MODELING AND SIMULATION OF IN SITU BIOREMEDIATION FOR TCE-CONTAMINATED GROUNDWATER THROUGH METHANE INJECTION IN KIMITSU CITY JAPAN

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ABSTRACT

A one-dimensional (1-D) numerical model was developed for simulating the *in situ* bioremediation process where trichloroeylene (TCE) in groundwater was cotabolically transformed by methane-degrading bacteria (methanotrophs). The model includes basic processes, such as advection, dispersion, and equilibrium sorption of methane, dissolved oxygen (DO), methanotrophs, and TCE. Monod kinetics with a modified competitive inhibition term between methane and TCE, cell inactivation by product toxicity from TCE transformation, and deactivation of the enzyme activity in the absence of methane were also incorporated into the model. The simulation result was compared with the data from the pilot biostimulation test at the Kururi site in Japan in 1998. The calibrated model provided good matches to the observed changes of the chemicals and methanotrophs concentrations at the two monitoring wells for the 180-day test.

KEYWORDS

bioremediation, modeling, methanotrophs, simulation, trichloroetylene

INTRODUCTION

Trichloroethylene (TCE) is a hazardous contaminant which persists for a long time in groundwater. One of the promising remediation technologies is *in situ* bioremediation, the use of microbes to convert the contaminant to safety products. Several groups of microbes can degrade TCE when grown on methane, aromatic compounds, and ammonia. This secondary oxidation process of the non-growth substrate is known as cometabolic transformation.

In Japan, a pilot test to remediate groundwater contaminated with TCE was carried out at Kururi, Kimitsu city, Chiba prefecture in 1998. Methane was selected as the lowest risky substrate for bioremediation because there are many houses near the typical contaminated sites and the groundwater is supplied as drinking water to large areas. In the pilot test, 10-20% of TCE removal was observed during the methane injection (Eguchi et al., 2001). The pilot test was successful from a safety standpoint although TCE removal efficacy was not so high.

Further public/social acceptance of *in situ* bioremediation to Japan is highly dependent on understanding the mechanism and the parameters affecting treatment efficacy of the new technology. As a method for the comprehensive study, modeling is increasingly becoming a useful tool to facilitate understanding the relative importance of various processes involved in *in situ*

bioremediation (Semprini and McCarty, 1992, Travis and Rosenberg, 1997, Soda et al., 2001). In this study, a 1-D model of TCE, methane, DO, and methanotrophs in groundwater was developed and applied to the field test data at the Kururi site.

SITE DESCRIPTION

The pilot test was carried out at 0.5-5.0 m under a private yard. Figure 1 shows the schematic recirculation system. Chemically augmented groundwater was circulated between the injection well and the recovery well located 2.25m apart (Eguchi et al., 2001). The pilot test was divided into three periods: pre-test, biostimulation test, and post-test. The pre-test was without any substrate injection for day 0-30 since 25th September 1998. The biostimulation test was operated with injection of the substrates for day 31-120. The average chemical concentrations injected into the aquifer are shown in Fig. 2. The post-test was without any substrate injection for day 121-180.

MODEL DEVELOPMENT

The aquifer was assumed to be homogenous with respect to the transport of TCE, methane, DO, and methanotrophs.

$$R\,\partial C/\partial t = \partial C/\partial x\left(D\,\partial C/\partial x\right) - U\left(\partial C/\partial x\right) + \left(dC/dt\right)^{*} \qquad \text{(Eq. 1)}$$

where C is to the aqueous-phase concentration (mg l^{-1}) of methane ([CH_4]), DO ([DO]), TCE ([TCE]), or methanotrophic population ([X]). x and t are the spatial coordinate (m) and time (d), respectively. D and U are dispersion coefficient (m^2 d^{-1}) and average hydrodynamic pore velocity of groundwater (l d^{-1}), respectively. The term $(dC/dt)^*$ refers to the biochemical reaction rate (mg l^{-1} d^{-1}).

$$R = 1 + \rho K_d / \theta \qquad \text{(Eq. 2)}$$

where R, ρ, θ and K_d are retardation factor (-), the bulk density of soil matrix (kg l^{-1}), the soil porosity (-), and the partition coefficient (l kg^{-1}), respectively. Since methane and oxygen are considered non-sorbing solute, R for those chemicals is unity. While, TCE and methanotrophs adsorb onto the aquifer solids. Eq. 1 is based on the linear and reversible equilibrium:

$$\overline{C} = K_d C \qquad \text{(Eq. 3)}$$

where $\overline{C}$ refers to the solid-phase concentration of TCE or methanotrophs (mg kg^{-1}).

