SIMULATION OF BIO-GEOCHEMICAL PROCESSES IN A COASTAL AQUIFER

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Numerical models which discuss about the bio-geochemical processes which take place in coastal aquifers are still limited. Bacteria mediated reduction is one of the main causes which directly contributes to the groundwater quality of coastal aquifers. In this study a two-dimensional numerical model was developed to simulate the bacteria mediated reduction processes which are occurring in the coastal aquifers. The model was applied to a cross section of Kujyukurihama coast in Chiba prefecture, Japan, where a reduced environment has been formed. The objective of this paper is not to provide an orthodox numerical simulation practice, but to convince the numerical modellers; the possibility of the simulation of bacterial reduction processes in coastal subsurface environments. This paper provides a preliminary numerical study of the reduction of MnO_2 and $Fe(OH)_3$ under anaerobic bacteria mediation. Further researches are needed to improve the numerical simulations on the reduction environments in coastal aquifers.

Key words: coastal aquifer, bacteria mediation, density dependent flow, numerical model, organic carbon, reduction processes

1. INTRODUCTION

A numerical study of the bio-geochemical aspects of the coastal aquifers is an interesting subject to address. So far numerical simulations which discuss about the bacteria mediated reduction processes, are not common in the scientific literature. Snyder et al.¹⁾ made detailed surveys on the bio-geochemical oxidation-reduction approach for the mixing zone formed in a shallow aquifer at the estuary of Sapelo Island, Georgia, USA. Based on the biogeochemical approaches, they have shown that the distribution of manganese, iron and sulphate ions are affected by the natural organic carbons and bacteria mediated reducing processes, which take place at the both sides of fresh and seawater transition zone. Hiroshiro et al.²⁾ analyzed the redox (oxidation-reduction) potential distribution in the monitoring wells and found out that the redox potential drastically decreased below the mixing zone from fresh water to reduced seawater.

Geochemical properties of the groundwater in a coastal aquifer would change with the depth from aerobic state to anaerobic state. The bacteria mediated redox reactions are significant in the geochemical property changes of the subsurface

water in a coastal aquifer. The availability of oxygen and other electron acceptors such as NO₃, MnO₂, $Fe(OH)_3$ and SO_4^{2-} with the organic carbon as the electron donor encourage the different bacteria to activate and form reduced environments in the subsoil. The gradual decrease of oxygen with the depth allows bacteria to use other electron acceptors and form Mn^{2+} , Fe^{2+} and HS^- rich reduced environments. The seawater below the mixing zone is almost anaerobic in the coastal aquifer, and bacteria mediated reduction processes are dominant. Depending on the availability of organic carbon, a sequence of redox zones of increasing redox potential may develop at the down gradient of the aquifer; zones of oxygen, NO₃, MnO₂, Fe(OH)₃ and SO_4^{2} reduction can be developed if the corresponding electron acceptors are present in the aquifer.

In this paper, a numerical study is discussed considering the reduced environment formed in the Kujyukurihama coast in Chousei village of the Chiba prefecture, Japan³⁾. **Fig. 1** shows the location of the selected place for this study. Due to the practical constrains, it is not possible to validate the model through a direct comparison between the measured data and numerically simulated results.



Fig. 1 Location map of the site³⁾

Some of the practical constraints can be listed as: (i) those processes have been taking place for thousands of years. (ii) history of the geological formation of the coastal aquifer is unknown. (iii) continuous measurement of chemical species which reside in that environment, is costly. Due to those reasons, a validation of the numerical model through a direct comparison is not discussed. Instead of that, authors tried to simulate the possible trends of bacteria mediated reduction processes. The availability of organic carbon is the major factor which influences the formation of reduced environments under the mediation of aerobic and anaerobic bacteria. In this numerical study, the behaviour of aerobic and anaerobic bacteria under the assigned organic carbon distribution and the formation of Mn^{2+} and Fe^{2+} at the reduction of MnO₂ and Fe(OH)₃ are discussed for the selected cross section of the site.

2. METHODOLOGY

Density dependent flow was involved in the coastal aquifer flow modelling due to the density difference of seawater and freshwater^{3,4)}. Therefore, the combination of density dependent flow with the bacteria mediated redox reactions have to be considered in this numerical study to simulate the bacteria mediated reduction processes. It will open a new research area to study the coastal reduced subsurface environments more extensively. In this study, a two - dimensional density dependent solute transport model and a two-dimensional bacterial mediated redox model are combined to describe the reduction processes which occur in the subsurface of the Kujyukurihama unconfined coastal aquifer. In the first part of the simulation, a density dependent two-dimensional solute transport model is used to obtain the steady state conditions for the chloride distribution and velocity distribution of the unconfined aquifer. The concentration distributions of chemical species in the freshwater and seawater are different due to the physical, chemical and biological processes in subsurface environments. For this reason, it is initially necessary to obtain the chloride distribution of the selected cross section of the aquifer. The initial distribution of chemical species in freshwater, mixing zone and seawater regions were assigned according to the obtained chloride distribution. These species distribution and velocity distribution were input to the twodimensional mass transport and bacteria mediated reduction model (redox model).

