Bioremediation by Denitrification in the Saturated Zone : Mathematical Model and Experiment

Eun-Jung Lee, Kang-Kun Lee, Young Kim*, Cheol-Yun Ha*
School of Earth and Environmental Sciences, Seoul National University
* *Dept. of Environmental Engineering College of Science and Technology Korea University*
piety99@snu.ac.kr

Abstract

The reactive transport model on the biologically mediated sequential nitrate transformation and its subsequent transport was developed and tested. This model was coded as a reaction module within the RT3D framework (Clement, 1997). Transports of the reasonable six mobile solutes (dissolved organic carbon, O_2, NO_3^-, NO_2^-, N_2O, N_2) and two immobile microbes were simulated. The simulation results gave a reasonable match with supposed transport pattern. For the next step, the developed model will be validated against experimental data.

key word: nitrate model, oxidized nitrogen, denitrification, transformation, transport, RT3D

1. Introduction

Nitrate that is hazardous for human is soluble and mobile in subsurface thus one of the most common pollutants in groundwater. In situ treatment methods are especially preferable, because there is the potential to provide safe and cost effective remediation of nitrate-contaminated groundwater with minimal site disturbance (Kilingstad et. al., 2002).

The objectives of this study are to develop the nitrate transport model describing stepwise reduction of NO_3^- to N_2, and to verify the developed reactive transport model.

2. Conceptual Model

In this study, we assumed that artificially injected fumarate as a carbon source is degraded by aerobic biodegradation and then by a process of denitrification. Sequential biological denitrification with the oxidation state of the nitrogen atom ($NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$) was selected as a conceptual reaction model (Keeney, 1986) and the transport, production, and reduction of nitrate, nitrite, and nitrous oxide were included to the model. In addition, we assumed that the degradation reactions occur only in the aqueous phase.

3. Mathematical Model

Biogeochemical reactions were assumed an equilibrium and a monod kinetic model for sorption and biological reactions, respectively. These rxns were supposed to be occurred in the aqueous phase, following the thermodynamically favorable sequences by the existing subsurface microbes : aerobic degradation, nitrate reduction, nitrite reduction, and nitrous oxide reduction. The microorganisms generally tend to adhere to aquifer materials, which was reflected on the model. From the analysis of the microbial community in the study site, Jochiwon, the denitrifying bacteria existed as a single species for denitrification. Thus it is assumed that the denitrifying bacteria uses nitrate, nitrite, and nitrous oxide as electron acceptors and is associated with all of the steps of denitrification.

To simulate biodegradation of fumarate via different degradation pathways, aerobic biodegradation, and three sequential steps of denitrification, rxns can be given by;

$r_{O_2}^{oxid} : C_4H_2O_4^{2-} + 3O_2 \rightarrow 2CO_2 + 2HCO_3^-$ (aerobic biodegradation)

$r_{NO_3}^{denit1} : 2C_4H_2O_4^{2-} + 12NO_3^- \rightarrow 4CO_2 + 4HCO_3^- + 12NO_2^-$ (nitrate reduction)

$r_{NO_2}^{denit2} : 2C_4H_2O_4^{2-} + 12NO_2^- + 11H^+ \rightarrow 3CO_2 + 5HCO_3^- + 6N_2O + 5H_2O$ (nitrite reduction)

$r_{N_2O}^{denit3} : C_4H_2O_4^{2-} + 6N_2O + H^+ \rightarrow 3CO_2 + HCO_3^- + 6N_2 + H_2O$ (nitrous oxide reduction)

The full Monod kinetic models of above rxns can be written as

1) aerobic biodegradation

$$r_{O_2}^{oxid} = \mu_{\max}^{oxid} X_h \left[\frac{k_{b,h}}{k_{b,h} + X_h}\right]\left[\frac{[C_4H_2O_4]}{K_{C_4H_2O_4} + [C_4H_2O_4]}\right]\left[\frac{[O_2]}{K_{O_2} + [O_2]}\right]$$

2) denitrification

① $NO_3^- \rightarrow NO_2^-$

$$r_{NO_3}^{denit1} = \mu_{\max}^{denit1} X_{d1}\left[\frac{k_{b,d1}}{k_{b,d1} + X_{d1}}\right]\left[\frac{k_{O_2,d1}^I}{k_{O_2,d1}^I + [O_2]}\right]\left[\frac{k_{NO_2,d1}^I}{k_{NO_2,d1}^I + [NO_2]}\right]\left[\frac{[C_4H_2O_4]}{K_{C_4H_2O_4} + [C_4H_2O_4]}\right]\left[\frac{[NO_3]}{K_{NO_3} + [NO_3]}\right]$$