Methane monooxygenase (MMO) can degrade TCE but its affinity for TCE is lower than that for methane. A modified competitive inhibition equation proposed by Chang and Alvarez-Cohen

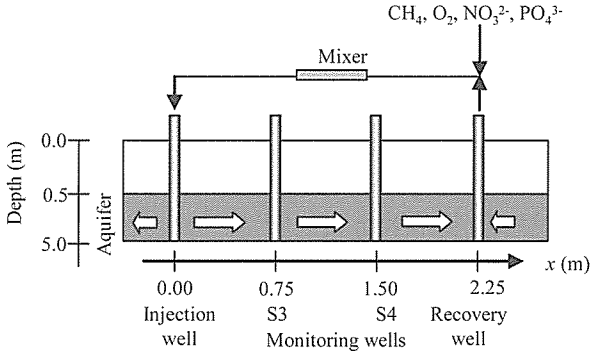

Figure 1. Scheme of the location of injection well, monitoring wells (S3 and S4), and recovery well at Kururi test site.

Table 1 Representive biochemical parameters

Parameter	Unit	Value	Literature values
k_{CH4}	mg $mg^{-1}d^{-1}$	3.0	0.53-3. 77
K_{CH4}	mg l^{-1}	0.2	0.20-6.85
K_{O2}	mg l^{-1}	0.5	0.01-1.0
k_{TCE}	mg $mg^{-1}d^{-1}$	1.0	0.152-4. 2
K_{TCE}	mg l^{-1}	5.0	1. 94-7. 0
b	d^{-1}	0.1	0.1-0. 55
b_d	d^{-1}	1.0	1. 0
Y	mg-cells mg-TCE^{-1}	0.35	0.33-0. 65
T_c	mg-TCE mg-$cells^{-1}$	0.03	0. 01-0.13
F_{TCE}	mg-DO mg-TCE^{-1}	0.3	0.3-0.49
F_{CH4}	mg-DO mg-CH_4^{-1}	2.2	2.2-4. 0
F_{decay}	mg-DO mg-$cells^{-1}$	1.42	1.42

(1995) was applied to cometabolic biodegradation between methane and TCE by metahnotrophs.

$$\left(\frac{d[CH_4]}{dt}\right)^* = -k_{CH4}\frac{[CH_4]}{[CH_4]+K_{CH4}(1+[TCE]/K_{TCE})}\frac{[DO]}{[DO]+K_{DO}}[X_{TL}] \quad \text{(Eq. 4)}$$

where k and K are maximum specific degradation rate (mg mg-cells^{-1} d^{-1}) and half saturation constant (mg l^{-1}). Eq. 4 assumes that methane is degraded by methanotrophs in both the aqueous phase X and the solid phase $\overline{X}$. Methanotrophic population on pore basis ([X_{TL}]) is defined as:

$$[X_{TL}] = [X] + \rho[\overline{X}]/\theta \quad \text{(Eq. 5)}$$

Nitrogen and phosphorous are also important factors for bacterial growth but those were added into the groundwater enough not to limit the biodegradation rates (Eguchi et al., 2001).

The net cell growth can be described as follows:

$$\left(\frac{d[X_{TL}]}{dt}\right)^* = -Y\left(\frac{d[CH_4]}{dt}\right)^* + \frac{1}{T_c}\left(\frac{d[TCE]}{dt}\right)^* - b\frac{[DO]}{[DO]+K_{DO}}([X_{TL}]-[X_{TLmin}]) \quad \text{(Eq. 6)}$$

where b, Y, and T_c are endogenous decay constant (d^{-1}), yield (mg-cells mg-CH_4^{-1}), and transformation capacity (Alvarez-Cohen and McCarty, 1991) (mg-TCE mg-cells^{-1}). It was assumed that methanotrophs maintain their minimum population X_{TLmin} because they can survive on naturally-occurring substrates even in the absence of methane.

