

Modeling Nitrogen Dynamics in a Soil Column with Reclaimed Water: Okinawa, Japan Application

W.K.C.N. DAYANTHI, Takayuki SHIGEMATSU, Hiroaki TANAKA,
Naoyuki YAMASHITA and Joseph E. ODENCRANTZ

Research Center for Environmental Quality Management, Graduate School of Engineering, Kyoto University,
1-2 Yumihama, Otsu, Shiga 520-0811, Japan

ABSTRACT

During a continuous irrigation of simulated reclaimed water on an unsaturated soil column, the characteristics of pore water at different depths, effluent, initial and final soil indicated the simultaneous occurrence of nitrification, denitrification and ammonium adsorption. Nitrification and adsorption significantly depleted ammonium (NH_4^+) of the influent at the upper soil layers. The nitrate–nitrogen (NO_3^- -N) concentration of the pore water and effluent increased to a maximum preceding the steady state. Total Nitrogen (T-N) did not exceed its value in the influent (23 mg/L), and NO_3^- -N was always less than 20 mg/L. The cumulative loss of T-N due to off-gassing to the soil air was 30.0%. The loss of total organic carbon of influent was 62.9%. The coupled material balance equations for both NH_4^+ -N and NO_3^- -N on entire soil volume were solved analytically to simulate the distribution of NO_3^- -N concentrations with time along the soil depth. First-order rate constants for nitrification (k_1) and denitrification (k_2) were varied within a wide range until the simulated NO_3^- -N concentrations fit properly with the measured values. The optimum k_1 and k_2 obtained using the measured effluent data were 0.09 d^{-1} and 0.003 d^{-1} , respectively. These are the global averages that represent the percolating water downward.

Keywords: Nitrate, Nitrification, Denitrification, Analytical modeling, Rate constants

INTRODUCTION

Reclaimed water irrigation has become a must in the present world to address the irrigation water scarcity. However, the environmental issues and health risks always follow the reclaimed water irrigation. Okinawa Island in Japan has been suffering from water scarcity and recently, the reclaimed water has been introduced as an alternative irrigation water source. A large-scale project on the reclaimed water irrigation has already been designed, and will be implemented during the next few years. According to that project, there will be no advanced treatment-unit process for the removal of excess nitrogen in the treatment train of reclaimed water (Dayanthi *et al.*, 2006). However, according to the same authors, the targeted secondary treated wastewater to produce reclaimed water contains NH_4^+ in high concentrations, which is likely to contribute to NO_3^- contamination in the subsurface water. Hence, NO_3^- tops the list of likely pollutants due to the irrigation of reclaimed water production on the island. NO_3^- is usually in the list of most likely pollutants due to the irrigation of reclaimed water elsewhere. As stated by El-Sadek *et al.* (2003), the fate of nitrogen in the soils is of major concern because of the potential hazard for nitrogen, applied in excess of the natural decomposing capacity of the soil, to contaminate shallow and deep aquifers. Hence, the study of nitrogen dynamics in soil is imperative in achieving precautionary measures to reduce the nitrate pollution.

Simulation of nitrogen dynamics using a

mathematical model is crucial in investigating nitrogen dynamics of soil because a model can estimate the NO_3^- -N concentration that may exist in the groundwater as a result of the reclaimed water itself. Modeling nitrogen dynamics has been attempted in number of fields with vastly different results. Especially, this issue has been constantly in the limelight of agricultural based studies. Much research on nitrogen dynamics can be found on the plant-soil system. Nitrogen dynamics in soil are of concern to the researchers representing different disciplines. Therefore, studies and modeling of soil nitrogen dynamics have so far been considered in wider perspective. The attempts of analytical modeling of soil nitrogen dynamics span several decades. In the initial stage, analytical models describing the simultaneous occurrence of nitrification, denitrification and nitrogen movement in soil water have been presented by McLaren (1969a, 1969b, 1970, 1971), Cho (1971) and Misra *et al.* (1974). The convective transport of nitrogen compounds has been the basis for these analytical models. In all of these attempts, nitrogen dynamics due to either an ammonium or nitrate salt have been modeled.

At present, the popularity of reclaimed water irrigation has made this issue be reexamined in the context of the current objectives, *i.e.* in terms of groundwater pollution. It has recently become an interest to the researchers in Environmental Engineering. However, so far, minimal attempts have been taken to simulate nitrogen dynamics caused by the reclaimed water. McLaren (1976) stated that in order to construct predictive mathematical models

for microbial transformations of elements, such as nitrogen in flowing systems in nature, it is essential to have realistic rate constants.

Therefore, this paper presents an estimation of nitrification and denitrification rate constants using an analytical model that simulates the nitrate dynamics in the unsaturated zone during a continuous irrigation of reclaimed water. The model is one-dimensional and incorporates nitrification, denitrification and sorption of ammonium processes.

