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DEGRADATION OF CHLORINATED ETHENES AT A GROUNDWATER REMEDIATION SITE USING IN-SITU BIOREMEDIATION

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SYNOPSIS

The aim of this paper is to evaluate the results of a field trial on groundwater remediation by in-situ bioremediation using reductive dechlorination of chlorinated ethenes at a site contaminated with tetrachloroethylene. Daughter products such as dichloroethylenes and ethene were observed which increased in the monitoring well during the field test in response to the increased reductive conditions of the aquifer. Moreover, it was shown that the first order rate constants of all chlorinated ethenes were several orders higher than those under natural aquifer conditions. These findings revealed that this technique can be used to accelerate reductive dechlorination of chlorinated ethenes in an aquifer.

INTRODUCTION

Groundwater extraction methods (Pump-and-Treat) are the most commonly employed methods of remediating aquifers contaminated with chlorinated ethenes such as tetrachloroethylene (PCE) and trichloroethylene (TCE). However, the technology required for such tasks is often difficult to apply at sites where contamination has spread over a large area and the concentration is low, where there is no sewage system at the surface, or where the contamination must be treated within a short period. At sites such as these, the application of an in-situ bioremediation technique that employs degradation is more useful than a Pump-and-Treat. There are several types of in-situ bioremediation techniques that can be used to biologically degrade chlorinated ethenes in an aquifer. Anaerobic biostimulation, which activates intrinsic microorganisms under the anaerobic conditions of the aquifer, is applied in this study.

Dichloroethylenes (DCEs) and vinyl chloride (VC) are often detected in aquifers contaminated by PCE and TCE, suggesting that PCE and TCE are reductively dechlorinated in the aquifer. Consequently, the acceleration of reductive dechlorination of chlorinated ethenes could facilitate an effective groundwater remediation strategy. While reductive dechlorination is generally slower than aerobic degradation, it is the only way to degrade PCE within an aquifer. This has meant that the application of in-situ bioremediation

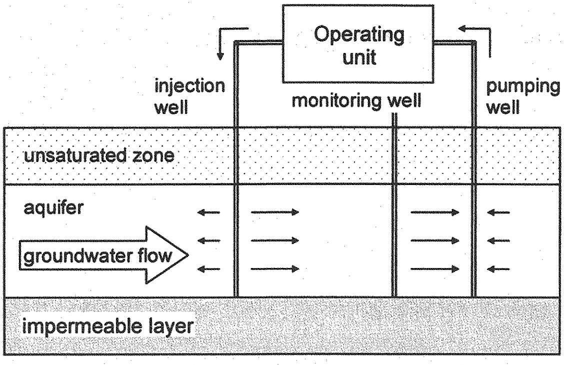

Fig. 1 Schematic illustration of the technology employed in the field test

using reductive dechlorination has increased recently. In this process, electron donors such as the polylactate ester (1), ethanol (2), carbohydrate solution with sodium sulfate (3), among others, have been supplied to aquifers in order to accelerate reductive dechlorination.

In this work, the authors have assessed the potential application of L-lactic acid as an electron donor for application to in-situ anaerobic bioremediation for several years. The results of a field test on groundwater remediation employing in-situ bioremediation at a site contaminated by PCE were evaluated. In the field test, groundwater was made to circulate at a remediation site by means of injection-and-pumping wells. Given that it is very important to consider the flow of groundwater when evaluating the degradation of chlorinated ethenes in detail, a numerical simulation was employed using field test data.

FIELD TESTS

Field test description

Figure 1 shows a schematic illustration of the technology employed in the field trial. Groundwater is made to circulate at a remediation site using injection-and-pumping wells. An additive is added to the groundwater in the operating unit at the surface, which activates the intrinsic microorganisms and subsequently accelerates the microbial degradation of chlorinated ethenes in the aquifer. The additive used in this study was a compost extract consisting of organic acids, mainly L-lactic acid, and several minerals.

Chlorinated ethenes are subject to a variety of microbial degradation processes, including reductive dechlorination, anaerobic oxidation, aerobic oxidation and aerobic cometabolism (4). In this study, reductive dechlorination was the most important degradation process because it is not possible for PCE to be biologically degraded in an aquifer by any other processes. Consequently, the purpose of the field test was to dechlorinate PCE via TCE, DCEs and VC to ethene within the aquifer of the study site.

