

Subsurface Volatilization and Ventilation for VOC Contamination

Timothy J. Mayotte • Brown & Root Environmental • Holt, MI

The presence of petroleum hydrocarbons, distillates, and chlorinated solvents in the subsurface environment frequently occurs from inadvertent discharges or unlawful release, and can pose a serious threat to human health and the environment. Due to strict environmental regulations, many industries are faced with significant financial and, potentially, criminal penalties associated with releases of these chemicals. In recent years, responsible industries have intensified efforts to remediate subsurface contamination problems. However, the excessive cost and lack of timely success of traditional remedial options have diminished many industries willingness to proactively engage in necessary cleanup efforts, as the expense of doing so may be prohibitive to the sustained economic health of the industry. A new technology that addresses each aspect of subsurface contamination by volatile organic compounds (VOCs) has been developed that serves to minimize the duration and cost of remedial efforts.

The Subsurface Volatilization and Ventilation System™ (SVVS) promotes in situ destruction of contamination by biodegradation, and air circulation to enhance volatilization and vapor capture to reduce VOC mass present in the subsurface as bulk product, aqueous phase and sorbed contamination, and vapors. Because all phases of VOC contamination are addressed simultaneously, the remediation process is greatly accelerated. In addition, because SVVS™ is simplistic in design and construction, remediation costs are typically well below those associated with more traditional treatment options.

Petroleum hydrocarbons (fuels) and halogenated aliphatics (solvents, degreasing agents, and cleaning solutions) collectively make up a group of chemicals often referred to as VOCs. Many VOCs are known to be toxic to human health and environmental biota. As a result, their presence in the environment is of major concern to state environmental protection officials and the U.S. Environmental Protection Agency (EPA). Stringent state and federal regulations and standards attempt to control the release of VOCs into the environment, and reduce or eliminate risks posed to public health and environmental receptors by VOC contamination after a release has been discovered. As a consequence, parties responsible for releases of VOCs often undertake rigorous remediation efforts to clean up affected subsurface media. Many of these efforts have failed, however, at great cost to responsible parties, because the technologies implemented have not adequately addressed all manifestations of the problem.

The Problem

Releases of VOCs into the subsurface environment frequently result in the contamination of unsaturated and saturated soils, and groundwater. Typically, liquid product



comprised of VOCs will migrate through the near-surface and subsurface soils under the influence of gravity. Some of the liquid is retained in the soil matrix along the path of migration, as the volume of the liquid along the margins of and behind the traveling liquid mass dissipates to a point at which capillary forces hinder further movement. If the volume released is sufficiently large, the bulk of the liquid mass will continue traveling downward. Along the way, the liquid will encounter lenses or zones within the soil that are less permeable than the surrounding matrix, such as clay and silt within sand, or soils of locally higher moisture content. As a result, the liquid will spread out and/or build up over these regions until enough hydraulic pressure has accumulated to drive the liquid into and through, or around the less permeable material. Such encounters serve to dissipate the bulk liquid volume further, thereby promoting the retention of fractions of the product in the soil. The remaining liquid will continue migrating to the underlying water table.

If the migrating product consists of petroleum hydrocarbons, the liquid will spread out, accumulate and essentially float on the water table. Conversely, if the product contains halogenated aliphatics, that are characterized by liquid densities greater than that of water, it will eventually build up and overcome the resistance posed by the water, penetrate the saturated soils, and migrate further downward under the influence of gravity.

As in the overlying unsaturated soils, the migration of this dense non-aqueous phase liquid (DNAPL) will proceed, often encountering local impedances resulting from permeability differentials in the saturated soils. Eventually, the volume of the DNAPL will either dissipate to such an extent that all the liquid is retained in the soil matrix under the condition of residual saturation, or will encounter a physical impedance of sufficient size and reduced permeability that the liquid simply spreads over and accumulates on its surface. In the latter case, if the impeding material has an inclined surface, the DNAPL will travel down slope until its volume is sufficiently dispersed or its movement is hindered by an obstruction.

