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TRANSFORMATION KINETICS OF TRACE-LEVEL HALOGENATED ORGANIC CONTAMINANTS IN A BIOLOGICALLY ACTIVE ZONE (BAZ) INDUCED BY NITRATE INJECTION

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ABSTRACT

Bae, W., Odencrantz, J.E., Rittmann, B.E. and Valocchi, A.J., 1990. Transformation kinetics of trace-level halogenated organic contaminants in a biologically active zone (BAZ) induced by nitrate injection. *J. Contam. Hydrol.*, 6: 53–68.

Laboratory experiments and numerical modeling were conducted to evaluate the secondary utilization of eight trace-concentration halogenated solvents in a denitrifying biologically active zone (BAZ) induced by nitrate injection into an acetate-fed porous-medium column. Results of column experiments indicated that carbon tetrachloride was removed most completely by the denitrifying BAZ, while bromoform, dibromoethane, tetrachloroethene, trichloroethene, and *1,2*- and *1,3*-dichlorobenzenes were removed, but to lesser degrees. *1,1,1*-trichloroethane removal was slight. Compounds were removed to higher degrees when the BAZ contact time was increased.

The steady-state, one-dimensional solute-transport equation was solved using an iterative finite-difference scheme and by employing a quasilinearization technique for the biofilm-reaction term. The model solved directly for the steady-state profiles of secondary substrates. One set of experimental results was used to obtain best-fit values of kinetic parameters, which were then used to predict the removal at different liquid flow velocities. The model predictions correctly described all experimental trends: removal of the halogenated compounds only in the BAZ, greater removal with increased BAZ contact time, and reduced specific removal rates caused by diffusion limitation in the biofilm.

INTRODUCTION

Halogenated organic compounds – such as halogenated methanes, ethanes, ethenes and benzenes – are used widely as industrial solvents, dry cleaning solvents, metal degreasing agents, and pesticides (Verschueren, 1983). Improper handling, storage and disposal of solvents are sources of groundwater contamination. A recent survey conducted by the U.S. Environmental Protection Agency revealed that at least 15% of 466 randomly selected finished groundwater supplies is contaminated with at least one halogenated organic compound (Westrick et al., 1984). The most frequently detected compounds were trichloroethene, tetrachloroethene and *1,1,1*-trichloroethane.

In situ bioreclamation is a promising approach to clean up aquifers

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containing hazardous contaminants, such as those mentioned on p. 53. The concept of in situ bioreclamation is to increase the active biomass by injecting into the subsurface nutrients which are in short supply and which limit the accumulation of the biomass. The most likely materials to be injected are an electron acceptor, a supplemental organic electron donor, or sources of nitrogen and phosphorus. Increasing the active biomass by several orders of magnitude over that naturally present can create a biologically active zone (BAZ) that could degrade hazardous compounds under the proper environmental conditions.

In many cases, a specific hazardous compound exists at a very low concentration that is insufficient to meet the minimum energy requirements needed to maintain a steady-state biomass. In such cases, each specific hazardous compound may be degraded by a secondary-utilization mechanism (Namkung et al., 1983), especially when the amount of accumulated biomass and the compound–biomass contact time are sufficiently large. Degradation by secondary-utilization is possible because the biomass is grown and sustained by its utilization of a primary substrate, which allows and governs the accumulation of biomass (Kobayashi and Rittmann, 1982; Namkung et al., 1983). The formation of a BAZ is one method for providing this biomass accumulation.

This paper reports results of an experimental program that investigated the degradability of several common halogenated solvents by a BAZ of a denitrifying microflora established through injection of NO_3^- as the electron acceptor into a porous-medium column which was fed with acetate as the primary substrate. The degradation kinetics of individual compounds in the BAZ and the effect of BAZ contact time, which constitute essential elements for assuring successful bioreclamation, are analyzed with the aid of one-dimensional solute-transport model that includes a biofilm-reaction term.

EXPERIMENTAL METHODS

Column construction and BAZ *development*

The experimental system was the one-BAZ system described by Odencrantz et al. (1990). Briefly, a 2.5-cm inside diameter by 22.5-cm long glass column was filled with 3-mm glass beads. Ports were placed every 2.5 cm. A radiolabeled electron donor (acetate at 7.5 mg SOC L^{-1}) in a mineral-salts solution was fed at 0.1-cm $min.^{-1}$ superficial flow velocity into the inlet end of the column, while electron-acceptor (nitrate at 7.3 mg NO_3^--N L^{-1}) solution was injected at 7.5 cm downstream of the column inlet through a planar-injection system. The column was inoculated with a mixed population of denitrifying bacteria. A schematic of BAZ development in the column is given in Fig. 1.

