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Optimizing First-order Rate Coefficients for Soil Nitrate Transformation Processes Applying an Inverse Method

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ABSTRACT

It is extremely challenging to measure first-order rate coefficients for soil nitrate transformation processes directly, either in the laboratory or in the field. In this study, an improved inverse method was proposed to optimize the first-order rate coefficients by considering the intermediate changing processes of the integrated functions. A numerical experiment was designed to test the accuracy of the method in optimizing the coefficients. Comparisons between the optimized and theoretical results indicated that all the relative errors were within 10%. Data collected from a field experiment were used to validate the optimization procedure and to demonstrate its applications in practice. Using the established model and the estimated values by the inverse method, the simulated source-sink term (SST) distributions of September 2-12, 2007, were in good agreement, with the root mean squared error (RMSE) between them being as low as 0.00021 mg cm^{-3} d^{-1}. Based on the established nitrate transformation model, the distributions of soil water content and nitrate concentration during September 2-12, 2007, were simulated, and compared well with the measured profiles, with the *RMSE* of 0.023 cm^3 cm^{-3} and 0.017 mg cm^{-3}, respectively. The improved inverse method should be useful for optimizing the first-order rate coefficients for nitrate transformation, establishing the nitrate transformation model, and simulating the nitrate transport in the soil-plant system.

Keywords: Numerical simulation**,** Root-nitrate-uptake**,** Soil nitrate Kinetics**,** Soil nitrate transformation.

INTRODUCTION

Nitrogen (N), an essential and key nutrient for plant growth and productivity, is meanwhile recognized as a major contributor to environmental pollution through nitrate (NO_3^--N) leaching and gaseous N emission (Arrobas and Rodrigues, 2013). The growing concern about the environmental impact of N fertilizer has enhanced the desire to simulate the transport and transformation of N in soils more accurately. Various simulation models of N turnover in the soil-plant system, differing in representation of processes, numerical algorithms and complexity have been developed in a number of countries (Cabon *et al*., 1991; Keating *et al*., 2003; Garnier *et al.,* 2003; Del Grosso *et al.,* 2005; Hansen *et al*., 2012). Comparisons reveal that the main discrepancies between models are often attributed to inadequate descriptions of the simultaneous processes of N turnover and incomplete definitions of input parameters (Wu and McGechan, 1998; Dinesh and Richter, 2002).

The nitrate transformation involves several complicated processes in soils, such as immobilization, nitrification, denitrification,

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and uptake by roots. First-order kinetics remains the most commonly used approach to quantify reaction rates for these processes (Ma and Shaffer, 2001). The corresponding rate coefficients are then modified for considering the effects of temperature, water content, pH, oxygen, and so on, depending on individual authors of various models. Theoretically, the rate coefficients should be similar under optimal conditions when the process is described as the first-order kinetics controlled by the same factors. However, the suggested rate coefficients vary from model to model. How to determine these rate coefficients accurately and effectively becomes one of the main obstacles in model applications (Ma and Shaffer, 2001). Since the rate coefficients are very difficult to measure directly, the trial-error method is often used to obtain coefficients related to these rates, which may not be optimized in a strict mathematical sense (Shaffer *et al*., 2001).

To solve similar problems, inverse methods have in recent years presented attractive alternatives. In order to establish the root-water-uptake (RWU) model, a few inverse methods were used to optimize *RWU* parameters by minimizing the residuals between simulated and measured soil water contents (Musters and Bouten, 2000). Zuo and Zhang (2002) developed an inverse method to estimate the average distributions of *RWU* rate. Shi *et al*. (2007) applied the method successfully to estimate the source-sink term (SST) in nitrate transport equation i.e. convection-dispersion equation (CDE), and optimize the root-nitrate-uptake (RNU) factor, one of the first-order rate coefficients. However, they neglected the other transformation processes such as ammonium nitrification, immobilization and denitrification through designing an ideal soil column experiment.

The objective of this study was to optimize the first-order rate coefficients related to nitrate transformations applying an improved inverse method. Thereupon, the SST model was established and the dynamics of soil nitrate was simulated. A numerical and a field experiment were designed to examine the feasibility of optimizing transformation rate coefficients and simulating soil nitrate transport in soil-plant systems using the inverse method.