Product retained in the unsaturated zone under residual saturation, or from accumulation over less permeable materials or the water table, will, like product in the saturated zone, be in direct contact with clean water passing over its surface. Fractions of VOCs from the product will dissolve into this water as the VOC molecules diffuse from the concentrated liquid (bulk product) to the less concentrated liquid (water) in an attempt to achieve a state of equilibrium. Consequently, the water passing over and migrating beyond the product accumulation will be contaminated with VOCs. The flowing contaminated water will continue along its path of travel through the region impacted by the release, encountering more bulk product along the way, thereby increasing in concentration. After flowing beyond the point of release, this groundwater will travel through and contaminate previously unaffected regions of the aquifer. The contaminated water will also come in contact with soil during its migration.

Many VOCs have a natural affinity for organic matter that often coats or is accumulated between soil grains, as well as for specific minerals components within the soil deposit. As a result, a portion of the VOC mass dissolved in infiltrating water and groundwater will partition onto the solid material for which it has an affinity. Therefore, it is possible to not only have product accumulations in the unsaturated and saturated soils,

and contaminated percolation water and groundwater, but also VOC mass sorbed to the soil matrix both above and below the water table. As water possessing decreased concentrations of VOCs eventually passes by the contamination sorbed to the solid surfaces, it becomes increasingly contaminated, as the sorbed VOCs partition back into the water in an attempt to maintain a state of chemical equilibrium.

In addition, because VOCs are volatile at the temperatures and pressures typical of subsurface environments, vapors will emanate from product accumulations, and, if of sufficient concentration, contaminated subterranean waters and soil in contact with the uncontaminated soil atmosphere. Typically, the VOC vapors, being of a greater density than the natural soil vapor, will then spread over the surface of the water table near the point of origin, and may enhance the proliferation of VOC contamination in groundwater and soil moisture as gaseous contaminants often redissolve in uncontaminated regions of the water table, again, in an attempt to maintain a state of equilibrium. Figure 1 illustrates how a spill or leak of VOC liquid may affect the subsurface.

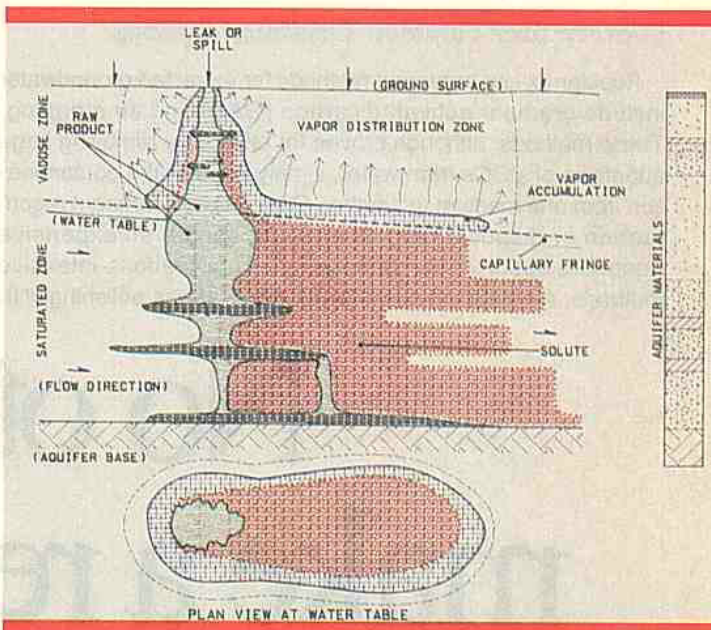


Figure 1

As has been described, four phases of contamination often result from a VOC release: residual bulk product, contaminated soil moisture and groundwater, soil-affixed contamination, and VOC vapors. Each phase interacts with the other phases to distribute the VOC mass in equal proportions (dynamic equilibrium). In terms of VOC remediation, dynamic equilibrium is an important concept because it reveals how effecting a reduction in concentration in one phase necessitates a shift in VOC mass transfer from the more contaminated phases towards the less contaminated phase. Because the shift does not occur instantaneously, but over extended periods of time, a significant reduction in VOC levels in one phase may appear as a permanent elimination of the undesirable VOC mass in that phase. However, given sufficient time, and provided the remedy causing the reduction did not target one or more of the other phases, the levels will rise again as VOC mass partitions into the "clean" phase from the remaining "dirty" phases. Each phase of contamination must therefore be addressed simultaneously.