Selection of halogenated organic compounds

Six chlorinated or brominated aliphatics and two chlorinated aromatics

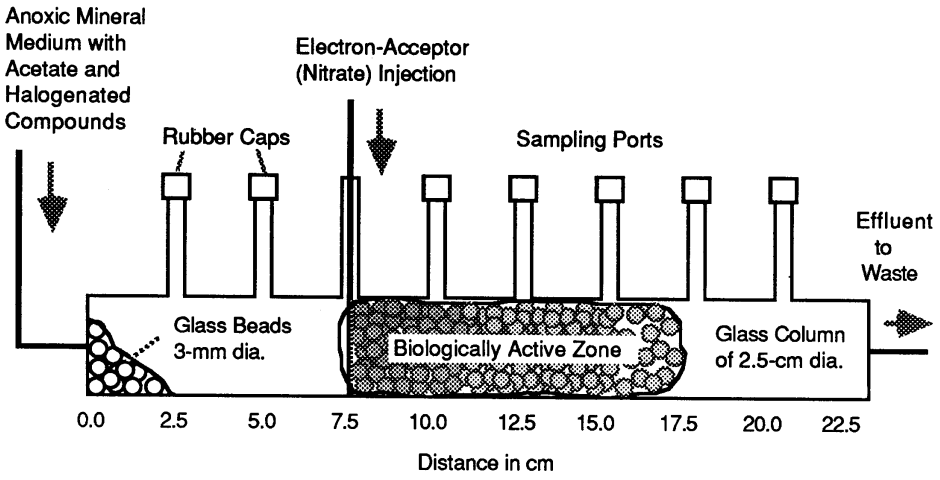

Fig. 1. Schematic of column reactor for secondary-utilization experiments.

were tested for their biodegradation kinetics in the denitrifying BAZ. The halogenated aliphatics contained three subgroups: carbon tetrachloride (CTC) and bromoform (BF), which are substituted methanes; *1,1,1*-trichloroethane (*1,1,1*-TCA) and dibromoethane (EDB), which are substituted ethanes; and tetrachloroethene (TeCE) and trichloroethene (TCE), which are substituted ethenes. The chlorinated aromatics were *1,2*-dichlorobenzene (*1,2*-DCB) and *1,3*-dichlorobenzene (*1,3*-DCB).

Column operation for secondary-utilization experiments

Secondary-utilization experiments were initiated after a fully stable denitrifying BAZ was developed as indicated by steady removals of SOC and nitrate after ~9 months of operation. The eight halogenated compounds selected were added to the feed solution at concentrations ranging from 50 to 100 $\mu g\,L^{-1}$ each.

The effect of BAZ contact time on secondary-substrate utilization was tested by varying the flow rate in the column, as summarized in Table 1. The superfi-

TABLE 1

Flow velocities and BAZ contact times

Run	Superficial flow velocity ($cm\,min.^{-1}$)	BAZ contact time* (min.)
a	0.1	50
b	0.04	125
c	0.01	500
d	0.1	50

*The extent of the BAZ was 12.5 cm.

cial flow velocity in the column for the initial experiment (run a) was 0.1 cm min.$^{-1}$, the same velocity used to develop the steady-state BAZ (Odencrantz et al., 1990). Subsequently, the flow velocity was reduced to 0.04 cm min.$^{-1}$ (run b) and then to 0.01 cm min.$^{-1}$ (run c). Thus, the BAZ contact time was increased by 2.5 and 10 times for runs b and c, respectively. Finally, the flow velocity was returned to the original flow velocity (run d) to check whether or not the BAZ had changed or adapted further to the halogenated compounds during runs a–c. Samples used to determine the removal of the halogenated compounds were taken after at least one month of continuous feeding of the compounds at the flow rate for that run.

Sampling and analytical methods

A syringe pump was used to withdraw liquid samples from each sampling port at a rate equal to the input feeding rate. The first sample was taken from the port nearest the outlet, and the sampling location then was moved stepwise toward the inlet. This sampling strategy was employed in order to minimize any effects of a flow-rate change caused by sampling another port. Syringe-pump sampling had two advantages: (1) it assured that the sample withdrawal rate was exactly the influent flow rate; and (2) it prevented volatilization losses during sampling. The glass syringe was connected to a stainless-steel sampling needle via a Teflon® tube, and this sampling apparatus – syringe, Teflon® tubing and needle – was flushed with effluent initially; thus, the potential sampling error due to adsorption of the halogenated compounds on the sampling apparatus was minimized.

Approximately 12 mL of liquid were collected from each sampling port. Exactly 10 mL of sample and 1 mL of dodecane or pentane were pipetted into a 15-mL hypo vial. The head space was minimized by adding distilled water, and the vial was tightly sealed with a Teflon®-faced Silicone® rubber cap. The vial was shaken vigorously for 3 min. to extract the halogenated compounds. After a 15-min. period for phase separation, 2 μL of the separated solvent phase were injected into a gas chromatograph equipped with an electron-capture detector (Hewlett-Packard®, model *5710*A). A *60/80* Carbopack B®, 0.1% sp-*1000* glass column was used for halogenated aliphatics, and a 1% sp-*1000* on *100/120* Supelcoport® was used for the DCB's. The same extraction and injection procedure was applied for standard solutions used for calibration. Dodecane was a superior extractant for the halogenated aliphatics, while pentane was superior for the dichlorobenzenes.

