Journal of Hydroscience and Hydraulic Engineering
Vol. 22, No.2 November, 2004, 105-111

NATURAL ATTENUATION OF TRICHLOROETHYLENE AND DICHLOROETHYLENE AT A GROUNDWATER REMEDIATION SITE

By

N. Egusa

Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan

T. Kakuo

Graduate School of Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan

T. Hirata

Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan

Y. Yoshioka

Hyogo Prefectural Institute of Public Health and Environmental Sciences,
3-1-27 Kotohiramachi, Sumaku, Koube 654-0037, Japan

and

O. Nakasugi

National Institute of Environmental Studies, 16-2 Onogawa, Tsukuba 305-0053, Japan

SYNOPSIS

The purpose of this paper is to evaluate the effects of natural attenuation of trichloroethylene (TCE) and dichloroethylene (DCE) at a groundwater remediation site. Field observations revealed that TCE was degraded in the aquifer and that concentrations of DCE, a daughter product of TCE, was maintained at levels of approximately 64% of TCE concentrations. In order to examine the rate of degradation of both substances in the aquifer, first order rate constants for TCE and DCE degradations were estimated by numerical simulation. The first order rate constants for TCE and DCE ranged between $1.5*10^{-3}$ to $15.0*10^{-3}$/day, and $3.1*10^{-3}$ to $31.0*10^{-3}$/day, respectively. The above findings suggest that DCE was degraded more easily than TCE in the aquifer and that this was probably attributed to anaerobic oxidation of DCE at this site.

INTRODUCTION

Since the late 1990s, the major emphasis of studies of soil and groundwater contamination by volatile organic compounds (VOCs) has shifted from the investigation of contamination mechanisms and the establishment of field survey methods, to the development of remediation techniques. These innovative techniques have been actively developed as an alternative to soil removal and groundwater extraction (usually called pump-and-treat) and treatments such as soil vapour extraction, air sparging, bioremediation, reactive barriers and others have become practicable.

The assessment of natural attenuation in aquifers, called monitored natural attenuation (MNA), is currently regarded as an important remediation method (McCarty and David (1)). Active remediation measures, such as pump-and-treat or soil vapour extraction techniques that forcibly extract contaminants from the subsurface environments, are most effective when contaminant concentrations are high. However, the effectiveness of these techniques decreases markedly as the contaminant concentrations decrease. This means that the cost benefits associated with remediation also decrease considerably with time and, consequently, extended periods of remediation cause a sharp increase in the total costs involved. In order to prevent such sharp increases in operation costs and to treat the subsurface environment effectively, MNA can be used in conjunction with an active remediation technique. For example, at sites where natural attenuation is low, active remediation techniques should be continued until such time as the contaminant concentrations are reduced to levels that meet environmental standards. Conversely, at sites where natural attenuation is

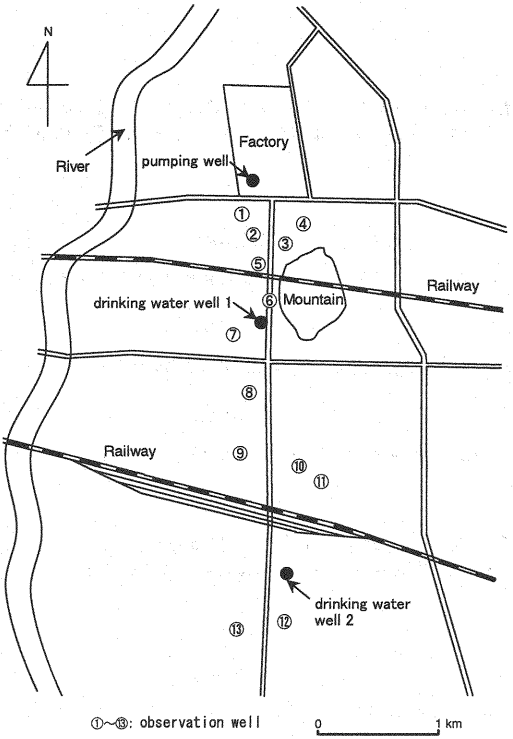

Fig. 1 Horizontal location of pumping well and observation wells

high, the decrease in contaminant concentrations by natural attenuation can be expected to occur. Active remediation techniques are thus stopped when the contaminant concentrations still exceed environmental standards, with natural attenuation bringing concentrations down to levels below environmental standards thereafter. In such cases, continuous monitoring of groundwater quality is undertaken once active remediation has ceased. As a result, the remediation time and costs can be reduced because the period over which active remediation is conducted can be shortened considerably.