Problems with Traditional Remediation Methods

An illustration of how the process of "dynamic equilibrium" has proven remedial efforts originally deemed successful to be incomplete is the discovery that many groundwater "pump-and-treat" actions undertaken to clean VOC-contaminated groundwater have failed in that attempt, and at excessive cost. Originally, it was believed that pump-and-treat would be successful by capturing all contaminated groundwater. In reality, what often occurred was that the water movement in the saturated zone was accelerated to a point where the rate of VOC mass transfer into the groundwater from product and sorbed soil contamination was far exceeded. As a result, VOC levels in the withdrawn water apparently dropped to favorable levels and remedial efforts were deemed complete. However, monitoring data for such sites often revealed a steady increase in VOC levels in groundwater, as, over time, VOC mass was transferred to the saturated zone from the phases not directly targeted by the pump-and-treat remedy.

Concern over Common Treatment Options

Popular ex situ treatment methods for extracted groundwater include granular activated carbon (GAC) and air stripping. These methods, although proven for effectively removing large quantities of VOCs from water, simply transfer the contamination from one medium to another. GAC requires frequent regeneration or disposal, and as a result, can be an expensive treatment option in comparison to less operations-intensive methods. Air stripping normally requires off-gas polishing with

vapor-phase carbon or by catalytic oxidation to ensure emissions do not exceed air quality standards. In addition, implementation of air stripping for VOC treatment commonly requires intensive air monitoring programs. For these reasons, air stripping can also become an expensive treatment alternative.

Common alternatives that use multiple technologies to attack residual product and sorbed contamination on unsaturated soil often involve excavation of the affected media in bulk for additional treatment processing or disposal. To responsible parties, the disposal option is becoming less attractive as it simply represents a transferral of the problem from one locale to another, and does little in the way of reducing liabilities. Treatment of excavated soils is frequently no better than disposal because the typical treatment processes, such as incineration and soil washing, are expensive and merely transfer the contamination from one medium to another.

Alternative Remediation Methods

In recent years, regulators have recognized the inherent lack of effectiveness of remedial alternatives that focus only on certain phases of VOC contamination, and have searched for new technologies that are integrated in approach, thereby addressing all phases of the contamination problem. Additionally, treatment methodologies that promote in situ destruction of VOCs without production of toxic byproducts are preferred.

Over the past few years, in situ bioremediation and soil vapor extraction (SVE) have become attractive alternatives for the remediation of VOC contamination in the subsurface. Both alternatives can be relatively inexpensive when compared to more traditional treatment options. In situ bioremediation promotes

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contaminant destruction in place; SVE enhances the transfer of VOC mass from the bulk liquid, aqueous, and solid phases to the vapor phase, and is effective for capturing and withdrawing the contaminated vapors for treatment above ground.

In Situ Bioremediation

Petroleum hydrocarbons are natural substrates, or sources of food, for many microorganisms that are indigenous to the subsurface. These microbes typically respire oxygen to complete the necessary biochemical reactions that convert the substrate to cell material and energy for metabolic processes. The byproducts of these reactions are typically harmless and normally include carbon dioxide and water. Some aerobes are also capable of metabolizing certain synthetic halogenated aliphatics possessing two or less halogens (e.g., chlorine, bromine) in their molecular structure. In addition, other aliphatic compounds containing more than two halogens may be fortuitously transformed to harmless end products following, or during, the process of metabolizing natural substrates. This process is often termed co-metabolism, and is not believed to result in beneficial microbial growth or energy production. It is currently accepted that subsurface microorganisms are capable of metabolizing degradable VOCs in the product and dissolved phases, and, to a certain extent, the vapor phase. Degradation of contamination sorbed to soils usually results upon desorption into the adjacent water and soil moisture being "cleansed" by the pertinent microbes.