MATERIALS AND METHODS

Water Flow in Soils

Successful simulation of NO_3^--N dynamics depends on accurate description of soil water movement. One-dimensional vertical soil water flow with *RWU* is simulated using Richards' Equation as follows (Wu *et al*., 1999):

$$C(h)\frac{\partial h}{\partial t}=\frac{\partial}{\partial z}\left[K(h)\left(\frac{\partial h}{\partial z}-1\right)\right]-S(z,t) \quad (1)$$

$$h(z,0)=h_0(z) \qquad 0\le z\le L \quad (2)$$

$$\left[-K(h)\left(\frac{\partial h}{\partial z}-1\right)\right]_{z=0}=-E(t) \qquad t>0 \quad (3)$$

$$h(L,t)=h_L(t) \qquad t>0 \quad (4)$$

Where, h is the soil matric potential (cm); $C(h)$ is the soil water capacity (cm^{-1}); $K(h)$ represents the soil hydraulic conductivity ($cm\ d^{-1}$); z *is* vertical coordinate originating from the soil surface and positive downward (cm); t *is* time (d); $h_0(z)$ is the initial soil matric potential in the profile (cm); $E(t)$ is the soil surface evaporation rate ($cm\ d^{-1}$); L represents the simulation depth (cm), and $L\ge L_r$, in which L_r is the rooting depth (cm); $h_L(t)$ is the matric potential at L (the lower boundary) (cm); and $S(z,t)$ is the *RWU* rate ($cm^3\ cm^{-3}\ d^{-1}$), defined by Wu *et al*. (1999) as follows:

$$S(z,t) = S(z_r,t) = \gamma(\theta) S_{\max}(z_r,t) = \gamma(\theta)\frac{T_p}{L_r} L_{nrd}(z_r) \quad (5)$$

Where, z_r $(= z/L_r)$ is the normalized root depth ranging from 0 to 1; $S_{\max}(z_r,t) =$ the maximal specific water extraction rate under the optimal soil water conditions (cm^3 cm^{-3} d^{-1}); $\gamma(\theta)$ is a dimensionless reduction function related to the effect of water stress; T_p represents the potential transpiration rate (cm d^{-1}); $L_{nrd}(z_r)$ is the normalized root length density distribution; and θ is the soil water content (cm^3 cm^{-3}).

Nitrate Transport in Soils

One-dimensional vertical movement of nitrate in the unsaturated zone is characterized by the CDE combined with a SST (Lafolie, 1991):

$$\frac{\partial[\theta C_N]}{\partial t} = \frac{\partial}{\partial z}\left[\theta D(\theta,v)\frac{\partial C_N}{\partial z} - qC_N\right] + SST_N(z,t) \quad (6)$$

$$C_N(z,0) = C_{N0}(z) \qquad 0 \le z \le L \quad (7)$$

$$\left[-\theta D(\theta,v)\frac{\partial C_N}{\partial z} + qC_N\right]_{z=0} = Q_s(t) \quad t > 0 \quad (8)$$

$$C_N(L,t) = C_{NL}(t) \qquad t > 0 \quad (9)$$

Where, C_N is the concentration of NO_3^--N, expressed as mass of NO_3^--N per volume of soil solution (mg cm^{-3}); q is the Darcy's flux (cm d^{-1}), $q = v\theta$, in which v is the pore water velocity (cm d^{-1}); $C_{N0}(z)$ is the initial NO_3^--N concentration distribution (mg cm^{-3}); $Q_s(t)$ represents the flux of NO_3^--N at soil surface (mg cm^{-2} d^{-1}); $C_{NL}(t)$ is the NO_3^--N concentration at the lower boundary (mg cm^{-3}); $SST_N(z,t)$ is the *SST* integrating the transformation processes of NO_3^--N in soils (mg cm^{-3} d^{-1}); $D(\theta,v) =$ the hydrodynamic dispersion coefficient (cm^2 d^{-1}):

$$D(\theta,v) = \lambda|v| + \frac{\theta^{\frac{7}{3}}}{\theta_s^2} D_0 \quad (10)$$

Where, D_0 is the diffusion coefficient for NO_3^--N in pure water (cm^2 d^{-1}); and λ represents the dispersivity (cm).

The $SST_N(z,t)$ unifies the transformation processes of NO_3^--N in soils, expressed as follows (Bradshaw *et al.*, 2013):

$$SST_N(z,t) = S_n(z,t) - S_m(z,t) - S_d(z,t) - S_u(z,t) \quad (11)$$

Where, $S_n(z,t)$, $S_m(z,t)$, $S_d(z,t)$, and $S_u(z,t)$, respectively, are the rates of ammonium nitrification, NO_3^--N immobilization, denitrification, and root uptake per unit soil volume (mg cm^{-3} d^{-1}), and defined by the following equations:

