

Biotransformation of Trichloroethylene in Soil

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Trichloroethylene was shown to degrade aerobically to carbon dioxide in an unsaturated soil column exposed to a mixture of natural gas in air (0.6%).

The organic contaminants that are most commonly detected in groundwater are low-molecular-weight, chlorinated aliphatic hydrocarbons such as trichloroethylene (TCE), tetrachloroethylene (PCE), 1,1,1-trichloroethane, carbon tetrachloride, and chloroform (15). The extent of contamination in industrial regions can be inferred from a survey undertaken by the state of New Jersey (8). More than a quarter of the wells sampled contained detectable concentrations of these compounds, and one 10th had concentrations in excess of 10 $\mu\text{g/l}$, but only 1 to 2% had concentrations in excess of 100 $\mu\text{g/l}$ (Table 1). The U.S. Environmental Protection Agency (16) has proposed recommended maximum contaminant levels of 0 for TCE, PCE, and carbon tetrachloride and 200 $\mu\text{g/l}$ for 1,1,1-trichloroethane. Recommended maximum contaminant levels are nonenforceable health goals. Maximum contaminant levels, which are enforceable standards under the Safe Drinking Water Act, are under discussion and may range from 5 to 50 $\mu\text{g/l}$ for TCE, PCE, and carbon tetrachloride.

This class of compounds is resistant to biodegradation in aerobic subsurface environments, which contributes to their persistence in polluted groundwaters (9, 11-13). However, these compounds can be biotransformed in anaerobic materials; Bouwer and McCarty (2) have shown that acetate-degrading methanogens can transform PCE, 1,1,1-trichloroethane, chloroform, and carbon tetrachloride. Surprisingly, chloroform and carbon tetrachloride were degraded to carbon dioxide in their study. Unfortunately, in subsurface materials these transformations are often incomplete and occasionally result in the accumulation of products (such as vinyl chloride from TCE or PCE) that are as much a problem as the original contaminant (6, 7).

Current technology for reclaiming groundwater polluted with these compounds involves pumping the water to the surface and either stripping out the compounds in aeration towers or removing the pollutant on a sorbent (5, 16). A process that permits treatment of the contaminated water in situ and results in destruction of the contaminants rather than simple transfer to another environmental medium should have economic and environmental advantages at many polluted sites.

It has been known for some time that the monooxygenase of methanotrophs will oxidize and dechlorinate halogenated methanes (3). It was recently reported that propane-oxidizing bacteria can epoxidate ethylene and that the epoxide is further metabolized (4). These observations suggest that the enzyme that epoxidates ethylene might transform TCE. To investigate this possibility, we exposed unsaturated soil to natural gas to enrich for methanotrophs and for organisms

that oxidized the other small alkanes present in natural gas and then examined the soil for the capacity to remove TCE from infiltrating water. As a control, the behavior of TCE in soil exposed to natural gas was compared to that of TCE in an earlier study (10), in which the same soil in the same experimental configuration was dosed with a solution of TCE but was not exposed to natural gas.

Sandy soil was packed into a glass column (5 cm, inner diameter) to a depth of 150 cm. Water containing TCE was applied at a rate of 21 cm per day (410 ml per day). The elution volume of the column was 41 cm (800 ml) of water. Water entering and leaving the column passed through 16-ml screw-capped test tubes that were sealed with a Teflon-faced septum. As appropriate, the tubes were removed for analysis of TCE by the purge-and trap method (1) according to U.S. Environmental Protection Agency test method no. 601 (14). The tubes were left in place long enough for 15 to 25 flushings before the samples were taken. With the exception of the sampling method, the construction and operation of the column was identical to that described in the earlier study.

A stream of air containing 0.6% natural gas by volume was passed over the head of the column. The gas was at least 96% hydrocarbons. Of the hydrocarbons, 77% was methane, 10% was ethane, 7% was propane, 2.4% was *n*-butane, 1% was *iso*-butane, 1.5% was pentanes, and 0.7% was hexanes. Three weeks were allowed for acclimation; the soil then received water containing TCE at an average concentration of 150 $\mu\text{g/liter}$. Concentrations of TCE in the column effluent were monitored for 2 weeks. Removal of TCE was extensive; less than 5% of the applied TCE passed through the soil (Fig. 1). This is in contrast to results of an earlier study (10). Without exposure to methane, there was no statistically significant degradation of TCE ($\alpha = 0.05$), as inferred from a mass balance of material applied, material that volatilized, and material in the column effluent. As a result, volatilization was the only removal process in the earlier study, resulting in a mean (\pm standard deviation) breakthrough of 28 ± 1 and $21 \pm 13\%$ of the TCE applied at 900 and 180 $\mu\text{g/liter}$, respectively. To confirm that the increased removal in the soil exposed to natural gas represented biological activity, the column was poisoned with water that contained 224 μg of TCE and 2 g of sodium azide per liter. Breakthrough of TCE increased dramatically (Fig. 1) to levels that were seen in the earlier study.