In general, when a preponderance of food is supplied to subsurface organisms, such as through a release of VOC liquid to the subsurface, microbe populations not toxically inhibited by the presence of high concentrations of the substrate will, in essence,

degrade the VOC until the oxygen in the soil atmosphere is depleted. At this point, the rate of subsequent degradation is a function of the rate of atmospheric circulation of oxygen in the soil. If oxygen were added to the subsurface at a greater rate, the indigenous microbes can become "stimulated" to metabolize more of the degradable VOC mass over a shorter period of time.

Soil Vapor Extraction

SVE has been proven successful for transferring VOC mass from the bulk liquid, dissolved, and sorbed phases to the vapor phase, as clean air is continuously drawn over the surface of these phases. In concept, SVE works much like an air stripping tower, with the soil matrix serving as the packing material which increases the surface area of air/VOC phase contact. The fact that uncontaminated air is circulated means that the partial pressure of the VOCs in the air stream is minimized, thereby providing a driving force for mass transfer as the VOC molecules partition from the aforementioned phases into the air in an attempt to maintain chemical equilibrium. Although the vapors withdrawn by extraction wells must be treated before release to the atmosphere, the implementation of SVE in concert with other technologies, such as pump-and-treat, can greatly accelerate remediation progress.

The SVVS™ Technology

The patented SVVS process is an integrated technology used for attacking all phases of VOC contamination, effecting a comprehensive and expedient remediation effort. SVVS emphasizes the aspects of in situ bioremediation and induced volatilization to reduce VOC concentration present in bulk liquid, dissolved,

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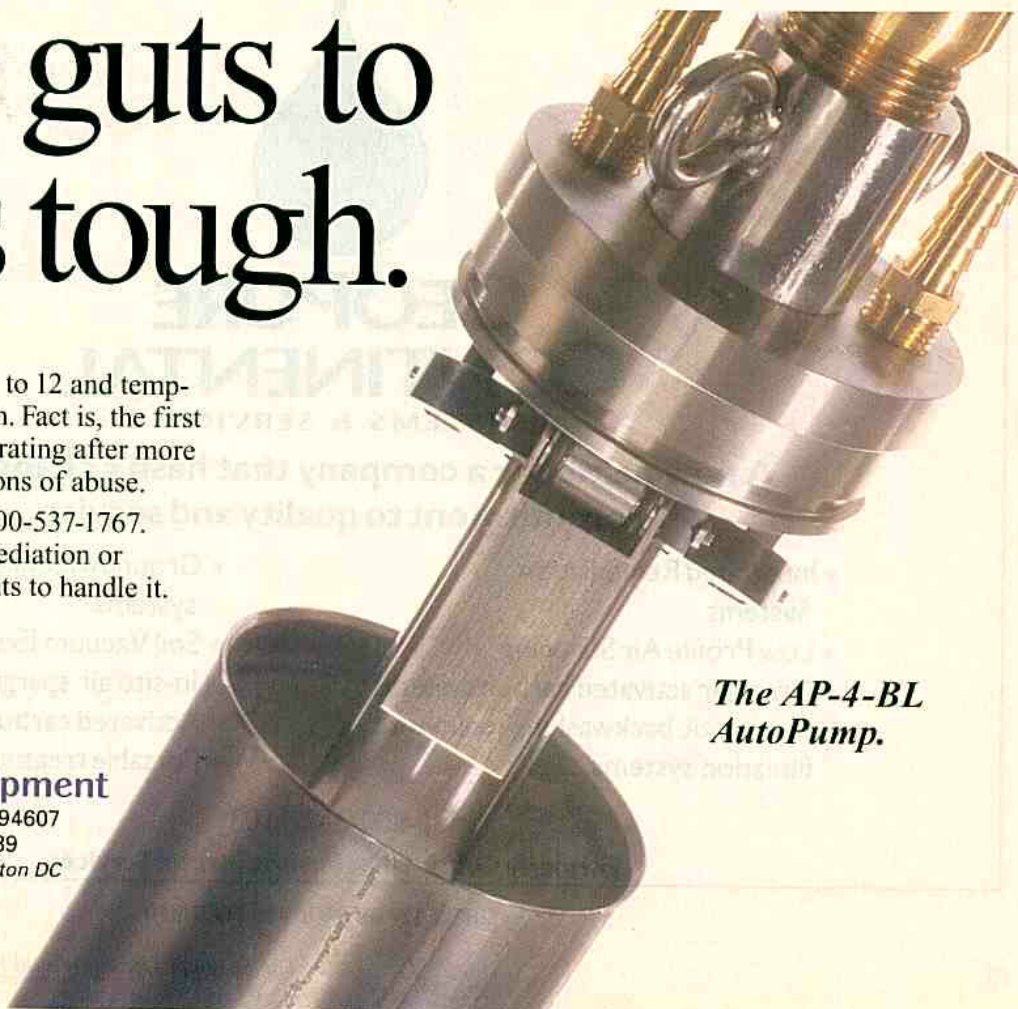
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sorbed, and vapor phases. The technology was developed by Billings and Associates of Albuquerque, New Mexico and is marketed and implemented by Brown & Root Environmental.

