

## Model Development for the Nitrification-Denitrification Coupled Process

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### Abstract

Nitrogen pollution in urban and rural groundwater is a common problem and poses a major threat to drinking water supplies based on groundwater. In this work, the kinetics of nitrification-denitrification coupled reactions are modeled and new reaction modules for the RT3D code (Clement,1997) describing the fate and transport nitrogen species, dissolved oxygen, dissolved organic carbon, and biomass are developed. The proposed nitrogen transformations and transport model showed very good match with results of a conceptual model. However, the model simulation results for the major reactive species should be tested for validation using experimental and field data.

**key word:** nitrogen model, transformation, transport, nitrification, denitrification, RT3D

### 1. Introduction

Nitrogen is one of the most common contaminants in groundwater, originating from agriculture, septic tank effluents, and waste disposal. Especially, the contamination of groundwater by excessive nitrate concentrations is a significant public health problem. In many cases, the study of nitrogen transport is complicated by the various nitrogen species and transformation that can occur in the saturated zone and the connection with microbial process.

The objectives of this paper are to develop nitrogen transformations and transport model in the saturated zone, to assess the performance of a reactive transport model which couples the sequential and biogeochemical processes and to apply in a field site contaminated by nitrogen. In this study, a mathematical model was developed to describe the nitrification-denitrification coupled process. The model was coded as a reaction module within the RT3D framework.

### 2. Conceptual Model

The bulk of the nitrogen in domestic wastewaters is in the form of dissolved ammonium. Most sediment and soil colloid surfaces are negatively charged, giving them the ability to act as cation exchangers. The positive ammonium ion can therefore be immobilized geochemically and adsorbed by aquifer sediments. Otherwise, this ammonium form will be rapidly oxidized to nitrite in the presence of oxygen and autotrophic ammonia-oxidizing bacteria. This is called nitrification. Nitrification is a

two-stage oxidation process by the autotrophic ammonia-oxidizing bacteria and the autotrophic nitrite-oxidizing bacteria. The ammonia-oxidizing bacteria are effective in converting ammonium to nitrite. The nitrite-oxidizing bacteria is oxidized nitrite to nitrate. Usually, nitrification occurred mostly in the unsaturated zone. However, Desimone and Howes (1998) suggested that nitrification in the suboxic saturated zone, along with oxidation of the residual organic carbon, may have buffered oxygen in the plume. Under groundwater table, nitrate is reduced to nitrogen gas by denitrification. This process occurs primarily in anoxic conditions and involves heterotrophic bacteria.

### 3. Mathematical Model

Mathematical modeling is a very useful tool for assessing the state of pollution in the groundwater environment and for predicting the efficiency of remediation alternatives. In this study, mathematical models for the transport and fate of nitrogen species, dissolved organic carbon, and dissolved oxygen and the growth of microbial populations in the groundwater environment were presented.

#### 3-1 Nitrogen transformation and transport

The multiple-Monod kinetics (Chen et al., 1992; Essaid et al., 1995) is appropriate for biodegradation reaction processes that involve several solutes. Thus, the multiple-Monod kinetics is used to describe the kinetic rate equation for all reaction processes in this model. The multiple-Monod kinetics for biodegradation reaction process,  $p$  is given by:

$$r^p = \mu_{\max}^p X_m I_b(X_m) I_{nc}(C_1) \left[ \frac{C_1}{K_1^p + C_1} \right] \left[ \frac{C_2}{K_2^p + C_2} \right] \Lambda \left[ \frac{C_n}{K_n^p + C_n} \right]$$

where  $r^p$  is the substrate utilization rate by reaction process,  $p$ ;  $\mu_{\max}^p$  is the maximum substrate utilization rate;  $X_m$  is the biomass concentration of the population  $m$  responsible for the reaction;  $C_1, C_2, \Lambda, C_n$  are the aqueous species concentrations;  $K_1^p, K_2^p, \Lambda, K_n^p$  are the half-saturation constants for the respective species. The kinetic equations for nitrification and denitrification have the following form.