MATERIALS AND METHODS

Laboratory Experiment

Soil column preparation Very large clumps (average diameter was 10–20 cm) of a high porous limestone soil obtained from an agricultural land on Okinawa, were air-dried and crushed manually and passed through a 0.4-cm square screen. Crushed soil was mixed well and 10 samples, each having 100 g soil, were grabbed from the soil mixture, for the analysis of the average moisture content. The average moisture content was 11.66%, and 29.9 kg of soil was weighed. It contained 26.78 kg oven-dry weight of soil. 5.2 kg of water was added on the uniformly spreaded soil on a mat, using a traditional watering can; and then soil was mixed well in order to achieve the homogeneity. The soil was then packed into a laboratory-scale acrylic plastic column (Fig. 1) of cylindrical shape (20 cm i.d. by 90 cm height) up to 85 cm height. Soil was filled in the columns as layers, each of 10 cm-thickness, so that the average bulk density of the soil inside a column was 1.34 g/cm³. There was a finely woven plastic mesh segregating the soil and the perforated base of the column. The soil surface was exposed to the atmosphere. The soil column was surrounded by a water jacket to maintain the temperature at 20°C. In order to collect the pore water (PW) at different depths (15, 35, 45, 55, 70 and 80 cm), 6 ports (PW1–6), each being 12.5 mm in internal diameter, were located around the column.

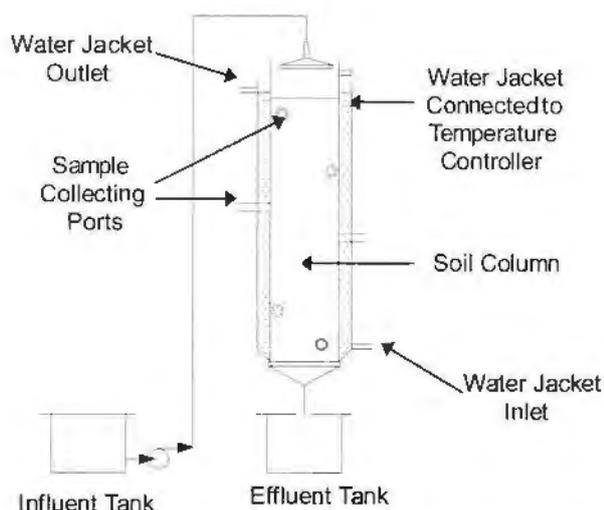


Fig. 1 Schematic diagram of the laboratory scale soil column.

Experimental procedure and sampling A peristaltic pump was used to pump up the influent into a shower hung approximately 5 cm above the soil surface. Simulated reclaimed water (SRW) was prepared with secondary treated wastewater obtained prior to chlorination from the Municipal Wastewater Treatment Plant, Otsu, Japan. It was filtered and mixed with anhydrous ammonium chloride so that the final NH₃-N concentration approximately became 18 mg/L in the SRW. The characteristics of both SRW and the raw soil are shown by Table 1. The characteristics of SRW was similar to that of the reclaimed water, produced in the experimental reclamation facility in Okinawa at present. Initially, both the columns were leached with deionized water continuously at 450 mL/h (14 mm/h) for 25 days until both PW and effluent did not receive any readily flushable contaminants from the soil. Then, SRW was continuously irrigated at a rate of 11 mL/h (0.35 mm/h). The application of reclaimed water was continued for 150 days. No significant height difference was observed before and after leaching.

Table 1 Characteristics of SRW and raw soil.

Description	SRW	Raw Soil (per kg of oven-dry soil)
NO ₃ ⁻ -N + NO ₂ ⁻ -N	2.5–3.5 mg/L	0.068 cmole
NH ₃ -N	18.0 mg/L	0.052 cmole
T-N	23 mg/L	8.2 cmole
pH	7.1–7.7	6.25
Conductivity	53–60 ms/m	—

The effluent from the column was collected once every day during the course of experiment. Pore water was collected twice a week by means of a porous cup soil water sampler (a product of Soilmoisture Equipment Corp., Santa Barbara, CA, USA; purchased from Namoto Trading Company, Chiba, Japan). The accumulated volume of water in the effluent tank by each effluent-sampling was recorded. Each effluent sample was filtered through a 0.45 µm filter paper. All the wastewater samples were frozen before analysis, and periodically (within 7 days after collection) analyzed for nitrogenous {NO₃⁻-N, Nitrite nitrogen (NO₂⁻-N), NH₃-N, T-N} compounds, conductivity and pH. Both conductivity and pH were analyzed as soon as the samples were collected. At the end of the experimental run, the soil column was unloaded in 5 cm thick-layers, without disturbing the orientation of the soil. Then, soil collected from each layer was mixed well and samples were taken for the analysis of the moisture content. Then, soil characteristics of each layer was obtained in terms of the gravimetric moisture content, NO₂⁻-N, NO₃⁻-N, NH₃-N and T-N.