(1) Density dependent solute transport model

The following set of equations is used for the numerical calculation of this model.

The equation of unsaturated-saturated flow can be written as:

$$(C_w + \alpha_0 S_s) \frac{\partial h}{\partial t} = -\frac{\partial u}{\partial x} - \frac{\partial v}{\partial y}$$
(1a)

$$u = -k \frac{\partial h}{\partial x}$$
 (1b); $v = -k \left(\frac{\partial h}{\partial t} + \frac{\rho}{\rho_f} \right)$ (1c)

where *t* is time, *h* is the piezometric head at the location of (x, y), *k* is the permeability, *u* and *v* are the velocity components in the *x* and *y* directions respectively. *S_s* is the specific storage coefficient, α_0 is a dummy number which takes 0 in unsaturated condition and 1 in saturated condition. *C_w* is the specific moisture capacity. ρ is the fluid density, ρ_f and ρ_s are the densities of freshwater and seawater.

The equation of mass transport for twodimensional advective-dispersive flow without chemical reaction term can be written as^{3,4}:

$$\frac{\partial(\theta C_{cl})}{\partial t} + \frac{\partial(u C_{cl})}{\partial x} + \frac{\partial(v C_{cl})}{\partial y} = \frac{\partial}{\partial x} \left(\theta D_{xx} \frac{\partial C_{cl}}{\partial x} + \theta D_{xy} \frac{\partial C_{cl}}{\partial y} \right) + \frac{\partial}{\partial y} \left(\theta D_{yy} \frac{\partial C_{cl}}{\partial y} + \theta D_{yx} \frac{\partial C_{cl}}{\partial x} \right)$$
(2)

where C_{cl} is the chloride concentration. D_{xx} , D_{xy} , D_{yy} , D_{yx} are the dispersion coefficients^{3,4)}, θ is the volumetric moisture content.

(2) Bacteria mediated redox model

The redox model describes the biological degradation of dissolved organic carbon (CH₂O) by different bacteria groups. Microbial mediated redox sequence of reactions (aerobic oxidation, nitrate reduction, Mn(IV) reduction, Fe(III) reduction and SO_4^{2-} reduction) are modelled with four bacteria groups named as X_1 , X_2 , X_3 and X_4 .



Fig. 2 Chemical species considered in the model and mass transfer processes between different phases.

Bacteria X_1 uses oxygen under aerobic conditions and nitrate under anaerobic conditions. Under anaerobic conditions bacterial groups X_2 , X_3 and X_4 use Mn(IV), Fe(III) and SO₄²⁻ as electron acceptors respectively and reduce them to Mn²⁺, Fe²⁻ and HS⁻.

The redox model takes into account three different phases: mobile pore water phase, immobile bio phase and matrix phase. The bio phase is assumed to include all bacterial growth and biological processes. The species located in three phases can transport between different phases according to the concentration gradients. Bacterial activities in bio phase generate concentration gradients between different phases. Redox model simulates the concentration variations due to the bacterial activities. **Fig. 2** shows the three phases, which are considered in the redox model. The chemical species, which reside in each phase are also shown in **Fig. 2**.

The fundamental two-dimensional partial differential equation governing the advectivedispersive solute transport of contaminants with the source/sink term for chemical reactions for the mobile phase species can be written as^{5} :

$$\frac{\partial(\theta C_{mob})}{\partial t} + \frac{\partial(u C_{mob})}{\partial x} + \frac{\partial(v C_{mob})}{\partial y} = \frac{\partial}{\partial x} \left(\theta D_{xx} \frac{\partial C_{mob}}{\partial x} + \theta D_{xy} \frac{\partial C_{mob}}{\partial y} \right) + \frac{\partial}{\partial y} \left(\theta D_{yy} \frac{\partial C_{mob}}{\partial y} + \theta D_{yx} \frac{\partial C_{mob}}{\partial x} \right) + \sum_{i=1}^{3} S_i$$
(3)

where C_{mob} is the mobile phase species concentration. S_i is the source/sink term which represents the solute exchange between different phases. The solute exchange processes are: (i) mass transfer between the mobile phase and the bio phase, $S_1 = \alpha(C_{bio} - C_{mob})$; (ii) mass transfer between the mobile phase and the matrix phase, $S_2 = \beta(C_{mat} - C_{mob})$; and (iii) mass transfer between the bio phase and the matrix phase, $S_3 = \gamma(C_{bio} - C_{mat})$. where C_{bio} and C_{mat} are the concentrations of solute in the bio phase and matrix phase, α , β and γ are the exchange coefficients between the different phases.