General Theory

As noted above, SVVS is an integrated technology used for the remediation of soil and groundwater contaminated with volatile and semi-volatile organic compounds. A typical SVVS system consists of a series of air injection and vacuum extraction wells designed to circulate air in the subsurface. The circulation of air serves to increase the concentration of dissolved oxygen in the groundwater, and the soil moisture within the capillary fringe and unsaturated zone. It also provides a delivery system for nutrient addition, if necessary. The pertinent indigenous microbes that use organic contaminants as a food source make use of the available dissolved oxygen and nutrients to mediate oxidation reactions that will result in the in situ transformation and destruction of the contaminants. Because oxygen is available in constant supply due to the injection of air, biodegradation rates are accelerated.

As an added benefit, the air percolating upward through the saturated and unsaturated zones from the air injection wells dynamically contacts the volatile and semi-volatile organic compounds, thereby enhancing the transfer of contamination from the liquid phase to the gas phase (e.g., stripping). The vapor-phase contaminants are then withdrawn from the subsurface by the network of vacuum extraction wells which are used primarily for vapor control, but also contribute somewhat to the bioremediation and stripping processes. Depending on

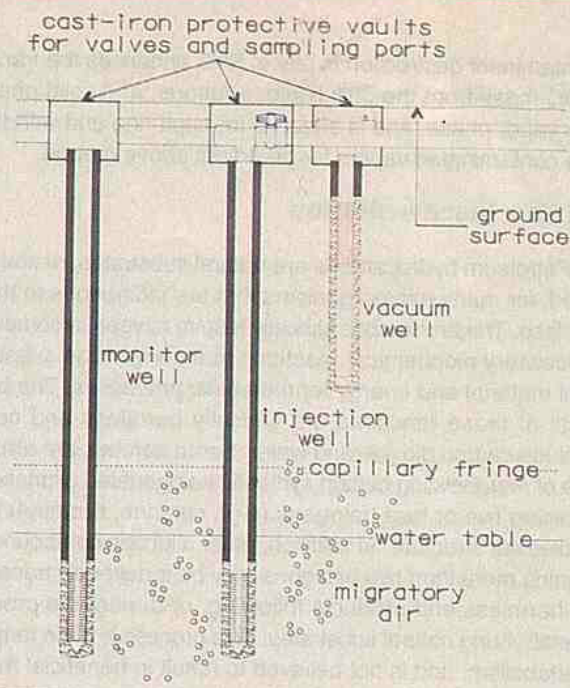


Figure 2

regulatory requirements, the extracted air may be treated aboveground or released directly to the atmosphere.

