LONG-TERM MONITORING TO OBSERVE NATURAL ATTENUATION IN THE LABORATORY

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ABSTRACT

Long-term studies to observe natural attenuation have been described for many field locations. Often the attenuation can only be inferred to be biodegradation, based on, for instance, the presence of *cis*-dichloroethylene (DCE) where only trichloroethylene (TCE) was a known contaminant. Because in several instances we had observed such transitions in the presence of plants, an unplanted control was set up to see if natural attenuation may arise "spontaneously." A cylinder 12 cm in diameter and 33 cm high was packed with a natural, sandy soil. The surface-volatilized gas phase was sampled intermittently over more than 1.5 years. Soil water was analyzed for contaminants on several occasions. Continuous feeding of TCE-contaminated water from the bottom resulted in release of only DCE, and relatively little of that. Both methanogenesis and methanotrophy were observed within the contaminated column. Surface monitoring currently indicates disappearance of >95% of the input TCE.

Key words: *natural attenuation, trichloroethylene, methanogensis, methanotrophy*

INTRODUCTION

Earlier studies in this laboratory reported the apparent degradation of several compounds including toluene and phenol supplied in groundwater to two planted channels of alfalfa (Davis et al., 1994a,b; Hoffman et al., 1994). However, it was not established whether the degradation process might have occurred without the added plants or the nutrients and bacterial inoculant that were introduced to the channels early in their life history.

Further studies (Narayanan et al., 1995, 1996) with trichloroethylene (TCE) introduced in the inlet water to the two-channel system showed significant conversion of TCE to *cis*-dichloroethylene. This occurred in the (presumably) anaerobic saturated zone so that the contaminant material in the outflow water was almost entirely DCE rather than TCE. The water residence time was long in this experiment because >90% was lost through evapotranspi-

ration before getting to the outflow. Very little TCE or DCE volatilization could be detected at the soil surface between the plants. An undetermined fraction of contaminant could have passed through the plants.

In experiments with TCE introduced as a NAPL, volatilization of DCE was observed at the soil surface in a six-channel system, even where plants were not present in the channel (Zhang et al., 1997). In this instance, it appeared that the reductive dechlorination was occurring but further metabolism of the DCE may have been minimal.

To specifically address the question of whether long-term degradative adaptation may occur without specific interventions, such as nutrient addition, planting, or bacterial inoculation, a groundwater fed cylinder was set up. Results obtained here may reasonably reflect what may occur under comparable conditions in the field with minimal interventions.

MATERIALS AND METHODS

A cylinder of 12 cm diameter x 33 cm depth (inside measurements) was set up September 11, 1998, and fed with a low level (25 µL/L) of trichloroethylene (TCE). The soil was silty sand from near the closed Riley County Landfill, as used in previous experiments. No microorganisms were deliberately introduced to this system, which is shown schematically in Figure 1. The water table was maintained at a few cm from the bottom, producing a saturated zone close to the soil surface.

As previously used with the two-channel system described by Davis et al. (1993), a mixing bottle of 13 L volume was continually stirred. Water was introduced into that bottle from an open reservoir which determined the overall hydraulic head of the system. The contaminant TCE was introduced into the mixer at a rate of 25 µL for each L water supplied to the head-maintaining reservoir. A nylon tube of ~3 mm O.D. passed from the mixer to a standard glass stopcock at the base of the cylinder. Inside, glass wool had been packed to prevent blockage by the silty soil. Over this was a ~1 cm layer of fine sand, then another layer of very fine sand. Both layers tapered in depth, away from the stopcock. Carefully, a half-liter of water was added; then the silty sand obtained at depth of 20-40 cm from the landfill site was packed on top of the washed sand. Another half liter of water was added, followed by silty sand "topsoil" from the landfill site to fill the cylinder completely.

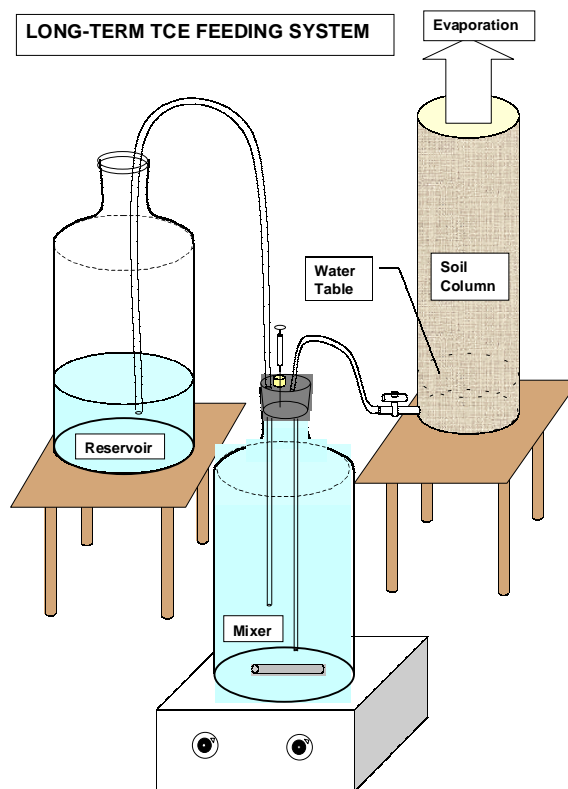Then the cylinder was saturated by introducing water, containing TCE, from the bottom,