Bacteria can utilize several substrates simultaneously. Bacteria growth is often controlled by availability of substrates. The specific growth rate of bacteria is assumed to be a function of the concentration of the substrates. As described by the ecological redox sequence, microbially mediated redox processes are described by following reactions⁵⁾:

Aerobic respiration (bacteria X1)

 $CH_2O + O_2 \rightarrow CO_2 + H_2O$

Denitrification (bacteria X1- under anaerobic condition)

 $CH_2O + 4/5NO_3^- + 4/5H^+ \rightarrow CO_2 + 2/5N_2 + 7/5H_2O$ Manganese dioxide-reduction (bacteria X_2)

 $CH_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 3H_2O + CO_2$

Iron hydroxide-reduction (bacteria X₃)

 $CH_2O + 4Fe(OH)_3 + 8H^+ \rightarrow 4Fe^{2+} + 11H_2O + CO_2$ Sulphate (SO_4^{-2}) -reduction (bacteria X₄)

 $CH_2O + 1/2SO_4^{2-} + 1/2H^+ \rightarrow CO_2 + 1/2HS^- + H_2O$

The growth of bacteria is described by the Double Monod kinetic equation as:

$$\frac{\partial X}{\partial t} = v_{\max} \frac{C_1}{K_{s1} + C_1} \cdot \frac{C_2}{K_{s2} + C_2} X$$
(4)

where v_{max} is the maximum growth rate, C_1 is the electron donor concentration in bio phases, C_2 is the electron acceptor concentration in bio phases, K_{s1} is the primary substrate half-saturation constant, K_{s2} is the secondary substrate half-saturation constant, and X is the bacterial concentration.

The concentration of the microbial population can increase on one or more respirative pathways. For example, many aerobic bacteria are facultatively anaerobic and can also grow under denitrifying conditions⁶⁾. The model extended to include the switching between aerobic and denitrifying growth conditions is based on the assumption that the same microorganisms are capable of either aerobic or denitrifying growth, depending on the oxygen concentration in their nearby environment. The switching function can be written as⁶⁾:

$$F([O_2]_{bio}) = 0.5 - \frac{1}{\pi} \tan^{-1} \{ [O_2]_{bio} - [O_2]_{thres} \} \times f_{s1} \}$$
(5)

where $F([O_2]_{bio})$ is the switching function, $[O_2]_{bio}$ is the concentration of oxygen O₂ in the bio phase, $[O_2]_{thres}$ is the threshold concentration of oxygen O₂, and f_{s1} is the slope of the switching function.

	Mobile phase			Matrix	
Species	Fresh	Sea	Bio phase	phase	
	water	water			
O ₂	0.3	0.15	0.3	-	
NO ₃ ⁻	0.2	0.10	-	-	
MnO ₂	-	-	0.05	5.0	
Fe(OH) ₃	-	-	0.05	5.0	
SO_4^{2-}	-	5.0	-	-	
CH ₂ O	0.0	10.0	10.0	10.0	

 Table 1. Assigned initial species' concentrations in different phases of the redox model (mg/l)

In the redox model, after oxygen is consumed up to the threshold oxygen concentration by bacteria X_1 , NO_3^- also starts to get reduced to N_2 by bacteria X_1 . When anaerobic condition takes place in the bio phase, MnO_2 and $Fe(OH)_3$ start to get reduced by the bacteria X_2 and bacteria X_3 and form Mn^{2+} and Fe^{2+} consecutively. SO_4^{2-} which initially resides in the seawater region of the mobile phase transfer to bio phase and gets reduced to HS^- following the order of redox reactions explained in page 3.

(3) Numerical simulation

In this study, the finite difference method and the method of characteristics are used as numerical solution techniques to solve the mathematical equations. The grid sizes in the horizontal (xdirection) and vertical (y-direction) directions of the finite difference grid system are 1.0 m and 0.2 m. The time increment was set to 5 minutes. The boundary conditions were selected concerning the existing geological conditions of the Kujyukurihama coast^{3,4)}. Table 1 describes the assumed initial chemical species distribution for the three phases in the numerical simulation. The model for the biologically mediated redox processes is highly complex, as it needs to involve a large number of parameters. Monod kinetic and switching function parameters were taken from several studies related to modelling and simulation of redox processes $^{5,6,7)}$. The values of the Monod kinetic and switching function parameters are listed in Table 2. The initial concentration of 0.001 mg/l is assigned for the bacteria X_1 , X_2 , X_3 and X_4 which reside in the bio phase.