At the end of the experiment, the calculations of the water flow balance, T-N and T-C mass balances were performed. In calculating the total cumulative mass of T-N and T-C discharged from each column as the effluent throughout the experimental period, both T-N

and T-C concentrations, respectively, of each effluent sample was multiplied by the respective total volume of accumulated water in the effluent tank. To obtain the initial T-N and T-C content of the soil, the total mass of T-N and T-C that flushed out with the effluent during the cleansing period was subtracted from the T-N and T-C of the raw soil, respectively. In calculating T-N and T-C of soil at the end of the experiment, it was assumed that the soil sample collected from each 5-cm thick layer had represented the total soil of that layer. T-N of soil at the end did not show any significant difference with that of raw soil. Therefore, the change of organic-N content in soil is negligible. The quantity of NO₃⁻-N and NH₃-N was only 1.5 % of T-N in raw soil. Therefore, it was very difficult to quantify the change of NO₃⁻-N and NH₃-N contents in soil at the end of the experiment, using the final T-N value of soil. Hence, T-N of soil after leaching was considered equal to the T-N of raw soil plus the content of accumulated NH₃-N and NO₃⁻-N in soil at the end of the experiment. We believe this is a reasonable assumption.

Analyses NO₃⁻-N and NO₂⁻-N of the wastewater were analyzed with a spectrophotometer (purchased from Shimadzu Corporation, Japan) and an ion chromatograph (purchased from Nihon DIONEX Corporation, Osaka, Japan). The NH₃-N of the wastewater samples was analyzed with a spectrophotometer using the phenate method. T-N was analyzed manually following the standard methods in the reference mentioned below. T-N was digested into NO₃⁻ and measured on a spectrophotometer. All the analyses of wastewater were in accordance with "Standard Methods for the Examination of Water and Wastewater, 1998". NO₃⁻, NO₂⁻ and NH₄⁺ of soil were extracted in 100 mL of 1M potassium chloride (KCl) from 10 g of soil. pH was measured in a solution of 15 g soil thoroughly mixed with 30 mL deionized water. T-N of soil was measured on a C-H-N analyzer, in which T-N is combusted into nitrogen gas (N₂). All the analyses of the soil were in accordance with Robertson *et al.* (1999).

Model Development

Simplified Materials-Balance Equation

Contaminant transport in porous media is governed by advection, molecular diffusion, hydrodynamic dispersion, sorption and transformation processes (Nazaroff *et al.*, 2001). Therefore, a simplified material balance equation for a contaminant transporting in an unsaturated soil column can be given by the equation:

$$\frac{\partial C_i}{\partial t} + \frac{(1-\phi)\rho_b}{\phi_w} \frac{\partial q_i}{\partial t} + \nu \frac{\partial C_i}{\partial x} - \epsilon_h \frac{\partial^2 C_i}{\partial x^2} - r_i = 0 \quad (1)$$

where C_i = solute 'i' concentration in soil solution (mg/L); t = time (d); φ = porosity; φ_w = volumetric moisture content; ρ_b = average bulk density of soil (g/cm³); q_i = Solute 'i' concentration on adsorbent phase (g solute/ g soil); ν = interstitial flow water velocity (cm/d); x = length along the soil column (cm); r_i = net effect of transformation of solute 'i' (sink-source

term) (mg/L.d); ε_h = dispersion coefficient (cm²/d). Each term in this equation has dimensions of contaminant quantity per unit total volume of the medium (including pores and soil grains) per unit time. Eq. (1) is subject to the following assumptions: the soil column is homogeneous; the fluid flow field is uniform and steady; the fluid flows with a velocity parallel to the 'x' axis and is in the direction of increasing 'x'; and radial dispersion.

Linear Form of Freundlich Isotherm for Sorption

The sorption process was represented by the linear form of Freundlich isotherm, in which sorption was assumed to be reversible and rapid as compared to advective and dispersive transport. The inherent assumption is the sorption-desorption reactions quickly transform into a reversible equilibrium state. Hence, q_i is given by:

$$q_i = K_{ads} C_i \quad (\text{Bohn } et al., 1985) \quad (2)$$

where K_{ads} = sorption partition coefficient (m³ soil solution/ g soil). Then, the Eq. (1) can be written as:

$$R \frac{\partial C_i}{\partial t} + \nu \frac{\partial C_i}{\partial x} - \epsilon_h \frac{\partial^2 C_i}{\partial x^2} - r_i = 0 \quad (3)$$

$$R = \left\{ 1 + (1-\phi) K_{ads} \frac{\rho_b}{\phi_w} \right\} \quad (4)$$

where R = retardation factor (Kinzelbach, 1986).

