Nitrogen Cycling in a River-Aquifer system

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1 Introduction

The aim of this project is to understand the role of organic matter mineralization in the removal of dissolved organics entering the groundwater from a contaminated river. Specifically, your task is to write a model that can predict the concentrations of DOM, O_2, NO_3, NH_3 and N_2 along the flow path of water from the river through the aquifer. First, you will use the model to fit the given profiles of O_2 and NH_3 in order to obtain the rate constants of aerobic DOM degradation, nitrification and groundwater aeration. Then you will apply the model to predict how the quality of potentially drinking water extracted from a well in the aquifer depends on the concentrations of DOM, NO_3 and NH_3 in the river. Your ultimate question is: How does the coupling of processes of aerobic respiration, nitrification-denitrification and groundwater aeration determine water quality along an aquifer adjacent to a river contaminated with organics?

2 Methods

To determine the infiltration of nitrogen from a river into the groundwater, several chemical equations have to be identified. First of all, there is aerobic respiration of dissolved organic matter (DOM). For the purposes of this model DOM is simplified to $(CH_2O)_{106}(NH_3)_{16}$, where the ratio between carbon and nitrogen is set to the Redfield ratio. Aerobic respiration can then be described by the following stoichiometric equation:

$$(CH_2O)_{106}(NH_3)_{16} + 106\,O_2 \longrightarrow 106\,CO_2 + 106\,H_2O + 16\,NH_3. \tag{1}$$

When oxygen is depleted, organic matter degradation is also possible through denitrification. Through this process nitrogen is lost from the system in gaseous form:

$$5\,(CH_2O)_{106}(NH_3)_{16} + 424\,NO_3^- + 424\,H^+ \longrightarrow 530\,CO_2 + 742\,H_2O + 80\,NH_3 + 212\,N_2. \tag{2}$$
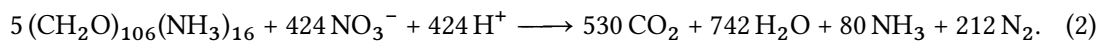
Both these processes lead to the formation of ammonium, which under oxic conditions can be transformed to nitrate in a process called nitrification:

$$NH_3 + 2\,O_2 \longrightarrow NO_3^- + H_2O + H^+. \tag{3}$$
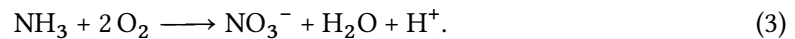
From these equations several species were identified as relevant for the model. First of all a primary goal of the model is to determine suitability of the groundwater for drinking water production. The regulations limit the concentrations of DOM, NO_3, and NH_3. Therefore, these parameters have to be modeled explicitly. Secondly oxygen is modeled for regulation of the processes, and nitrogen is modeled to track the final loss of nitrogen from the groundwater.

2.1 Assumptions

To simplify the problem the following points are assumed:

- River and groundwater directly connected, no unsaturated zone in between

- Only 1 dimensional transport along streamline

- Once nitrogen degases it is permanently lost from the system

- DOM is only removed through aerobic respiration and denitrification, other removal processes are ignored.

2.2 Equations

$$\frac{\partial [DOM]}{\partial t} = D\frac{\partial^2 [DOM]}{\partial x^2} - u\frac{\partial [DOM]}{\partial x} - R_{org.rem} \tag{4}$$

$$\frac{\partial [O_2]}{\partial t} = D\frac{\partial^2 [O_2]}{\partial x^2} - u\frac{\partial [O_2]}{\partial x} - R_{aero} - R_{nit} + R_{aeration} \tag{5}$$

$$\frac{\partial [NO_3]}{\partial t} = D\frac{\partial^2 [NO_3]}{\partial x^2} - u\frac{\partial [NO_3]}{\partial x} - R_{denit} + R_{nit} \tag{6}$$

$$\frac{\partial [NH_3]}{\partial t} = D\frac{\partial^2 [NH_3]}{\partial x^2} - u\frac{\partial [NH_3]}{\partial x} + R_{org.rem} - R_{nit} \tag{7}$$

$$\frac{\partial [N_2]}{\partial t} = D\frac{\partial^2 [N_2]}{\partial x^2} - u\frac{\partial [N_2]}{\partial x} + R_{denit} + R_{degas} \tag{8}$$

$$R_{org.rem} = k_1[DOM] = R_{aero} + R_{denit} \tag{9}$$

$$R_{aero} = R_{org.rem}\left(\frac{[O_2]}{k_{O_2} + [O_2]}\right) \tag{10}$$

$$R_{denit} = R_{org.rem}\left(\frac{[NO_3]}{k_{NO_3} + [NO_3]}\right)\left(\frac{k_{O_2}}{k_{O_2} + [O_2]}\right) \tag{11}$$

$$R_{nit} = k_2[NH_3][O_2] \tag{12}$$

$$R_{aeration} = k_3\left(1 - \frac{[O_2]}{S_{O_2}}\right) \tag{13}$$

$$R_{degas} = k_3\left(1 - \frac{[N_2]}{S_{N_2}}\right) \tag{14}$$

Table 1: Given parameters of the system

Parameter	Value	Unit
Velocity, u	10	cm/h
Porosity, ϕ	0.4	m^3_{pw}/m^3
Dispersivity, α_L	1.5	m
Affinity O_2, k_{O_2}	20	μmol/L
Affinity NO_3, k_{NO_3}	35	μmol/L
Temperature, T	10	˚C
Salinity, S	0	

The following values are given as initial guesses for the fitting.

$$k_1 \approx 1 \times 10^{-3} \, \frac{1}{h} \tag{15}$$

$$k_2 \approx 5 \times 10^{-4} \, \frac{1}{\mu mol_{O_2} \, L \, h} \tag{16}$$

$$\frac{k_3}{S_{O_2}} \approx 5 \times 10^{-4} \, \frac{1}{h} \tag{17}$$

The value for k_3 is given as a fraction because the notation of the rate law is different.

From the given values Table 1 we can calculate the dispersion coefficient:

$$D \approx \alpha_L u \tag{18}$$

$$= 10 \, \frac{cm}{h} \times 1.5 \, m \tag{19}$$

$$= 0.15 \, \frac{m^2}{h} \tag{20}$$

$$\tag{21}$$

2.3 Boundary conditions

2.4 Regulations

$$DOM < 3 \, \frac{mg_C}{L} \tag{22}$$

$$NO_3 < 25 \, \frac{mg_{NO_3}}{L} \tag{23}$$

$$NH_3 < 0.05 \, \frac{mg_{NH_3}}{L} \tag{24}$$

Table 2: Boundary conditions for the state variables

Parameter	Upper	Lower
DOM	$[DOM] = 6\,\mathrm{mg_C/L} = 0.5\,\mathrm{mmol_C/L} = 4.71\,\mathrm{\mu mol_{DOM}/L}$	$\frac{\partial[DOM]}{\partial x} = 0$
O_2	$[O_2] = 210\,\mathrm{\mu mol_{O2}/L}$	$\frac{\partial[O_2]}{\partial x} = 0$
NO_3	$[NO_3] = 100\,\mathrm{\mu mol_{NO3}/L}$	$\frac{\partial[NO_3]}{\partial x} = 0$
NH_3	$[NH_3] = 0\,\mathrm{\mu mol_{NO3}/L}$	$\frac{\partial[NH_3]}{\partial x} = 0$
N_2	$[N_2] = S_{N_2}$	$\frac{\partial[N_2]}{\partial x} = 0$

3 Results

4 Discussion

DOM infiltrates farther then expected because some removal processes are ignored. k_1 is the potential maximum removal rate which is never reached

5 Conclusion