The groundwater contamination at the site was caused by the leakage of PCE from drums left outside. Geological characteristics of the site are the surface soil from the ground surface to G.L. - 0.5 m, loam from G.L. - 0.5 m to G.L. - 1.5 m, sand layer from G.L. - 1.5 m to G.L. - 3.5 m, and gravel layer from G.L. - 3.5 m to G.L. - 4.5 m with an impermeable clay layer underlying the gravel layer, making the aquifer unconfined. The aquifer is approximately 1 m thick and the actual groundwater velocity is 3.0 m/d.

Figure 2 shows the location of monitoring and injection-and-pumping wells. The field test was conducted in a part of the contaminated site by means of seven injection-and-pumping and four monitoring wells constructed at the study site. One of the monitoring wells was constructed downstream from the contaminated site and is not shown in Figure 2. This monitoring well was also used as a pumping well to prevent contamination from spreading.

Table 1 lists the operating conditions for the field tests. Two different operations were conducted over a 10-week period to evaluate the relative efficacies of two methods for the reductive dechlorination of chlorinated ethenes. The former 5-week operation is referred to as Run 1 and the latter as Run 2 in this paper, each of which were continuous operations. The injection and pumping rate of groundwater and the application rate of additive in Run 2 were less than those used in Run 1. The placement of injection-and-pumping wells was also revised in Run 2 because the direction of groundwater flow differed from that estimated before conducting the field test. However, this revision did not affect the direction of groundwater flow near monitoring well No. 2. The concentrations of chlorinated ethenes were measured by

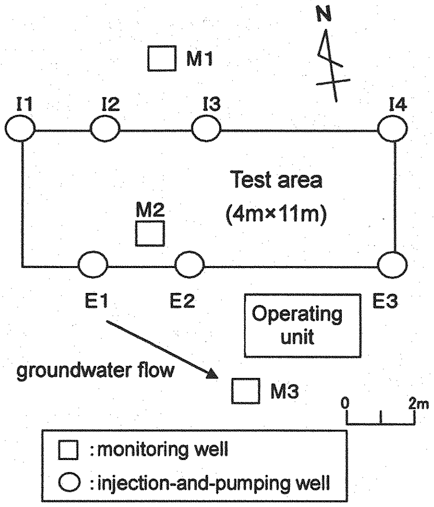

Fig. 2 Location of monitoring and injection-and-pumping wells

Table 1 Operating conditions

	Run1	Run2
monitoring well	M1,M2,M3	
injection well	I1-I4	E1, I1-I3
injection rate (m^3/d)	30.96	5.472
pumping well	E1-E3	E2,E3
pumping rate (m^3/d)	30.96	5.472
rate of additive (L/d)	1.64	0.8

means of a gas chromatograph (HP6890/5972 or HP6890).

Concentrations of electron acceptors

Figure 3 shows the variations in the concentrations of electron acceptors in monitoring wells No. 1, No. 2 and the operating unit at the surface over time. No nitrates were detected in monitoring well No. 2 inside the field test area at the time of initiating Run 1 as a result of adding additive. Similarly, no oxygen was detected at the beginning of Run 2, and sulfate concentrations decreased markedly as a result of adding an additive. In monitoring well No. 1 outside the field test area, except for the nitrate concentrations on the 13th of February, only minor changes were observed in the concentrations of electron acceptors while the study was being carried out. On the other hand, the concentrations in the operating unit changed as much as those in the monitoring well No.2 but were a little higher than those in the monitoring well No.2.

Assays of the concentrations of electron acceptors revealed that the reductive condition of the aquifer outside the field test area did not change during the field test. However, since the reductive condition of the aquifer at the study site continued to increase over the course of the experiment, the aquifer in Run 2 had a higher reductive potential than it did in Run 1.

