

EPA Ground Water Issue

TCE Removal from Contaminated Soil and Ground Water

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Background

The Regional Superfund Ground Water Forum is a group of EPA professionals, representing EPA's Regional Superfund Offices, committed to the identification and the resolution of ground water issues impacting the remediation of Superfund sites. The Forum is supported by and advises the Superfund Technical Support Project. Remediation of trichloroethylene-contaminated soils and ground waters is an issue identified by the Forum as a concern of Superfund decision-makers. For further information contact Hugh H. Russell (FTS-743-2444), John E. Matthews (FTS-743-2408), or Guy W. Sewell (FTS-743-2232).

Introduction

Trichloroethylene (TCE) is a halogenated aliphatic organic compound which, due to its unique properties and solvent effects, has been widely used as an ingredient in industrial cleaning solutions and as a "universal" degreasing agent. TCE, perchloroethylene (PCE), and trichloroethane (TCA) are the most frequently detected volatile organic chemicals (VOCs) in ground water in the United States (Fischer et al., 1987). Approximately 20% of 315 wells sampled in a New Jersey study contained TCE and/or other VOCs above the 1 ppb detection limit (Fusillo et al., 1985). The presence of TCE has led to the closure of water supply wells on Long Island, N.Y. and in Massachusetts (Josephson, 1983). Detectable levels of at least one of 18 VOCs, including TCE, were reported in 15.9% of 63 water wells sampled in Nebraska, a State having a low population density and industrial base (Goodenkauf and Atkinson, 1986).

Trichloroethylene per se is not carcinogenic; it is thought to become a human health hazard only after processing in the human liver (Bartseh et al., 1979). Epoxidation by liver oxidase enzymes confers a suspected carcinogenic nature (Apfeldorf and Infante, 1981; Tu et al., 1985). However, processing in the human liver is not the only way in which TCE may become a health hazard. Reductive dehalogenation of TCE through natural or induced mechanisms may result in

production of vinyl chloride (VC) which, in contrast to TCE, is a known carcinogen [Fed. Regist. 1984, 49:114, 24334(11)].

Wastewater or municipal water supply treatment systems which utilize coagulation, sedimentation, precipitative softening, filtration and chlorination have been found ineffective for reducing concentrations of TCE to non-hazardous levels (Robeck and Love, 1983). Other methods are required for remediation of water contaminated with TCE if such water is to be used for human consumption. The purpose of this paper is to: 1) present a synopsis of physico-chemical properties and reactive mechanisms of TCE, and 2) delineate and discuss promising remediation technologies that have been proposed and/or demonstrated for restoring TCE-contaminated subsurface environmental media.

Physical and Chemical Properties of Trichloroethylene

Preliminary assessment of remediation technologies feasible for reclamation of subsurface environmental media contaminated with TCE must involve consideration of the compound's physical and chemical properties (i.e., distribution coefficients, reactivity, solubility, etc.). These properties are directly responsible for behavior, transport and fate of the chemical in the subsurface environment. Knowledge of a compound's physico-chemical tendencies can be used to alter behavior and fate of that compound in the environment. Important considerations derived from physical and chemical properties of TCE presented in Table 1 are:

Density (1.46 g/ml) - Density can be defined as the concentration of matter, and is measured by the mass per unit

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volume. In relation to liquids, these units are grams per milliliter. The density of a substance is usually referenced to pure water which is taken to be 1 gram per milliliter. TCE is heavier than water; therefore, a spill of sufficient magnitude is likely to move downward through the subsurface until lower permeability features impedes its progress. This often results in formation of a plume or pool(s) of dense nonaqueous phase liquid (DNAPL) in the aquifer plus a trail of residual saturation within the downward path. Implicit in this statement is the fact that residual saturation also will serve as source areas for contamination and migration of TCE within an aquifer system. There is an inherent difficulty associated with location of DNAPL in the subsurface and subsequent removal of DNAPL pools or plumes using a standard pump and treat regime. A major reason for this difficulty of removal is that water coning using conventional extraction wells results in poor DNAPL/water ratios.

A density difference of about 1% above or below that of water (1.0 gm/ml) can significantly influence movement of contaminants in saturated and unsaturated zones (Josephson, 1983). This does not mean that density differences of less than 1% do not influence movement of contaminants. These density differences may even be apparent at low solute concentrations (Short, 1991, personal communication). At a site in New Jersey, it was determined that although soil and shallow ground water at the source area were contaminated with benzene, toluene and other volatile organic compounds with relatively low specific gravities, the compounds did not migrate downward into deeper municipal supply wells (Spayd, 1985). This is in contrast with what could happen if the source area were contaminated with chlorinated aliphatics, including TCE. Areas containing insoluble TCE, i.e., DNAPL pools, can serve as source areas for spreading of contamination. As ground water moves through and/or around these source areas, equilibrium concentrations partition into the aqueous phase. Aqueous phase TCE is then spread through the aquifer by advection and dispersion. As a result small source areas can serve to contaminate large portions of an aquifer to levels exceeding drinking water standards. At a site in Texas, for example, Freeberg et al. (1987) determined that 8 kg of non-aqueous phase TCE was responsible for contaminating 12.3 x 10⁶ gallons of water at an average concentration of 176 ppb.