In an attempt to identify the products of the biotransformation, a second column was acclimated to natural gas and then dosed with a solution of [¹⁴C]TCE. After 1.6 elution volumes of water had been applied, $15.8 \pm 0.3\%$ ($\alpha = 0.05$) of the applied radiolabel appeared in the column effluent. When the column effluent was adjusted to pH 11, the

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TABLE 1. Frequency of detection of organic pollutants in wells in an industrial state

Compound	% of 670 wells with concn greater than: ^a		
	100 µg/liter	10 µg/liter	MRC
TCE	1.8	4.0	26
PCE	0.3	2.4	23
1,1,1-Trichloroethane	0.7	9.7	21
Carbon tetrachloride	0.3	0.8	27
Chloroform	0.4	3.6	15

^a Data summarized from reference 8. MRC. Minimum reported concentration.

radiolabel could not be purged by conditions of vigorous aeration that could remove 99% or more of the label from the [¹⁴C]TCE dose solution. At least 95% ($\alpha = 0.05$) of the label was purged from the effluent when the pH was adjusted to 2, and at least 93% ($\alpha = 0.05$) of the label precipitated with barium hydroxide. After 2.9 elution volumes, the label in the effluent increased to $24.6 \pm 0.4\%$ ($\alpha = 0.05$) of the applied label. Again, essentially all of it precipitated in the presence of barium hydroxide. Apparently the TCE was degraded to carbon dioxide. Because the soil used in this study has little organic matter (0.4% at the surface, 0.04% at 150 cm) and essentially no structure, we believe that anaerobic microhabitats are unlikely to occur and that the transformation was an aerobic process.

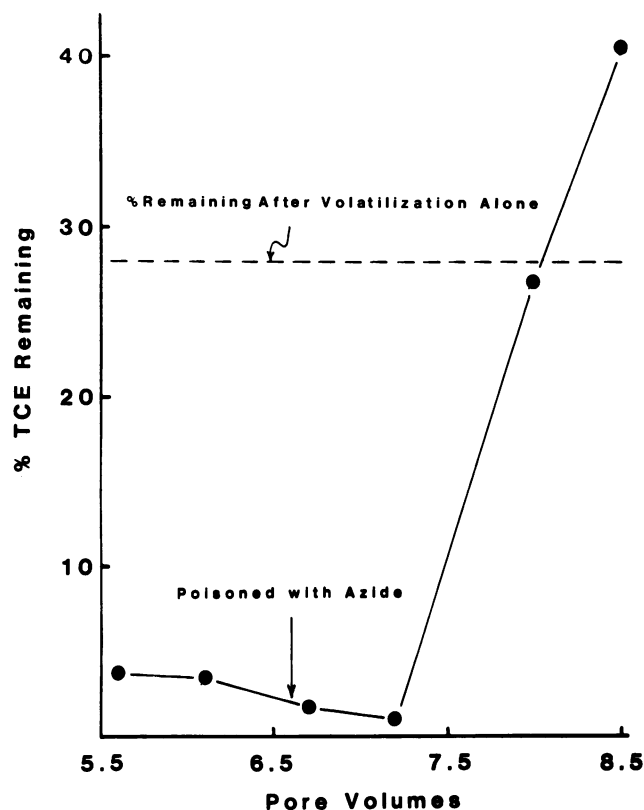


FIG. 1. Removal of TCE during passage through unsaturated soil exposed to an atmosphere of 0.6% methane (vol/vol) in air.

Biological activity lowered the concentration of TCE by roughly 1 order of magnitude during the 2-day residence time of water in the column. Such a rate is adequate for in situ reclamation. Work is in progress at the Robert S. Kerr Environmental Research Laboratory to identify which of the other chlorinated aliphatic hydrocarbons are subject to the process, to determine any other end products of the biotransformation, and to adapt the process to aquifers rather than unsaturated soil.

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