Concentrations of chlorinated ethenes

Figure 4 shows the variations in the concentrations of chlorinated ethenes in the monitoring wells No. 1, No. 2 and the operating unit at the surface over time. Before Run 1, in monitoring well No. 2 within the field test area, the concentrations of PCE, TCE and DCEs were higher than VC. The concentration of VC was one order lower than those of the other chlorinated ethenes assayed and ethene was not detected. Except on the 13th of February, the concentrations of PCE and TCE were one order lower than the initial values during the field test. The concentrations of DCEs and VC were similar to initial values. The concentration of ethene began to increase soon after the initiation of Run 2 and reached 0.1 mg/L upon termination of Run 2. Subsequent to Run 2, the concentrations of chlorinated ethenes returned to their initial values, as the

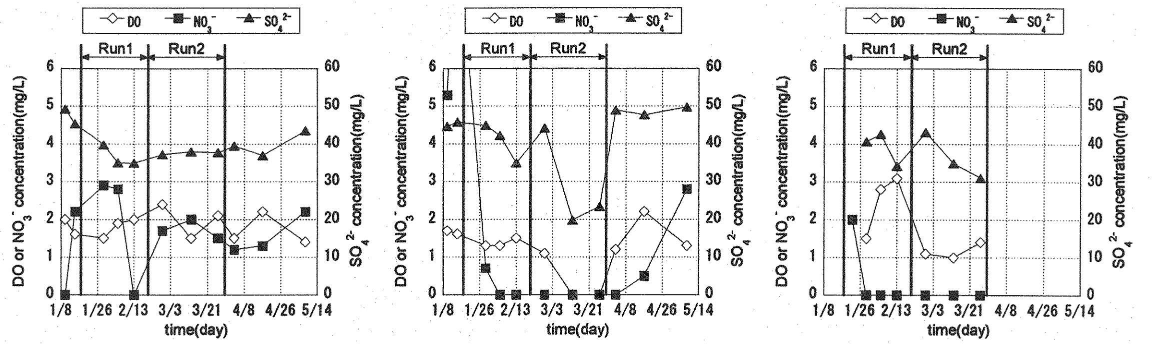

Fig. 3 Concentrations of electron acceptors
(Left : Monitoring well No. 1, Center : Monitoring well No. 2, Right : Operating unit)

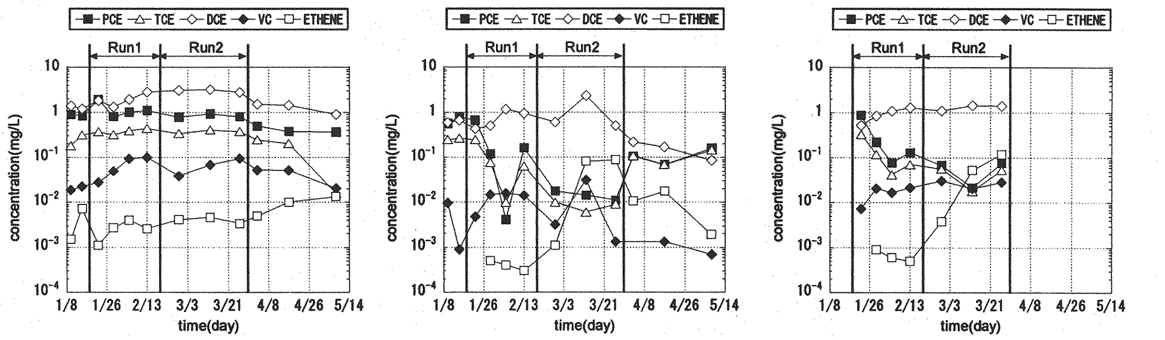

Fig. 4 Concentrations of chlorinated ethenes
(Left : Monitoring well No. 1; Center : Monitoring well No. 2; Right : Operating unit)