-Nitrification: ammonium → NO_3^--N (Cabon *et al.*, 1991):

$$S_n(z,t) = k_1\varphi_1(T',\theta)C_0(z,t)\theta(z,t) \quad (12)$$

$$\varphi_1(T',\theta) = \begin{cases} 1.07^{[T'(z,t)-T_m]}\dfrac{\theta(z,t)}{\theta_f(z)} & \theta(z,t) \le \theta_f(z) \\ 1.07^{[T'(z,t)-T_m]}\dfrac{\theta_f(z)}{\theta(z,t)} & \theta(z,t) > \theta_f(z) \end{cases}$$

-Immobilization: NO_3^--N → Organic matter (Cabon *et al*., 1991):

$$S_m(z,t) = k_2\varphi_2(T^{'},\theta)C_N(z,t)\theta(z,t) \tag{13}$$

$$\varphi_2(T^{'},\theta) = \begin{cases} k_2 1.05^{\left[T^{'}(z,t)-T_m\right]}\dfrac{\theta(z,t)}{\theta_f(z)} & \theta(z,t) \le \theta_f(z) \\ k_2 1.05^{\left[T^{'}(z,t)-T_m\right]}\dfrac{\theta_f(z)}{\theta(z,t)} & \theta(z,t) > \theta_f(z) \end{cases}$$

-Denitrification: NO_3^--N → N_2O (McGechan and Wu, 2001):

$$S_d(z,t) = k_3\varphi_3(T^{'},\theta)C_N(z,t)\theta(z,t) \tag{14}$$

$$\varphi_3(T^{'},\theta) = \begin{cases} 0 & \theta(z,t) \le \theta_d(z,t) \\ 1.07^{\left[T^{'}(z,t)-T_m\right]}\dfrac{\theta(z,t)-\theta_d(z,t)}{\theta_f(z)-\theta_d(z,t)} & \theta_d(z,t) \le \theta(z,t) \le \theta_s(z) \end{cases}$$

$$\theta_d(z,t) = 0.627\theta_f(z) - 0.0267\frac{\theta_s(z)-\theta(z,t)}{\theta_s(z)}\theta_f(z)$$

-*RNU* (Schoups and Hopmans, 2002):

$$S_u(z,t) = \delta\, S(z,t)C_N(z,t) \tag{15}$$

Where, k_1, k_2, k_3, and δ, respectively, are the first-order rate coefficients for nitrification of ammonium, immobilization, denitrification, and root uptake of NO_3^--N. δ is usually abbreviated as the dimensionless RNU factor ($\delta \ge 0$); $C_0(z,t)$ is the concentration of ammonium in the soil solution (mg cm^{-3}); $T^{'}(z,t)$ is the soil temperature (ºC); T_m is the optimum temperature (ºC) and chosen as $T_m = 35$ ºC in this study (Cabon *et al*., 1991); $\theta_f(z)$= the field water capacity (cm^3 cm^{-3}); and $\theta_d(z,t)$ is the threshold water content (cm^3 cm^{-3}).

Range of the First-order Rate Coefficients in the Literature

Retrieval results have shown that the immobilization coefficient, k_2, was neglected in many cases (Keating *et al*., 2003; McGechan and Hodda, 2010; Liu *et al*., 2011; Hansen *et al*., 2012), but occasionally used in very few models, with the value of around 0.02 d^{-1} (Cabon *et al*., 1991). It is generally accepted that the *RNU* factor δ may depend on the types of solute, plant species, and nutrient status of the plant. A value of $\delta \le 1$ corresponds to a passive *RNU*, and $\delta > 1$ would correspond to active uptake (Schoups and Hopmans, 2002). The first-order rate coefficients for nitrification (k_1) and denitrification (k_3) changed greatly with location and model, but were generally within the range of 0.005-1.0 and 0.00016-0.006 d^{-1}, respectively.

Optimization Procedure for the First-order Rate Coefficients

The average $\overline{SST}_N(z_i,T)$ may be calculated as follows:

$$\overline{SST}_N(z_i,T) = \frac{1}{T}\int_0^T SST_N(z_i,t)\mathrm{d}t = \frac{k_1}{T}\int_0^T f_1\mathrm{d}t - \frac{k_2}{T}\int_0^T f_2\mathrm{d}t - \frac{k_3}{T}\int_0^T f_3\mathrm{d}t - \frac{\delta}{T}\int_0^T C_N(z_i,t)S(z_i,t)\mathrm{d}t \tag{16}$$

In order to minimize the errors brought about by the numerical integration, the following procedures were proposed to improve the method introduced by Shi *et al.* (2007).

(1) Solve Equations (1)-(4) using the implicit finite difference method to obtain $h(z,t)$ and $\theta(z,t)$.

(2) Estimate the average distribution of $\overline{SST}_N(z,T)$ from 0 to T using the inverse method (Shi *et al.*, 2007).