It was assumed that TCE is degraded only in the aqueous phase.

$$\left(\frac{d[TCE]}{dt}\right)^* = -F_a k_{TCE}\frac{[TCE]}{[TCE]+K_{TCE}(1+[TCE]/K_{CH4})}\frac{[DO]}{[DO]+K_{DO}}[X_{TL}] \quad \text{(Eq. 7)}$$

where F_a is the fraction of methanotrophic population active towards the cometabolic transformation (Semprini and McCarty, 1992). The model assumes that when methane is absent, deactivation of MMO activity occurs and the value of F_a decreases.

$$\begin{cases} F_a = 1.0 & (d[X_{TL}]/dt)^* \geq 0 \\ dF_a/dt = -b_d F_a & (d[X_{TL}]/dt)^* < 0 \end{cases} \quad \text{(Eq. 8)}$$

where b_d (d^{-1}) is the rate constant for a first-order deactivation process. Whenever net growth of methanotrophs occurs, F_a is rest to unity.

The electron acceptor DO is consumed by methane oxidation, TCE degradation, and cell decay.

$$\left(\frac{d[DO]}{dt}\right)^* = -F_{CH4}\left(\frac{d[CH_4]}{dt}\right)^* - F_{TCE}\left(\frac{d[TCE]}{dt}\right)^* - F_{decay}b\frac{[DO]}{[DO]+K_{DO}}([X_{TL}]-X_{TLmin}) \quad \text{(Eq. 9)}$$

where F_{CH4}, F_{TCE}, and F_{decay} are the stoichiometric ratio of consumed oxygen to methane, TCE, and cells in the reactions, respectively.

The initial condition was set at a spatially constant value for methane 0.0 mg l^{-1}, TCE 0.0 mg l^{-1}, dissolved oxygen 5.0 mg l^{-1} and methanotrophs 3.0x10^{-5} mg l^{-1}. The inlet boundary conditions were defined as shown in Fig. 2. A transmissive boundary condition was used for the outlet boundary.

RESULTS AND DISCUSSION

The biochemical parameter values used in this study is summarized in Table 1. The rate coefficients were assumed to be constant in time and independent of groundwater temperature. Information on the biochemical parameters is lacking but the values were calibrated within the reported range.

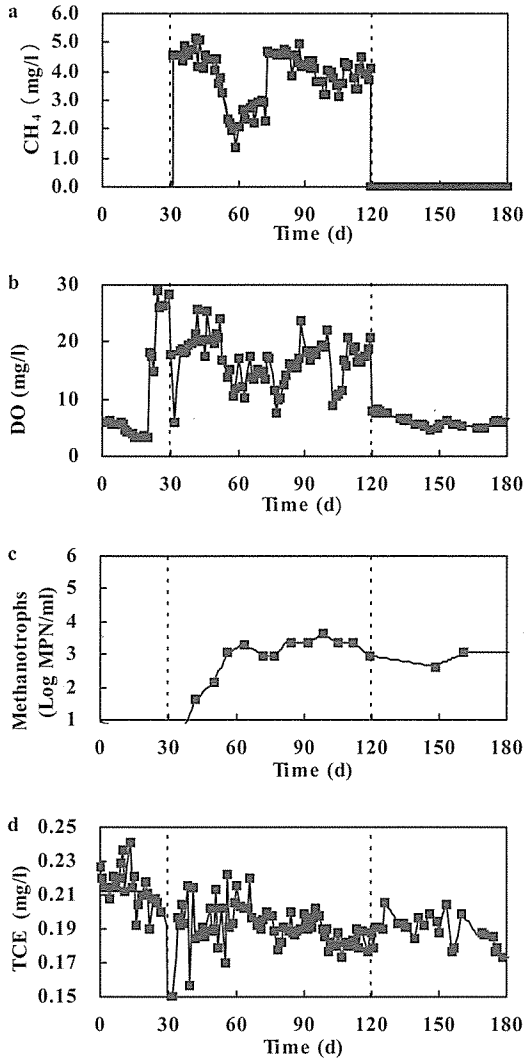

Figure 2. Boundary conditions used for simulation at the injection. (a)CH_4, (b) DO, (c) methanotrophs, and (d) TCE. The boundary conditions (line) were prepared by linear interpolation of the field data (closed square).

