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In-Situ Treatment of Soil Contaminated by Benzene (A BTEX Compound)

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Introduction

Gasoline is a complex solution of different hydrocarbons. Naturally occurring petroleum contains aromatic hydrocarbons, a class of unsaturated hydrocarbons that includes benzene, toluene, ethylenzene, and xylene (collectively known as BTEX). Since the EPA banned lead additions to gas in 1973, aromatic hydrocarbons were added to increase the octane concentration, thereby maximizing the burn rate of gasoline in the engine cylinders (Cole 1994). Unleaded and premium gasoline contains 4% and 5% benzene by weight, respectively (Cole 1994).

BTEX compounds are the most toxic compounds of gasoline except for methane, which is a non-hydrocarbon additive. Benzene is the most toxic chemical of the BTEX compounds and is a known carcinogen (Brauner and Killingstad 1996). When ingested, liver enzymes cannot break benzene into more soluble components that are passed through the kidneys. Rather, benzene is stored in the fatty tissues of the liver and causes damage to the liver and bone marrow. Inhalation of benzene fumes at 50-250 ppm causes headaches, nausea, and light-headedness. Recovery is usually rapid after getting some fresh air. However, exposure to higher concentrations (5-10 minutes exposure to 20,000 ppm or 60 minutes to 3,000-7,000 ppm) can lead to death (Cole 1994).

Gasoline becomes an environmental contaminant when it leaks from underground storage tanks or petroleum storage facilities. Underground storage tanks installed before 1988 are unprotected steel structures that often leak gasoline into the environment (Cole 1994). In the United States, there are approximately 1-2 million gasoline storage tanks. Out of this number, it is estimated that 100,000 to 400,000 tanks are leaking gasoline into the soil or directly into the groundwater. Leakage from underground storage tanks is a major source of groundwater contamination (Brauner and Killingstad 1996). BTEX compounds are the hydrocarbons most frequently reported as groundwater contaminants (Brauner and Killingstad 1996). Since over 50% of the drinking water supply in the United States comes from underground wells, the BTEX compounds is the single most common source of drinking water contamination. (Brauner and Killingstad 1996).

During the 1980’s, Congress provided for UST (underground storage tank) regulations. Determining who is responsible for the clean up of the polluted site is the focus of many lawsuits. The "Superfund Law" was passed in an effort to delineate responsibility and to provide funds for sites contaminated by various pollutants (Cole 1994).

Benzene Dynamics and Consequences for Remediation

When gasoline leaks into the soil, it separates into the following phases: free liquid, vapor, adsorbed onto soil particles, and aqueous or dissolved in water. The soil texture, soil porosity, and age of the contamination plume affect the distribution of the phases. Approximately 60% of benzene tends to separate into the vapor phase, 35% into the aqueous phase, and 5% adsorbed onto soil particles. The vapor phase occurs in the vadose zone (i.e., the unsaturated zone under the surface). Although petroleum hydrocarbons are generally considered to be insoluble in water, lighter hydrocarbons like benzene are more soluble in water in comparison to hydrocarbons such as the polycyclic aromatic hydrocarbons (PAHs) that are often components of diesel fuel (e.g., naphthalene, anthracene, or pyrene). In addition, benzene adsorbs readily onto soil particles and is more strongly adsorbed to clay than to either sand or silt particles (Cole 1994).

Fluctuations between the various physical phases complicate remediation of hydrocarbons. As the hydrocarbon moves through the soil, part vaporizes into the spaces in the vadose zone that are not occupied by water or the free hydrocarbon liquid. As it moves down into more water-saturated zones, hydrocarbons either dissolve into aqueous solution or are adsorbed onto soil particles. Any vertical water movement through the soil leaches some hydrocarbons off the soil particles into aqueous solution. Hydrocarbons in the bulk liquid form get trapped when the groundwater levels fluctuate. They often break into globules called "ganglia." Fluctuations in the groundwater cause parts of the ganglia to become aqueous. When the groundwater levels drop, parts of ganglia get "smeared" onto soil particles. Both the ganglia and adsorbed soil particles provide a continual source of contamination (Cole 1994).