The portion of the sample that was not extracted was filtered and counted for ^{14}C concentration to determine the soluble organic carbon (SOC) concentration. A liquid scintillation counter (Beckman®, model LS-*100*) was used, and details can be found elsewhere (Rittmann et al., 1988; Odencrantz et al., 1990).

RESULTS FOR SECONDARY UTILIZATION EXPERIMENTS

Removal of halogenated aliphatics in the acetate-grown BAZ

The results for the halogenated aliphatics, as well as SOC, are shown in Fig. 2 for runs a–d. Sample concentrations are normalized to the measured concentration at the sampling port immediately upstream of the NO_3^- injection (5-cm location; see Fig. 1), and the concentrations of each compound at the 5-cm port are given in Table 2.

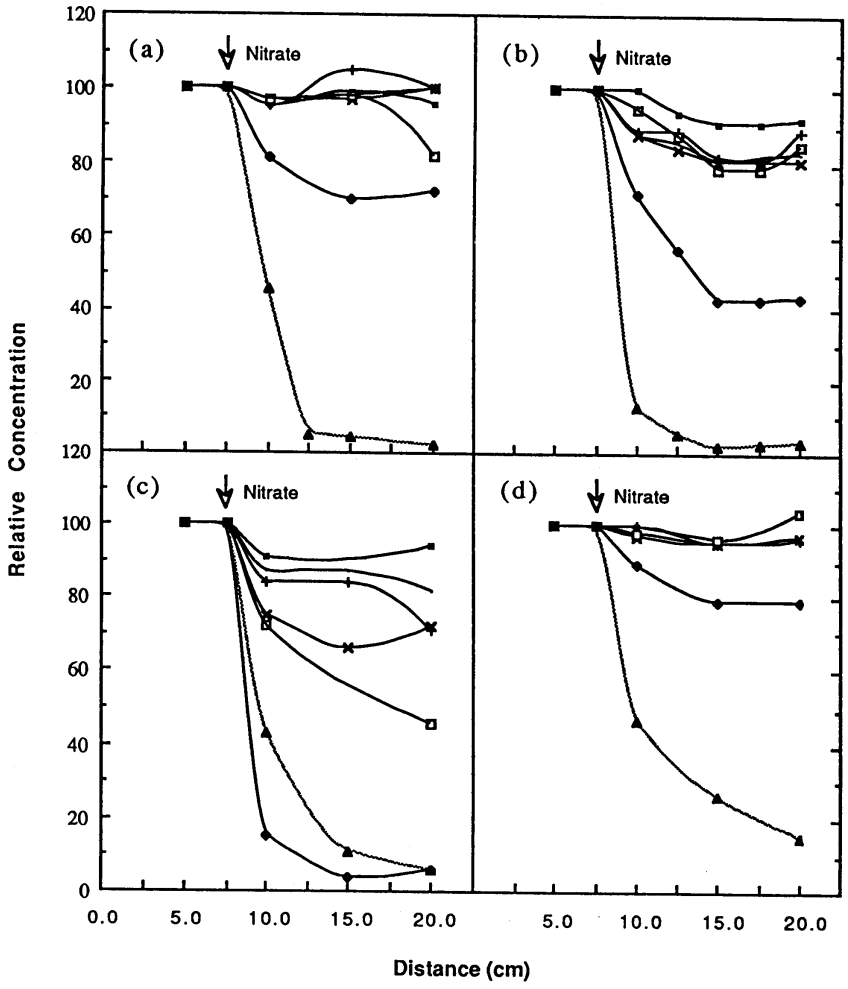

Fig. 2. Removal of halogenated aliphatic compounds and SOC in a denitrifying column at given superficial flow velocities: (a) 0.10 cm min.$^{-1}$; (b) 0.04 cm min.$^{-1}$; (c) 0.01 cm min.$^{-1}$; and (d) 0.10 cm min.$^{-1}$. Symbols represent: ■ = *1,1,1*-TCA; · = EDB; + = TCE; × = BF; □ = TeCE; ◆ = CTC; and ▲ = SOC.

TABLE 2

Initial concentrations ($\mu g\,L^{-1}$) of secondary compounds and acetate SOC

Compound	Run			
	a	b	c	d
Aliphatics runs:				
CTC	81	69	53	62
BF	106	57	54	59
1,1,1-TCA	84	99	112	94
EDB	87	69	45	45
TeCE	79	55	50	66
TCE	95	62	88	87
SOC	6,600	5,100	4,900	6,300
Aromatics runs:				
1,2-DCB	–	–	42	35
1,3-DCB	–	–	29	23
SOC	–	–	7,300	7,200

– = not determined.