Kinetics of Microbial Transformation of Nitrogen

In this analytical model, first-order kinetics were assumed for both nitrification and denitrification. Therefore, the net rates of transformation of ammonium (r₁) and nitrate (r₂) can be given by:

$$r_1 = -Rk_1 C_1 \quad (4)$$

$$r_2 = -Rk_1 C_1 - k_2 C_2 \quad (5)$$

where k₁ = first order oxidation rate constant of NH₃ in soil and solution (d⁻¹); C₁ = concentration of NH₃-N in solution (mg/L); k₂ = first order reduction rate constant of NO₃⁻ in solution (d⁻¹); C₂ = concentration of NO₃⁻-N in solution (mg/L). It was assumed that an instantaneous equilibrium between the ammonium ions on the solid and liquid phases occurred. Therefore, 'r₁' contains "R" that depicts adsorbed ammonium too undergoes nitrification. In this model, NO₃⁻-N was not subject to sorption. Therefore, the governing equations for NH₃-N and NO₃⁻-N dynamics that incorporate the advection, dispersion, sorption and transformation are given by:

$$R \frac{\partial C_1}{\partial t} + \nu \frac{\partial C_1}{\partial x} - D_1 \frac{\partial^2 C_1}{\partial x^2} - Rk_1 C_1 = 0 \quad (6)$$

$$\frac{\partial C_2}{\partial t} + \nu \frac{\partial C_2}{\partial x} - D_2 \frac{\partial^2 C_2}{\partial x^2} - Rk_1 C_1 + Rk_2 C_2 = 0 \quad (7)$$

where D₁ = apparent molecular diffusion coefficient for NH₃ (cm²/d); D₂ = apparent molecular diffusion

coefficient for NO₃ (cm²/d). 'ε_h' was replaced with 'D₁' and 'D₂' by considering that the dispersive effect is negligible due to the very low pore water velocity.

Analytical Solutions for the Governing Equations

The following boundary conditions were considered. The duration of the entire course of experimental run is equal to 'T'.

$$\begin{aligned} C_1 &= C_1^0 = C_2^0 & x &= 0 & 0 < t < T \\ C_1 &= C_2 &= 0 & x &= 0 & t > T \\ C_1 &= C_2 &= 0 & x &\geq 0 & t = 0 \\ C_1 &= C_2 &= 0 & x &\rightarrow \infty & t \geq 0 \end{aligned}$$

Eq. (6) and (7) were solved using the Laplace transformation techniques (Riley *et al.*, 1998; Schiff, 1999; Abramowitz and Stegun, 1972) subject to aforementioned boundary conditions as:

$$C_1(x, t) = C_1^0 F(x, t) \tag{8}$$

$$C_2(x, t) = C_2^0 Q(x, t) + \frac{Rk_1C_1^0}{(k_1R - k_2)} [Q(x, t) - P(x, t) + S(x, t) - F(x, t)] \tag{9}$$

where

$$\begin{aligned} F(x, t) &= \frac{1}{2} \left[\exp\left\{\frac{x}{2D}(\nu - \sqrt{\nu^2 + 4Dk_1R})\right\} \times \operatorname{erfc}\left(\frac{x - t\sqrt{\nu^2 + 4Dk_1R}}{\sqrt{4Dt/R}}\right) + \exp\left\{\frac{x}{2D}(\nu + \sqrt{\nu^2 + 4Dk_1R})\right\} \times \operatorname{erft}\left(\frac{x + t\sqrt{\nu^2 + 4Dk_1R}}{\sqrt{4Dt/R}}\right) \right] \\ Q(x, t) &= \frac{1}{2} \left[\exp\left\{\frac{x}{2D}(\nu - \sqrt{\nu^2 + 4Dk_2})\right\} \times \operatorname{erfc}\left(\frac{x - t\sqrt{\nu^2 + 4Dk_2}}{\sqrt{4Dt}}\right) + \exp\left\{\frac{x}{2D}(\nu + \sqrt{\nu^2 + 4Dk_2})\right\} \times \operatorname{erft}\left(\frac{x + t\sqrt{\nu^2 + 4Dk_2}}{\sqrt{4Dt}}\right) \right] \\ P(x, t) &= \frac{1}{2} \left[\exp\{-At\} \exp\left\{\frac{x}{2D_2}(\nu - \sqrt{\nu^2 + 4Dk_2 - 4DA})\right\} \times \operatorname{erfc}\left(\frac{x - t\sqrt{\nu^2 + 4Dk_2 - 4DA}}{\sqrt{4Dt}}\right) + \exp\{-At\} \exp\left\{\frac{x}{2D}(\nu + \sqrt{\nu^2 + 4Dk_2 - 4DA})\right\} \times \operatorname{erft}\left(\frac{x + t\sqrt{\nu^2 + 4Dk_2 - 4DA}}{\sqrt{4Dt}}\right) \right] \\ S(x, t) &= \frac{1}{2} \left[\exp\{-At\} \exp\left\{\frac{x}{2D_1}(\nu - \sqrt{\nu^2 + 4Dk_1R - 4DAR})\right\} \times \operatorname{erfc}\left(\frac{x - t\sqrt{\nu^2 + 4Dk_1R - 4DAR}}{\sqrt{4Dt/R}}\right) + \exp\{-At\} \exp\left\{\frac{x}{2D_2}(\nu + \sqrt{\nu^2 + 4Dk_1R - 4DAR})\right\} \times \operatorname{erft}\left(\frac{x + t\sqrt{\nu^2 + 4Dk_1R - 4DAR}}{\sqrt{4Dt/R}}\right) \right] \\ A &= \left(\frac{k_1R - k_2}{R - 1}\right) \end{aligned}$$

where erfc = complementary error function. It was assumed that D = D₁ = D₂ for the simplicity of the solutions.