Water solubility - Water solubility can be defined as the maximum concentration of a solute which can be carried in water under equilibrium conditions and is generally given as ppm (parts per million) or mg/l (milligrams per liter). The water solubility limit of TCE is 1000 mg/l, the maximum concentration of TCE that can be in aqueous solution at 20° C. Water solubility of a compound has a direct relation on distribution coefficients and biodegradability of a particular compound. A compound that is relatively insoluble in water will prefer to partition into another phase; i.e., volatilize into soil gas or sorb to organic material. Compounds that are relatively insoluble also are not as readily available for transport across the bacterial membrane, and thus less subject to biological action.

K_{oc} value - K_{oc} is defined as the amount of sorption on a unit carbon basis. The K_{oc} can be predicted from other chemical properties of compounds such as water solubility and octanol water coefficient. The low K_{oc} value of 2.42 for TCE

translates into little retardation by soil or aquifer organic materials. Since the retardation is so low, pump-and-treat technologies appear attractive as remediation alternatives. Mehran et al. (1987) through field and laboratory investigations determined a retardation factor of approximately 2.0 for TCE which agrees with the data of Wilson et al. (1981) and falls within the range of 1-10 given by Mackay et al. (1985) for sand and gravel aquifers with low organic content. Measured partition coefficients, however, may be considerably higher than calculated values, especially at lower aqueous concentrations. Johnson et al. (1989) found that at equilibrium concentrations of approximately 1 ppm, the measured partition coefficient of TCE was significantly higher than calculated values. These authors also report that other workers who have observed the same effect theorize that this higher value may be related to clay interactions.

If the retardation factor is considered to be 2.0, TCE should migrate at half the speed of water through soil and aquifer materials low in organic carbon content, and theoretically somewhat slower in material with a high organic carbon content.

Henry's Law Constant - Henry's Law states that the amount of gas that dissolves in a given quantity of liquid at constant temperature and pressure, is directly proportional to partial pressure of the gas above the solution. Henry's coefficients, as a result, describe the relative tendency of a compound to volatilize from liquid to air. The Henry's Law Constant for TCE is 0.00892 which is high enough, when combined with its low solubility in water and high vapor pressure, for efficient transfer of TCE to the atmosphere. The evaporation half-life of TCE in water is on the order of 20 minutes at room temperature in both static and stirred vessels (Dilling, 1975; Dilling et al., 1975).

Table 1. Physico-chemical Properties of Trichloroethylene

Density	1.46 g/ml
Water Solubility	1000 mg/L
Henry's Law Constant (atm-m ³ /mol @ 20° C)	0.00892
Molecular Weight	131.4
Boiling Point	86.7° C
Log Octanol-Water Partition Coefficient	2.42

The chemical structure of TCE bestows chemical reactivity. Three chlorine atoms attached to the carbon-carbon double bond make TCE a highly oxidized compound. Oxidized molecules readily accept electrons (reduction) under appropriate conditions, but resist further oxidation. As a result, chemical reactivity of TCE is greatest under a reducing atmosphere, conditions that favor transfer of electrons to TCE.

Due to their size, the three carbon atoms surrounding the double bond are responsible for steric hinderance. This lowers the rate at which large nucleophilic groups can approach or react with the carbon-carbon double bond.

Due to its chemical nature, TCE can (under the appropriate conditions) undergo a number of abiotic transformations, or interphase transfers. The ease with which any chemical can undergo such reactions is an important indicator of that chemical's susceptibility to abiotic remediation processes.

Environmental Distribution of Trichloroethylene

While it has been estimated that about 60% of the total TCE produced in the United States is lost to the atmosphere, with negligible discharge into water bodies (Cohen and Ryan, 1985), widespread contamination of terrestrial subsurface environmental media also has occurred. Given the wide use of TCE as a degreasing solvent plus its recalcitrance and chemical properties, this type of distribution pattern is not surprising.

Trichloroethylene contamination exists in both vadose and saturated zones of the subsurface environment. This contamination results from spills, leaking transfer lines, storage tanks and poor environmental awareness. Because of its density and low K_{oc} , TCE will ultimately move downward in the vadose zone until an impermeable barrier is reached. Such a scenario occurs when a TCE spill is of sufficient magnitude or deep enough in the vadose zone for volatilization to be restricted.

