



Ground Water Issue

Evaluation of Soil Venting Application

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Introduction

The Regional Superfund Ground-Water Forum is a group of scientists, representing EPA's Regional Superfund Offices, organized to exchange up-to-date information related to ground-water remediation at Superfund sites. One of the major issues of concern to the Forum is the transport and fate of contaminants in soil and ground water as related to subsurface remediation.

The ability of soil venting to inexpensively remove large amounts of volatile organic compounds (VOCs) from contaminated soils is well established. However, the time required using venting to remediate soils to low contaminant levels often required by state and federal regulators has not been adequately investigated. Most field studies verify the ability of a venting system to circulate air in the subsurface and remove, at least initially, a large mass of VOCs. They do not generally provide insight into mass transport limitations which eventually limit performance, nor do field studies generally evaluate methods such as enhanced biodegradation which may optimize overall contaminant removal. Discussion is presented to aid in evaluating the feasibility of venting application. Methods to optimize venting application are also discussed.

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Determining Contaminant Volatility

The first step in evaluating the feasibility of venting application at a hazardous waste site is to assess contaminant volatility. If concentrations of VOCs in soil are relatively low and the magnitude of liquid hydrocarbons present in the soil is negligible, VOCs can be assumed to exist in a three-phase

system (i.e., air, water, and soil), as illustrated in Figure 1. If soils are sufficiently moist, relative volatility in a three-phase system can be estimated using equation (1) which incorporates the effects of air-water partitioning (Henry's constant) and sorption (soil-water partition coefficient).

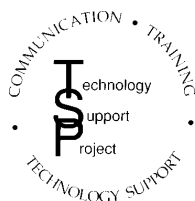
$$\frac{C_g}{C_t} = \frac{1}{(\rho_g K_{oc} f_{oc} / h) + \phi} \quad (1)$$

where:

- C_g = Vapor concentration of VOCs in gas phase (mg/cm³ air)
- C_t = Total volatile organic concentration (mg/cm³ soil)
- ρ_g = Bulk density (g/cm³)
- K_{oc} = Organic carbon-water partition coefficient (cm³/g)
- f_{oc} = Fraction of organic carbon content (g/g)
- K_h = Henry's Constant (mg/cm³air/mg/cm³water)
- θ = Volumetric moisture content (cm³/cm³)
- ϕ = Volumetric air content (cm³/cm³)

Caution must be exercised when using this approach since this relationship is based on the assumption that solid phase sorption is dominated by natural organic carbon content. This assumption is frequently invalid in soils below the root zone where soil organic carbon is less than 0.1%.

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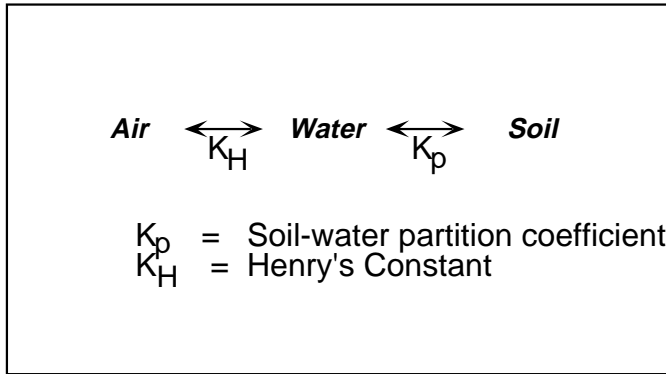


Figure 1. Three phase system.

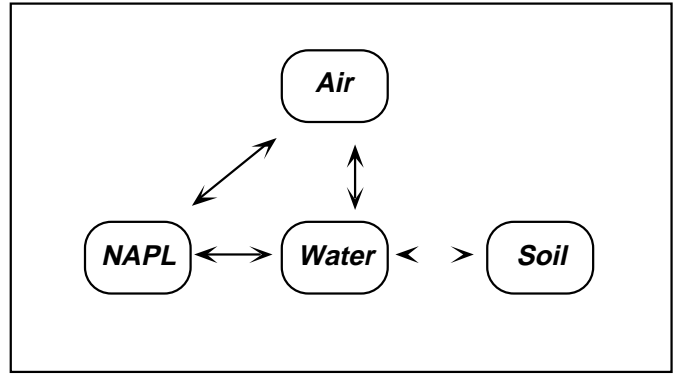


Figure 2. Four phase system.