$$r^1 = \mu_{\max}^{nit_1} X_1 \left[ \frac{k_b}{k_b + X_1} \right] \left[ \frac{NH_4}{K_{NH_4} + NH_4} \right] \left[ \frac{O_2}{K_{O_2} + O_2} \right]$$

$$r^2 = \mu_{\max}^{nit_2} X_2 \left[ \frac{k_b}{k_b + X_2} \right] \left[ \frac{NO_2}{K_{NO_2} + NO_2} \right] \left[ \frac{O_2}{K_{O_2} + O_2} \right]$$

$$r^3 = \mu_{\max}^{denit} X_3 \left[ \frac{k_b}{k_b + X_3} \right] \left[ \frac{k_{O_2}}{k_{O_2} + O_2} \right] \left[ \frac{CH_2O}{K_{CH_2O} + CH_2O} \right] \left[ \frac{NO_3}{K_{NO_3} + NO_3} \right]$$

where  $r^1$  is the substrate utilization rate by ammonium oxidation nitrification;  $r^2$  is the substrate utilization rate by nitrite oxidation nitrification;  $r^3$  is the substrate utilization rate by denitrification;  $X_1$  is the concentration of autotrophic ammonia-oxidizing biomass;  $X_2$  is the concentration of the autotrophic nitrite-oxidizing biomass.  $X_3$  is the heterotrophic biomass concentration.

The fate and transport of ammonium, nitrite, nitrate and nitrogen gas in a multi-dimensional saturated porous media can be written as:

$$R_{NH_4} \frac{\partial[NH_4]}{\partial t} = \frac{\partial}{\partial x_j} \left( D_{ij} \frac{\partial[NH_4]}{\partial x_j} \right) - \frac{\partial(v_i[NH_4])}{\partial x_i} + \frac{q_s}{\phi} [NH_4]_s - r^1$$

$$R_{NO_2} \frac{\partial[NO_2]}{\partial t} = \frac{\partial}{\partial x_j} \left( D_{ij} \frac{\partial[NO_2]}{\partial x_j} \right) - \frac{\partial(v_i[NO_2])}{\partial x_i} + \frac{q_s}{\phi} [NO_2]_s + y_{NO_2/NH_4} \cdot r^1 - r^2$$

$$R_{NO_3} \frac{\partial[NO_3]}{\partial t} = \frac{\partial}{\partial x_j} \left( D_{ij} \frac{\partial[NO_3]}{\partial x_j} \right) - \frac{\partial(v_i[NO_3])}{\partial x_i} + \frac{q_s}{\phi} [NO_3]_s + y_{NO_3/NO_2} \cdot r^2 - r^3$$

$$R_{N_2} \frac{\partial[N_2]}{\partial t} = \frac{\partial}{\partial x_j} \left( D_{ij} \frac{\partial[N_2]}{\partial x_j} \right) - \frac{\partial(v_i[N_2])}{\partial x_i} + \frac{q_s}{\phi} [N_2]_s + y_{N_2/NO_3} \cdot r^3$$

where  $y_{NO_2/NH_4}$ ,  $y_{NO_3/NO_2}$ ,  $y_{N_2/NO_3}$  are the ratio of secondary substrate to primary substrate consumed, as determined from stoichiometry.

### 3-2 Dissolved organic carbon(DOC) and dissolved oxygen(DO) transport

The nitrogen losses through denitrification do require a suitable carbon substrate to maximize biological activity in the saturated zone. The kinetic equations for DOC oxidation have the following form.

$$r^4 = \mu_{max}^{oxid} X_3 \left[ \frac{k_b}{k_b + X_3} \right] \left[ \frac{CH_2O}{K_{CH_2O} + CH_2O} \right] \left[ \frac{O_2}{K_{O_2} + O_2} \right]$$

where  $r^4$  is the substrate utilization rate by denitrification.