Model Application

Input data A computer program was developed to incorporate equations (8) and (9) using Microsoft Visual Basic. The 'erfc' was computed using a numerical approximation given by Abramowitz and Stegun (1972). **Table 2** shows the input parameters in the model. The soil parameters shown in Table 2 are the average values of the soil before and after leaching. The particle density of soil was assumed as 2.65 g/cm³ (GLOBE, 2002) in calculating the air-filled porosity. The average effluent rate of the entire course of experiment (9.98 mL/h) was divided by the cross sectional area of the column and the volumetric moisture content, to obtain 'v'.

Calibration of the Model The model was calibrated in terms of 'k₁' and 'k₂', by applying it to the experimental results of the soil column. Transient and steady state NO₃⁻-N concentrations at depths, 15 cm, 35 cm, 45 cm, 55 cm, 70 cm, 80 cm and 85 cm, were computed for each 0.01 d⁻¹ increment of 'k₁' from 0.01 to 0.7 d⁻¹ and 'k₂' from 0.001 - 0.1 d⁻¹. These ranges are the common ranges in which existing 'k₁' and 'k₂' values lie. Then, the optimum 'k₁' and 'k₂' were obtained for each depth using the sum of squares of error between each estimated and measured NO₃⁻-N concentration. When applying the model to optimize the rate constants at each depth, it was considered that the control volume is from the soil surface to each depth. Then, the optimized 'k₁' and 'k₂' per each depth, except 85 cm, were averaged out. These average 'k₁' and 'k₂' represent the pore water inside the soil column, since measured NO₃⁻-N concentrations in the pore water samples were used for the initial optimization. The 'k₁' and 'k₂' at 85 cm depth were considered as the global averages of 'k₁' and 'k₂' in the soil column because those values were optimized using the measured

Table 2 Input data.

Parameter	Value	Note
D	1.4 cm ² /d	Reference: Odencrantz et. al. (1990)
K _{ads}	2 cm ³ /g	Reference: Gusman et. al. (1999)
φ	0.62	Average of initial and final soil
φ _w	0.375	Average of initial and final soil
ρ _s	1.378 g/cm ³	Average of initial and final soil
R	3.79	Calculated
v	2.033 cm/d	Calculated using average effluent rate
C ₁ ⁰	18 mg/L	Measured
C ₂ ⁰	3 mg/L	Measured

NO₃⁻-N concentrations in the effluent samples. The average 'k₁' and 'k₂' of the pore water and the global averages were considered as the calibration parameters of the model.

RESULTS AND DISCUSSION

Model Simulations of Experimental Results

The 'k₁' and 'k₂' optimized for each port location are shown by Table 3. The 'k₁' and 'k₂' for each depth were optimized using the measured data of pore water samples at the respective depth. Table 3 also depicts the correlation coefficient (R²) and the sum of squares of errors between the measured and simulated (using the respective 'k₁' and 'k₂' for each depth) NO₃⁻-N at each depth. The average 'k₁' and 'k₂' that represent the pore water in the soil column were 0.045 d⁻¹ and 0.011 d⁻¹, respectively. The global averages of 'k₁' and 'k₂' were 0.09 d⁻¹ and 0.003 d⁻¹, respectively. Table 4 shows R² and the sum of squares of errors between the measured and simulated (using the average 'k₁' and 'k₂' for the pore water samples and the global average 'k₁' and 'k₂' for the effluent) NO₃⁻-N at each depth. Figure 2 shows the variation of the simulated and measured NO₃⁻-N at each depth. The simulated values for the pore water and effluent depths have been obtained using the average and global average 'k₁' and 'k₂', respectively, depicted by Table 4.

As seen in Table 4, there is a significant difference between the constants optimized using the pore water and effluent. The heterogeneous nature and sampling techniques in the column are the main candidates in explaining the variation. Pore water samples were collected at the vertical centre line of the column. Each pore water

Table 3 Optimum 'k₁' and 'k₂' for each depth.

Depth (cm)	k ₁ (d ⁻¹)	k ₂ (d ⁻¹)	R ²	Sum of squares of errors
0-15	0.04	0.02	0.69	116
0-35	0.05	0.02	0.86	144
0-45	0.05	0.01	0.89	120
0-55	0.03	0.006	0.88	149
0-70	0.04	0.005	0.88	186
0-80	0.06	0.005	0.92	111

Table 4 Calibration data of the model.