Figure 1. Long-term TCE feeding system.

with the reservoir raised so the water table reached the top of the cylinder. After a day, the inlet was shut off and the soil was packed down gently to provide a smooth surface and well-settled column. Then it was allowed to dry down until the saturated zone was down to ~20 cm. At that point, the reservoir was lowered to give a 10 cm (from bottom) water table and the stopcock was reopened. The column was wrapped in black plastic to inhibit algal growth.

Surface fluxes of TCE and DCE (cis-1,2-dichloroethylene) were monitored by sampling vented containers placed on, then pressed into, the surface of the soil. The volatiles were detected by FID gas chromatography. Water usage was determined over long periods of time by record of the amount of water added to the hydraulic reservoir to maintain a constant head.

Water use rates varied with season of the year, as expected, with higher usage during the winter and summer and lower usage in the spring and fall when relative humidity was higher. Rates varied from 1 L/ 2 wk to 1 L/ mo. When plants were present, the water use was higher.

Soil water was sampled by using a sharpened brass cylinder forced into the soil to a determined depth, after which the core was quickly transferred to a bottle and sealed with a Mininert valve. The soil was allowed to equilibrate and then the head-space gas was sampled. The soil amount was determined by weighing the soil and bottle wet. The water content was deduced by the difference in weight after drying. Using the Henry constant and appropriate volume calculations, the equivalent concentration in the aqueous phase was determined. A linear correction was made for sorption to soil organic matter, which was only 1% of the soil mass.

Levels of TCE in the inlet water were determined by adding known volumes of the water to bottles stoppered with Mininert valves. Head-space gas was sampled and aqueous-phase concentration was calculated using the Henry constant. Comparing head-space TCE content with soil vs large glass beads allowed estimation of the sorption coefficient. On a soil mass basis, it was a correction factor of two; that is, half of the aqueous-phase TCE became sorbed to the soil organic matter.

RESULTS

No surface flux of TCE from the cylinder was measurable, even during the first few months; instead the dominant detectable gas was DCE with some methane during the first year. Initially, the flux of DCE over short periods of time (15 -40 min) was about half of

Table 1. Surface DCE efflux at 90 days of exposure to TCE[a].

Time	relative pk ht
6 min	5, 4, 4.5
16 min	16, 10.5, 11.5
30 min	16, 16.5, 16
185 min	46, 55, 56
24 hr	82, 68, 88

a. Sample flux calculation. Water use 1 L/ 2 wk or 336 h = <3 mL/h. TCE level is 25 µL/L = 25 nL/mL = 0.29 µmol/mL (from density and formula wt). For 3 mL/ h, 0.87 µmol or ~22 µL/h TCE gas volatilization is predicted based on water flux. Gas phase sample is obtained from covering 1/ 2.25 portion of surface area = ~10 mL/ h for the area captured. This is collected into a 150 mL container so that ~ 70 nL/mL/h (ppm/h) is the predicted accumulation rate in the gas phase. Observed accumulation rate converted to concentration by comparison to a standard of TCE gives a concentration of 3 nL/mL/6 min or ~30/70 of the expected flux. Accumulation is non-linear over time, as can be seen by graphing the data from this table.

the contaminant flux predicted from water usage averaged over a week-long period (Table 1). After a year, this had declined somewhat, while the methane flux was less than 3% of the input TCE carbon. After several further months of exposure to TCE, the surface flux of DCE decreased several-fold and methane was no longer observable (Table 2).

Soil sampling at two months from initiation of feeding indicated that high levels of DCE and some methane both were present in the fully saturated zone. No TCE was detectable in the top 15 cm of the column.

After five months, the column was partially dried down, then watered from the top with Hoagland's solution for ~two weeks and planted with successive crops of sunflowers. It was possible to observe transfer of DCE into the stems of the sunflower plants, as reported elsewhere (Davis et al., 1999). Water use was greater during this time and some organic carbon may have been introduced when the plant roots decayed.

At a year, several months after the plants had been removed, the amount of methane in the deep soil water was only a small fraction of the input TCE concentration, less than 10% of carbon (Table 3). Plant roots presumably had not entered the saturated zone.

Now, after 20 months from the initiation of the column, no TCE is detectable in the top ~20 cm of soil in the cylinder and surface flux of DCE is only 6% of the amount expected on the basis of water use. There is no detectable methane release from the soil surface, although the methane level in the deep water remains at 7% of TCE carbon concentration.

DISCUSSION

This system appears to have evolved into an effective remediation without intentional addition of any specific micro-organisms. It is likely that the same soil could do so in its natural

Table 2. Surface flux at several times.