In Fig. 2a, which is for the original flow velocity (0.1 cm min.$^{-1}$), out of six halogenated aliphatic compounds, only CTC showed significant removal (28%) through the BAZ. The other compounds, except TeCE, showed slight decreases in concentration, but the average losses in downstream samplings from the 10-, 15- and 20-cm ports were not greater than 2%, which was statistically insignificant. TeCE showed only a 1.5% loss up to the 15-cm sampling port. The abrupt loss of TeCE at the 20-cm location was probably due to analytical error.

Run b had a 0.04 cm min.$^{-1}$ flow velocity, which made the BAZ contact time 2.5 times greater than in run a. The results of run b are presented in Fig. 2b, which shows that the removal of CTC was more significant (57%). Also, the other compounds, except *1,1,1*-TCA, had 15–20% removal. *1,1,1*-TCA had the lowest removal efficiency, $\sim 10\%$.

The observed removals were associated with biological reactions in the BAZ. This was evident from a subsequent control experiment with TeCE performed in the same denitrifying column with a flow velocity of 0.04 cm min.$^{-1}$, but under suppressed biological activity. The suppression of the biological activity was achieved by stopping the TeCE feeding for several months (thus, the biological capability to degrade TeCE was lost) and by removing the electron donor (acetate) from the feed during the experiment (thus, the main metabolic function in the cell was minimized). TeCE was fed for ~ 1 week, and its profile was measured; there was $\geqslant 99\%$ recovery of TeCE at all ports. Thus, losses due to sorption and volatilization accounted for $< 1\%$ removal of TeCE in the control experiment.

Sorption and volatilization losses for the other compounds should be similar

to or less than those of TeCE, because TeCE has the highest octanol–water partition coefficient (thus, was the most sorbable to cells) and a relatively high Henry's law constant (thus, was among the most volatile) for all the compounds tested (Callahan et al., 1979; Lyman et al., 1982). Therefore, the gradual decreases in the halogenated aliphatics shown in Fig. 2b were biologically mediated losses.

Although biodegradation of several of the halogenated aliphatics (i.e. TeCE, *1,1,1*-TCA and EDB) under denitrifying conditions was not shown conclusively before (Bouwer and Wright, 1988), their removal as electron acceptors seems plausible on a thermodynamic basis. Reduction of the halogenated aliphatics produces more free energy than does reduction of NO_3^- to NO_2^- (Vogel et al., 1987). Biodegradation of CTC and BF under denitrifying conditions has been observed previously (Bouwer and McCarty, 1983; Bouwer and Wright, 1988).

Fig. 2c shows the results of run c, which had a flow velocity of 0.01 cm $min.^{-1}$ and a BAZ contact time ten times greater than for run a. CTC was removed almost completely (94%), as its concentration decreased from 53 to 3 $\mu g\,L^{-1}$ across the BAZ. Significant removals of TeCE (~50%), BF (~30%), TCE (15%–30%) and EDB (~20%) occurred in response to the increased contact time between the compounds and the BAZ. Removals for these compounds were higher than the removals in run b and confirmed that these halogenated aliphatics were degraded under denitrification conditions. *1,1,1*-TCA showed a percentage removal comparable (~10%) to run b.

Fig. 2d shows the results obtained from run d, in which the flow velocity was increased back to the original value of 0.1 cm $min.^{-1}$ used in run a. The removals of halogenated compounds were very similar to those in Fig. 2a. Thus, the increased removals in runs b and c probably were not the result of physiological or genetic adaptation, but occurred because of the increased contact time.

During runs b and c, the loading of primary substrate (acetate) to the BAZ was reduced proportionally to the reduction in flow velocity. This decreased loading probably caused the biomass in the BAZ to decline. Thus, the substrate-removal capacity of the BAZ may have declined during runs b and c. Such an effect was observed by Rittmann and Brunner (1984) when they transiently increased the substrate loading to a biofilm that was slowly decaying. Evidence of biomass decay during runs b and c was provided by the substantial increases in effluent SOC (1.25 ± 0.35 $mg\,L^{-1}$; 83% removal) during run d compared to the SOC during run a (0.16 ± 0.04 $mg\,L^{-1}$; 98% removal).