Various *ex-situ* and *in-situ* treatments have evolved to clean up benzene contamination. *Ex-situ* soil treatments consist of treating excavated soil. The excavated soil is either put into landfills or subsequently treated in landfarming or composting operations. *Ex-situ* treatments of contaminated groundwater includes pump and treatment methods or physically containing the contaminated water by installing slurry walls or some other permanent structure (Brauner and Killingstad 1996, Cole 1994).

In some cases, petroleum contamination is too pervasive through the soil and groundwater for *ex-situ* treatments to be financially feasible. *In-situ* treatments of benzene are used instead of *ex-situ* treatments because of lower costs, less disruption to the surface, and more effective treatment of benzene concentrations in groundwater (Cole 1994).

Two common *in-situ* treatments are soil vapor extraction and enhancement of the aerobic and anaerobic biodegradation of benzene. The soil vapor extraction technique strips the benzene in its vapor form from the soil. Removal of the vapor changes the equilibrium between the various phases. The change in vapor pressure causes the hydrocarbons adsorbed onto soil particles to slowly turn into vapor. This in turn causes any free liquid to be adsorbed onto the soil particles (Cole 1994). The extracted vapors from this method must be treated in a filter before release to the atmosphere (Cole 1994).

Soil vapor extraction typically removes the majority of benzene but biodegradation removes any remaining benzene that is either dissolved in water or adsorbed to soil particles. Low levels of microbes, the lack of proper electron acceptors (i.e., oxygen, sulfate, nitrate, or carbon dioxide), excess water, or deficient amounts of water can limit biodegradation. In addition, the lack of nutrients, especially nitrogen and phosphorous, can limit biodegradation. The optimum C:N:P ratio is 25:1: 0.5 (Cole 1994).

Some techniques enhance biodegradation by seeding microbes in the soil or adding more nutrients. Biodegradation of benzene occurs most quickly under aerobic conditions. Adding hydrogen peroxide, using bioventing or biosparing techniques enhances aerobic biodegradation. In anaerobic situations, most research indicates that benzene is usually recalcitrant. However, a recent study indicates that adding iron compounds may break down benzene.

Soil Vapor Extraction (SVE)

Soil vapor extraction (SVE), also known as volatilization, venting, or soil vacuuming, is a technique used to remove vapor-phase petroleum contaminants from the vadose zone (Dupont et al. 1991, Cole 1994). SVE consists of a system of small diameter vertical wells and lateral trenches linked to piping network that ends in a vacuum pump at the wellhead (Dupont et al. 1991). Soil vapor extraction works by creating negative pressure gradients in a series of zones within the unsaturated soil; this negative pressure causes a subsurface airflow. The air in the soil is replaced with fresh air that strips the vapor phase hydrocarbons from spaces between soil particles in the vadose zone (Urlings et al. 1991). SVE changes the equilibrium so that benzene in its aqueous or adsorption phase moves to the vapor phase (Cole 1994).

The success of soil vapor extraction depends on the following factors: soil moisture content, depth to the water table, volatility of the contaminant, soil porosity, and temperature. Lighter, more volatile contaminants such as BTEX chemicals are extracted more easily than heavier contaminants such as diesel fuel, heating oil, or fuel oil. (Cole 1994, Dupont et al. 1991). Water saturated soil also decreases the removal rate to the wellhead (Cole 1994). SVE does not work if most of the benzene is in the groundwater that undergoes seasonal water table fluctuations or if the groundwater is close to the surface (Cole 1994). SVE also does not work well in tight non-porous clay soil. (Cole 1994). The soil should be fairly permeable (Dupont et al. 1991). The injected air may have to be heated in colder climates but soil porosity has a bigger impact on the recovery rate (Cole 1994).

The extracted vapors from SVE must be treated before release into the atmosphere. Charcoal adsorption or catalytic incineration is often used to treat the extracted soil vapor. Granulated charcoal filters effectively clean the vapor but the filters must be replaced often and are expensive. The catalytic converters oxidize benzene vapors to carbon dioxide and water but this method has high maintenance costs (Cole 1994, Urlings, 1991).