Natural attenuation includes processes such as biotic and abiotic degradation, dispersion, dilution, absorption, and volatilization of a contaminant in an aquifer. The processes of biotic and abiotic degradation are known to be particularly important destructive attenuation mechanisms in MNA; therefore it is necessary to evaluate the effects of the processes associated with biotic and abiotic degradation in detail.

This paper evaluates the effects of natural attenuation on decreases in the concentrations of trichloroethylene (TCE) and dichloroethylene (DCE) at a groundwater remediation site where a pump-and-treat technique was conducted. In addition to field observations, a numerical simulation was performed in order to estimate the rates of TCE and DCE degradation at the site.

FIELD OBSERVATIONS

Site description

Figure 1 illustrates the location of a pumping well and observation wells at the site. Geological characteristics of the site are gravel sand from the ground surface to G.L.-1.3m and clay sand from G.L.-1.3 m to G.L.-2.3 m. Sand gravel, with a thickness of about 34 m, underlies the clay sand layer and below that are clay, gravel with cobblestone, and sand with clay layers to G.L.-100 m. Groundwater is encountered at about G.L.-5 m and mainly flows from the north to the south at an average velocity of about 1.0 m/day.

Groundwater contamination by TCE was discovered about 20 years ago. The cause of the contamination was the leakage of Dense Non-Aqueous Phase Liquid (DNAPL), mainly TCE, from underground pipelines in a factory (see Figure 1). A boring investigation conducted at the factory revealed that a large amount of DNAPL was present in the subsurface environment. Soil removal and pump-and-treat

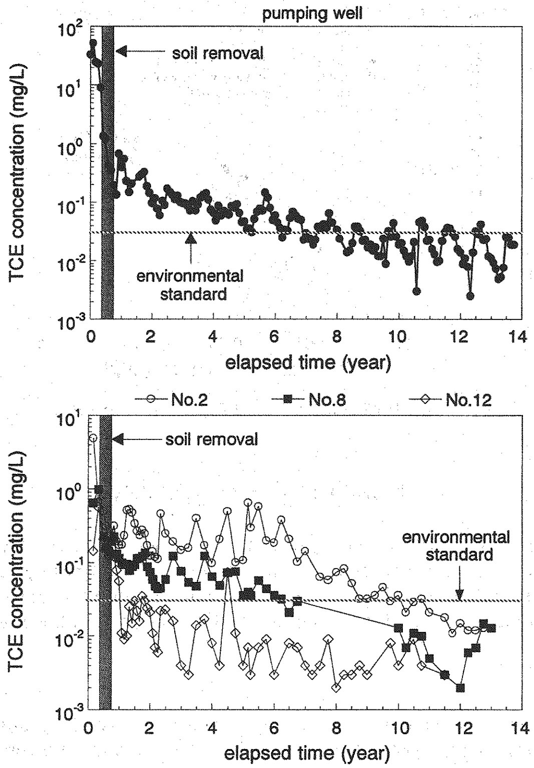

Fig. 2 Variations of TCE concentrations in pumping well and some observation wells over time

techniques were subsequently conducted to treat the unsaturated zone and the aquifer respectively. Approximately 1000 m^3 of soil containing TCE at concentrations of more than 1.0 mg/kg-dry soil was removed from the unsaturated zone just after the contamination was discovered. Since the discovery of the contamination, $2*10^5$ to $4*10^5$ m^3/year of groundwater has been extracted from the aquifer.

Observation results

Figure 2 shows the variations of TCE concentrations in the pumping well and some of the observation wells over time. The horizontal axis indicates the time that has elapsed since the contamination was discovered. The concentration in the pumping well was more than 30 mg/L when the contamination was discovered but quickly decreased to levels less than 1 mg/L after the contaminated soil was removed. After that, the concentration of TCE decreased gradually due to the effects of groundwater extraction in large part and fell far below the environmental standard after a period of 13 years. In the meantime, the concentrations in all observation wells also started to decrease as soon as the soil removal and pump-and-treat techniques started, but the concentration levels in well No.2 was maintained for 4 years at levels that were reached 2 years after the contamination was discovered. As groundwater extraction during this period was limited, the TCE transported downstream increased in quantity. However, after 11 years the concentrations dropped to less than the environmental standard in all observation wells.

