quadrilateral mesh with a predefined finer setting; the element size ranged from 0.001 to 0.035 m. Transient simulations were solved using an implicit backward differentiation formula (BDF) scheme with free time stepping, and results were output at a 1 d interval over a total simulation period of 40 d. The porosity and Darcy velocity were set to 0.4 and 0.04 m/d, respectively, as baseline parameters of the conceptual profile according to the hydrogeological background of the Dagou aquifer and previous reactive nitrogen transport modeling in coastal aquifers [4,10], and were kept constant across all scenarios to ensure direct comparison of the effects of nitrogen input pattern and DBC addition. A time-varying inflow boundary was assigned at the upper boundary, whereas the lower boundary was treated as a free outflow boundary. The model tracked NO_3^- -N, O_2 , DOC, and the redox-active DBC fractions in groundwater. Denitrification was represented by two pathways, namely direct denitrification driven by DOC and DBC-mediated denitrification, and the gradual decline in DBC activity during the reaction process was also considered.

Under the baseline condition, the initial concentrations of NO_3^- -N, DOC, and O_2 were uniformly set to 0.8, 0.6, and 0.06 mol/m³, respectively. DBC was initially distributed only in the upper 0.3 m of the profile, where the initial concentrations of DBCred and DBCox were both 0.25 mol C/m³; below this depth, the initial DBC concentration was set to zero. In all nitrogen management scenarios, parameters other than the upper-boundary NO_3^- -N input pattern and the presence or absence of DBC were kept the same as those under the baseline condition.

Three groups of nitrogen management scenarios were established, including total nitrogen input scenarios (N0–N5), nitrogen application frequency scenarios (F1–F3), and nitrogen release rate scenarios (R1–R3). The total nitrogen input group was used to compare the effects of different nitrogen loading levels, where N3 was defined as the conventional nitrogen input scenario, N1 and N2 represented 40% and 20% nitrogen reduction, respectively, N4 and N5 represented 20% and 40% nitrogen increase, respectively, and N0 represented a low-background input scenario without fertilization. The nitrogen application frequency group was used to compare one-time, two-split, and four-split applications under the same total nitrogen input, corresponding to F1, F2, and F3, respectively. The nitrogen release rate group was used to compare rapid, conventional, and slow nitrogen release, corresponding to R1, R2, and R3, respectively. In addition, three representative scenarios, namely conventional nitrogen input, 40% nitrogen reduction, and slow-release nitrogen input, were selected to establish no-DBC control scenarios (C1–C3) for direct

comparison of remediation performance with and without DBC. Detailed scenario settings are shown in Table 1.

In all scenarios, the upper-boundary NO_3^- -N input was represented by a time-varying concentration boundary to simulate differences in nitrate infiltration after nitrogen application, while a low background input was retained during non-fertilization periods. The main evaluation indices included cumulative bottom NO_3^- -N leaching, denitrification removal, and bottom NO_3^- -N concentration. Cumulative bottom leaching was used to characterize nitrate leaching risk at the lower boundary of the profile, denitrification removal was used to reflect the nitrate transformation capacity of the system, and bottom NO_3^- -N concentration was used to describe the temporal response of nitrate output under different management conditions.

Among all scenarios, conventional nitrogen input, 40% nitrogen reduction, and slow-release nitrogen input were selected as representative cases for comparison with and without DBC because they reflect three practically meaningful management situations, namely baseline input, source reduction, and controlled-release management. This design allowed the additional remediation effect of DBC to be evaluated under different nitrate-input backgrounds while keeping the comparison framework concise and directly comparable.

Table 1. Nitrogen management scenario settings.

Scenario	Description	DBC condition
N0	Low-background N input	With DBC
N1	40% nitrogen reduction relative to conventional N input	With DBC
N2	20% nitrogen reduction relative to conventional N input	With DBC
N3	Conventional N input	With DBC
N4	20% increase relative to conventional N input	With DBC
N5	40% increase relative to conventional N input	With DBC
F1	One-time application	With DBC
F2	Two split applications	With DBC
F3	Four split applications	With DBC
R1	Rapid release	With DBC
R2	Conventional release	With DBC
R3	Slow release	With DBC
C1	Conventional N input without DBC	Without DBC
C2	40% nitrogen reduction without DBC	Without DBC
C3	Slow-release nitrogen input without DBC	Without DBC

