

## A Mathematical Model Development for the Nitrification-Denitrification Coupled Process

이미선, 이강근, T. Prabhakar Clement\*

서울대학교 지구환경과학부

\*Department of Civil Engineering, Harbert Engineering Center, Auburn University, USA

juyouk77@snu.ac.kr

### 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 describing the fate and transport of nitrogen species, dissolved oxygen, dissolved organic carbon, and biomass are developed and tested. The proposed nitrogen transformations and transport model showed very good match with the results of other public codes.

**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

#### 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:

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

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.

$$r^1 = \mu_{\max}^{nit_1} X_1 \left[ \frac{k_{b_1}}{k_{b_1} + X_1} \right] \left[ \frac{NH_4}{K_{NH_4} + NH_4} \right] \left[ \frac{O_2}{K_{O_2} + O_2} \right]$$

$$r^2 = \mu_{\max}^{nit_2} X_2 \left[ \frac{k_{b_2}}{k_{b_2} + X_2} \right] \left[ \frac{NO_2}{K_{NO_2} + NO_2} \right] \left[ \frac{O_2}{K_{O_2} + O_2} \right]$$

$$r^3 = \mu_{\max}^{denit} X_3 \left[ \frac{k_{b_3}}{k_{b_3} + X_3} \right] \left[ \frac{k_{O_2}}{k_{O_2} + O_2} \right] \left[ \frac{CH_2O}{K_{CH_2O} + CH_2O} \right] \left[ \frac{NO_3}{K_{NO_3} + NO_3} \right]$$

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

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

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

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

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

#### 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.

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

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 Verification

To verify that this developed model adequately describes the behavior of the nitrogen compounds, dissolved oxygen, dissolved organic carbon, and biomass as it undergoes reaction, three one-dimensional simulation cases are presented. The Case 1 is a comparison to numerical results presented by *Kindred et al.*(1989) for aerobic biodegradation and denitrification. The Case 2 and Case 3 are compared with modeling results of *Widdowson et al.*(1988) for multiple electron acceptor respiration(oxygen-based and nitrate-based respiration) limited biodegradation of a carbonaceous substrate and nutrient limited biodegradation, respectively.

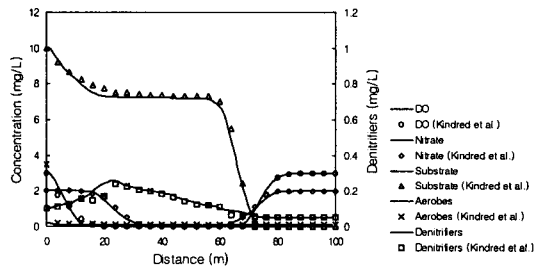
### 4-1 Description of problem

The problem considered for the Case 1 is a one-dimensional aquifer, which is 100m long. Its assumed an initial substrate, dissolved oxygen and nitrate concentrations of 0, 3, and 2mg/l, respectively. The concentrations of substrate, dissolved oxygen and nitrate at the left boundary are held fixed at 10, 3, and 2mg/l, respectively. The Case 2 considers a one-dimensional tracer transport in a hypothetical laboratory scale column experiment (50cm). Initial substrate, oxygen, nitrate, ammonia, and biomass are assumed as 1.0mg/l, 2.0mg/l, 5.0mg/l, 6.0mg/l and 0.565mg/l, respectively to be uniform across the domain. The substrate, oxygen, nitrate, ammonia, and biomass concentrations at the left boundary of the domain are fixed at 20.0mg/l, 2.0mg/l, 5.0mg/l, 6.0mg/l, and 0.565mg/l, respectively.

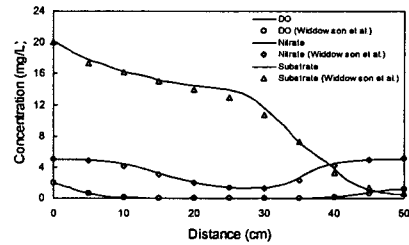
### 4-2 Numerical simulation results and discussion

In both cases the model results compared favorably. Therefore, the developed model was verified by comparing simulation results obtained using the code developed by *Kindred et al.*(1989) and *Widdowson et al.*(1988).

(a)



(b)



<Figure> Numerical simulation results for (a) Case 1, and (b) Case 2

## 5. Conclusions

In this study, a mathematical model was developed to describe the coupled nitrification-denitrification process. The model was coded as a reaction module within the RT3D framework. The model was tested by comparing simulation results obtained using the code developed by *Kindred et al.*(1989) and *Widdowson et al.*(1988). In both cases the model results compared favorably. It is evaluated that developed model describing nitrification and denitrification in the saturated zone is effective in this study. 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

1. Clement,T.P., 1997. RT3D-A modular computer code for simulating reactive multi-species transport in 3-dimensional groundwater aquifers, Pacific Northwest National Laboratory Report, PNNL-11720(<http://bioprocess.pnl.gov/rt3d.htm>).
2. DeSimone,L.A., Howes,B.L., 1998. Nitrogen transport and transformations in a shallow aquifer receiving wastewater discharge: A mass balance approach. *Water Resour. Res.* 34(2), 271-285.
3. Kindred,J.S., Celia,M.A., 1989. Contaminant transport and biodegradation 2. Conceptual model and test simulations. *Water Resour. Res.* 25(6), 1149-1159.
4. Widdowson,M.A., Molz,F.J., Benefield,L.D., 1988. A numerical transport model for oxygen- and nitrate-based respiration linked to substrate and nutrient availability in porous media. *Water Resour. Res.* 24(9), 1553-1565.

## Acknowledgement

This research was supported by a grant (code : 3-5-1) from Sustainable Water Resources Research Center of 21st Century Frontier Research Program.