Once in the vadose zone, TCE can become associated with soil pore water, enter the gas phase because of its Henry's constant, or exist as nonaqueous phase liquid (NAPL). It is therefore conceivable that upward or downward movement of TCE can occur in each of these three phases, thereby increasing areal extent of the original spill in both the vadose and saturated zones. While movement of large concentrations of TCE through the vadose zone may be rapid, surface tension exerted at the capillary fringe may retard further downward movement of smaller spills.

Nonaqueous phase concentrations of TCE which are large enough to overcome capillary forces will move downward into the aquifer. Once the water table is penetrated, lateral flow may be mediated by the regional ground-water flow. Due to its high density, the movement of free-phase TCE is still directed vertically until lower permeability features are encountered. Once an impermeable layer is encountered, horizontal movement will occur. Such movement may even be directed against the natural ground-water flow by the effects of gravity.

Since permeability is a function of the liquid as well as the medium, the vertical movement of TCE through an aquifer is determined by geological properties of the aquifer material; i.e., granular size of sand or clay lenses. Trichloroethylene will tend to pool near these impermeable features. Water passing over and around these pools solubilize TCE that can be spread throughout the aquifer.

Reaction Mechanisms for Trichloroethylene

Oxidation

Highly oxidized chemicals such as TCE have a high reduction potential and are thereby resistant to further oxidation. This is

the reason that aerobic biological mediated degradation of TCE was once thought to be illogical.

It is, however, possible to oxidize TCE using chemicals such as potassium ferrate. Delucca et al. (1983) determined in laboratory experiments that 30 ppm potassium ferrate would completely oxidize 100 ppb TCE in less than fifty minutes (after an initial 5 to 20 minute delay) at 23 degrees Celsius and a pH of 8.3. These experiments, however, were conducted using water that had been double distilled, deionized and passed through resin columns. These purification steps effectively removed all organic and inorganic species that might have inhibited the oxidation of TCE through a competitive process. The presence of other solutes with lower oxidation states or more accessible electrophilic binding sites would effectively lower the concentration of the radicals by reacting first, thus leaving fewer radicals to combine with TCE.

In wastewater treatment, ozone has been shown effective at the removal of organic material. Ozonation, however, is generally used to remove less oxidized chemicals than chlorinated aliphatics. The actual mechanism in this case is either the direct reaction of ozone with the carbon-carbon double bond or nucleophilic substitution by hydroxyl radicals which are generated upon the decomposition of ozone. Destruction of TCE by ozone has been reported by Glaze and Kang (1988) and Francis (1987), and with some success by Cheng and Olvey (1972); however, the low concentration and reactivity with other solutes of hydroxyl radicals is still a problem. To overcome this problem, investigators have tried to couple chemical reactions designed to increase production of hydroxyl radicals. Glaze and Kang (1988) have described four ways to enhance the oxidation potential of ozone: 1) variation in pH, 2) addition of hydrogen peroxide, 3) addition of ultraviolet light and 4) addition of a combination of peroxide and ultraviolet radiation. Their results indicate that direct ozonation of TCE in high alkalinity ground water is a slow process. The addition of hydrogen peroxide at a ratio of 0.5-0.7 (w/w hydrogen peroxide: ozone) accelerated the oxidation rate by a factor of two to three. They concluded that oxidation of TCE under certain conditions is a promising destruction process.

Reduction

Compounds such as TCE also are susceptible to reduction. While transition metals may play a role in abiotic reductions, the major reductive components may be electrons or reducing equivalents produced from biological reactions or molecular hydrogen (Barbash and Roberts, 1986). Reduction of TCE may be possible by any organic compound that has a sufficiently low oxidation potential for efficient hydrogen transfer under ambient conditions.

Dehalohydrolysis

Natural dehalohydrolysis of TCE (or other halogenated VOCs), with the subsequent production of an alcohol, is possible. Half-lives of such reactions are on the order of days to centuries (Barbash and Roberts, 1986). Natural dehalohydrolysis proceeds by either hydrolysis in an aqueous phase or nucleophilic substitution and elimination reaction at unsaturated carbons (ethene bond). Removal of a chlorine

atom from one carbon coincides with removal of a hydrogen atom from the adjacent carbon. Given the number of soil and aquifer systems contaminated with TCE, however, natural dehalohydrolysis is not considered to be a significant mechanism of degradation.

The rate determining step in nucleophilic attack is hydroxyl ion (or other nucleophile) reaction with the double bond. The rates of unimolecular and bimolecular nucleophilic substitution depend on: 1) structure of the carbon bearing the leaving group (general order of reactivity in bimolecular reactions methyl > primary > secondary > tertiary), 2) concentration and reactivity of the leaving group, 3) nature of the leaving group (I > Br > Cl > F), 4) nature and polarity of the solvent (concentration of ions such as bicarbonate) and, 5) in the case of S_N2 type reactions, the concentration of the radical. It is quite evident then, should nucleophilic substitution occur, the daughter product or products (dichloroethylene or vinyl chloride) would be increasingly resistant to nucleophilic displacement, yet still be of environmental consequence. This fact, coupled with the low rates of natural dehydrohalogenation of TCE point to the need for some type of catalyst or enhancement of reactivity.