Removal of dichlorobenzenes in the acetate-grown BAZ

Profiles of *1,2*-DCB and *1,3*-DCB along the column are shown in Fig. 3. Fig. 3a shows DCB removals from run c, while Fig. 3b is from run d. Fig. 3a shows that *1,2*-DCB decreased from 35 to 23 $\mu g\,L^{-1}$, a 34% removal across the BAZ. The removal of *1,3*-DCB was slightly better (35%) than that of *1,2*-DCB in Fig. 3a. As with the halogenated aliphatics, BAZ contact time was a critical

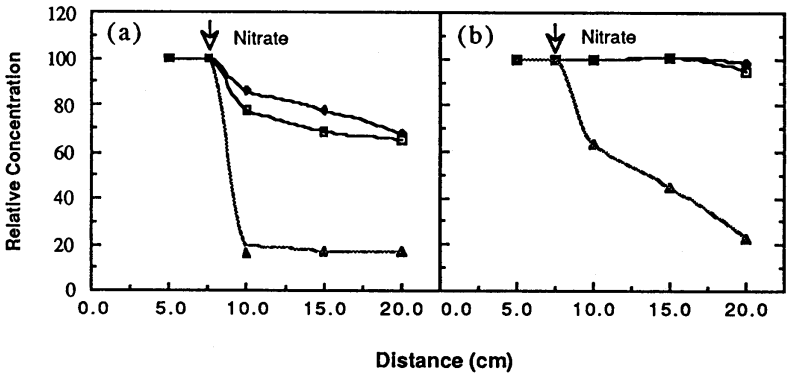

Fig. 3. Removal of DCB's and SOC in a denitrifying column at given superficial flow velocities: (a) 0.01 cm min.$^{-1}$; and (b) 0.10 cm min.$^{-1}$. Symbols represent: ◆ = *1,2*-DCB; □ = *1,3*-DCB; and ▲ = SOC.

parameter in the extent of DCB removal. At the reduced contact time used in run d, no significant removal was observed (Fig. 3b).

The observation of DCB removal in a denitrifying column is very important, because these compounds were thought to be biologically persistent under anoxic conditions (Bouwer and McCarty, 1983; Bouwer, 1987). To investigate any nonbiological reactions which might have been responsible for the removal, two potential alternative pathways, sorption and volatilization, were examined.

DCB's have moderately high octanol–water partition coefficients, with a typical log(K_{ow})-value around 3.4 (Callahan et al., 1979; Miller et al., 1985). Therefore, DCB's could sorb onto or into hydrophobic parts of cells produced from the primary substrate. However, two factors indicate that sorption was not responsible for the removals in these experiments. First, the liquid samples were not filtered before DCB extractions; thus, any DCB's sorbed to effluent cells would have been measured. Second and more important, the DCB's were fed continuously for the duration (5 months) of the experiment. Because DCB samplings were made almost at the end of the period, we estimated that any sorption capacity of the cells in the column would have been saturated long before samples were taken.

Volatilization of DCB's into the nitrogen gas produced during the denitrification reaction or through the sampling ports could have taken place. Because the gas production rate was trivial compared to the liquid flowrate (0.4% by volume), volatilization losses into the nitrogen gas phase were < 1% of the observed DCB removals and would not explain the substantial removal of DCB's. Volatilization through the sampling ports was not responsible mechanism for the DCB removals, because abiotic removal of TeCE in the control column at a flow velocity of 0.04 cm min.$^{-1}$ was not significant (< 1%). DCB's have at least four times lower Henry's law constant (as vapor pressure/aqueous solubility) than does TeCE (Callahan et al., 1979), signifying that

DCB's are at least four times less volatile; therefore, volatilization losses for DCB's could not have been significant, even at the four times lower flow velocity (0.01 cm min.$^{-1}$) which was used in the DCB experiment shown in Fig. 3a. Moreover, it was shown that *1,1,1*-TCA in run c (velocity = 0.01 cm min.$^{-1}$) had a much lower percentage removal ($\sim$ 10%) than for the DCB's, even though it has at least two times higher Henry's law constant (Callahan et al., 1979; Lyman et al., 1982). As there was no significant alternative pathway for DCB removal in these experiments, the removal can be attributed to biodegradation.

DEVELOPMENT OF THE SECONDARY-UTILIZATION MODEL

Secondary utilization of a trace-level halogenated organic compound can be achieved when biomass is grown and sustained by its utilization of a primary substrate. Namkung et al. (1983) demonstrated how to model secondary utilization. Such a model requires knowledge of the kinetic parameters of the secondary-substrate removal, as well as the distribution of biomass, which is determined by primary-substrate utilization.

The mass-balance equation for each secondary substrate was the steady-state solute-transport equation:

$$0 = D_H(d^2S/dx^2) - v(dS/dx) - aJ \quad (1)$$

where S is the dissolved secondary-substrate concentration ($M_s L^{-3}$, where M_s = mass of substrate, L = length); D_H is the hydrodynamic dispersion coefficient ($L^2 T^{-1}$, where T = time); v is the specific discharge (superficial flow velocity, $L T^{-1}$); a is the specific surface area of the porous medium (L^{-1}); and J is the substrate flux into the biofilm ($M_s L^{-2} T^{-1}$).