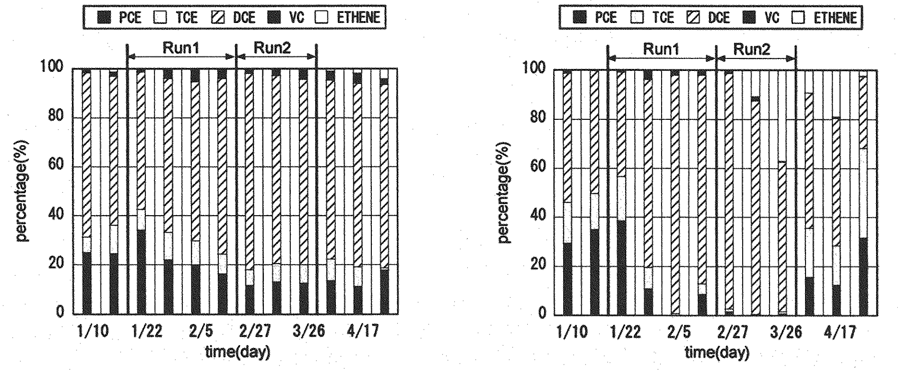

Fig. 5 Percentages of mole concentrations of chlorinated ethenes
(Left : Monitoring well No. 1; Right : Monitoring well No. 2)

contaminated groundwater flowed in the field test area from the outside contamination area. However, except for the concentration of ethene at the end of Run 2, the concentrations of chlorinated ethenes in monitoring well No. 1 were higher than those in monitoring well No. 2 with these concentrations remaining relatively unchanged. While slightly higher than those in the well, the concentrations of chlorinated ethenes in the operating unit changed as much as those in the monitoring well No. 2.

In order to evaluate the extent of the various reductive dechlorination reactions of chlorinated ethenes in detail, Figure 5 shows the percentages of mole concentrations of chlorinated ethenes in the monitoring wells No. 1 and 2. The percentages of PCE and TCE decreased while that of DCEs increased over time in monitoring well No. 2 during Run 1. During Run 2, the percentages of ethene increased while that of DCEs decreased over time. However, the ratios of chlorinated ethenes in monitoring well No. 1 were not found to change during the field test.

According to the results of the field test, the reductive dechlorination of chlorinated ethenes did not increase outside the field test area. However, the ratios of less chlorinated ethenes such as the DCEs and ethene within the field test area were observed to increase over time. These data proves that by supplying additive to the aquifer the rate of reductive dechlorination can be accelerated. Furthermore, the increase in the concentration of ethene observed during Run 2 meant that this technology could be used to completely purify a groundwater contaminated by PCE. Although the period over which this study was conducted was relatively short, the findings confirmed a decrease in the concentrations of PCE and TCE, maintenance of VC concentrations, and an increase in the concentration of ethene. However, the concentration of DCEs remained relatively unchanged and high. PCE is reductively dechlorinated via TCE, DCEs and VC to ethene, suggesting that the degradation rate of each chlorinated ethene is very important for evaluating reductive dechlorination in an aquifer. In the numerical simulation described below, the monitoring data is used to evaluate reductive dechlorination from the viewpoint of degradation rate.

NUMERICAL SIMULATION

Model description

The thickness of the aquifer is approximately 1 m and the screen lengths of injection-and-pumping wells were the same as the thickness of the aquifer, which meant that the vertical flow of groundwater was considered to be negligible. A horizontal two-dimensional model was adopted in this study.

Groundwater flow equation:

$$S\frac{\partial h}{\partial t}=k\frac{\partial^2 h}{\partial x^2}+k\frac{\partial^2 h}{\partial y^2}\pm Q\delta(x-x')(y-y') \tag{1}$$

PCE transport equation:

$$\begin{aligned}&\frac{\partial C_P}{\partial t}+\frac{\partial(v_x C_P)}{\partial x}+\frac{\partial(v_y C_P)}{\partial y}=\frac{\partial}{\partial x}\left(D_{xx}\frac{\partial C_P}{\partial x}+D_{xy}\frac{\partial C_P}{\partial y}\right)+\frac{\partial}{\partial y}\left(D_{yx}\frac{\partial C_P}{\partial x}+D_{yy}\frac{\partial C_P}{\partial y}\right)\\&-K_P C_P\pm QC'_P\delta(x-x')(y-y')\end{aligned} \tag{2}$$