3 Results and discussion

3.1 Effects of nitrogen management practices on groundwater nitrate leaching risk

Under different nitrogen management practices, cumulative bottom NO_3^- -N leaching showed consistent differences, indicating that groundwater nitrate leaching risk was affected not only by total nitrogen input, but also

by the application frequency and release pattern of nitrogen input. The spatiotemporal distributions of NO_3^- -N under contrasting total nitrogen input scenarios (Figure 1) and the cumulative bottom leaching results (Figure 2a) together show that total nitrogen input strongly affected nitrate behavior in groundwater. Compared with N0, N5 showed a larger high-concentration zone, deeper downward migration, and longer persistence of NO_3^- -N within the profile, while cumulative bottom NO_3^- -N leaching increased progressively with increasing total nitrogen input. Under the same total nitrogen input, increasing application frequency reduced cumulative bottom NO_3^- -N leaching (Figure 2b), suggesting that split application can alleviate nitrate accumulation and leaching pressure in the lower part of the profile by avoiding short-term concentrated nitrogen input. In the release-rate scenarios, cumulative bottom NO_3^- -N leaching was highest under rapid release and lowest under slow release (Figure 2c), indicating that delayed nitrogen release was more favorable for reducing long-term leaching risk. Overall, although the magnitude of variation among different management scenarios was moderate, the direction of change was consistent, confirming that nitrogen management influences groundwater nitrate leaching risk by altering how and when NO_3^- -N enters the subsurface.

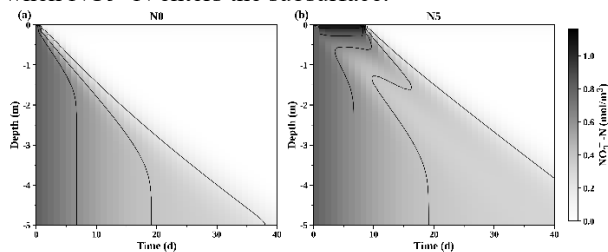


Figure 1. Spatiotemporal distributions of NO_3^- -N under contrasting total nitrogen input scenarios: (a) N0; (b) N5.

In addition, the temporal response of bottom NO_3^- -N concentration also differed among nitrogen management scenarios, indicating that groundwater nitrate output was controlled not only by total nitrogen input, but also by the application frequency and release pattern of nitrogen input. Overall, reducing nitrogen input, redistributing application timing, and delaying nitrogen release all helped lower leaching risk, although their effects on groundwater nitrate behavior were not identical.

These differences indicate that the three management practices reduced groundwater nitrate risk through partly different mechanisms. Lower total nitrogen input directly decreased the nitrate mass available for downward migration, whereas split application mainly weakened short-term concentration peaks by redistributing nitrate input over time. In contrast, slow-release input moderated the persistence of nitrate infiltration and was therefore more effective in reducing the longer-term accumulation of nitrate near the lower boundary. This distinction is important because it shows that nitrogen management affects not only the magnitude of nitrate leaching, but also the temporal pattern by which nitrate risk develops within the profile [11].

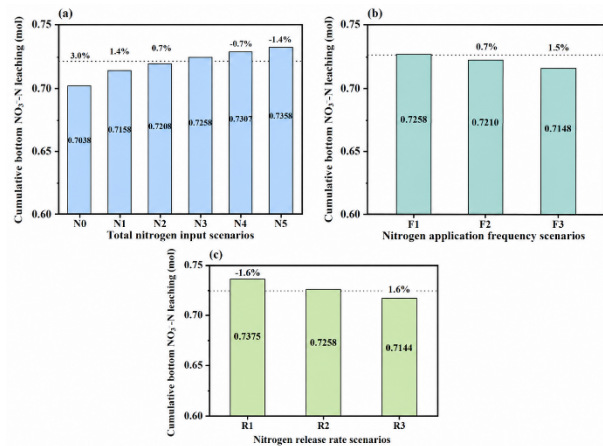


Figure 2. Comparison of cumulative bottom NO_3^- -N leaching under different nitrogen management scenarios: (a) total nitrogen input scenarios; (b) nitrogen application frequency scenarios; (c) nitrogen release rate scenarios.

3.2 Additional remediation effect of DBC under representative nitrogen management scenarios

Figure 3 shows that, under all three representative nitrogen management scenarios, the addition of DBC reduced cumulative bottom NO_3^- -N leaching and increased denitrification removal, indicating that DBC provided a stable additional remediation effect under different nitrogen management conditions. Across the three scenarios, denitrification removal increased by approximately 5.5% to 6.0% after DBC addition, whereas cumulative bottom NO_3^- -N leaching decreased by 1.7% to 1.8%. These results indicate that DBC not only reduced nitrate loss at the lower boundary of the profile, but also enhanced nitrate transformation within the profile. Therefore, DBC is better considered a supplementary remediation measure under optimized nitrogen management, rather than an alternative to nitrogen input control itself.