Biofilters are especially useful if the vapors no longer provide enough fuel for the catalytic converters (Jutras et al. 1997). Biofilters can be packed with a filler material such as *Spaghnum* peat moss and filled with bacteria. As vapors pass through the filter, contaminants are adsorbed onto the surface of the filter where microbes can degrade them (Cole 1994). Justras et al. (1997) tested the effectiveness of a field scale compost based biofilter in an Arizona site contaminated by gas leaking from an underground storage tank. During the first three months of treatment, the gas emitted from soil vapor extraction was incinerated. After three months, however, the BTEX compounds had decreased to such an extent that there was not enough fuel to run the catalytic converter. Propane was added to make up the fuel deficit. The biofilters were packed with 4:1 diatomaceous earth: composted horse manure. Results of the five-month study indicated that between 78.5-90% of the benzene in its vapor phase was eliminated. Different bacteria colonies showed different affinities for the respective BTEX compounds. The flow rate determined how effectively the biofilter treated the vapor gas. For example, during high flow rates (greater than 70 m3 h-1) and low flow rates (less than 50 m3 h-1), gas emitted into the atmosphere did not satisfy the EPA emission standards of emitting less than 1.36 kg per day of the contaminated vapors. Justras et al. (1997) determined that the proper flow rate (50-70 m3 h-1) allowed the extracted vapors enough time to reside in the biofilter for biodegradtion process. Using a biofilter is cheaper than providing propane for the catalytic converter, especially if the treatment takes longer than originally expected (Justras et al. 1997).

Biodegradation

Benzene is usually not completely removed from the soil by soil vapor extraction alone because part remains in solution (aqueous) and/or adsorbed onto soil particles. Biodegradation is used to remove residual contaminants that do not readily move into the vapor phase (Dupont 1991). Biodegradation is a process where microbes, which include bacteria or fungi, break down hydrocarbons and produces carbon dioxide and water (Cole 1994). Most microbial activity occurs in the aqueous layer on the surface of the soil particles (Cole 1994).

Biodegradation Enhanced By Bacteria

Adding microbes or "seeding" may enhance biodegradation although the benefits are ambiguous. Microbes are seeded based on the rationale that the indigenous microbes may be overwhelmed if there is a sudden influx of hydrocarbons. Microbial populations present in the soil may take a long time to build to sufficient levels to decompose the benzene and other BTEX compounds. In addition, indigenous microbes may not be capable of breaking down complex hydrocarbons. The main advantage of seeding is to decrease the lag time before the indigenous microbes build in sufficient numbers to effectively break down the hydrocarbons (Atlas 1991).

Introduced microbes need to have compatibility with the indigenous microbes, grow quickly, effectively breakdown the hydrocarbons, and have a non-toxic effect on the environment. (Atlas 1991). Finding the appropriate microbe that can operate under the specific soil conditions of the remedial site can be difficult. Indigenous microbes are highly adapted to the site and will naturally increase after a hydrocarbon leak into the soil. Eventually, indigenous bacteria will outcompete any foreign microbes and negate their ability to decompose benzene. Thus, adding microbes may be unnecessary (Atlas 1991).

Atlas (1991) described a multipurpose genetically modified microbe containing a *Pseudomanas* strain capable of oxidizing benzene along with the other BTEX compounds. Concern has been expressed about the possible detrimental health effects on humans when seeding microbes. No test protocols have been developed and implemented to test the pathogenicity of seed cultures (Atlas 1991).

Adding indigenous enriched microbes, however, may counter some of the concern of using foreign microbes. Weber and Corseuil (1994) conducted a field study to test the effectiveness of enriched indigenous microbes in biodegradation. They implemented a biologically active carbon (BAC) system that uses carbon as a substrate medium for growth of microbes. The carbon was also inoculated with benzene. Microbes were rubbed off the carbon. Adding enriched indigenous microbes, *Arthrobacter* sp., decreased the time of degradation from 12 days (the control) to 10 hours. Practically all (99%) of the benzene was removed. Under lower concentrations, the enriched microbes also provided complete degradation but at a somewhat slower rate (Weber and Corseuil 1994).