Assays of DCE, a daughter product of TCE, were only initiated 12 years after the contamination was discovered. Figure 3 shows the positive correlation that exists between the ratios of TCE and DCE concentrations in the groundwater. Given that the power of the TCE concentrations in the regression equation of Figure 3 is approximately 1.0, the concentration of DCE is thought to be maintained at levels approximately 64% of the TCE concentration in the aquifer. Stoichiometrically, it is likely that the concentration of TCE in the aquifer has decreased by a factor of 46% through the effects of degradation. This implies that the degradation of TCE plays an important role in the decrease in TCE concentrations. However, in addition to degradation, the processes of advection and dispersion also contribute to a decrease in TCE and DCE concentrations, and DCE is also degraded in the aquifer. Consequently, a mass transport analysis that considers the degradation process is necessary to examine the effects of natural attenuation in detail.

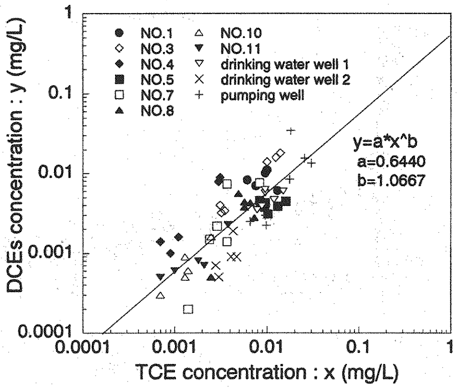

Fig. 3 Ratio of TCE and DCE concentrations

NUMERICAL SIMULATION

The field observations showed that TCE concentrations decreased by degradation, and that the ratio between TCE and DCE concentrations was fixed in the aquifer. These findings are both related to the rates of degradation of both substances. Accordingly, a numerical simulation by means of field observation data was carried out in order to estimate the rates of degradation of TCE and DCE in the aquifer.

Model description

A two or three dimensional model is an appropriate way in which to simulate the effects of natural attenuation that considers abiotic and biotic degradation, longitudinal and transverse dispersions and others at a site. However, it is difficult to collect sufficient two or three-dimensional information for features such as geological characteristics, groundwater velocity, contaminant concentration and others at a site. In such instances, a one-dimensional model may be more effective in obtaining accurate simulation results. Such was the situation at the site examined here where a lot of necessary information could not be collected. Furthermore, it was impossible for a numerical simulation model for mass transport using an advective-dispersive equation to simulate the decrease in contaminant concentrations caused by soil removal. For these reasons, it was difficult to establish an initial condition for a two-dimensional model at the site. Consequently, a one-dimensional model was applied in this paper.

When the *x*-axis is taken to represent the downstream direction of groundwater, mass transport equations of TCE and DCE are shown as follows:

Transport equation of TCE in an aquifer

$$\frac{\partial C_T}{\partial t} + v'\frac{\partial C_T}{\partial x} = D\frac{\partial^2 C_T}{\partial x^2} - K_T C_T \tag{1}$$

Transport equation of DCE in an aquifer

$$\frac{\partial C_D}{\partial t} + v'\frac{\partial C_D}{\partial x} = D\frac{\partial^2 C_D}{\partial x^2} + YK_T C_T - K_D C_D \tag{2}$$

where C_T and C_D = concentrations of TCE and DCE respectively (mg/L); v' = groundwater velocity (m/day); D = dispersion coefficient ($=a_L|v'|+D_M$) (m^2/day); a_L = longitudinal dispersivity (m); D_M = molecular diffusion coefficient (m^2/day); K_T and K_D = first order rate constants for TCE and DCE degradation, respectively (1/day); Y = molecular weight ratio between DCE and TCE. In this simulation, a first order reaction model was applied to simulate the decreases in TCE and DCE concentrations by degradation; therefore, the rates of degradation of both substances could be evaluated using the first order rate constants. The second right-hand term in eq. (1) shows the degradation of TCE, the second right-hand term in eq. (2) shows the production of DCE by degradation of TCE, and the third right-hand term in eq. (2) shows the degradation of DCE. The method of characteristics was applied to solve eqs. (1) and (2).