In the early stages of SVVS implementation, the overall rate of mass transfer of contamination to the vapor phase, may exceed biodegradation rates. It is during this period, which lasts anywhere from two weeks to a few months, that extracted vapors



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may need to be treated above ground before release to the atmosphere. However, the magnitude of treatment will decrease steadily over this period until biodegradation rates surpass the net rate of transfer of contaminant mass into the circulating air. When this point is reached, the vapor extraction off-gas will consist predominantly of carbon dioxide, which is the major gaseous byproduct resulting from the biodegradation process. The extent of ex situ treatment is reduced significantly over that required by conventional SVE systems. To reduce these costs further and promote additional VOC destruction, the SVVS design uses proprietary biofilters for treatment of the extracted vapors.

Schematic diagrams of the general SVVS components and conceptual layout are provided on Figures 2 and 3.

Design

In the SVVS design, coordinated air injection and vacuum extraction wells form reactor lines. Reactor lines are linked together to form an SVVS unit. Typically, a single reactor line is comprised of no more than six injection and extraction wells, and is operated by a single valve used to control air input and vacuum rates. However, some units include valve control at each well head. Through these arrangements, remediation stress can be precisely managed during remediation. If a portion of the site is responding slowly, more remediation stress is applied through valve adjustment. Conversely, less stress may be directed to portions of the site that are remediating at a faster rate or have been cleaned up to regulatory standards.

Considerable knowledge and experience is required to properly operate an SVVS system and meet treatment objec-

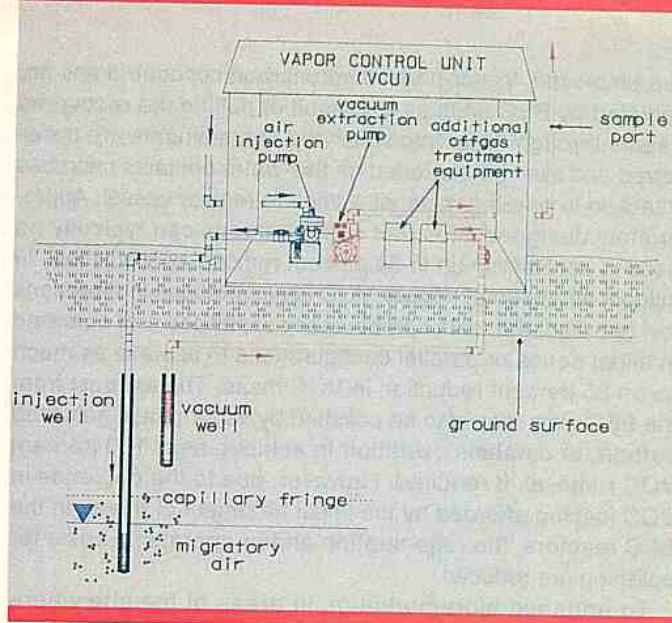


Figure 3

tives in a cost-effective and timely manner. In general, SVVS operation is directed towards enhancing subsurface conditions, through air flow adjustment and/or nutrient addition, to optimize the viability and activity of the indigenous microbial strains that are most effective for degrading VOCs. Often, this is a site-specific endeavor, and is a dynamic process requiring close observation and revision.

When treatment of the extracted vapors is required, the patent-pending Biological Emissions Control™ (BEC™) units

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are employed. Vapor-phase hydrocarbon concentrations are reduced by BEC units as the result of pulling the recovered vapors through water into which the contaminants are transferred and then biodegraded as this water contacts microbes attached to packing material within the reactor vessel. Appropriately designed BEC unit configurations can typically be used to accomplish up to 50 percent removal of VOC mass in influent air streams. If lower VOC concentrations in emissions are required, the units can be easily expanded and operated in either series or parallel configurations to achieve as much as an 85 percent reduction in VOC mass. The exhaust from the BEC units may also be polished by vapor phase activated carbon, or catalytic oxidation to achieve near 100 percent VOC removal, if required. However, due to the decrease in VOC loading afforded by the initial treatment of the air in the BEC reactors, the regeneration and/or operations costs for polishing are reduced.

To enhance bioremediation in areas of the site where indigenous microbe populations are less prolific, the patent-pending BioTrans™ technique may be employed. This entails collecting soil and/or groundwater samples from biologically active portions of a site and isolating the dominant strains of the indigenous, hydrocarbon-degrading microbes in the laboratory. The microbes are then cultivated until a sufficient population has been produced. The less biologically active portions of the site are then inoculated with the laboratory-cultivated indigenous microbes. While the populations of these microbes are grown ex situ, they remain acclimated to site conditions.