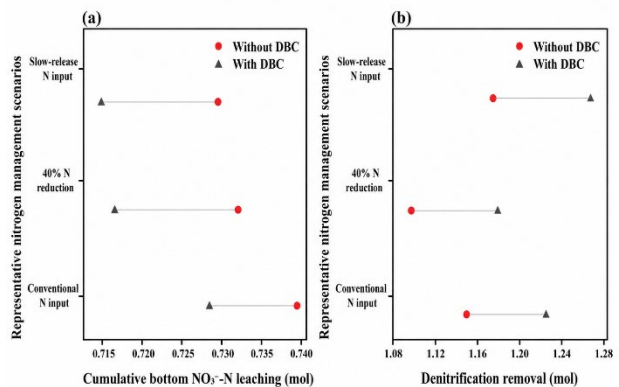


Figure 3. Comparison of remediation performance with and without DBC under representative nitrogen management scenarios: (a) cumulative bottom NO_3^- -N leaching; (b) denitrification removal.

Figure 4 further shows that the effect of DBC was also reflected in the temporal variation of bottom NO_3^- -N

concentration. Under all three representative nitrogen management scenarios, bottom NO_3^- -N concentration decreased gradually with time, and the curves with and without DBC began to diverge mainly during the later stage of the simulation. At 40 d, bottom NO_3^- -N concentration decreased by 14.7%, 18.3%, and 18.6% after DBC addition under conventional nitrogen input, 40% nitrogen reduction, and slow-release nitrogen input, respectively. This indicates that the influence of DBC on the lower boundary was not immediate, but became evident after a certain period of migration and reaction. In addition, the slightly greater reduction observed under reduced and slow-release nitrogen input suggests that optimized nitrogen management can provide more favorable conditions for the additional remediation effect of DBC to be expressed.

This pattern suggests that the additional effect of DBC may be more readily expressed under reduced or slow-release nitrogen input, where nitrate accumulation near the lower boundary is more effectively constrained.

These results further indicate that the remediation role of DBC should be understood in relation to nitrogen-input conditions rather than as an independent substitute for source control. When nitrate input remains high, the effect of DBC on nitrate transformation can still be observed, but its contribution to lowering lower-boundary leaching risk remains comparatively limited. By contrast, under reduced or slow-release input, nitrate migration is less concentrated, and the additional promoting effect of DBC on in-profile denitrification becomes more evident. Therefore, the present results support a combined strategy in which nitrogen management remains the primary means of risk reduction, whereas DBC acts as a supplementary measure to further improve nitrate attenuation within groundwater.

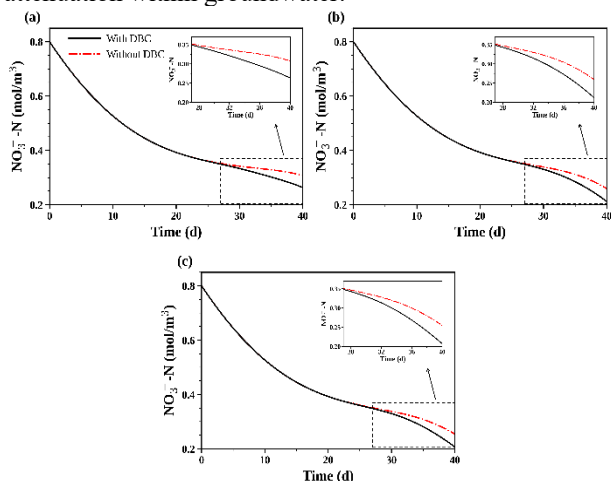


Figure 4. Comparison of bottom NO_3^- -N concentration profiles with and without DBC under representative nitrogen management scenarios: (a) conventional nitrogen input; (b) 40% nitrogen reduction; (c) slow-release nitrogen input.

4 Conclusions

Figure 2 shows that cumulative bottom NO_3^- -N leaching increased with total nitrogen input, but decreased with increasing application frequency and with delayed

nitrogen release, indicating that moderate-to-low input, split application, and slow-release input were the three more favorable practices for lowering groundwater nitrate leaching risk.

Under the three representative scenarios, DBC further reduced cumulative bottom NO_3^- -N leaching by 1.7%-1.8% and increased denitrification removal by 5.5%-6.0%, indicating that nitrogen management optimization is the primary measure for risk control, whereas DBC functions as a supplementary remediation measure under optimized nitrogen management.

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