Table 1 shows the simulation parameters used for the model. Three constant velocities were used in the numerical simulation because the seasonal change in groundwater velocity was unknown at the site. 1.0

Table1 Simulation parameters

Parameter			Value	
Groundwater velocity	v'	(m/day)	(1)	0.1
			(2)	1.0
			(3)	10.0
Longitudinal dispersivity	a_L	(m)		10.0
Molecular diffusion coefficient	D_M	(m^2/day)		8.6×10^{-5}
Molecular weight ratio between DCE and TCE	Y			0.737
Scale increment	Δx	(m)		10.0
Time increment	Δt	(day)	(1)	1.0
			(2)	1.0
			(3)	0.1

m/day was chosen for the average groundwater velocity and the others, considered as representative of the lowest and highest velocities of 0.1 m/day and 10.0 m/day respectively, were chosen for the purpose of making comparisons.

The initial condition of TCE concentration was taken as the concentration observed after one year in Figure 3 when the influence of soil removal on the decrease in TCE concentration in the pumping well had disappeared. The upstream boundary (x=0m) was observation well No.1, which was the closest to the pumping well, and Dirichlet boundary conditions were used. The pumping well in the factory where the DNAPL infiltrated into the aquifer was subject to peculiar environmental conditions because groundwater extraction was being conducted at this location and DNAPL was also dissolving into the groundwater around the pumping well. As a result, the concentration in the pumping well could not be used as a boundary condition in this one-dimensional model. In addition, the observed concentrations of DCE could not be used as the initial and boundary conditions either because assays of DCE concentrations were only initiated 12 years after the contamination was discovered. Consequently, the initial and upstream boundary DCE concentrations were taken as 64% of the observed TCE concentrations. At the downstream boundary (x=2500m), Neumann boundary conditions were used in eqs. (1) and (2). As a constant groundwater velocity was used, that is, the seasonal change in the groundwater velocity was not considered, this simulation had difficulty in expressing seasonal changes in the TCE and DCE concentrations. Moving averages for TCE and DCE concentrations were, therefore, employed as the initial and boundary conditions.

Rates of Degradation

Figure 4 shows the simulation results of TCE concentrations. The horizontal axis represents the time that has elapsed since year one in Figure 3. The first order rate constants for TCE and DCE were determined by trial and error. However, as assays of DCE concentrations were only initiated after 12 years, the simulated concentration of DCE from 12 years after was compared with the observed data. The rate constants for TCE were $1.5*10^{-3}$ to $2.5*10^{-3}$/day at a groundwater velocity of 1.0 m/day, $0.5*10^{-3}$ to $1.5*10^{-3}$/day at 0.1 m/day, and $5.0*10^{-3}$ to $15.0*10^{-3}$/day at 10.0 m/day, respectively. The rate constants for DCE were $3.1*10^{-3}$ to $5.1*10^{-3}$/day at a groundwater velocity of 1.0 m/day, $1.0*10^{-3}$ to $3.1*10^{-3}$/day at 0.1 m/day, and $10.0*10^{-3}$ to $31.0*10^{-3}$/day at 10.0 m/day, respectively. These findings revealed that the rate constant for DCE was larger than TCE in every instance.

When velocity was taken as 0.1 m/day, the simulated TCE concentrations did not approximate the concentrations observed in the field with a high degree of accuracy. Consequently, the results obtained using velocities of 0.1 m/day were not considered appropriate for the determination of rate constants. Conversely, good results were obtained for wells No. 7 and 11 using the velocities of 1.0 m/day and 10.0 m/day, which meant that ranges for TCE and DCE rate constants could be taken as $1.5*10^{-3}$ to $15.0*10^{-3}$/day and $3.1*10^{-3}$ to $31.0*10^{-3}$/day respectively. However, for well No.2, no differences were observed in the variations of simulated TCE concentrations for a given rate constant. This suggests that the decrease in TCE concentrations observed in well No.2 was less affected by degradation, and that the pump-and-treat technique was more effective in decreasing TCE concentrations.