(3) Approximate $SST_N(z,t)$ in Equation (6) with the estimated $\overline{SST}_N(z,T)$, and solve Equations (6)-(9) numerically for the distributions of $C_N(z,t)$ from 0 to T using the implicit finite difference method.

(4) Piecewise calculate the integrals of Equation (16) using the trapezoidal formula, on the basis of the continuous distributions of $\theta(z_i,t)$ and $C_N(z_i,t)$ from 0 to T, which were obtained by Step (1) and (3), respectively.

(5) Optimize the coefficients k_1, k_2, k_3, and δ simultaneously based on Equation (16) using the linear multivariate least-squares procedure, with the retrieval range of the coefficients in the literature as the constraint conditions.

Numerical Experiment

A numerical experiment was designed to test the accuracy and convergence of the method in optimizing the first-order rate coefficients for nitrate transformation processes as follows:

(1) Input a set of data related to water flow and nitrate transformation in soils, which are listed in Table 1.

(2) Solve Equations (1)-(4) using implicit finite difference method to obtain distributions of matric potential $h(z,t)$.

(3) Solve Equations (6)-(9) using implicit finite difference method to obtain the theoretical distributions of soil nitrate concentration $C_N(z,t)$ at time $t= T$ on the basis of Equations 11)-(15) and the input data in step (1).

(4) Choose some values $C_N(z_i,t)$ from $C_N(z,t)$ according to a specified spatial interval (SI) as the "measured" data points.

(5) Fit the "measured" points $C^*_N(z_i,t)$ to a continuous and smooth nitrate concentration curve using the following algebraic polynomial (Huang, 2010):

Table 1. Soil properties, *RWU* and nitrate transformation parameters, initial and boundary conditions in the numerical experiment.

Parameters and data
Soil properties (Carsel and Parrish, 1988): θ_s = 0.450 cm^3 cm^{-3}, θ_r= 0.067 cm^3 cm^{-3}, K_s= 10.8 cm d^{-1}, α= 0.020 cm^{-1} and n= 1.41 in van Genuchten's Equation (1980).
RWU parameters (Musters and Bouten, 2000): L_r= 150 cm, T_p= 0.6 cm d^{-1}.
Hydrodynamic dispersion (Valente *et al.*, 2004): D_0= 1.64 cm^2 d^{-1}, λ= 0.3 cm.
Nitrate transport and transformation parameters (Cabon *et al.*, 1991; Lafolie, 1991; Schoups and Hopmans, 2002): k_1= 0.3 d^{-1}, k_2 = 0.02 d^{-1}, k_3= 0.003 d^{-1}, δ= 1.3, T'= 25ºC.
Ammonium concentration: C_0 (z, t)= 0.02 mg cm^{-3}.
Initial soil water content distribution:
θ (z, 0)= 0.3663+5.76(z-83.57)×10^{-4}-2.0(z-83.57)^2×10^{-6} (cm^3 cm^{-3});
Upper boundary conditions: E (t)= 0.03 cm d^{-1}; $Q_s(t)$= 0.
Lower boundary conditions:
h(180, t)= -34.123, then L= 160 cm, h(L, t) was linearly interpolated;
C_N (L, t)= (0.334 -0.00994t)/10 mg cm^{-3}.

$$P_m(z) = a_1 + a_2(z - \bar{z}) + a_3(z - \bar{z})^2 + ... + a_m(z - \bar{z})^{m-1};\ \bar{z} = \frac{1}{M}\sum_{i=1}^{M} z_i \quad (17)$$

(6) Estimate the average distribution of *SST* in *CDE* using the generated soil nitrate concentration distributions in Step (5) and the inverse method (Shi *et al*., 2007).

(7) Optimize k_1, k_2, k_3, and δ using the proposed method, and calculating the errors between the optimized k_1, k_2, k_3, and δ and their theoretical values (Table 2).

Field Experiment

A field experiment was conducted to validate the optimization procedure and demonstrate its applications in practice. The experiment, performed at an experimental station of China Agricultural University in Quzhou, China (Latitude: 36°52'N; Longitude: 115°01'E), was carried out between August 8 and September 14, 2007. Summer maize (*Zea mays* L. *cv.* Zhengdan 958) was planted in three duplicate 8×8 m^2 plots and was studied at the growth stages between tasseling and harvest. The amount of applied fertilizer in each plot was kept at the same conventional level (about 140 kg ha^{-1} of N as urea). Time domain reflectometry (TDR 100, Campbell, USA) probes were installed horizontally in each plot to measure distributions of soil water content at depths of 5, 10, 15, 20, 30, 50, 70, 90, and 110 cm from the surface. Three duplicate microlysimeters, made of PVC pipe with 15 cm height and 10 cm inner diameter each, were installed in each plot and weighed at the same time every afternoon. Multi-point thermometer sensors (CB-0221, CID, Beijing, China) were installed horizontally to observe soil temperature at depths of 5, 10, 20, 40, and 80 cm from the surface.