TCE transport equation:

$$\begin{aligned}&\frac{\partial C_T}{\partial t}+\frac{\partial(v_x C_T)}{\partial x}+\frac{\partial(v_y C_T)}{\partial y}=\frac{\partial}{\partial x}\left(D_{xx}\frac{\partial C_T}{\partial x}+D_{xy}\frac{\partial C_T}{\partial y}\right)+\frac{\partial}{\partial y}\left(D_{yx}\frac{\partial C_T}{\partial x}+D_{yy}\frac{\partial C_T}{\partial y}\right)\\&+Y_{T/P}K_P C_P-K_T C_T\pm QC'_T\delta(x-x')(y-y')\end{aligned} \tag{3}$$

where $\boldsymbol{S}$ = specific storage coefficient; $\boldsymbol{h}$ = hydraulic pressure head; $\boldsymbol{k}$ = hydraulic conductivity; $\boldsymbol{Q}$ = injection or pumping rate; C_P, C_T = concentrations of PCE and TCE; v_x, v_y = actual groundwater velocities; D_{xx}, D_{xy}, D_{yx}, D_{yy} = dispersion coefficients; K_P, K_T = first order rate constants for PCE and TCE degradation; $Y_{T/P}$ = molecular weight ratio between TCE and PCE; $\delta(x-x')(y-y')$ = dilac function; x',y' = grid points of the injection or pumping wells; C'_P, C'_T = concentrations of PCE and TCE in the operating unit (at injection points) or in a pumping well (at pumping points). The transport equations of DCEs and VC are not shown in this paper because they have the same forms as equation (3).

A first-order kinetic was applied to simulate changes in the concentrations of chlorinated ethenes by microbial degradation. The third right-hand term in equation (2) shows the degradation of PCE. The third right-hand term in equation (3) shows the production of TCE due to the degradation of PCE, while the fourth right-hand term in equation (3) shows the degradation of TCE. The Monod kinetic was found to be suitable for the simulation of reductive dechlorination of chlorinated ethenes in an aquifer (5). However, it was quite difficult to derive a correct half-saturation constant for use with the Monod kinetic equation using a field data, and differences of a few orders were reported for values obtained for laboratory experiments (5,6). Alternately, a zero-order kinetic has proved to be more appropriate than the first-order kinetic for concentrations above a few μM or above the low mg/L range (5). However, since the concentrations of chlorinated ethenes at our study site were approximately 1 mg/L or less, we applied the first-order kinetic to our numerical simulations.

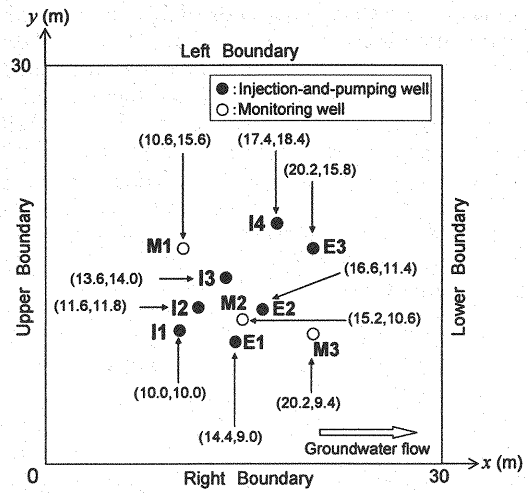

Fig. 6 Simulation area

Table 2 Simulation parameters

Parameter	Value
Space increment: $\Delta x, \Delta y$ (m)	0.2,0.2
Time increment: Δt (s)	60
Hydraulic conductivity (m/s)	4×10^{-4}
Specific storage coefficient: (1/m)	0.25
Longitudinal dispersivity: α_L (m)	0.5
Transverse dispersivity: α_T (m)	0.05
Molecular diffusion coefficient: D_M (m^2/s)	1.0×10^{-9}
Pumping and ingection rate in Run1: Q (m^3/s)	3.58×10^{-4}
Pumping and ingection rate in Run2: Q (m^3/s)	6.33×10^{-5}

Figure 6 shows the simulation area to which the finite difference method was applied. The monitoring data for groundwater level and the concentrations of chlorinated ethenes in the monitoring wells before Run 1 were linear interpolated to yield the initial values for all grid points. The Dirichlet boundary condition was used as the upper boundary condition for groundwater flow and transport equations. The values of the upper boundary for the groundwater flow equation were given by the monitoring data for groundwater level in the monitoring wells No.1 and the average hydraulic gradient in the site. The monitoring data for the concentrations of chlorinated ethenes in the monitoring wells No.1 were used as the values of the upper boundary for the transport equations. The left, right and lower boundaries were given by Neumann boundary conditions.