In a review of natural attenuation of VOCs, Wilson et al. (2) reported that the rate constants of TCE and DCE ranged from $0.23*10^{-3}$ to $4.4*10^{-3}$/day and $0.5*10^{-3}$ to $5.11*10^{-3}$/day, respectively. Based on field observation data, Hanadai et al. (3) calculated the rate constants for TCE and DCE as $6.9*10^{4}$ to $4.7*10^{-3}$/day and $9.4*10^{-4}$ to $1.9*10^{-2}$/day, respectively. Chapelle and Bradley (4) computed the rate constants using field observation data and found that for TCE it was $5.0*10^{-3}$ to $2.0*10^{-2}$/day in strong sulfate reduction conditions,

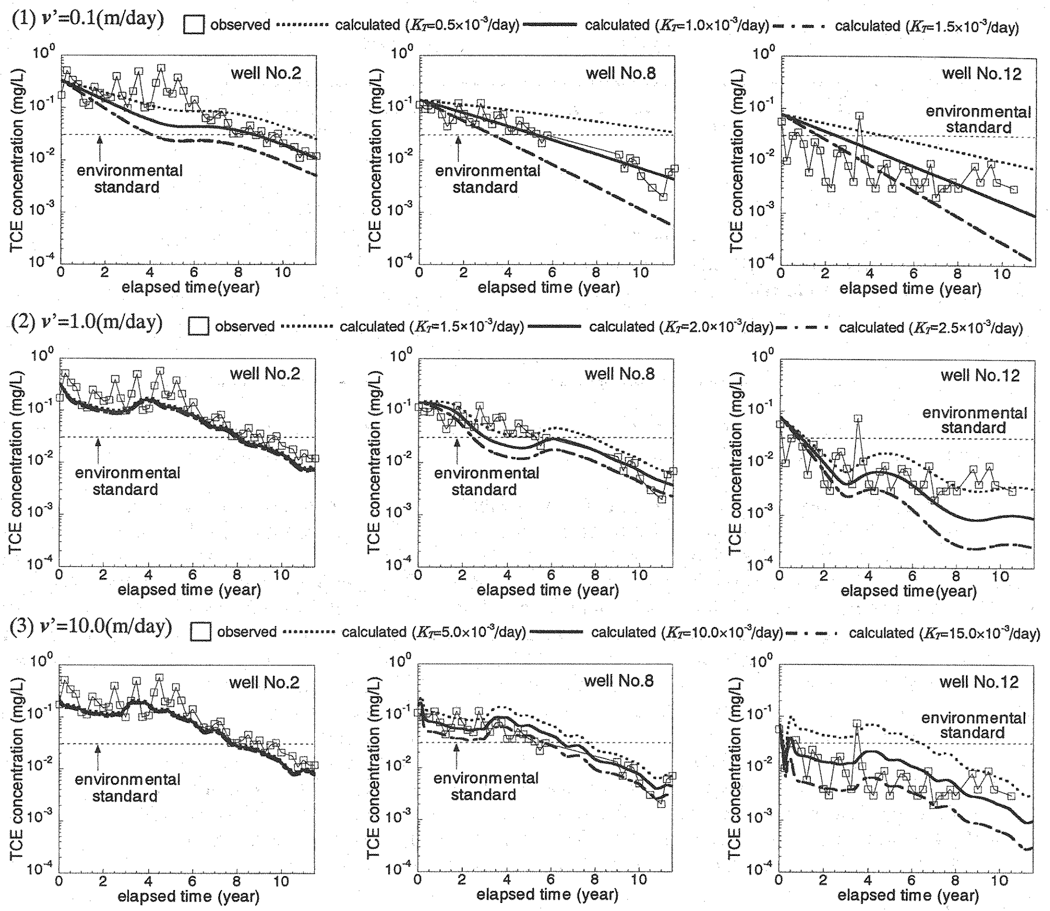

Fig.4 Simulation results

while for DCE a rate constant of $1.0{*}10^{-2}$ to $4.0{*}10^{-2}$/day was obtained in the absence of strong sulfate reduction conditions. Although the geochemical conditions at these sites were different, most of the rate constants were close to 10^{-3}/day. The rate constants at the site where investigations were conducted were also about 10^{-3}/day. Consequently, the most probable value for the rate constants of TCE and DCE in a field-scale would be at a scale of about 10^{-3}/day.