In regards to catalysts, a number of chemical compounds or processes have been developed, or borrowed from the wastewater treatment industry. Ultraviolet radiation has been suggested as one method to enhance reaction rates through the formation of reactive hydroxyl radicals. Ultraviolet light may be an important mechanism for the degradation of recalcitrant chemicals in surface waters and the photolytic zone (top 1-2 mm) of soil (Miller et al., 1987). In a laboratory setting with a six-fold molar excess of dissolved oxygen, under an oxygen atmosphere, the photooxidizable half-life of TCE has been determined to be 10.7 months (Dilling et al., 1975). Given the interphase transfer potential of TCE, photodegradation should not occur to any extent before transfer to the atmosphere.

Surface Treatment Technologies

Air Stripping

Air stripping is an applicable technology for removal of TCE from contaminated water. A constant stream of air is used to drive TCE from solution, taking advantage of the low Henry's Law constant and water solubility. Since TCE is fairly recalcitrant to other remediation efforts, air stripping seems to be the current method of choice to return water to potability. A number of pilot-scale demonstration and full-scale case studies have shown this alternative to be effective for removal of TCE from contaminated water. This process, however, only shifts the compound to another medium. New restrictions on venting of volatile organic compounds to the atmosphere may preclude the use of such technologies or require treatment of the air-stripped off-gases by carbon adsorption.

The typical air stripper is designed to allow for percolation of large volumes of air through contaminated water. This has the effect of changing conditions to favor volatilization of TCE. Application limitations usually occur as the concentration of TCE falls below a threshold level where volumes of air larger than logistically possible are required to continue the stripping process.

In 1982, 10-12 United States utilities were using some form of aeration technique to strip volatile organic chemicals such as TCE from water supplies. The air strippers used were of three principal types: redwood slat aerators, packed towers and spray towers, all of which are designed to allow maximum contact of water, air and TCE (Robeck and Love, 1983). Since that time many sites and municipal supply systems have utilized air strippers (generally packed towers) as a method for removing VOCs from contaminated ground water.

Wurtsmith AFB - At Wurtsmith AFB, Oscoda, Michigan, TCE was detected in drinking water at a concentration of 6,000 ppb, with a concentration of 10,000 ppb in the centerline of the plume (Gross and Termath, 1985). The remedial design selected was for two packed towers that could be run parallel or in series. The towers were run constantly for one year, consistently obtaining effluent concentrations below 1.5 ppb. The one problem encountered was bacterial growth which plugged the towers. This had the effect of lowering the surface area available for transfer of TCE into the gas phase. Constant chlorination was found to retard bacterial growth, while not affecting operational efficiency of the tower.

Savannah River, Georgia - TCE was found in ground water at the Savannah River Plant in 1981 near an abandoned settling basin which had been used for storage of process waters (Boone et al., 1986). The horizontal area of the plume contour at 100 ppb total concentration chlorocarbons was estimated to be 360 acres. The total mass of chlorocarbons was thought to be 360,000 pounds. In 1983, air stripping was thought to be the best available technology for remediation; therefore, two pilot air stripping units of 20 and 50 gpm capacity were designed. The two pilot strippers, when operated properly, reduced the concentration of total chlorinated hydrocarbons in ground water from 120,000 ppb to less than detection limits of 1 ppb. Data from these pilot units were used to design a production tower to process contaminated water at a rate of 400 gpm.

In 1985, the production tower (400 gpm column) was placed on line and fed by a network of 11 recovery wells. As of 1986, some 65,000 pounds of chlorinated solvents had been recovered from the aquifer through the combined operation of pilot and production towers. In 13 months, the production tower alone, which was reported to operate at 90% efficiency, had removed some 33,500 pounds of chlorocarbons from 115 million gallons of water.

Refrigerator Manufacturing Facility - In the late 1960's, a refrigerator manufacturing facility was granted permission for a waste disposal area in the upper of two peninsulas formed by the "S" meander of a river. This practice resulted in the contamination of the underlying aquifer with chlorinated aliphatics. TCE concentrations were approximately 35 ppm.

The treatment system consisted of installation of 14 wells for extraction of ground water which was processed by air-stripping. Effluent from the "stripper" was then discharged through a recharge basin that was capped with 1.5 feet of pea gravel. Recharge through the pea gravel was thought to serve two purposes: 1) additional removal of TCE by percolation through the gravel, and 2) flushing residual TCE contamination from the vadose zone.