Table 2 shows the simulation parameters used for the model. The hydraulic conductivity was calculated using Darcy's law. The actual groundwater velocity was 3.0 m/d, groundwater gradient was 0.021 and volumetric water content was 0.25 at the site before the field test. The specific storage coefficient of the unconfined aquifer was calculated by means of volumetric water content (0.25) and aquifer thickness (1 m). The longitudinal dispersivity was defined after considering scale dependency. The field test area was 11 m*4 m and a value of 0.5 m (from the literature) was used for longitudinal dispersivity (7). One tenth of the longitudinal dispersivity was applied for transverse dispersivity.

Groundwater flow

Figure 7 shows the groundwater flows at the steady state in Run 1 and Run 2. In Run 1, the rate of groundwater flow near monitoring well No. 2 was calculated as 23.2 m^3/d using simulated flow nets made using injection wells I1, I2, and I3, and pumping wells E1 and E2. This value was almost equal to the injection volume of injection wells I1, I2 and I3. Therefore, it was found that almost all of the groundwater that flows near monitoring well No. 2 circulated in the field test area. The average actual velocity within the field test area was 10.0 m/d, which was larger than that observed outside the area.

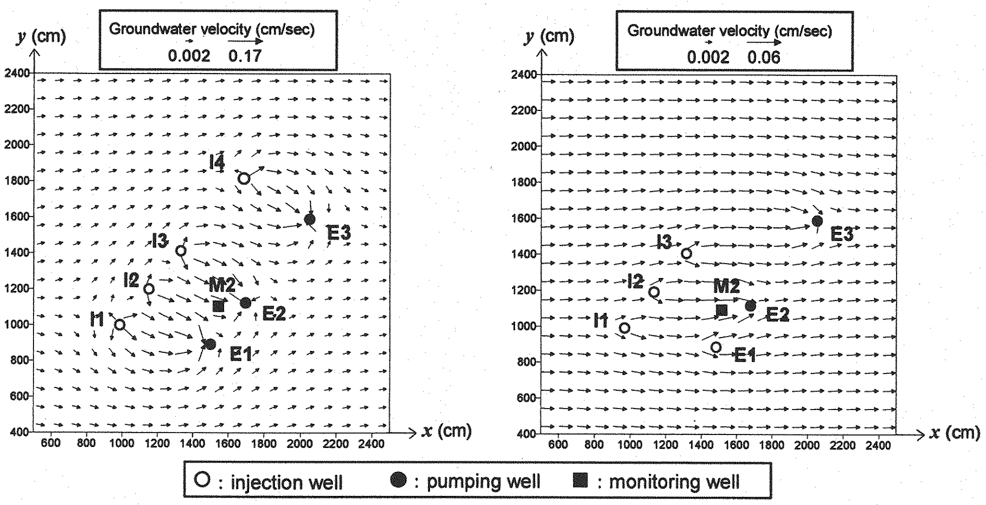

Fig. 7 Simulated groundwater flow (Left : Run 1; Right : Run 2)

Table 3 First order rate constants of chlorinated ethenes obtained in the numerical simulation

	week	PCE	TCE	DCE	VC
		K_P (1/d)	K_T (1/d)	K_D (1/d)	K_V (1/d)
Run1	1	0.75	2.40	1.70	95.00
	2	1.88	4.00	1.77	40.00
	3	9.50	7.75	0.15	8.65
	4	–	0.28	0.90	43.00
Run2	1	4.15	9.00	1.50	185.00
	3	4.50	12.00	0.09	4.00
	5	5.00	9.20	1.65	350.00

However, in Run 2, the rate of groundwater flow near monitoring well No. 2, calculated using simulated flow nets made using injection wells I1 and I2 and pumping well E2, was 3.57 m^3/d. This was larger than the injection volume of 2.74 m^3/d from injection wells I1 and I2. Therefore, groundwater flows near monitoring well No. 2 consisted of 2.74 m^3/d circulating groundwater and 0.83 m^3/d groundwater from upstream. The average actual groundwater velocity within the field test area was 4.0 m/d; slightly larger than that outside the field test area.