Effects of Natural Attenuation

The dominant destructive mechanism of TCE is reductive dechlorination in the subsurface environment, where TCE is transformed into DCE (Chapelle (5)). However, DCE is degraded by anaerobic oxidation as well as reductive dechlorination (Chapelle (5)). DCE is transformed into vinyl chloride (VC) by reductive dechlorination and is degraded into H_2O and CO_2 by anaerobic oxidation. In general, as the degree of halogenation in these substances diminishes, the dechlorination rate decreases. Therefore, the dechlorination of DCE is normally slower than TCE, which is a higher halogenated substance than DCE. A reductive environment stronger than nitrate reductive conditions is necessary for the dechlorination of DCE. However, Chapelle and Bradley (4) demonstrated that the rate constant of DCE in a weakly reductive environment was larger than that of TCE in a sulfate reductive environment. This means that the degradation rate of DCE by anaerobic oxidation occurs faster than that of TCE by reductive dechlorination. Similar results were obtained elsewhere (Wilson (2)). Consequently, DCE is likely to degrade more easily than TCE in an aquifer that is not subject to strong reductive conditions such as sulfate reductive or methanogenic conditions.

At the site where our study was conducted, the aquifer is situated at approximately G.L.-5m and the main geological feature is sand gravel, and the reductive potential of the groundwater is thus unlikely to be similar to strong sulfate reductive conditions. Consequently, the anaerobic oxidation of DCE in the groundwater contributed to faster degrading than TCE at this site.

CONCLUSION

The main purpose of this study is to evaluate the effects of natural attenuation of TCE and DCE at a groundwater remediation site. Field observations revealed that TCE was degraded in the aquifer and the concentrations of DCE, a daughter product of TCE, were maintained at approximately 64% of TCE concentrations. In order to assess the degradation rates of both substances in the aquifer, first order rate constants for TCE and DCE degradations were estimated by means of a numerical simulation. The first order rate constants of TCE and DCE were $1.5*10^{-3}$ to $15.0*10^{-3}$/day and $3.1*10^{-3}$ to $31.0*10^{-3}$/day respectively, and it can be deduced by referring to the rate constants at the other sites that the most probable value for the rate constants of TCE and DCE in a field-scale is at a scale of about 10^{-3}/day. Given that a first order rate constant (K) can be converted into a half-life ($t_{1/2}$) using the equation $K=\ln 2/t_{1/2}$, with the simulated rate constants for TCE and DCE of $2.0*10^{-3}$/day and $4.2*10^{-3}$/day, the half-lives for both substances at this site are 0.95 and 0.45 years respectively. This suggests that DCE degrades more easily than TCE in this aquifer, probably because of the increased susceptibility of DCE to anaerobic oxidation.

REFERENCES

1. McCarty, P.L. and E.E. David: Natural Attenuation, Innovative Approaches to the On-Site Assessment and Remediation of Contaminated Sites, Kluwer Academic Publishers, pp.141-181, 2001.
2. Wilson, J.T., D.H. Kampbell and J.W. Weaver: Environmental chemistry and the kinetics of biotransformation of chlorinated organic compounds in ground water, Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water, pp.133-136, 1996.
3. Hanadai S. Rifai et al.: Intrinsic Bioremediation, Battelle Press, pp.1-29, 1995.
4. Chapelle, F.H. and P.M. Bradley: Selecting Remediation Goals by Assessing the Natural Attenuation Capacity of Groundwater Systems, Bioremediation Journal, Vol.2, No.3&4, pp.227-238, 1998.
5. Chapelle, F. H.: Ground-Water Microbiology and Geochemistry (2nd Edition), John Wiley and Sons, INC., pp.403-445, 2001.

APPENDIX – NOTATION

The following symbols are used in this paper:

C_T = concentrations of TCE (mg/L);

C_D = concentrations of DCE (mg/L);

v' = groundwater velocity (m/day);

D = dispersion coefficient ($=a_L|v'|+D_M$) (m^2/day);

a_L = longitudinal dispersivity (m);

D_M = molecular diffusion coefficient (m^2/day);

K_T = first order rate constant of TCE (1/day);

K_D = first order rate constant of DCE (1/day); and

Y = molecular ratio of DCE and TCE (1/day).

(Received December 8, 2003 ; revised February 26, 2004)