It was reported that the system operated at an influent flow rate of 210 gpm (4000 ppb TCE) and a TCE removal efficiency of 78% (Thomsen et al., 1989). Additional removal attributed to spraying of process water over and percolation through the gravel raised the TCE removal efficiency to greater than 95%. Full scale operation began in the summer of 1987. From July 1987 to October 1987, approximately 24.5 million gallons of ground water were treated, and 775 pounds of TCE were removed.

Combined Air Stripping and Carbon Adsorption

A currently popular method for remediating water contaminated with TCE is to combine the technologies of air stripping and granular activated carbon (GAC) adsorption. This treatment train is attractive because it ameliorates shortcomings of both technologies.

In the case of air stripping, the residual concentration of TCE in treated effluent may be above local or regional drinking water standards, thereby necessitating a "polishing" step prior to use or discharge. Limitations associated with GAC adsorption are:

1) a given sorbent has a finite capacity for sorption of a given contaminant; once this limit is reached, contaminant breakthrough occurs. This breakthrough results from competition between contaminants and normal solutes for unbound sites; less tightly bound solutes are displaced by those solutes having a greater affinity. When loss of binding efficiency becomes great enough, breakthrough of contaminants occurs. Once breakthrough occurs, the sorbent must be changed or cleaned. Adsorption of TCE to GAC, based on equilibrium concentrations of 1 ppm at neutral pH and 20°C, is 28 mg/g (Amy et al., 1987).

2) high dissolved organic carbon (DOC) and other contaminants can compete with TCE for binding sites available on the sorbent, thus increasing the likelihood of breakthrough. A concentration of 10 ppm natural organic matter in river water has been shown to reduce TCE adsorption by up to 70% (Amy et al., 1987).

Recognizing the limitations of sorption (the first may only be economically limiting), use of this technology as a polishing step following air stripping can be a viable link in a surface treatment process for TCE. Air stripping can be used to remove the majority of TCE, followed by adsorption which is used to polish the stripper effluent. This approach will lower construction costs of the air stripper and increase life expectancy of the adsorbent.

Rockaway Township - In 1979, ground-water contamination by TCE and lesser amounts of diisopropyl ether and methyl tertiary butyl ether was discovered in three of the water supply wells serving Rockaway, New Jersey. The first technology used to treat the ground water was sorption utilizing GAC. Quick breakthrough of ether contaminants resulted in rapid loss of GAC sorptive effectiveness. This led to consideration and ultimate use of air stripping as a primary treatment technology (McKinnon and Dykson, 1984). A counter current packed tower with a water flow rate of 1400 gpm and an air flow rate of 37,500 cfm was installed and placed on line Feb. 4, 1982. By July 1983, the GAC system was taken off line

because of the excellent performance of the packed tower in addition to reduced influent levels of the ether compounds.

Subsurface Remediation Technologies

Soil Venting

Soil venting is an in situ air stripping technique used to remove volatile contaminants from the vadose zone. Air is forced into the soil subsurface through a series of air inlets, then vented or extracted under vacuum through extraction pipes. Air laden with organic vapors moves along an induced flow path toward withdrawal wells where it is removed from the unsaturated zone and treated and/or released to the atmosphere (Baehler et al., 1988). Success of the method depends on rate of contaminant mass transfer from immiscible and water phases to the air phase, and on ability to establish an air-flow field that intersects the distributed contaminant. In many cases, treatment of off-gases may be required due to air quality standards.

Trichloroethylene, due to its high potential for interphase transfer to the gaseous phase, should be an excellent candidate for soil venting technologies. Cary et al. (1989) suggested that by forcing air into the water table below the contamination and maintaining sufficient air entry pressure throughout a significant volume of soil, TCE should be trapped at the soil water interface and released to the gas phase. This release to the gaseous phase would favor transfer to the soil surface.

Field results reported by Mehran et al. (1987) link the TCE concentration in soil gas with current levels in ground water; therefore, the theory suggested by Cary et al. would appear to be correct for contamination at or near the soil-water interface. This also may point to the possibility that movement of gaseous TCE from the saturated zone into the soil gas phase may act to further spread contamination. Soil venting technology for removal of TCE has not been fully tested in the field or, at least, has not been reported in refereed literature; however, results from two pilot-scale tests demonstrate the potential applicability of the technology for removal of TCE from the vadose zone (Coia et al., 1985 and Danko et al., 1989).

The first test site was an area where open burning of solvents such as TCE had occurred for over thirty years (Coia et al., 1985). The site consisted of sandy glacial soils with a TCE concentration of 5,000-7,000 mg/kg. A closed, forced ventilation system was installed. The system consisted of perforated PVC pipes extended vertically into the vadose zone, and separate extraction pipes. For 14 weeks, two pilot systems were run, one designated the high-contaminated zone (50-5,000 ppm TCE) and the second the low (5-50 ppm TCE) zone. In the low-contaminated zone, extraction pipes were installed on 20 foot spacing and air was forced into the soil at 50 cfm. In contrast, in the high-contaminated zone, extraction pipes were installed on 50 foot spacing and air was forced into the soil at 50-225 cfm. At the end of the study, 1 kg of TCE was removed from the low-contaminated zone and 730 kg (10-20%) from the high-contaminated zone.