3. RESULTS AND DISCUSSION

Redox model simulates the solute transport with biochemical reaction processes. They are complex because they involve many biochemical parameters. Parameter sensitivity analysis is important to determine the degree of influence of the various input parameters. Sensitivity analyses were conducted by several authors^{5),6),7)}. They have found out that maximum growth rate v_{max} of the bacteria,

Table 2 Parameters used for the simulation.

Pai	Value					
	α	3 day^{-1}				
coefficient	β	0.5 day^{-1}				
	γ	0.05 day ⁻¹				
Diamonaivity	α_L	0.36 cm				
Dispersivity	α_T	0.036 cm				
soil diameter	а	0.01mm				
Half saturation	K _{CH2O}	0.10 mmol/L				
constant	K _{O2} , K _{NO3} , K _{MnO2} ,	1.0 x 10 ⁻³				
	K _{Fe(OH)3} , K _{SO4}	mmol/L				
	Yield Coefficient	0.10 mol cell-				
Aerobic bacteria	Y ₀₂	C/mol OC				
X ₁	Max. growth v_{max}	5.0 day ⁻¹				
	Decay rate <i>v</i> _{X1dec}	1.05 day ⁻¹				
	Yield Coefficient	0.08 mol cell-				
Denitrification	Y _{NO3}	C/mol OC				
bacteria	Max. growth v_{max}	4.05 day ⁻¹				
\mathbf{X}_1	Decay rate <i>v</i> _{X1dec}	1.05 day ⁻¹				
Mn(II)-	Yield Coefficient	0.015 mol cell-				
reduction	Y _{MnO2}	C/molOC				
bacteria	Max. growth v_{max}	0.5 day ⁻¹				
X_2	Decay rate <i>v</i> _{X2dec}	0.075 day ⁻¹				
Fe(III)-	Yield Coefficient	0.015 mol cell-				
Reduction	Y _{Fe(OH)3}	C/molOC				
bacteria	Max. growth v_{max}	0.5 day ⁻¹				
X_3	Decay rate v_{X3dec}	0.075 day ⁻¹				
Sulfata	Yield Coefficient	0.015 mol cell-				
Reduction	Y _{SO4}	C/molOC				
bacteria	Max. growth v_{max}	0.45 day ⁻¹				
X_4	Decay rate <i>v</i> _{X4dec}	0.045 day^{-1}				
	Threshold	1.5 x 10 ⁻² mmol/L				
Switching	Concentration					
parameter	$[O_2]_{\text{thres}}$					
F	Slope of switch f_{sl}	40.0				

exchange coefficients α , β , γ and the initial distribution of concentrations of CH₂O, MnO₂ and Fe(OH)₃ in the bio and matrix phases influence the growth of bacteria X₂ and X₃ under anaerobic conditions. Fig. 3 illustrates the steady state chloride distribution and velocity profile obtained from the two-dimensional density dependent flow model. The validity of the numerical solution for chloride distribution was confirmed^{3),4)}. Table 3 shows the rough measurements carried out on 1998 July for the chemical species of Kujyukurihama coast subsurface^{3),4)}. Measurement points depicted in Fig. 3 as A, B, C, D, and E. Points located in the seawater region show negative ORP (oxidationreduction potential) and those points represent higher DOC and TOC values than point D which is located in the freshwater region. Measured Fe²⁺ and



Fig. 3 Steady state chloride distribution (%) and velocity distribution for the two-dimensional density dependent solute transport model. (*Selected cross section of Kujyukurihama coast, Chousei village, Chiba, Japan*)



Fig. 5 (Freuburements were done in 1996 July)									
Point	Α	В	С	D	E				
pH	7.2	8.2	6.9	7.6	7.9				
Na ⁺ (mg/l)	5900	4500	5500	120					
K^+ (mg/l)	220	170	210	15					
Ca^{2+} (mg/l)	240	190	220	45					
Fe^{2+} (mg/l)	0.2	< 0.1	< 0.1	< 0.1					
Total – Mn (mg/l)	1	0.06	0.17	0.04					
Cl- (mg/l)	9500	7300	9100	230					
SO_4^{2-} (mg/l)	1200	1000	980	40					
DO (mg/l)	(2.9)	(4.1)	< 0.5	3.5	< 0.5				
DOC (mg/l)	5	5	11	<1					
TOC (mg/l)	14	7	20	1					
ORP (mV)	-99	-66	-380	78					
S^{2} (mg/l)	< 0.5	< 0.5	11	< 0.5					