② $NO_2^- \rightarrow N_2O$

$$r_{NO_2}^{denit2} = \mu_{\max}^{denit2} X_{d1}\left[\frac{k_{b,d1}}{k_{b,d1} + X_{d1}}\right]\left[\frac{k_{O_2,d2}^I}{k_{O_2,d2}^I + [O_2]}\right]\left[\frac{k_{NO_2,d2}^I}{k_{NO_2,d2}^I + [NO_2]}\right]\left[\frac{[C_4H_2O_4]}{K_{C_4H_2O_4} + [C_4H_2O_4]}\right]\left[\frac{[NO_2]}{K_{NO_2} + [NO_2]}\right]$$

③ $N_2O \rightarrow N_2$

$$r_{N_2O}^{denit3} = \mu_{\max}^{denit3} X_{d1}\left[\frac{k_{b,d1}}{k_{b,d1} + X_{d1}}\right]\left[\frac{k_{O_2,d3}^I}{k_{O_2,d3}^I + [O_2]}\right]\left[\frac{k_{NO_2,d3}^I}{k_{NO_2,d3}^I + [NO_2]}\right]\left[\frac{[C_4H_2O_4]}{K_{C_4H_2O_4} + [C_4H_2O_4]}\right]\left[\frac{[N_2O]}{K_{N_2O} + [N_2O]}\right]$$

where r is the electron donor (ED) degradation rate (mg/L/day), μ is the maximum substrate utilization rate for ED (1/day), X_h is the heterotroph concentration (mg/L), X_{d1} is the denitrifying bacteria concentration (mg/L), K is the saturation constant (mg/L), and $k_{b,dn}$ and $k^I_{EA,dn}$ are inhibition constant of the biomass and EA (mg/L), respectively.

The fate and transport of fumarate, oxygen, oxidized nitrogens and nitrogen gas in saturated porous media can be written as

$$R_{C_4H_2O_4}\frac{\partial[C_4H_2O_4]}{\partial t}=\frac{\partial}{\partial x_j}\left(D_{ij}\frac{\partial[C_4H_2O_4]}{\partial x_j}\right)-\frac{\partial(v_i[C_4H_2O_4])}{\partial x_i}+\frac{q_s}{\phi}[C_4H_2O_4]_s-r_{O_2}^{oxid}-r_{NO_3}^{denit1}-r_{NO_2}^{denit2}-r_{N_2O}^{denit3}$$

$$R_{O_2}\frac{\partial[O_2]}{\partial t}=\frac{\partial}{\partial x_j}\left(D_{ij}\frac{\partial[O_2]}{\partial x_j}\right)-\frac{\partial(v_i[O_2])}{\partial x_i}+\frac{q_s}{\phi}[O_2]_s-Y_{O_2/C_4H_2O_4}\cdot r_{O_2}^{oxid}$$

$$R_{NO_3}\frac{\partial[NO_3]}{\partial t}=\frac{\partial}{\partial x_j}\left(D_{ij}\frac{\partial[NO_3]}{\partial x_j}\right)-\frac{\partial(v_i[NO_3])}{\partial x_i}+\frac{q_s}{\phi}[NO_3]_s-r_{NO_3}^{denit1}$$

$$R_{NO_2}\frac{\partial[NO_2]}{\partial t}=\frac{\partial}{\partial x_j}\left(D_{ij}\frac{\partial[NO_2]}{\partial x_j}\right)-\frac{\partial(v_i[NO_2])}{\partial x_i}+\frac{q_s}{\phi}[NO_2]_s+Y_{NO_2/NO_3}\cdot r_{NO_3}^{denit1}-r_{NO_2}^{denit2}$$

$$R_{N_2O}\frac{\partial[N_2O]}{\partial t}=\frac{\partial}{\partial x_j}\left(D_{ij}\frac{\partial[N_2O]}{\partial x_j}\right)-\frac{\partial(v_i[N_2O])}{\partial x_i}+\frac{q_s}{\phi}[N_2O]_s+Y_{N_2O/NO_2}\cdot r_{NO_2}^{denit2}-r_{N_2O}^{denit3}$$

$$R_{N_2}\frac{\partial[N_2]}{\partial t}=\frac{\partial}{\partial x_j}\left(D_{ij}\frac{\partial[N_2]}{\partial x_j}\right)-\frac{\partial(v_i[N_2])}{\partial x_i}+\frac{q_s}{\phi}[N_2]_s+Y_{N_2/N_2O}\cdot r_{N_2O}^{denit3}$$