A. 4.5 months	
Time	Relative pk ht
7 min	4, 4, 6.5
15 min	8, 11.5, 6.5
32 min	16.5, 8, 25

B. 5.5 months	
Time	Relative pk ht
10 min	5, 8, 12
21 min	13, 18, 16
33 min	21, 26, 21

C. 6.3 months	
Time	Relative pk ht
10 min	1.5, 1, 1
40 min	5.5, 7, 5

D. 13 months	
Time	Relative pk ht
16 min	1, 1.5, 1
60 min	3, 2,5, 2.5

E. 16 months	
Time	Relative pk ht
20 min	2, 2, 2
40 min	4, 3, 4.5
24 hr	15, 17, 13

All values are relative, normalized to the same units used in Table 1.

setting, if both anaerobic and aerobic zones were present.

Surface release of DCE has declined at least five-fold and release of methane has become undetectable. Given that instrumental responses and sampling techniques have remained the same and the water use continues relatively constant, we can only conclude that degradation is occurring within the column.

This system is not unique. During experiments with TCE NAPL phase in a six-channel system, DCE was observed (Zhang et al., 1997). Following these experiments, we observed the presence of an additional peak indicative of DCE being slowly desorbed, during the course of a later study intended to examine methyl-*tert*-butyl ether (MTBE) migration. During later studies with the six-channel system, we attempted to determine the transfer to plants and surface flux of both MTBE and TCE in a single channel, when they were introduced in the groundwater. Much to our regret, no TCE was detectable in the gas-phase flux from the soil surface, although it was present at the expected level in the inlet water. Most likely it was converted to DCE, which elutes at the same position as MTBE in the gas chromatograph, obscuring it.

ACKNOWLEDGMENTS

REFERENCES

Davis, L.C., C.T. Chaffin, N. Muralidharan, V.P. Visser, W.G. Fateley, L.E. Erickson, and R.M. Hammaker, 1993. Proceedings of the Conference on Hazardous Waste, Kansas State University, pp 236-249. Monitoring the beneficial effects of

Table 3. Contaminant analysis at 20 months.

Depth in column (cm)	Concentration (rel)[a]
0 - 8	19
8 - 16	63
16 - 24	105

a. compared to inlet water in the presence of the same soil, corrected for DCE vs TCE response and relative water volume in the analyzed sample. "Contaminant" is the sum of amounts of DCE and TCE. TCE was observed only in the 16-24 cm sample and was less than 1/4 the total.

plants in bioremediation of volatile organic compounds.

Davis, L.C., N. Muralidharan, V.P. Visser, C. Chaffin, W.G. Fateley, L.E. Erickson, and R.M. Hammaker, 1994a. American Chemical Society Symposium Series # 563 Bioremediation through rhizosphere technology T.A. Anderson and J. Coats, Eds., pp 112-122. Alfalfa plants and associated microorganisms promote biodegradation rather than volatilization of organic substances from groundwater.

Davis, L.C., C.T. Chaffin, L.E. Erickson, W.G. Fateley, R.M. Hammaker, R.M. Hoffman, N. Muralidharan, and V.P. Visser, 1994b. 4 pg extended abstract in Proceedings of the 20th annual Risk Reduction Engineering Laboratory research meeting. Using Fourier transform infra-red spectroscopy (FT-IR) to monitor progress of plant-based bioremediation efforts.

Davis, L.C., D. Lupher, J. Hu, and L.E. Erickson, 1999. Proceedings of the Conference on Hazardous Waste, Kansas State University, pp 203-209. Transport of trichloroethylene through living plant tissues.

Hoffman, R.M., V.P. Visser, L.C. Davis, L.E. Erickson, N. Muralidharan, R.M. Hammaker, and W.G. Fateley, 1994. In Proceedings of the Conference on Hazardous Waste Research, Kansas State University; D. Tillison, L.E. Erickson, S.C. Grant, and J.P. McDonald, eds. pp 108-116. Monitoring plant bioremediation of volatile organic compounds (VOCs) using open path Fourier transform infrared (FT-IR) spectrometry.

Narayanan, M., L.C. Davis, and L.E. Erickson, 1995. Proceedings of the 25th Annual Biochemical Engineering Conference, pp 11-20. Biodegradation studies of chlorinated organic pollutants in a chamber in the presence of alfalfa plants.

Narayanan, M., L.C. Davis, L.E. Erickson, R.M. Hoffman, N.K. Russell, R.M. Hammaker, and W.G. Fateley, 1996. Proceedings, Fifth World Congress on Chemical Engineering, Vol III, pp 694-699. Modeling and analysis of transport and biodegradation in laboratory chambers with plants.

Zhang, Q., L.C. Davis, and L.E. Erickson, 1997. Proceedings of the 27th Annual Biochemical Engineering Symposium, pp 122-132. An experimental study of trichloroethylene fluxes to the atmosphere.