Soil texture of the experimental field from 0 to 110 cm depth was silt loam. Soil water retention data and saturated hydraulic conductivity were measured by the pressure membrane method and constant-head method using soil samples taken from the field with six duplicates for each soil. The soil dispersivity was obtained as λ= 0.34 cm by analyzing the breakthrough curve (BTC) of Cl^- with the optimization software CXTFIT (Toride *et al*., 1999).

Soil and root samples were taken 4 times during the experimental period, on August 11, 21, September 2, and 12, 2007, respectively. Soil cores were sampled using a 15 cm high and 10 cm inner diameter auger. At each sampling time, soil samples at depths of 5, 10, 15, 20, 30, 50, 70, and 90 cm were collected to measure nitrate and ammonium concentration with the continuous flow analyzer (TRAACS 2000, Bran+Luebbe, Norderstedt, Germany). The remaining samples were put into a meshwork (with grids of 0.05 cm in diameter) and washed out soil for roots. All the roots collected from each soil core were scanned with a Snapscan 1236 scanner (AGFA, Germany) and analyzed with a Win Rhizo Pro software package (Regent Instruments Inc., Canada) to obtain the root length density distributions.

Table 2. Comparison of optimized first-order rate coefficients using M1 and M2.

	k_1 (d^{-1})	k_3 (d^{-1})	δ
Range	0.005-1	0.00016-0.006	≥0
Theoretical	0.3	0.003	1.3
Optimized (M1)	0.045 (85%)[a]	0.0002 (93%)	0.696 (46%)
Optimized (M2)	0.295 (1.7%)	0.0028 (6.7%)	1.278 (1.7%)

[a] The number in the parentheses represents the relative error between the theoretical values and the optimized results.

RESULTS AND DISCUSSION

Numerical Experiment

With the RWU and nitrate transformation parameters (Table1), distributions of soil nitrate concentration at t= 10 d was simulated using implicit finite difference method. The "measured" nitrate concentrations for spatial interval SI= 5-10 cm (i.e. SI= 5 cm for $0 \le z \le 30$ cm and SI= 10 cm for $z > 30$ cm) were generated according to Step (4) in Section on "MATERIALS AND METHODS─Numerical Experiment", and then fitted using Equation (17).

Since the first-order rate coefficient for immobilization k_2 was just occasionally employed as 0.02 d^{-1} in very few cases, in this study, it was fixed as the retrieval value and not involved in the optimization process. The remaining coefficients i.e. k_1, k_3, and δ were then optimized simultaneously using the method (M1) proposed by Shi *et al.* (2007) and the improved method (M2) in this study, respectively, and compared with the theoretical values in Table 2. The results showed that the relative errors between the theoretical and optimized coefficients using M1 were more than 40%, without an acceptable range. However, reliable optimization results were obtained by M2, with all the relative errors not more than 10%. Without considering the intermediate changing processes of the integrated functions, it would be almost impossible to get satisfactory and reliable optimization results using M1. In general, the improved method (M2) would be worth being recommended to optimize the first-order rate coefficients for soil nitrate transformation processes through applying the inverse method to estimate the SST of soil nitrate transport equation.

Field Experiment

Considering that the numerical experiment might not represent the practical situation, we discussed the applicability of the optimization procedure in further using the field experiment. The measured soil water content, nitrate and ammonium concentration distributions above the rooting depths on August 11, 21, September 2 and 12, 2007, are shown in Figures 1 and 2, respectively. Figure 2 indicated that the values of soil nitrate concentration near the

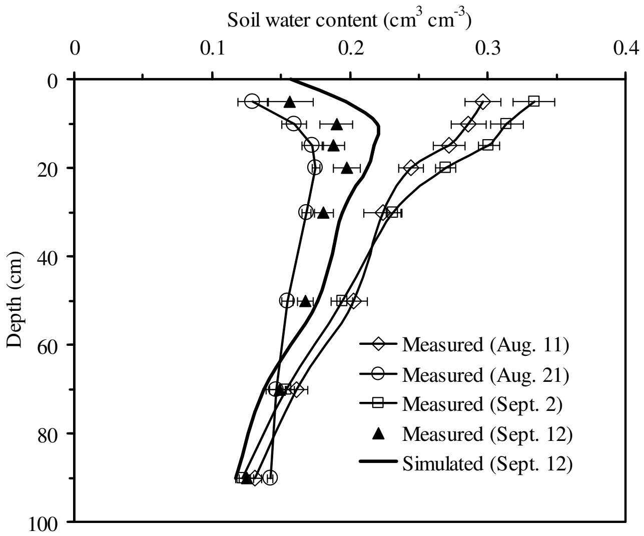

Figure 1. Measured and simulated soil water content distributions from August 11 to September 12, 2007 in the field experiment. Horizontal bars are standard errors.