The second test site was the Verona Superfund site in Battle Creek, Michigan (Danko et al., 1989). A number of private

and city wells in the Verona Field were discovered to be contaminated with VOCs, in August 1981. The predominant contaminants based on total mass were perchloroethylene (PCE), cis/trans-dichloroethylene (DCE), TCE, 1,1,1-trichloroethane (TCA) and toluene. A Record of Decision (ROD) was issued in 1985 specifying corrective action which would include a network of ground-water extraction wells, followed by air stripping plus a soil vapor extraction system for vadose zone contamination.

A soil vapor extraction system was installed to specifically remove VOCs from the most contaminated vadose zone source area. The system design consisted of a network of 4" PVC wells screened from approximately 5 ft. below grade to 3 ft. below the water table. A surface collection manifold connected to a centrifugal air/water separator was attached to a carbon adsorption system. The outlet end of the carbon adsorption system was connected to a vacuum system which pulls air from the subsurface into the extraction wells. The pilot system began operation in November 1987. By August 1989, total mass of VOCs removed was reported to be 40,000 lbs.

In-Well Aeration

Another remediation method based on interphase transfer potential of TCE is in-well aeration. In-well aeration can be accomplished using either an air lift or electric submersible pump and sparger. The air lift pump may or may not be used with a sparger.

In-well aeration has been tested at sites near Collegeville, PA and at Glen Cove, NY (Coyle et al., 1988). At the Pennsylvania site, the air lift pump run used with a sparger removed 78% of the TCE; the electric pump run concurrently with a sparger removed 82%. At the New York site, the air lift pump without a sparger removed 65% of the TCE; with sparging, the same pump removed approximately 73%.

Technologies based strictly on volatilization of TCE, however effective at subsurface remediation, do not satisfy the intent of Section 121 of CERCLA. This Section states that "remedial actions in which treatment permanently and significantly reduces the volume, toxicity or mobility of the hazardous substances, pollutants, and contaminants, in a principal element, are to be preferred over remedial actions not involving such treatment." Air stripping simply transfers TCE from one medium (soil or water) to another (atmosphere) without any significant reduction in volume or toxicity.

Bioremediation

Biological remediation is one methodology which has the potential to satisfy the intent of Section 121 of CERCLA. Although bioremediation of environments contaminated with TCE can best be described as in its infancy, this technology remains attractive since the possibility exists for complete mineralization of TCE to CO₂, water, and chlorine instead of simply a transfer from one medium to another. In the case of biological degradation, bacteria may produce necessary enzymes and cofactors which act as catalysts for some of the chemical processes already described.

Anaerobic degradation - Because of the oxidized state of TCE, ecological conditions under which degradation is most

likely to occur is a reducing environment. Biological degradation (and possibly mineralization) of TCE under anaerobic conditions has been studied for a number of years (Bouwer and McCarty, 1983; Bouwer et al., 1981). The first reported biological attenuation of TCE was that of the obligate anaerobic methanogenic bacteria through a process known as reductive dehalogenation. Under anaerobic conditions, oxidized TCE can function as an electron sink and is readily reduced by electrons (or reducing equivalents) formed as a result of metabolism (oxidation) of organic electron donors by members of methanogenic consortia. Volatile fatty acids and toluene may serve as oxidizable substrates (electron donors) which can be coupled to reduction of haloorganic molecules such as TCE with the resultant removal of a chlorine atom (Sewell et al., 1990). Freedman and Gossett (1989) reported conversion of PCE and TCE to ethylene without significant conversion to carbon dioxide. The conversion occurred in an anaerobic system stimulated with electron donors such as hydrogen, methanol, formate and acetate, with added yeast extract. Presumably, the electron donors provided the electrons or reducing equivalents necessary for complete chlorine removal by reductive dehalogenation. PCE mineralization has been reported by other authors (Vogel and McCarty, 1985), although it seems that in the absence of sufficient oxidizable organic compounds a buildup of DCE(s) or vinyl chloride also will occur (Bouwer and McCarty, 1983; Bouwer et al., 1981). Theoretically, under anaerobic conditions, with sufficient quantities of other readily oxidizable substrates and the necessary auxiliary nutrients, methanogenic consortia may be capable of converting TCE to harmless end-products. More research is needed, however, to determine how effective this remediation may be, and what actual requirements are needed to drive the process. Advantages of anaerobic processes are that there appears to be no apparent lower concentration limit to activity nor is there a need to perfuse the subsurface with copious amounts of oxygen.