Biodegradation Enhanced By Oxygen

Electrons released during the hydrocarbon breakdown must be accepted by another element or compound (i.e., nitrate, sulfate, carbon dioxide, or oxygen). Benzene biodegradation occurs most quickly under aerobic conditions (Brauner and Killingstad 1996). The availability of oxygen in soils and aquifers can be limited depending on the type of soil (mix of sand, silt, and clay) and whether the soil is waterlogged (Atlas 1991).

In conventional biodegradation, water is used to carry oxygen or the alternative electron acceptors. However, these efforts have met with limited success because water is an inadequate carrier of oxygen. Massive amounts of water are needed to provide the necessary amount of oxygen. For example, 22,000 g of oxygen-saturated water are needed to provide 1 gram oxygen whereas 14 g of air are needed to provide 1 gram of oxygen. Moreover, the problem of providing adequate amounts of oxygen in water is compounded by the large amounts of oxygen needed by benzene in its degradation. Biodegradation of benzene requires at least 3 grams of oxygen per gram of benzene (Dupont et al. 1991).

Dupont et al. (1991) noted that Wilson and Ward were among the first to suggest using the soil vapor extraction system to provide additional oxygen to the vadose zone. Thus, the soil vapor extraction system could serve the dual purpose of extracting hydrocarbons in the vapor form and also providing oxygen to stimulate biodegradation in the vadose zone (Dupont et al. 1991). Using the soil vapor extraction system to supply oxygen or any electron acceptor is called bio-venting. SVE used in conjunction with biodegradation is usually effective (Cole 1994). However, Urlings (1991) noted that out of 23 sites, only two sites used bioventing over the water based technology to supply oxygen to the vadose zone.

Van Eyk and Vreeken (1991) tested the effectiveness of bioventing at a gas station in the Netherlands that leaked gasoline from an underground storage tank. They selected this particular site because the test site had to have hydraulic permeability of at least 10 –5 mfs because lower permeability result in a long clean up times. The groundwater table had to be at least 2 m below ground surface to make it economically favorable in comparison to ex-situ excavation treatments. The shallow ground water was heavily contaminated; the deeper groundwater was only slightly contaminated. Two pumping wells were installed. After three months of bioventing, gaseous benzene was at 4% of its original amount. An additional 6 months was needed before benzene concentrations in the groundwater and shallow water tables decreased to levels as required in the Netherlands (van Eyk and Vreeken 1991).

In some cases, the emphasis is placed more on biodegradation rather than soil vapor extraction. Treating the contaminated vapors produced during SVE can represent at least 50% of the total treatment costs whereas biodegradation is cheaper (Miller et al. 1991)

If the soil permeability is too small, biodegradation takes a long time to complete. Pneumatic fracturing is used in low permeability formations (i.e., clay-rich) to increase the soil permeability. Pneumatic fracturing involves the injection of air or other gases into the soil at a sufficient pressure and flow rate to create artificial fractures. (van Eyk and Vreeken 1991).

A field pilot demonstration at a gasoline-contaminated site in Pennsylvania tested the effectiveness of pneumatic fracturing of a primarily silty-clay texture in removing benzene. Soil tests at the end of the project indicated substantial BTEX amounts were removed from the site. At 0.3 –0.9 m bgs (below ground surface), substantially all of the benzene was removed. (The data for benzene was not given for the other levels.) Substantial amounts of the other BTEX compounds were removed at different levels. At 0.3 –0.9 m bgs, 81% of BTEX compounds were removed. At 1.5-2.1 m bgs and 2.7-3.4m bgs, 33% and 50% of the BTEX compounds were removed respectively. After 1 year, 79% of the BTEX concentrations had been removed. (Venkatrman et al. 1998).

Biosparging is similar to bioventing except that air is forced through water. With biosparging, a compressor is used to inject air below the water table and provides additional oxygen in shallow aquifers and the adjacent areas where "smearing" tends to occur. Biosparging is more effective than bioventing in providing oxygen in low permeability or saturated soil. As air moves through the water or saturated soil, benzene is forced out of solution into its vapor state. Constant biosparging is typically required to aid the biodegradation in the water-saturated zones (Griffin et al. 1991, Lovley 1997).