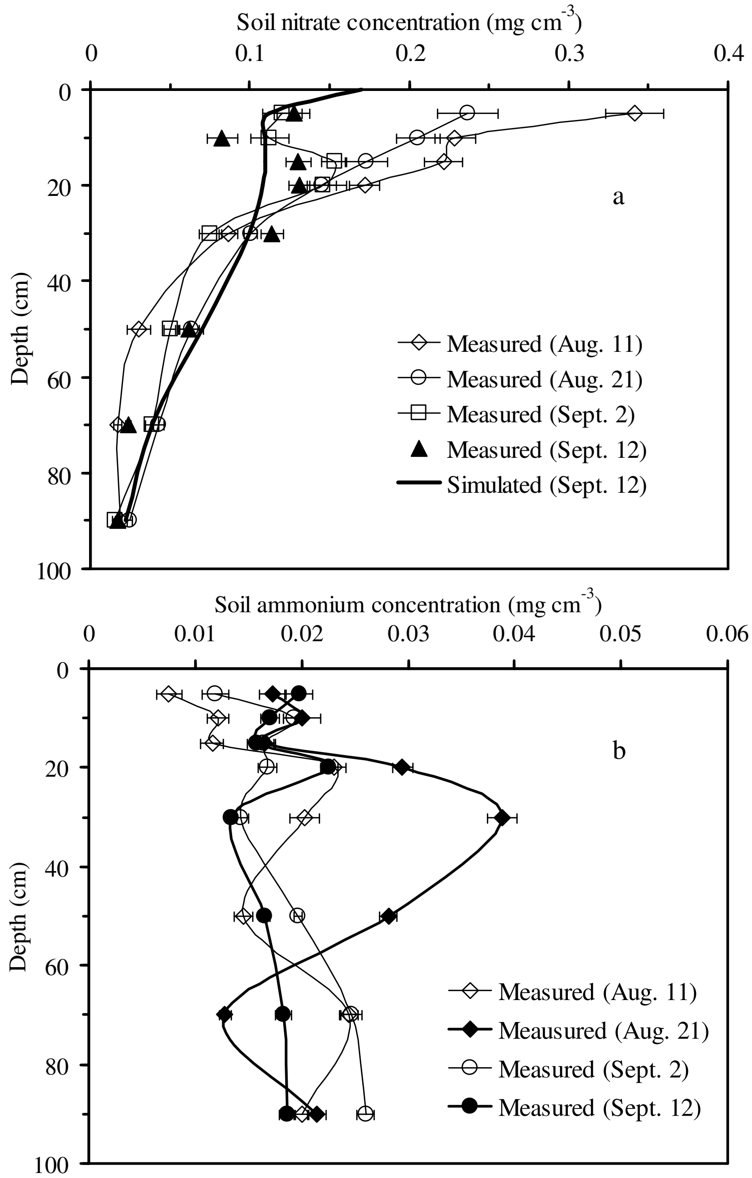

Figure 2. Distributions of: (a) Measured and simulated soil nitrate concentration; and (b) Measured soil ammonium concentration, from August 11 to September 12, 2007 in the field experiment. Horizontal bars are standard errors.

soil surface ($0 \leq z \leq 30$ cm) were relatively high, and decreased with increasing depth. However, soil ammonium concentration distribution did not show a regular tendency and its values showed relatively small changes in the whole profile, except for the depth from 20 to 50 cm on August 21, 2007.

Estimating RWU and SST

With the measured soil water content, nitrate, and ammonium concentration profiles, the average distributions of *RWU* rate and *SST* during the experimental period were estimated using the inverse method

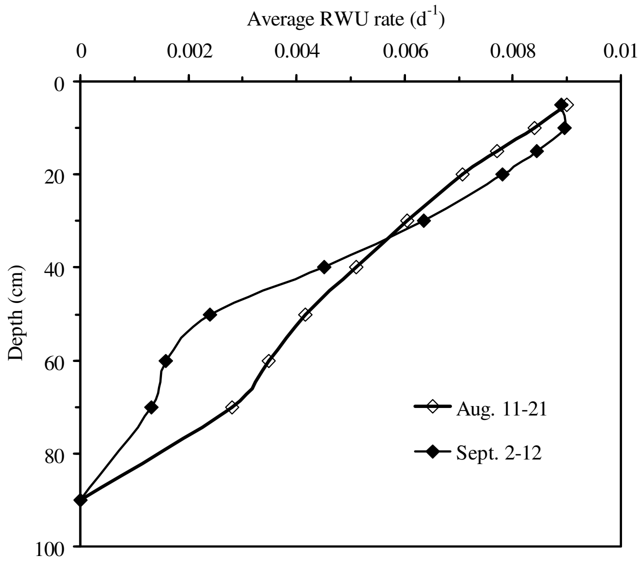

Figure 3. Estimated average *RWU* rate distributions from August 11 to September 12, 2007 in the field experiment.