Fig. 5 Growth of bacteria X₁, X₂, X₃ and X₄

total Mn^{2+} show high concentrations at A, B and C points, which are located in the seawater. Moreover, at point C the S²⁻ has higher value. These observations provide evidences for the reduction of MnO_2 , Fe(OH)₃ and SO₄²⁻ under anaerobic conditions. Point C, which is located at the bottom part of the aquifer, shows highly reduced conditions with -380 mV ORP value, high S²⁻ and high total Mn^{2+} concentrations. Point A represents the bottom part of the mixing zone while point D represents the freshwater region where DO shows high concentration. Point E locates in the mixing zone and only pH and DO values are available. Other measurements were not conducted for the point E. The values shown of DO for the points A and B are uncertain due to measurement errors. Because of that they are shown in brackets.

Fig. 4 and Fig. 5 show the numerical results of the selected species, which are included in the redox model, along the X-Y line shown in Fig. 3. Fig. 4 shows the numerical results for the assumed condition, where initial CH₂O in mobile freshwater is 0.0 mg/l and 10.0 mg/l in seawater. In the seawater region, the development of redox condition is illustrated by the gradual increase of Mn²⁺ and Fe^{2+} concentrations at the expense of CH₂O. The gradual decrease of MnO_2 and $Fe(OH)_3$ in the matrix phase shows the metabolism of bacteria X₂ and X_3 at the reduced conditions. In Fig. 4(e) around 12.0 m elevation an increased of $Fe(OH)_3$ can be seen with time. It is due to the precipitation of $Fe(OH)_3$ by formed Fe^{2+} and available O_2 . Precipitation of Fe(OH)₃ starts with the formation of Fe^{2+} in the reduced region. Fe^{2+} is transported to the mixing zone with the advective flow and precipitated as Fe(OH)₃. The patterns of formation of Mn^{2+} and Fe^{2+} (**Fig. 4**((a) and (b)) and reduction of MnO_2 and $Fe(OH)_3$ (Fig. 4((d) and (e)) are compatible. It shows that the redox model functions correctly for the assumed initial CH₂O distribution.

Fig. 5 ((a) to (d)) describes the numerical results of bacterial growth. Generally, the aerobic bacteria X1 should be grown in the oxygen abandon freshwater region if CH2O is available. In this numerical simulation the provided CH₂O in the freshwater region is 0.0 mg/l. Therefore, bacteria X_1 do not grow in the freshwater region. As shown in **Fig. 5**(a) up to 10 days, bacteria X_1 grows rapidly in the CH₂O rich seawater region consuming the available oxygen and NO_3 . After that its growth decreases due to the lack of oxygen and NO_3^- , creating anaerobic conditions. Consequently, bacteria X_2 and X_3 as shown in **Fig. 5** ((b) and (c)) start to grow in the anaerobic environment consuming available CH₂O meantime the MnO₂ and $Fe(OH)_3$ start to get reduced. The growth of SO_4^{2-1} reducing bacteria X₄ starts slowly at the beginning. Its growth accelerates with the slow down of bacteria X₂ and X₃. The metabolism of bacteria is compatible with the species' formation shown in Fig. 4. It implies that the developed model is capable of simulating the expected reduction processes. The illustration of the concentration variations of Mn²⁺, Fe²⁺, CH₂O, MnO₂ and Fe(OH)₃ provide numerical evidences for the behaviour of aerobic/anaerobic bacteria in the coastal aquifer and the formation of reduced environments under the availability of organic carbon as the electron donor.

Even though a direct simulation of above discussed chemical species formation is difficult, the numerical model developed in this study can provide an insight for the formation of redox conditions and the growth of aerobic/anaerobic bacteria at the existence of CH_2O . This numerical approach is important for better understanding of the geophysical and geochemical processes in a coastal aquifer.

5. CONCLUSION

The results from this study showed that it is generally possible to simulate the formation of redox environments at the subsurface of coastal aquifer using the bacteria mediated solute transport model. The model is able to simulate the behaviours of the selected chemical species present in the coastal subsurface under the availability of organic carbon as the electron donor for the aerobic and anaerobic bacteria. In the natural environment the formation of reduced environments involves large number of chemical reactions and it takes very large time period also. It is not easy to include all the reactions taking place in a coastal aquifer to a numerical model. While, a simplified numerical simulation which is combined with the density dependent flow, is practical and important to understand the transport of species and bacteria mediated reduction processes which take place in the coastal aquifers.

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