The flux of secondary substrate was computed from its own kinetic parameters and the biofilm accumulation (thickness $\times$ density). The biofilm accumulation was controlled by primary-substrate utilization and was computed as part of the modeling procedure described in detail by Odencrantz et al. (1990). The secondary substrates were assumed not to affect the overall growth rate or accumulation of the biomass. The pseudo-analytical solution of Rittmann and McCarty (1981), which was based upon the work of Atkinson and How (1974), was utilized to estimate J for a secondary substrate into the biofilm. The pseudo-analytical solution is expressed by:

$$J = \eta q_m X_f L_f [S_s/(K + S_s)] \quad (2)$$

where η is the effectiveness factor; q_m is the maximum specific rate of substrate utilization ($M_s M_x T^{-1}$; where M_x = mass of bacteria); X_f is the biofilm density ($M_x L^{-3}$); L_f is the biofilm thickness (L); K is the half-maximum-rate concentration ($M_s L^{-3}$); and S_s is the substrate concentration at the diffusion layer–biofilm interface ($M_s L^{-3}$). S_s is related to S through the traditional relationship for external mass-transport resistance:

$$S_s = S - JL/D \quad (3)$$

where D is the diffusion coefficient (L^2T^{-1}); and L is the diffusion layer thickness (L). The effectiveness factor, η, represents the ratio of actual flux to the flux with no diffusion limitation within the biofilm and is a nonlinear algebraic function of S_s (Atkinson and How, 1974; Rittmann and McCarty, 1981). An iteration procedure is needed to simultaneously solve eqs. 2 and 3 for S_s, η and J (Rittmann and McCarty, 1981; Rittmann et al., 1988).

The steady-state eq. 1 for each secondary substrate was solved using the same quasilinearization strategy employed in Odencrantz et al. (1990) for the primary substrate. When the substrate concentration (S^m) at an iteration m is known, a first-order Taylor series is used to approximate the flux at the next iteration:

$$J(S^{m+1}) = J(S^m) + [dJ/dS]^m(S^{m+1} - S^m) \quad (4)$$

As long as $[dJ/dS]^m$ can be computed, substitution of eq. 4 into eq. 1 yields a linear ordinary differential equation for S^{m+1}. The resultant equation was solved using a standard finite-difference technique, as discussed in Odencrantz et al. (1990).

Unlike the case for the primary substrate, the internal complexity of the algorithm to compute $J(S)$ for the secondary substrate did not permit an explicit expression for computation of $[dJ/dS]^m$. Therefore, a forward finite-difference approach was employed to compute $[dJ/dS]^m$ for any S^m, that is:

$$[dJ/dS]^m = [J(S^m + \Delta S) - J(S^m)]/\Delta S \quad (5)$$

The iterative solution of eqs. 2 and 3 was used to compute $J(S^m)$ and $J(S^m + \Delta S)$, which were used in eq. 5 to compute $[dJ/dS]^m$. The evaluation of $[dJ/dS]^m$ was not sensitive to the differencing interval, ΔS, which ranged from 0.01% to 0.1% of S. The convergence and accuracy of the secondary utilization model were very similar to those of the primary-substrate model presented Odencrantz et al. (1990).

MODEL APPLICATION TO SECONDARY-SUBSTRATE PROFILES

The laboratory profiles of the secondary substrates were modeled using the framework summarized in the previous section. The primary-substrate profile was modeled first. From the results for the primary-substrate, the steady-state biofilm thickness was calculated at each grid point. The result was a profile of biomass (X_fL_f) throughout the length of the column. The X_fL_f-values then served as inputs to compute the flux of a particular secondary substrate into the biofilm (Rittmann and McCarty, 1981; Namkung et al., 1983), which was needed to solve the solute-transport equation for each secondary substrate by quasilinearization.

Before the secondary-substrate experiments were started, the column had been operated for 9 months at the same flow velocity and input concentrations of acetate and nitrate. The same flow velocity was used for two more months for run a. Because of the long time used to establish the steady-state biofilm and

the relatively short times the reactors were run at the new flow rates (for runs b and c, 5 weeks each), it was assumed that the biomass distribution remained the same for runs a–d. However, it was possible that the BAZ lost active biomass during runs b and c.

The strategy for modeling the secondary substrates was to choose q_m- and K-values that provided a good fit to the experimental results for one experiment. This fitting exercise was needed because the q_m- and K-values of these secondary substrates were not determined independently. However, recall that the reactor parameters and the kinetic parameters of the primary substrate were known independently (Odencrantz et al., 1990). The criteria of best fit combined a least-squares evaluation and modeler judgement. The least-squares analysis (Dennis and Schnabel, 1983) gave sums of squares of deviations that were negligibly different for a broad range of kinetic parameters (q_m and K) close to the optimal solution. Therefore, judgement was used to select the parameters that gave no systematic deviations with the laboratory data. The fitted q_m- and K-values were used to predict the results for other experiments (i.e. for different flow velocities) with the same secondary substrates. The secondary-substrate modeling was evaluated with five halogenated aliphatics: CTC, BF, EDB, TeCE and TCE.