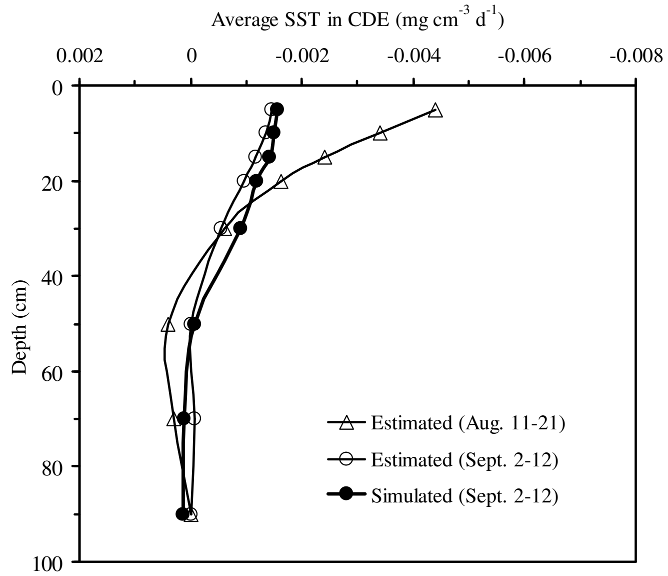

Figure 4. Estimated (using the inverse method) and simulated (using the established nitrate transformation model) distributions of the *SST* in *CDE* from August 11 to September 12, 2007 in the field experiment.

(Zuo and Zhang, 2002; Shi *et al*., 2007) as shown in Figures 3 and 4, respectively. The values of average *SST* during August 11-21 and September 2-12 in the upper area (about $0 \leq z \leq 45$ cm) was negative and became positive when $z > 45$ cm. The results indicated that the nitrate transformation in the upper parts of 0-45 cm was mainly by root uptake, immobilization, and denitrification, while in the depths below 45 cm, especially with the decrease of *RNU* rate, nitrification became predominated. The changing tendency of average *SST* was also consistent with the distributions of soil nitrate and ammonium concentration (Figure 2) and RWU rate (Figure 3).

Optimizing the First-order Rate Coefficients

To establish the nitrate transformation model, two measured soil nitrate profiles on August 11 and 21, 2007, were used to optimize the first-order rate coefficients for nitrate transformation processes through the improved method. Similar to that in the numerical experiment, the first-order rate coefficient for immobilization k_2 was also taken as 0.02 d^{-1}. The other coefficients for nitrate transformation were optimized as: k_1= 0.275 d^{-1}, k_3= 0.0024 d^{-1}, and δ= 1.53. With the established soil nitrate transformation model, measured soil nitrate and ammonium concentration distribution, and other related information, the average distribution of *SST* during September 2-12, 2007, was simulated through Equations (6)-(9) using the implicit difference method. The simulated average *SST* profile agreed well with the estimated distribution using the inverse method (Figure 4), with the *RMSE* between them as low as 0.00021 mg cm^{-3} d^{-1}. The result showed that the optimization procedure using the improved method would be reliable and effective to optimize the first-order rate coefficients and establish soil nitrate transformation model in the field.

Simulating Soil Water Flow and Nitrate Transport

Since the measured soil water content and nitrate concentration profiles during August 11-21, 2007, were used to establish the nitrate transformation model, only the dynamics of soil water and nitrate during September 2 to 12, 2007, were simulated. Equations (1)-(4), which describe the soil water flow in the soil-maize system, were solved using the implicit difference method. With the measured distributions of normalized root length density on September 2 and 12, 2007, and other information, soil water flow during September 2-12, 2007, was simulated. The simulated soil water content distribution on September 12, 2007, was comparable with the measured profile (Figure 1), with the *RMSE* of 0.023 cm^3 cm^{-3} between them.