Equation (1) can be used to evaluate individual VOC contaminant reduction trends and attainment of soil-based remediation standards. Vapors should be collected from dedicated vapor probes under static (venting system not operating) conditions. This estimate is valid only for soils in the immediate vicinity of the probe intake. This approach minimizes sample dilution and collection of vapor samples under nonequilibrium conditions. It, however, necessitates periodic cessation of venting. When the vapor concentration for a VOC approaches a corresponding total soil concentration, actual soil samples can be collected to confirm remediation. This approach has several benefits over conventional soil samples collection and analysis. At lower VOC concentration levels, collection of static vapor samples is likely more sensitive than soil collection and analysis due to VOC loss in the latter procedure. Siegrist and Jenssen (1990) demonstrated substantial VOC loss during normal soil sample collection, storage, and analysis. Also, comparing contaminant reduction trends strictly with soil samples is difficult due to spatial variability in soils. No two soil samples can be collected at the exact same location. In addition, soil gas analyses can be accomplished more quickly and inexpensively than soil sample collection, thus enabling more frequent evaluation of trends. A potential disadvantage of using this approach is inability to distinguish VOC vapors emanating from soils as opposed to ground water. Hypothetically, soils could be remediated to desired levels with probes still indicating contamination above remediation standards. This concern could be alleviated to some degree by determining the presence of a diffusion vapor gradient from the water table using vertically placed vapor probes.

If soils are visibly contaminated or the presence of nonaqueous phase liquids (NAPLs) is suspected in soils based on high contaminant, total organic carbon, or total petroleum hydrocarbon analysis, contaminants are likely present in a four phase system as illustrated in Figure 2. Under these circumstances, most of the VOC mass will be associated with the immiscible fluid and assuming that the fluid acts as an ideal solution, volatilization will be governed by Raoult's Law.

$$P_a = X_a P_a^0 \quad (2)$$

where:

- P_a = vapor pressure of component over solution (mm Hg)
- X_a = mole fraction of component in solution
- P_a^0 = saturated vapor pressure of pure component (mm Hg)

In a four-phase system, contaminant volatility will be governed by the VOC's vapor pressure and mole fraction within the immiscible fluid. The vapor pressure of all compounds increases substantially with an increase in temperature while solubility in a solvent phase is much less affected by temperature. This suggests that soil temperature should be taken into account when evaluating VOC recovery for contaminants located near the soil surface (seasonal variations in soil temperature quickly dampen with depth). For instance, if conducting a field test to evaluate potential remediation of shallow soil contamination in the winter, one should realize that VOC recovery could be substantially higher during summer months, and low recovery should not necessarily be viewed as venting system failure.

As venting proceeds, lower molecular weight organic compounds will preferentially volatilize and degrade. This process is commonly described as weathering and has been examined by Johnson (1989) in laboratory experiments. Samples of gasoline were sparged with air and the concentration and composition of vapors were monitored. The efficiency of vapor extraction decreased to less than 1% of its initial value even though approximately 40% of the gasoline remained. Theoretical and experimental work on product weathering indicate the need to monitor temporal variation in specific VOCs of concern in extraction and observation wells.

Evaluating Air Flow

Air permeability (k_a) in soil is a function of a soil's intrinsic permeability (k_i) and liquid content. At hazardous waste sites, liquid present in soil pores is often a combination of soil water and immiscible fluids. Air permeability (k_a) can be estimated by multiplying a soil's intrinsic permeability (k_i) by the relative permeability (k_r).

$$k_a = k_i k_r \quad (3)$$

The dimensionless ratio k_r varies from one to zero and describes the variation in air permeability as a function of air saturation. Equations developed by Brooks and Corey (1964) and Van Genuchten (1980) are useful in estimating air permeability as a function of air saturation or liquid content. The Brooks-Corey equation to estimate relative permeability of a non-wetting fluid (i.e. air) is given by:

$$k_r = (1 - S_e)^2 (1 - S_e^{(2+\lambda)/\lambda}) \quad (4)$$

where:

$$\begin{aligned} S_e &= \text{effective saturation} \\ \lambda &= \text{a pore distribution parameter} \end{aligned}$$

The effective saturation is given by:

$$S_e = \frac{\left(\frac{\theta}{\varepsilon} + \frac{\theta_r}{\varepsilon}\right)}{\left(1 - \frac{\theta_r}{\varepsilon}\right)} \quad (5)$$