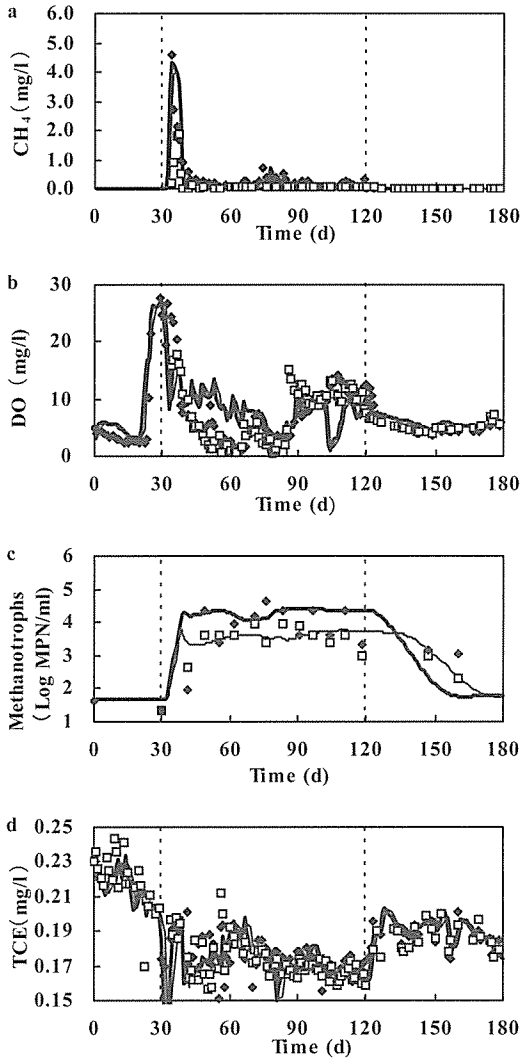

Figure 3. Simulated concentrations of (a)CH_4, (b) DO, (c) methanotrophs, and (d) TCE vs time at the S3 (bold line) and S4 (fine line) wells. The field data at the S3 (closed diamond) and S4 (open square) wells are also shown.

Methane, DO, methanotrophs, and TCE concentrations at sampling wells S3 and S4 are shown in Fig. 3. The simulated methane concentration showed good match with the field data. The methane concentration at the S3 well reached 4.6 mg/l on day 34 and decreased rapidly below the detection limit. The DO concentration reached 28 mg/l on day 31, subsequently decreased mainly by the methane oxidation.

Methanotroph population increased remarkably in the biostimulation test period with decrease in methane concentration. For convenience, it was assumed that 1.0mg of the methanotroph population corresponds to 10^8 MPN (most-probable-number) to compare the simulation results with the field data. F_a at the S3 and S4 wells in day 31-40 was unity when the population grew rapidly, and fluctuated between 0.0-1.0 in day 41-120 (data not shown). In the post-test period, MMO was deactivated ($F_a = 0.0$) and methanotrophic population decreased gradually by endogenous decay.

Corresponding to the establishment of the methanotroph population, decrease in TCE concentration was observed after day 40. TCE degradation depended highly on the methane concentration at the injection well (Fig. 2a). Responding to the fluctuations of the injected methane concentration, the simulated TCE concentration was about 0.16-0.17 mg/l during day 40-55, increased to 0.17-0.19 during day 60-75, then decreased again 0.16-0.17 mg/l during day 75-120. After methane injection was stopped on day 120, the TCE concentration returned rapidly to the original level.

CONCLUSIONS

The simulation results successfully recreated the time changes of methane, DO, TCE, and methanotrophs concentrations. Model studies comparing the simulated and field data of the *in situ* bioremediation process are very scarce. Such model works for bioremediation of TCE-contaminated groundwater utilizing methanotrophs were reported by only at the Moffet Federal Airfield (Senprini and McCarty, 1992) and the U. S. Department of Energy's Savannah River site (Travis and Rosenberg, 1997) as far as we know. The model developed in this study is a successful effort to understanding its mechanism, considering the complexity of the problem. The simulation models coupled with experimentally-based approaches will allow discussing the efficacy and the safety of bioremediation.

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