On the basis of soil water flow simulation, the established nitrate transformation model, Equations (6)-(9) were solved using the implicit finite difference method to simulate soil nitrate transport between September 2 and 12, 2007. The simulated distribution of soil nitrate concentration on September 12, 2007, was also shown and compared with the measured profile in Figure 2, which demonstrated that the simulated results and changing tendency matched the measured values well. The *RMSE* between the simulated and measured nitrate concentration distributions was 0.017 mg cm^{-3}. In the simulation, soil ammonium concentration between September 2 and 12, 2007, was linearly interpolated using the measured ammonium concentrations on September 2 and 12, 2007. The results showed that the linear interpolation of the ammonium concentration had little influence on the simulation, and the inverse method would be applicable to establish nitrate transformation model and simulate soil nitrate transport in the field.

It should be noted that the *RNU* factor δ used in this study only included the root uptake of nitrate, not considering the uptake of soil ammonium. Moreover, the information about the distribution of ammonium concentration had to be given as the measured values because the transport and transformation of soil ammonium were not incorporated, which would be inconvenient for the numerical simulation in practice. To understand the characteristics of N turnover in the soil-plant system well, it would be better to couple simulation of the nitrate and ammonium transport in soils simultaneously. However, many researchers have shown that the concentration of nitrate is often much higher than that of ammonium in dry land soils (Ju *et al.*, 2004; Mohsenabadi *et al.*, 2008). In this case, it would be reasonable to suppose that the root uptake of soil N could be predominated by *RNU* and the movement of ammonium could be ignored. Therefore, the optimization procedure proposed in this study would be useful for analyzing the *RNU* of the plant and the dynamics of nitrate in the soil-plant system.

The numerical and field experimental results showed that the inverse method could be a useful alternative to optimize the first-order rate coefficients for nitrate transformation processes, establish the transformation model, and simulate nitrate transport in soils. However, to understand the cycling of soil N in the soil-plant system completely, further attention should be paid to coupling simulation of soil nitrate and ammonium transformation and transport.

CONCLUSIONS

Due to the fact that the first-order rate coefficients for nitrate transformation processes are very difficult to measure directly, an improved inverse method was applied to optimize them. A numerical experiment and a field experiment were designed to test the accuracy and effectiveness of the method in optimizing these coefficients. The results showed that the inverse method could be a useful alternative to optimize the first-order rate coefficients for nitrate transformation processes, establish the transformation model, and simulate nitrate transport in soils. However, to understand the cycling of soil N in the soil-plant system completely, further attention should be paid to coupling simulation of soil nitrate and ammonium transformation and transport.

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بهینه سازی ضریب درجه اول نرخ فرایند دگرگونی نیترات خاک با کاربرد روش معکوس

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چکیده

اندازه گیری مستقیم ضریب درجه اول نرخ فرایند دگرگونی نیترات خاک در آزمایشگاه و نیز در مزرعه چالشی بزرگ است. در پژوهش حا ضر، روش معکوس اصلاح شده برای بهینه کردن ضریب درجه اول نرخ فرایند مزبور با در نظر گرفتن تغییرات فرایندهای بینابینی درکل فرایند دگرگونی پیشنهاد و استفاده شد. به این منظور، آزمونی عددی برای درست آزمایی روش مزبور در تعیین ضریب های بهینه طراحی شد. مقایسه نتایج بهینه شده و مقادیر تئوریک(نظری) نشان داد که همه خطاهای نسبی در محدوده ۱۰٪ بود. نیز، داده های گردآوری شده از یک آ زمون مزرعه ای برای اعتبار سنجی روش بهینه سازی ونشان دادن کاربرد آن در عمل استفاده شد. بر پایه مدل به دست آمده و ارقام برآورد شده در روش معکوس ، توزیع عبارت منبع-مخزن (source-sink term) داده های بازه زمانی ۱۲-۲ سپتامبر ۲۰۰۷ توافق و هماهنگی خوبی داشتند و ریشه میانگین مربعات خطا ها (RMSE)بین آنها به کمی 0.00021 mg cm^{-3} d^{-1} بود. بر پایه مدل به دست آمده برای دگرگونی نیترات، توزیع مقدار آب خاک و غلظت نیترات در بازه زمانی ۱۲-۲ سپتامبر ۲۰۰۷ شبیه سازی شد که نتایج با مقادیر اندازه گیری شده در نیمرخ خاک به خوبی مقایسه می شد و ریشه میانگین مربعات خطا ها به ترتیب برابر 0.023 cm^{3} cm^{-3} و 0.017 mg cm-3 بود. به این قرار، روش معکوس اصلاح شده برای بهینه سازی ضریب درجه اول نرخ دگرگونی نیترات خاک و ایجاد مدل دگرگونی نیترات و شبیه سازی انتقال نیترات در سامانه گیاه- خاک مفید می نماید.