Depth (cm)	k ₁ (d ⁻¹)	k ₂ (d ⁻¹)	R ²	Sum of squares of errors
15			0.64	166
35			0.86	169
45	0.045	0.011	0.87	127
55			0.90	120
70			0.88	261
80			0.91	378
85 (Effluent)	0.09	0.003	0.99	20

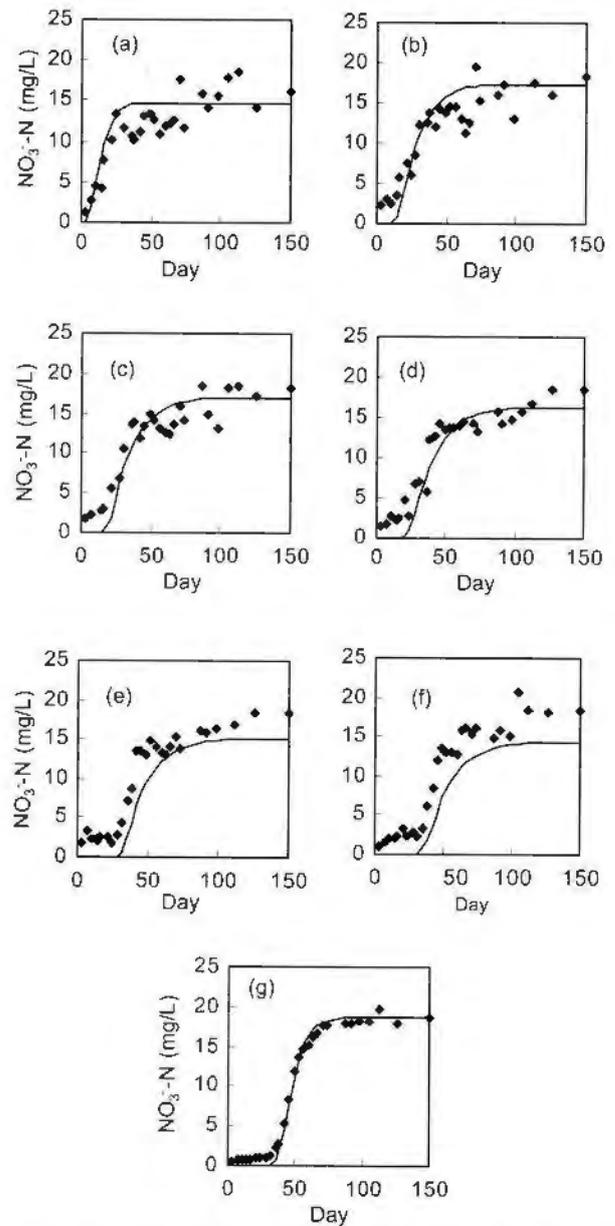


Fig. 2 Simulated (lines) and measured (diamonds) NO₃⁻-N concentrations at various PWs and effluent (a) Pore Water 1 (PW1 @ 15 cm), (b) PW2 @ 35 cm, (c) PW3 @ 45 cm, (d) PW4 @ 55 cm, (e) PW5 @ 70 cm, (f) PW6 @ 80 cm and (g) Effluent @ 85 cm.

sample represents only one point of the column. In addition, the pore water represents both mobile and immobile water. Therefore, the NO₃⁻-N concentration of pore water samples largely represents localized conditions. However, the effluent represents the total percolated water or column-averaged conditions. The constants derived using the measured data of the effluent samples are referred to as the global average of the rate constants, 'k₁' and 'k₂', in the column.

Nitrogenous Compounds Dynamics (Experimental Results)

Figure 3 shows the steady-state distribution of NH₃-N, NO₃⁻-N and T-N concentrations along the

soil column. The presence of nitrification is clearly visible in the obtained profiles of $\text{NO}_3^- - \text{N}$ (measured data of Fig. 2) and $\text{NH}_3 - \text{N}$ (Fig. 3). Nitrification was greater above 15 cm depth, since concentration of $\text{NO}_3^- - \text{N}$ in the pore water samples at 15 cm exceeded the concentration of the influent within 7 days of the commencement of the application. In addition, the transient and steady-state $\text{NH}_3 - \text{N}$ concentrations of all pore water and effluent samples were almost invariant at values less than 1.7 mg/L. The presence of ammonium adsorption onto soil is also apparent. Hence, ammonium present in the influent has undergone both nitrification and adsorption. It is apparent that the adsorbed ammonium has also nitrified and leached into the solution because the $\text{NO}_3^- - \text{N}$ concentration is close to the level of $\text{NH}_3 - \text{N}$ in the influent. According to the measured data of Fig. 2, $\text{NO}_3^- - \text{N}$ concentration of the pore water samples and the effluent gradually reached the steady-state in a succession. The successive attainment of the steady-state by all the pore water and effluent samples occurred within 75 days of the experimental run. At various depths, it exhibited similar profiles. Steady-state concentrations at ports greater than 70 cm were slightly higher than those of upper ports. Since the pore water does not necessarily represent the flowing water, a local condition may have been represented by this observation. Denitrification may have been higher in those areas of the column.