Aerobic Degradation - It has long been thought that TCE is resistant to degradation under aerobic conditions due to its already oxidized state. Recently, a number of monooxygenases produced under aerobic conditions have been shown to degrade TCE (Nelson et al., 1987; Harker and Young, 1990). Under these conditions, there is no buildup of vinyl chloride, and complete mineralization is possible. An aromatic compound such as toluene or phenol is required, however, for induction of the enzymes responsible. As a result any application of this system would require the presence of a suitable aromatic compound or other inducer. The inducer requirement might be alleviated by manipulation of the proper genetic sequence for monooxygenase production, but other carbon and/or energy sources would probably be required for growth.

Methylotrophic degradation - The enzyme methane monooxygenase (MMO) produced by methylotrophic bacteria growing in the presence of oxygen at the expense of methane has a wide range of growth substrates and pseudosubstrates; one of which is TCE. This enzyme epoxidates TCE. The resulting chemical complex is unstable and quickly hydrolyzes to various products dependent on the pH of the menstruum. TCE epoxide in phosphate buffer at pH 7.7 has a half-life of 12 seconds (Miller and Guengerich, 1982). If TCE epoxidation by MMO follows enzyme kinetics similar to that of a true growth substrate and inhibitor rather than some enzyme

modification due to its reaction with MMO, the question arises as to whether or not methane necessary for production of MMO will competitively inhibit TCE epoxidation (or more correctly overcome the TCE inhibition). If such is the case, only a certain percentage of TCE may be epoxidated before it is transported away from the bacteria in a flow situation. Since this process is co-metabolic, methane is a strict requirement. Removal of the true substrate will result in rapid loss of production of MMO, thereby reducing the ability to epoxidate TCE. Methods to enhance this ability are genetic in nature. Genetic recom-bination resulting in constitutive expression of the MMO genes is required in order that methane will no longer be required for induction. Even if constitutive expression is achieved, small amounts of methane still may be needed as a carbon and energy source.

Mixed Consortia Degradation

Recently, it has been shown that a mixed consortia of bacteria can effectively mineralize TCE (Henson et al., 1988; Wilson and Wilson, 1985). This involves co-metabolism of TCE (epoxidation) by bacteria that oxidize gaseous hydrocarbons such as methane, propane and butane, followed by hydrolysis of the TCE epoxide. The hydrolysis products are then utilized by other naturally occurring bacteria. Wackett et al. (1989) surveyed a number of propane oxidizing bacteria for their ability to degrade TCE. While TCE oxidation was not common among the bacteria surveyed, unique members could oxidize TCE. High concentrations (>15% v/v) of the gaseous hydrocarbons was found to inhibit co-metabolism of TCE. Oxygen concentrations also could be limiting in aqueous treatment systems since oxygen is required by the gaseous, alkane-utilizing and heterotrophic population.

Bioremediation of Extracted Ground Waters/ Subsurface Air Streams

Surface bioreactors could be used to remediate TCE-laden ground water or subsurface air streams extracted using any type of pump-and-treat system. Water treatment technology would consist of passing contaminated water along with suitable concentrations of methane or other gases such as propane through the reactor. The methylo-trophic or gaseous hydrocarbon-utilizing portion of the mixed population would epoxidate the TCE. This would spontaneously hydrolyze the TCE to glyoxylate, formate and carbon monoxide which would then be utilized by the heterotrophic population. Laboratory work at the Robert S. Kerr Environmental Research Laboratory in Ada, Oklahoma (RSKERL-Ada) has shown that TCE can be removed from water utilizing surface bioreactors (Wilson and Pogue, 1987; Wilson and White, 1986). A trailer-mounted pilot-scale system has been designed and constructed for use in field trials (Miller and Callaway, 1991).

Treatment of extracted air streams would consist of passing off-gases stripped from pumped ground waters or collected from soil venting systems through surface bioreactors. A suitable concentration of hydrocarbon gases would be added to the feed stream to initiate the cometabolic process.

Systems developed for treatment of contaminated air streams would not be limited by the oxygen concentration. Treatment of contaminated air streams such as those resulting from air stripping operations or soil venting processes would have the additional advantage of eliminating any role water chemistry

may play on the treatment process. Variations in water chemistry from site to site could be virtually ignored if contaminants are first transferred into an air stream prior to treatment.

In Situ Bioremediation

In situ bioremediation for removal or reduction of TCE contamination in the saturated zone is still in the research mode at this time. The RSKERL-Ada has an active research program directed toward this promising technology.