First order rate constants

The first order rate constants for chlorinated ethenes were determined by trial and error. The concentrations of chlorinated ethenes were measured at one- or two-week intervals during the field test. Consequently, first order rate constants were determined such that the numerical simulation results corroborated the decreases observed in concentrations of chlorinated ethenes during each measurement interval. In short, the first order rate constant for every measurement interval was derived for the simulation. Also, since first order rate constants under natural aquifer conditions were not clear, values reported in the literature were adopted (8), namely, 3.5×10^{-4}/d for PCE, 7.0×10^{-4}/d for TCE, 7.5×10^{-4}/d for DCEs and 6.0×10^{-3}/d for VC.

Table 3 shows the first order rate constants determined by numerical simulation. The value of PCE for the fourth week could not be calculated because the PCE concentration at monitoring well No. 2 was larger than it was at the injection wells. We assumed that the first order rate constant of PCE was the same as that of the natural aquifer and calculated those of the other three chlorinated ethenes accordingly. Consequently, the values obtained for TCE, DCEs and VC have low accuracies. Figure 8 shows the concentrations of chlorinated ethenes determined by means of a numerical simulation and by assay. A comparison of these values reveals that the values derived using the numerical simulation corroborates those measured in the field

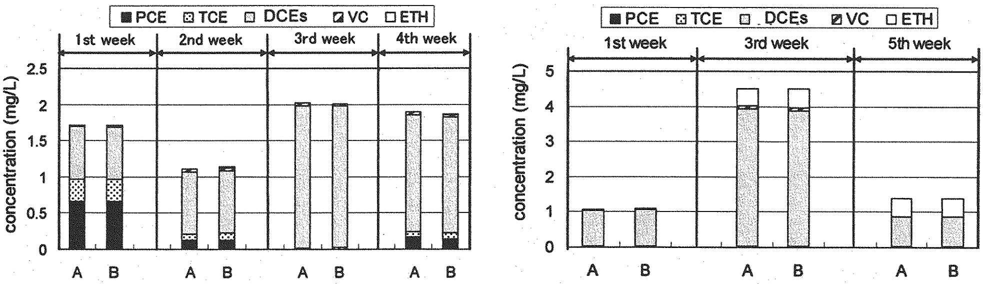

Fig. 8 Monitored and calculated concentrations of chlorinated ethenes
(A : Monitored; B : Calculated; Left : Run 1; Right : Run 2)

Table 4 Previously published first order rate constants for chlorinated ethenes under natural aquifer conditions

References	First order rate constant (×10^{-3}/d)			
	PCE	TCE	DCE	VC
Nakashima et al. (2002), (1)	0.41	2.2	0.55	—
Clement et al. (2000), (8)	0.32-0.40	0.45-0.90	0.65-0.85	4.0-8.0
Barton et al. (2000), (9)	0.28-1.6	0.36-2.0	0.5-2.5	—
Clement et al. (2002), (10)	5.0	5.0	5.0	0.6
Yunwei suna et al. (2001), (11)	—	3.1	2.5	3.8
Chapelle and Bradley (1998), (12)	—	5.0-20	10-40	—

very well.

Table 4 shows first order rate constants under natural aquifer conditions in the literature, with most ranging between 10^{-4}/d to 10^{-2}/d. On the other hand, the range in first order rate constants simulated in this study were from 10^{-2}/d to 10^{2}/d, which was larger than that observed under natural aquifer conditions by more than a few orders. Based on these findings, it became clear that reductive dechlorination of chlorinated ethenes was accelerated by means of this technology.

Characteristics of degraded chlorinated ethenes

In this section, the characteristics of microbially-degraded chlorinated ethenes are evaluated using the obtained first order rate constant. The first order rate constants of PCE and TCE exhibited similar tendencies. In Run 1, the first order rate constants tended to increase except for the values of the fourth week when the accuracy of the simulation was low. In Run 2, however, the first order rate constants were more stable and larger than those obtained in Run 1. According to the concentration of electron acceptors in Figure 3, the reductive condition of the aquifer in Run 2 was greater than it was in Run 1. As a result, the stable reductive dechlorination of PCE and TCE may have had the effect of increasing the first order rate constants.