Then, the fate and transport of heterotroph and denitrifier can be written as

$$\frac{dX_h}{dt}=Y_h\cdot r_{O_2}^{oxid}-d_h\cdot X_h\,,\qquad \frac{dX_{d1}}{dt}=Y_{d1}(r_{NO_3}^{denit1}+r_{NO_2}^{denit2}+r_{N_2O}^{denit3})-d_{d1}\cdot X_{d1}$$

4. Model Application

A domain that is a 100 m × 10 m section of unconfined aquifer was used for testing of the model. Groundwater flowed with hydraulic gradient of 0.001 and the aquifer thickness was 10 m. Initial concentrations of DO, NO_3^-, and DOC in all domain were assume to be 7 mg/ℓ, 10 mg/ℓ, and 7 mg/ℓ, respectively. Transports of reactive species were simulated for 200 days. Figure 1 shows the changes of solute concentrations at 73 m down spot according to the elapsed, which describes the denitrification process well.

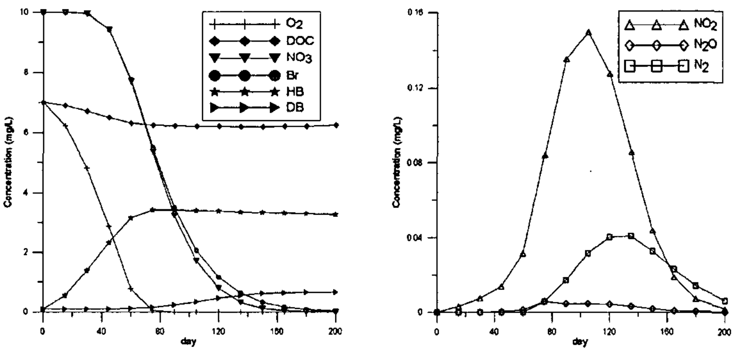

Figure 1. The variations of concentrations versus the time at 73 m down spot.

5. Field Application

To prove that this developed model adequately describes the reactive transport of nitrate, in situ field experiments will be performed in Jochiwon. 8 wells were developed in the study site and slug tests were conducted at the 4 wells. From the slug test results, geometric mean of hydraulic conductivity of this aquifer was 1.23×10^{-3} cm/s. Using results of transport test, the model was calibrated to evaluate goodness of fit between field test data and simulation data for bromide and nitrate through their time series (Figure 2). From the error analysis, the longitudinal dispersivity and retardation factor of bromide and nitrate were calibrated to 1.0 m and 1.0, respectively.

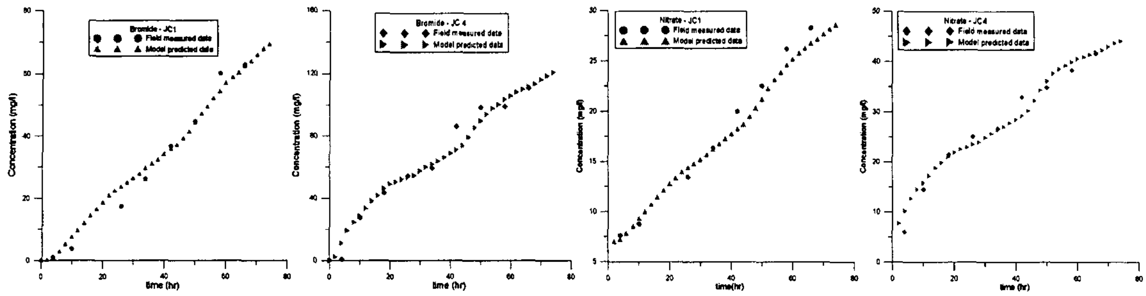

Figure 2. Comparison of field measured and model predicted concentrations of bromide and nitrate at JC1, JC4.

6. Conclusions

The reactive transport model on the biologically mediated transformation of oxidized nitrogen and its subsequent transport was developed and tested. The model is able to quantify adequately the process of denitrification and nitrate transport in the saturated zone. In the study, transport test was performed and analyzed to obtain the hydraulic parameters, such as longitudinal dispersivity and retardation factor, at Jochiwon site. The validation of the overall model, which represents substrate degradations using oxygen, nitrate, nitrite, and nitrous oxide as electron acceptors, is left for further studies. The model is expected to evaluate possible remedial methods as well as to estimate the remediation cost.

7. Acknowledgement

This research was supported by the BK21 project of the Korean government and AEBRC at POSTECH.

8. References

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