After the data were fit with the best q_m- and K-values, it was observed that equally good fits were achieved for higher values of q_m and K, so long as the ratio q_m/K was constant. This pattern is indicative of first-order kinetics in S for which the ratio q_m/K is a first-order rate coefficient. Therefore, the parameters are presented as a q_m/K ratio and the minimum K to give the first-order response.

Carbon tetrachloride

The q_m/K-value which gave the best fit for CTC and a flow velocity of 0.1 cm min.$^{-1}$ was 0.00667 L (mg cells)$^{-1}$ day^{-1} (Table 3). Curve *1* in Fig. 4 shows the results of the numerical fitting for this flow velocity. Clearly, all of the points are well represented by the numerical result, and there are no systematic deviations.

In order to evaluate the predictive ability of the numerical model, the

TABLE 3

Summary of q_m/K-values and lowest K-values for CTC, BF, EDB, TeCE and TCE

Compound	q_m/K (L (mg cells)$^{-1}$ day^{-1})	Lowest K (mg L^{-1})
CTC	0.00667	0.45
BF	0.00137	0.77
EDB	0.00100	0 91
TeCE	0.00220	0.70
TCE	0.00111	0.90

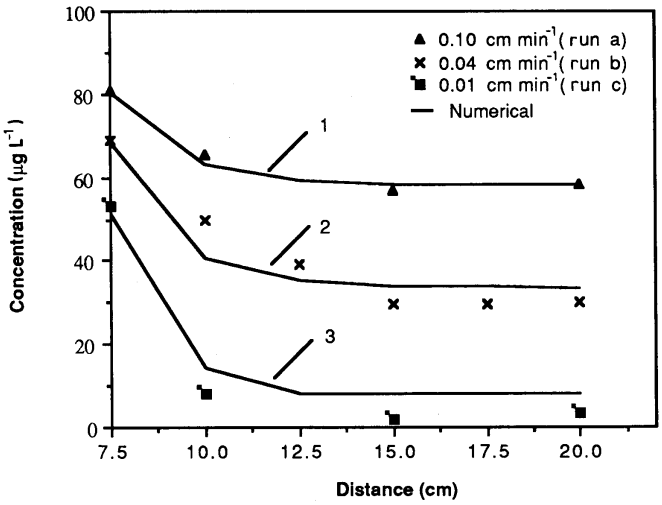

Fig. 4. Fitted CTC profile at a superficial velocity of 0.10 cm min.$^{-1}$ (curve *1*) and predicted CTC profiles at superficial velocities of 0.04 and 0.01 cm min.$^{-1}$ (curves *2* and *3*, respectively). The q_m/K-value is 0.00667 L (mg cells)$^{-1}$ day^{-1}.

profiles at the other two flow velocities (runs b and c) were calculated using the same q_m- and K-values. The superficial velocity and influent concentration were suitably modified for each of the other runs. Curve *2* in Fig. 4 shows the results of the numerical prediction compared to the laboratory data for a superficial velocity of 0.04 cm min.$^{-1}$, while curve *3* shows the results of the numerical prediction for a superficial velocity of 0.01 cm min.$^{-1}$. The numerical and experimental results have the same trends: rapid decrease in the first part of the BAZ (where most of the biomass was located) and an approach to a plateau concentration at the downstream part (15-cm position) of the BAZ. The absolute values of the plateau concentration differ slightly, but they are close and have the correct trend.

Bromoform, ethylene dibromide, tetrachloroethene and trichloroethene

For secondary substrates other than CTC, no detectable removal was observed at a superficial velocity of 0.1 cm min.$^{-1}$, due to insufficient contact time with the biomass. As a result, the kinetic parameters were found for the superficial velocity of 0.04 cm min.$^{-1}$. Table 3 lists the best-fit kinetic parameters for each aliphatic compound. Curve *1* in Fig. 5 shows the results of the numerical fitting between the experimental values and the model results for BF. As for CTC, most removal of BF occurred in the upstream part of BAZ, from 7.5 to 12.5 cm.