The first order rate constant of DCEs was smaller than those of PCE and TCE. The tendency to undergo reductive dechlorination decreases with decreasing number of chlorine atoms present in the molecule. Given their relatively fewer chlorine atoms, the first order rate constant for DCEs were smaller than those of PCE and TCE. As a result, the concentrations of DCEs would not be observed to decrease during the field test. However, DCEs could be anaerobically oxidized to CO_2 and chloride under iron- and manganese-reducing conditions (4), and a larger first order rate constant for DCEs relative to TCE in an aquifer that was under iron and manganese-reducing conditions has been reported (12). The aquifer conditions in this field test changed from being aerobic or nitrate-reducing to sulfate-reducing, indicating that the aquifer has been under iron- or manganese-reducing conditions at one stage. However, the first order rate constant of DCEs was never larger than that of TCE during this study. Since there are many uncertainties associated with the anaerobic oxidation of DCEs, further investigations are necessary.

The first order rate constant of VC was the largest of the four chlorinated ethenes. Since the degradation of VC is the final stage in the detoxification of PCE, this finding indicates that this technology had the effect of completely purifying a groundwater contaminated by PCE. However, the slower reductive dechlorination of VC relative to the other chlorinated ethenes could not stoichiometrically be explained by the finding that its first order rate constant was more than several-fold higher than those of PCE and TCE. Other processes may have contributed to the rates of VC-degradation at the site. For example, VC can be anaerobically oxidized to CO_2 and chloride under iron-reducing conditions. Based on aquifer conditions during the field test, the first order rate constant of VC may have increased relative to the other ethenes due to the anaerobic oxidation of VC. However, it was not possible to examine other degradation processes of VC in detail using the field test data. However, relatively higher first order rate constants for VC compared to other chlorinated ethenes has been reported previously (8,11), indicating that a similar finding in this study is not atypical. The degradation processes associated with VC therefore need to be further investigated because the increase in the degradation of VC directly affects the performance of bioremediation efforts.

CONCLUSION

This paper evaluated the results of a field test on in-situ anaerobic biostimulation at a site contaminated with PCE. The results obtained in this study can be summarized as follows:

First, in a monitoring well within the test area in the field, it was found that the ratios of chlorinated ethenes with fewer chlorides increased over the duration of this study. Of particular relevance was the increase in the concentration of ethene observed at the end of the field test, indicating that the application of this technology could render PCE harmless.

Secondly, the results of numerical simulations revealed that the first order rate constants of chlorinated ethenes were larger than those under natural aquifer conditions by more than a few orders. This finding provides evidence that this technology is very useful for accelerating the reductive dechlorination of chlorinated ethenes in an aquifer.

Thirdly, the first order rate constants of PCE and TCE tended to be high and stable under highly reductive conditions.

Fourthly, the first order rate constant of DCEs increased to levels that were higher than those normally observed under natural aquifer conditions, but remained less than those of PCE and TCE. This was because of the tendency of reductive dechlorination to decrease in proportion to the number of chlorine atoms present in a molecule.

Finally, the first order rate constant for VC was the largest of the four chlorinated ethenes assayed in this study. However, degradation by processes such as aerobic and anaerobic oxidation, as well as abiotic degradation, may have contributed to the relatively higher first order rate constant of VC in the aquifer.

The results of this field test demonstrated the potential of this technology to successfully remediate a groundwater site contaminated by PCE. Future research should concentrate on elucidating those degradation processes that could not be determined in this study, and should also focus on optimizing the application of this technology.

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APPENDIX – NOTATION

The following symbols are used in this paper:

S = specific storage coefficient;

h = hydraulic pressure head;

Q = injection or pumping rate;

C_P, C_T = concentrations of PCE and TCE;

D_{xx}, D_{xy}, D_{yx}, D_{yy} = dispersion coefficients;

K_P, K_T = first order rate constants for PCE and TCE degradation;

$Y_{T/P}$ = molecular weight ratio between TCE and PCE;

$\delta(x-x')(y-y')$ = dilac function; and

C'_P, C'_T = concentrations of PCE and TCE in the operating unit.

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