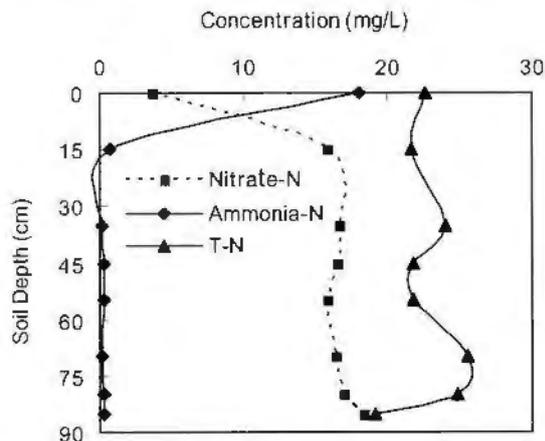


Fig. 3 Steady-state distribution of $\text{NH}_3 - \text{N}$, $\text{NO}_3^- - \text{N}$, and T-N concentrations along the soil column.

As shown by Fig. 4, there is a gap between the influent and effluent profiles of cumulative mass of T-N. The gap between the cumulative mass of T-N in the influent and effluent indicates that the balance amount of T-N may have either accumulated on soil or off-gassed to the soil air, most likely as N_2O , NO_x , N_2 or all. Table 5, which shows the components of the input and output in terms of ultimate cumulative mass of T-N, indicates that the latter caused the gap between the influent and effluent profiles.

Table 5 shows the ultimate cumulative mass of T-N lost by off-gassing is the ultimate cumulative T-N in the influent minus that in the effluent plus accumulated T-N in soil. The mass of T-N that has been lost by

off-gassing to the soil air is 30.0 %, relative to the ultimate cumulative mass of T-N applied via the influent. In addition, the carbon mass balance indicated that the ultimate cumulative mass of TOC, supplied by the influent that was lost is 62.9 %. Figure 5 shows the variation of cumulative T-C and TOC in the influent and the effluent. This provides evidence that the dissolved organic carbon in the soil solution may have been used for denitrification. As stated by DeBusk *et al.* (2001), microbial utilization is one means of removing organic compounds during transportation. Also Brye *et al.* (2001) reported that the dissolved organic carbon is considered to be a readily available substrate for soil microorganisms. Further, DeBusk *et al.* (2001) reported that the facultative anaerobic bacteria are capable of using NO_3^- or NO_2^- as terminal electron acceptors, coupled with the oxidation of organic carbon in the absence of oxygen gas. Further, Dayanthi *et al.* (2008) indicated that denitrification progressed more rapidly due to the

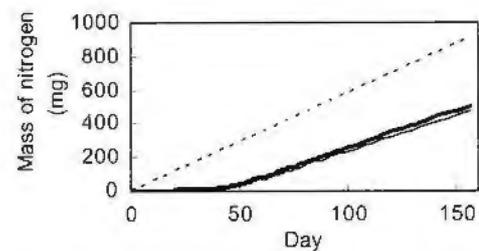


Fig. 4 Variation of the cumulative mass of T-N applied on the column via influent (dashed line), and the cumulative mass of T-N (thick solid line) and $\text{NO}_3^- - \text{N}$ (thin solid line) discharged via the effluent for the entire experimental run (150 days).

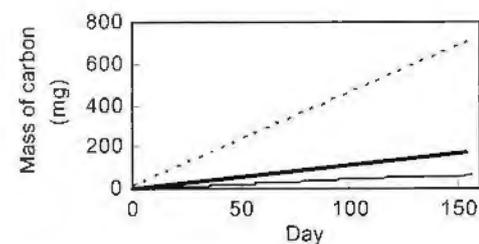


Fig. 5 Variation of the cumulative mass of T-C (thin dashed line) & TOC (thick solid line) applied on the column via influent, and the cumulative mass of T-C (thick dashed line) and TOC (thin solid line) discharged as E.

Table 5 Nitrogen mass balance of the experiment.

Description	Value
Cumulative T-N supplied as influent (mg)	900
Accumulated T-N in soil after leaching (mg)	168
Cumulative T-N discharged as effluent (mg)	506
Cumulative $\text{NO}_3^- - \text{N}$ discharged as effluent (mg)	470
Cumulative T-N lost by off-gassing to the soil air (mg)	281

continuous irrigation of reclaimed water than the intermittent irrigation, in a soil column experiment conducted on a low porous soil obtained from the Okinawa Island; and Shigematsu *et al.* (2006) verified it using an analysis of nitrogen stable isotopes. The acceleration of denitrification in the continuous application could also be attributed to the high retention time owing to the less percolation rate, and the water saturation conditions that have created an anoxic environment.

Evaluation of the Model

The model simulates the measured values quite well and consistently throughout the column. All simulations of $\text{NO}_3^- - \text{N}$ showed a reasonable agreement with the experimental results. The correlation coefficients between the measured and simulated concentrations of the pore water at all depths were more than 0.85, except at 15 cm depth. The correlation coefficient was 0.99 for the effluent. The shapes of the profiles are captured with the model that suggests all the transients are well-represented with the model. Although, this model has some limitations, the $\text{NO}_3^- - \text{N}$ dynamics are satisfactorily described. The measured data verified that the nitrification, denitrification and adsorption of ammonium processes dominate the nitrogen dynamics in the soil column. The calibration data of the model also indicate that the nitrification and denitrification both had a significant effect on the nitrate dynamics. Therefore, the estimated rate constants in this paper reflect the nitrogen dynamics suitable for all practical purposes.