During a test in Australia, the effect of biosparging on the decrease of benzene was split between vapor extraction and biodegradation. Vapor extraction removed most of the benzene but biodegradation played a role. Biosparging caused benzene to evaporate into the vapor phase from the water (Johnson et al. 1998).

Biodegradation Enhanced By Hydrogen Peroxide

To overcome a limited supply of oxygen, hydrogen peroxide can be added in appropriate and stabilized formulations. When hydrogen peroxide decomposes, it releases oxygen that can support microbial degradation of hydrocarbons. Excessive hydrogen peroxide, however, kills bacteria. Moreover, hydrogen is not stable and decomposes rapidly (Atlas 1991). Hydrogen peroxide reacts with any reduced species such as plant detritus, reduced iron, and ammonia produced in the degradation process itself (Cole 1994). However, this treatment has been effectively used to stimulate microbial degradation of hydrocarbons (Atlas 1991).

In an anaerobic, methane-saturated groundwater Canadian field site, hydrogen peroxide at non-toxic levels was supplied as the oxygen source. Batch biodegradation experiments were conducted with groundwater and core samples obtained from a Canadian landfill. The benzene, along with the other BTEX compounds, underwent rapid biodegradation (Atlas1991).

Anaerobic Biodegradation Possibly Enhanced by Iron Chelates

Some aquifers are anaerobic because microbial respiration consumes any available oxygen. Moreover, oxygen is replaced from the atmosphere at very slow rates. (Lovley 1997). The other potential electron acceptors besides oxygen for BTEX compounds are nitrate, Mn (IV), Fe (III), sulfate, and methane (Lovley 1997). No matter what electron acceptors were available, benzene is the most recalcitrant BTEX compounds to anaerobic biodegradation (Lovley 1997, Krumholz et al. 1996).

Only a few field and lab studies indicated that biodegradation of benzene occurred under anaerobic conditions. Some of these studies, however, did not provide enough experimental data to evaluate the results. For example, in a filed study at an Amsterdam dune site, the anaerobic conditions were not well defined. The data as provided made it difficult to evaluate if benzene was actually removed through an anaerobic process. In other cases, care was not taken to isolate the cause of the benzene biodegradation. For example, in a Dutch ground water study, benzene levels decreased but no attempt was made to remove oxygen from the groundwater prior to the study (Krumholz et al. 1996).

After field tests, Lovley (1997) determined that degradation of benzene occurs after adding synthetic Fe(III) chelates to the sediment. Chelates cause Fe(III) to become more soluble and accessible to benzene. Adding humic acids, which may be a more environmentally acceptable method, also stimulates benzene biodegradation (Lovley 1997). However, iron chelates were probably already in the soil and may not the reason for benzene's biodegradation. Additional investigation regarding anaerobic degradation of benzene is needed (Krumholz).

Conclusion

The two common different *in situ* treatments, soil vapor extraction and biodegradation, treat benzene in its different phases. The soil vapor extraction method is a proven technique that removes most of the benzene in its vapor form. Treatment of the extracted benzene vapors is an expensive component of soil vapor extraction that invites further research into new techniques such as biofiltrations that could potentially reduce costs. Biodegradation breaks down benzene in its aqueous and adsorbed onto soil particle phases. Biodegradation is enhanced by microbe seeding or by providing additional oxygen through the application of hydrogen peroxide, bioventing, or biosparging. Given the ability of indigenous microbes to build up in numbers in response to benzene contamination, seeding microbes may be unnecessary. The use of genetically modified microbes should be guided by established protocols. Using enriched indigenous microbes may be a more politically viable option.

Since benzene is recalcitrant under anaerobic conditions, more research is needed to determine the effectiveness and practicality of adding iron chelates. Although biosparging and pneumatic fracturing provide oxygen to saturated zones that enhance biodegradation, they are expensive options. Considering the number of leaking underground storage tanks that could contaminate drinking water, providing financially feasible yet effective alternatives that treat benzene in all its forms is necessary.

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