Anaerobic processes without support of secondary organic compounds often lead to the production of vinyl chloride as the final end product. Aerobic processes, on the other hand, require presence of an inducer compound which may not be available. Since stimulation of populations of mixed consortia and methylo-trophs will usually require injection of methane, oxygen and other nutrients, aerobic processes also are subject to mass transport limitations. For example, given a retardation factor of 2.0 for TCE as the standard, it is possible that injection of required stimulants may result in transport of TCE partitioned into the aqueous phase away from appropriate bacteria before such bacteria are stimulated and begin actively producing the enzyme MMO. If injection does not result in complete transport of aqueous-phase TCE, its concentration may be diluted such that the TCE:methane or TCE:substrate ratio is too low for effective treatment. In situ processes utilizing methanotrophs or mixed consortia require modification of the currently conceived design of in situ bioremediation in the saturated zone to account for the possibility of aqueous-phase TCE transport away from the biologically activated portion of the aquifer.

Coupling of anaerobic in situ processes to surface based aerobic reactors is a promising variation of this technology also under consideration. In such a system, in situ anaerobic bacteria would be stimulated to reductively remove chlorine atoms from TCE. Resultant daughter products more susceptible to aerobic degradation could then be pumped to the surface and effectively treated in a bioreactor.

Moffet Field Study - A form of in situ aquifer bioreclamation has been studied at a test site on the Moffet Field Air Station in California (Roberts et al., 1989; Semprini et al., 1987). The test aquifer was shallow, confined, and composed of coarse-grained alluvial sands. To create the test zone, an extraction well and injection well 6 meters apart with 3 intermediate monitoring wells were installed. The 3 monitoring wells were used to gather data for tracer and degradation studies. Parameters including methane, oxygen and halogenated solvent concentrations were continuously monitored.

Test zone microbiota were stimulated by injecting ground water containing methane and oxygen in alternating pulses. Within a few weeks, complete methane utilization was observed. This confirmed the presence of indigenous methanotrophic bacteria. Although methanotrophic bacteria utilize methane as a carbon source, atmospheric oxygen also is required for growth.

During the initial phase of the field test, TCE was injected at an average concentration of 100 g/l; concentrations were then lowered to 60 g/l to determine the effect of sorption on observed concentration losses. Early breakthrough results at the first monitoring well, after normalizing concentrations to

account for adsorption, indicated that microbial degradation could have been as high as 30%.

A second phase of this study involved injection of approximately 1 ppm normalized concentrations of vinyl chloride, trans-DCE, cis-DCE and TCE. At 2-4 meters from the injection well, transformation rates were found to be 95%, 90%, 45% and 29%, respectively. The recalcitrance of TCE was attributed to a number of factors, including degree of chlorination and low solubility of methane and oxygen.

Results from the Moffet Field study do not provide a wholesale license for initiation of in situ bioremediation of aquifers contaminated with TCE. Injection of methane, oxygen and other nutrients into an aquifer to stimulate a methylotrophic population would, in aquifers having little TCE sorption potential, push aqueous-phase TCE from the microbially stimulated portion of the aquifer before the appropriate bacteria could adapt or be stimulated. This technological limitation may be overcome in the future by redesigning the injection protocols currently utilized for in situ biological remediation. Such scenarios have been developed by Roberts et al. (1989). However, given the low rates of TCE degradation in initial field tests, this scenario awaits documentation.

Summary

Due to its chemical structure and unreactive nature, TCE is not easily transformed to environmentally safe compounds. The most efficient and cost effective method for removal of TCE from polluted ground water at this time appears to be air stripping, especially for aquifers which are utilized as potable water sources. Aquifers subjected to bioremediation would require further treatment of the ground water before human consumption, thus increasing the overall cost.

The primary alternative now being studied for removal of TCE from contaminated soil in the vadose zone is soil venting. Soil venting appears to be both efficient and cost-effective for VOC removal from the vadose zone in many instances. Limitations will occur in soil contaminated with a mixture of waste (TCE mixed with low volatility waste) as well as in highly impermeable soils. These limitations highlight the need for continued research into soil bioventing, including anaerobic and aerobic techniques based on co-metabolism of TCE driven by the less volatile constituents.

With new restricted air emissions standards, the use of air stripping and soil venting technologies may require that off-gases from them be treated in some manner before discharge to the atmosphere. Use of biological reactors to treat air or water streams from air strippers or soil venting operations may be a cost effective alternative to GAC. The movement toward clean air will require that research and demonstration studies be conducted pertaining to development of efficient cost-effective technologies.

Biological remediation, though unproven at this point, could destroy TCE completely, thus meeting the intent of Section 121 of CERCLA. More research is required, however, before full-scale implementation of such technology. Anaerobic treatment of aquifers contaminated with TCE may be a viable

option. Extensive monitoring would be necessary to assure that the final product of this remediation is not vinyl chloride. Extensive protocols also may be developed for utilization of native methylotrophs in aquifers through stimulation with methane and oxygen before contact with TCE contaminated ground water. Additionally, biological methods may be designed to effectively treat off-gases from air strippers or soil vacuum extraction systems.

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