As a result of the concentration of $\text{NH}_4^+ - \text{N}$ being negligible and lack of a particular pattern, the calibration of the model was done with $\text{NO}_3^- - \text{N}$ concentrations. It is assumed that the process of oxidation of ammonium to nitrite is very quick and therefore, that process has been omitted from the transformation terms. $\text{NO}_2^- - \text{N}$ never existed in significant concentrations in either pore water or effluent samples.

This model represents a simplified version for the heterogeneity of the unsaturated porous media in the column. Since, the overall material balance equations of $\text{NH}_4^+ - \text{N}$ and $\text{NO}_3^- - \text{N}$ were solved using analytical techniques, it was important to preserve the linearity of the equations. In addition, analytical solutions are possible for these equations because they have relatively simple initial conditions and boundary conditions. In order to preserve the linearity of the equations and making the analytical solutions, a number of simplifying assumptions were made such as steady state water flow was assumed; a uniform hydrogeologic condition were assumed in the soil column whereas it is different from the reality. The interstitial pore water velocity was most likely not uniform in the column because of unsaturated conditions. As per Lafolie *et al.* (1991), a better prediction of the water flow including macropore and soil structure effects is probably a major challenge in modeling not only water flow but also the transport of fertilizer and chemical substances.

Another important assumption was first-order kinetics for the microbial transformation of nitrogen

compounds. According to Starr *et al.* (1974), many factors such as microbial growth kinetics, temperature, pH, and the supply of oxygen and carbon and a host of other environmental parameters are implicitly included in the rate coefficients. Starr *et al.* (1974) describes that under steady-state conditions, the transformations are generally zero or first-order rate reactions for relatively large or small concentrations, respectively. According to the same author, for more dilute solutions and/or where oxygen or carbon supplies are limited, the net rate of oxidation of ammonium, oxidation of nitrite and reduction of nitrate can be given by first order kinetics. McLaren (1976) mentioned that the rate constants obtained in the field or laboratory soil studies are usually arbitrary because the rate constants depend on both time and biomass or microbial number. Doner *et al.* (1974) indicated that the microbial numbers are as important as are other parameters including flow rates, organic matter content, soil pH and redox potential etc. These facts show that the estimated rate constants, k_1 and k_2 , in this paper are subject to some limitations. However, these values may represent the apparent constants into which the aforementioned various factors have been lumped together. In addition, the model presented in this paper is oriented toward a simple simulation using physico-chemical aspects rather than microbial processes. If microbial dynamics were taken into account, the model would be non-linear, and would unable to be solved analytically. In addition, the model would also require more input parameters.

In the developed model, sorption was subject to several simplified assumptions. It was further assumed that the ammonium on both solid and solution phases would undergo nitrification. Krupp *et al.* (1972) stated that the microbial oxidation can involve NH_4^+ ions on both phases, together with the existence of both mobile and immobile soil water. The measured data support this statement. It is considered that the adsorbates both on the adsorbent and in solution are in local equilibrium with each other. However, in reality, the adsorbate initially tends to be sorbed irreversibly, only after some time a reversible sorption-desorption equilibrium is potentially established.

CONCLUSIONS

The dynamics of ammonium and nitrate due to a continuous irrigation on a high porous soil in a soil column were simulated using a simple analytical model. The model was developed using the coupled material balance equations for $\text{NH}_4^+ - \text{N}$ and $\text{NO}_3^- - \text{N}$ on entire soil volume that incorporate convection, dispersion, adsorption and biological transformation of the solute. The transformation processes incorporates nitrification, denitrification and adsorption of ammonium onto soil as those were the dominating processes in determining the fate of nitrogen in the soil column experiment. In order to preserve the linearity of equations, several assumptions were used to interpret the above processes in the model. First-order rate constants were determined for

nitrification and denitrification processes.

The calibration parameters of the models were apparent rate constants of nitrification and denitrification. In this study, a unique approach was followed in order to estimate the apparent rate constants in which the optimization of the rate constants using a large database of simulated $\text{NO}_3^- - \text{N}$, was implemented with a computer program and statistics. The nitrification and denitrification rate constants derived using the measured data of the effluent samples, which represent the global averages, were 0.09 d^{-1} and 0.003 d^{-1} , respectively. These rate constants indicate that the nitrification and denitrification both had a significant effect on the nitrate dynamics of these soil column experiments.

With the global averages of the rate constants, the model can be used to make reasonable predictions of nitrate leaching to groundwater systems. The model can also be used to predict the nitrate concentration as a result of continuous irrigation in a porous soil. Therefore, the model can be used as means of testing alternatives and assessing risks.

The developed model, with the global averages of the rate constants, could give reasonable predictions to the steady state $\text{NO}_3^- - \text{N}$ that may exist in the groundwater of the fields containing high porous soil in Okinawa, due to the continuous drip irrigation under a green house or field applications.

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