The fate and transport of DOC, and DO in a multi-dimensional saturated porous media can be written as:

$$R_{CH_2O} \frac{\partial[CH_2O]}{\partial t} = \frac{\partial}{\partial x_j} \left( D_{ij} \frac{\partial[CH_2O]}{\partial x_j} \right) - \frac{\partial(v_i[CH_2O])}{\partial x_i} + \frac{q_s}{\phi} [CH_2O]_s - r^4$$

$$R_{O_2} \frac{\partial[O_2]}{\partial t} = \frac{\partial}{\partial x_j} \left( D_{ij} \frac{\partial[O_2]}{\partial x_j} \right) - \frac{\partial(v_i[O_2])}{\partial x_i} + \frac{q_s}{\phi} [O_2]_s - y_{O_2/NH_4} r^1 - y_{O_2/NO_2} r^2 - y_{O_2/CH_2O} r^4$$

## 4. Model Application To Test Case

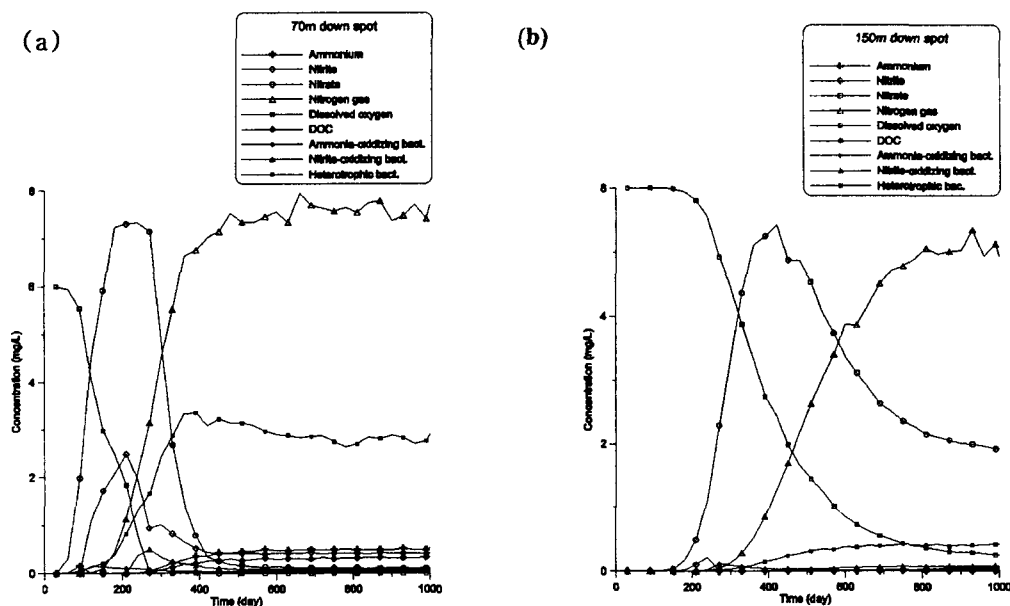
### 4-1 Description of problem

The domain is a 410m×270m section of unconfined aquifer with a flow gradient from left (starting head=65m) to right (starting head=61m) and thickness of 70m. The grid consists of 27 rows and 41 columns. The source location is (14, 12, 1), and contaminants involved nitrogen and organic carbon are leaching at the location shown. Initial levels of ammonium, nitrate, DO, DOC, and microbial population are assume to be 4 mg/l, 40 mg/l, 0 mg/l, 4 mg/l, and  $2 \times 10^{17}$  mg of bacteria/mg of soil, respectively. In uncontaminated part, dissolved oxygen concentration is 6 mg/l and is supplied to all domain.

### 4-2 Numerical simulation results and discussion

Simulations were completed for 1000 days to simulate nine reactive species. The

variations of concentrations according to the simulation time are given in figure, (a) and (b). The figures shows well nitrification–denitrification coupled process. The process generally occur in the early time of the simulation.



<Figure> Time series for nitrogen species, dissolved oxygen, dissolved organic carbon, and biomass (a) at 70m down spot and (b) at 150m down spot.

## 5. Conclusions

In test case, it is evaluated that developed model describing nitrification and denitrification in the saturated zone is effective in this study. This nitrogen model can be used to simulate a rural field problem. The model must be able to quantify adequately the process of nitrogen transformation and transport. Such model can be used to predict evolution of contaminant plumes in a shallow aquifer. The model is expected to assess nitrogen pollution and the effects of localized nitrate reduction measures, as well as to estimate the cost of the pollution–reduction actions.

## 6. References

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