Curve *2* in Fig. 5 shows the prediction of the numerical model for the 0.01-cm-min.$^{-1}$ experiment, using the kinetic parameters from the superficial velocity of 0.04 cm min.$^{-1}$. The numerical model predicted a slightly lower

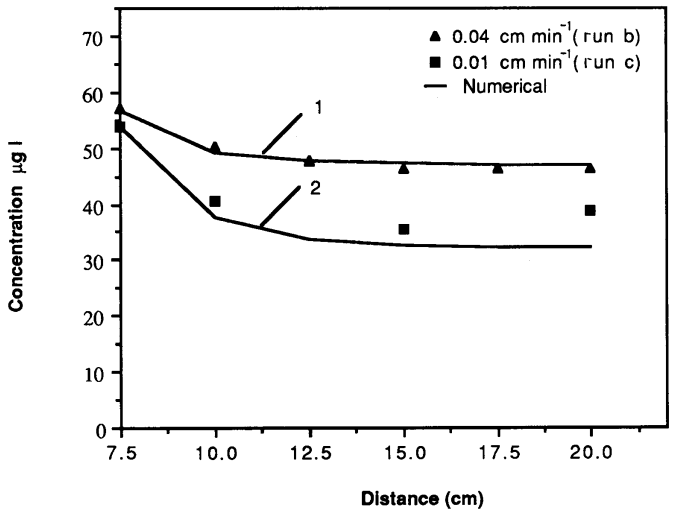

Fig. 5. Fitted BF profile at a superficial velocity of 0.04 cm min.$^{-1}$ (curve *1*) and predicted BF profile at superficial velocity of 0.01 cm min.$^{-1}$ (curve *2*). The q_m/K-value is 0.00137 L (mg cells)$^{-1}$ day^{-1}.

plateau concentration than was measured in the laboratory. This difference in removals perhaps can be attributed to biofilm loss between runs b and c. Modeling predictions for the 0.1-cm-min.$^{-1}$ experiment gave a prediction of only 1.5% removal of BF (results not shown). This predicted negligible removal was consistent with the insignificant removal observed for runs a and d.

Because the numerical fits to the laboratory data for TeCE, EDB and TCE were similar to those shown for BF in Fig. 5, their curves are not presented. The same trend of somewhat greater predicted removals for run c occurred for each compound.

Comparing the q_m/K-values in Table 3 indicates two categories of kinetics. CTC had a q_m/K-value of $\sim 0.0067\,L\,mg^{-1}\,day^{-1}$, while the other aliphatic compounds had lower values of 0.0010–0.0022 L mg^{-1} day^{-1}. Thus, CTC was more rapidly biodegraded, leading to its greater fractional removal at all flow velocities.

Table 4 shows the calculated fractional distribution of biomass in the three segments of the BAZ after injection, as well as the corresponding distribution of fractional removals of the halogenated aliphatic compounds in runs b and c. The first conclusion from these data is that all removals occurred within 12.5 cm downstream of the injection, which defined the extent of the BAZ. Second, although 72% of the biomass was located in the first segment, 55–59% of the halogenated-compound removal was located in the first segment. The specific removal activity was lower in the first segment than in the other two segments because of diffusional resistance inside the biofilm present in the first segment of the column. Diffusion limitation in the biofilm is described by the effectiveness factor (η), which is the ratio of the actual flux to the flux that would occur when there is no diffusional resistance. The η-values calculated for

TABLE 4

Fraction of the total biomass, fraction of the total removal, and effectiveness factors for the halogenated aliphatic compounds in each segment of the BAZ

	Segment		
	7.5–10 cm	10–15 cm	15–20 cm
Calculated biofilm mass	0.72	0.26	0.02
Halogenated aliphatics removal*			
CTC	0.59	0.37	0.04
Other aliphatics	0.55	0.38	0.07
η-value*			
CTC	0.75	0.98	1.0
Other aliphatics	0.92	0.998	1.0

* Computed as average for runs b and c.

each segment are listed in Table 4. Whereas the η-values downstream of the injection port approached unity, the η-values in the first segment were significantly less than unity, due to the larger L_f. Also, the effects of diffusional resistance were greatest for the most rapidly degraded compound, CTC.

SUMMARY AND CONCLUSIONS

Laboratory experiments were conducted to evaluate the secondary utilization of eight trace-concentration halogenated solvents in a BAZ induced by nitrate injection. Results of these experiments indicate that carbon tetrachloride was removed most completely by a denitrifying BAZ, while bromoform, dibromoethane, tetrachloroethene, trichloroethene and *1,2-* and *1,3*-di-chlorobenzene were removed to lesser degrees. *1,1,1*-trichloroethane removal was slight. A significant result was that the dichlorobenzenes also were removed; these compounds have previously been considered refractory under denitrifying conditions.

An efficient numerical model that coupled solute-transport and biofilm kinetics was developed to interpret the laboratory results. The steady-state, one-dimensional solute-transport equation was solved using an iterative finite-difference scheme and by employing a quasilinearization technique for the biofilm-reaction term. The model was capable of solving directly for the steady-state profiles of secondary substrates. Since independently determined kinetic parameters did not exist for the secondary substrates, one set of results from the column experiments was used to obtain best-fit kinetic parameters, which were then used to predict the results for experiments conducted with different liquid flow velocities. The model results correctly described all trends: (1) removal of the halogenated compounds only in the BAZ; (2) greater removal

with increased BAZ contact time; and (3) reduced specific removal rates caused by diffusion limitation in the biofilm.

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