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System Flexibility and Cost

The design of SVVS allows for flexibility both in terms of system expansion and operation. Because of the simplicity of system construction and the reserve capacity of air injection and vapor extraction capabilities built into a typical design, the cost of system expansion is normally no greater than 10 percent to 20 percent of a project's total budget. Typical SVVS systems are installed and operated at costs ranging between \$150,000 and \$500,000. In addition, SVVS systems are operated in a dynamic fashion to provide the most favorable in situ conditions for the destruction of VOCs by the pertinent indigenous microbes. The system not only allows for the delivery and circulation of air, and therefore oxygen, but also certain nutrients necessary to optimize microbe viability. Because of the complexities of conditions necessary to enhance the activity of many microbes favorable for VOC destruction, the system operation requires extensive knowledge and experience.

Effectiveness

SVVS has been employed at over 30 sites consisting of petroleum hydrocarbon releases over the past five years. The soil and groundwater, including bulk product accumulations at several of these sites have been cleaned to applicable regulatory standards within this and shorter periods of time. A short list of recent successful applications is provided in Table 1. SVVS has also been implemented to attack halogenated aliphatic compounds in the subsurface. Presently, the EPA Office of Research and Development is evaluating the efficiency of SVVS for treating chlorinated compounds in soil, sludge, and groundwater at an audio



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Site	Soil Type	Depth To Groundwater (feet)	Contaminants	Cleanup Time ¹ (months)	Initial Groundwater concentration (ppm)	Final Groundwater concentration (ppm)
Isleta Site ²	Alluvial sands, silts, clays	6.5 - 16	Leaded Gasoline	2	BTEX: 4 - 25	BTEX: 0.25 - 8
Conservancy Site ²	Silty sand, interfering clay layer	6.5	Gasoline	5	Benzene: 3 - 6	59% average benzene reduction
Buddy Beene Site ²	Clay	10 - 15	Gasoline	2	Bulk product	8.5% reduction/month
Los Chavez Site ²	Clay	4 - 6	Gasoline	9	Bulk product	40% benzene, xylene reduction 60% toluene reduction 30% ethylbenzene reduction
Arenal Site ²	NR	10 - 12	Gasoline	10	Benzene: > 30	Benzene: < 5

BTEX = Benzene, toluene, ethylbenzene, and xylene

ppm = parts per million

¹ Cleanup times indicate the time interval between the initial and final groundwater concentrations reported. Total site remediation time may be longer

² Nested injection and extraction wells.

Table 1

manufacturing facility in southwest Michigan under the Superfund Innovative Technology Evaluation (SITE) program. The SITE demonstration is expected to be complete in 1994.

Although SVVS is not a cure-all, as it may not be an economically beneficial alternative for remediation of materials of very low permeability, it is an attractive option for effecting rapid cleanup in most subsurface conditions at a significantly reduced cost compared to traditional remediation methods. In addition, SVVS presents a way for industry to minimize liabilities through emphasis on contaminant destruction rather than transferral of VOC mass to another medium. These facts emphasize that, at a minimum, consideration should be given to SVVS when assessing the technical and economic feasibility of various remedial alternatives for addressing VOC contamination in the subsurface.

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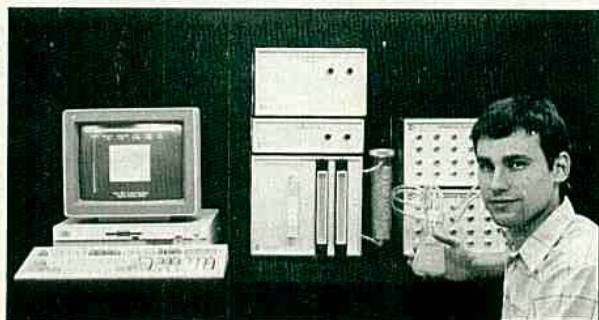
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