Where:

$$\begin{aligned} \theta &= \text{volumetric moisture content} \\ \varepsilon &= \text{total porosity} \\ \theta_r &= \text{residual saturation} \end{aligned}$$

The pore size distribution parameter and residual water content can be estimated using soil-water characteristic curves which relate matric potential to volumetric water content. When initially developing an estimate of relative permeability for a given soil texture and liquid content, values for ε , θ_r , S_e , and λ can be obtained from the literature. Rawls et al. (1982) summarized geometric and arithmetic means for Brook-Corey parameters for various USDA soil textural classes. Figure 3 illustrates relative permeability as a function of volumetric moisture content for clayey soils assuming $\varepsilon = 0.475$, $\theta_r = 0.090$, and $\lambda = 0.131$.

The most effective method of measuring air permeability is by conducting a field pneumatic pump test. Using permeameters or other laboratory measurements provide information on a

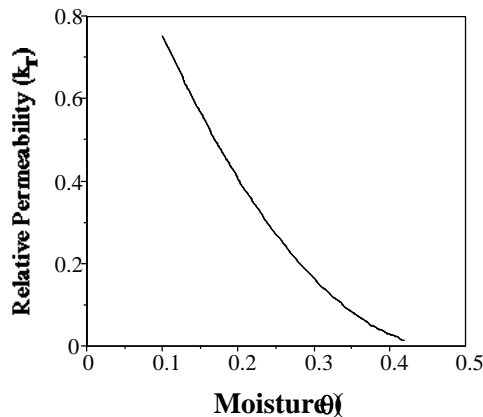


Figure 3. Relative permeability vs moisture content of clay.

relatively small scale. Information gained from pneumatic pump tests is vital in determining site-specific design considerations (e.g., spacing of extraction wells). Selecting the placement and screened intervals of extraction and observation wells and applied vacuum rates during a pump test is often based on preliminary mathematical modeling.

Evaluating Mass Transfer Limitations and Remediation Time

The effects of mass transport limitations are usually manifested by a substantial drop in soil vapor contaminant

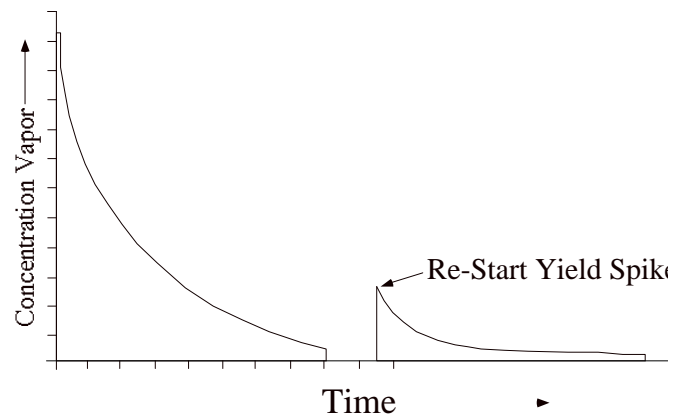


Figure 4. Concentration vs. time.

concentrations as illustrated in Figure 4 or by an asymptotic increase in total mass removal with operation time. Typically, when venting is terminated, an increase in soil gas concentration is observed over time. Slow mass transfer with respect to advective air flow is most likely caused by diffusive release from porous aggregate structures or lenses of lesser permeability as illustrated in Figure 5. The time required for the remediation of heterogeneous and fractured soils depends on the proportion of contaminated material exposed to direct bulk airflow. It would be expected that long-term performance of venting will be limited to a large degree by gaseous and liquid diffusion from soil regions not exposed to direct airflow.

Regardless of possible causes, the significance of mass transport limitations should be evaluated during venting field tests. This can be achieved by pneumatically isolating a small area of a site and aggressively applying vacuum extraction until mass transport limitations are realized. Isolation can be achieved by surrounding extraction wells with passive inlet or air injection wells as shown in Figure 6. Quantifying the effects of mass transport limitations on remediation time might then be attempted by utilizing models incorporating mass transfer rate coefficients.

The discrepancy frequently observed between mass removal predicted from equilibrium conditions using Henry's Law constants and that observed from laboratory column and field studies is sometimes reconciled by the use of "effective or lumped" soil-air partition coefficients. These parameters are

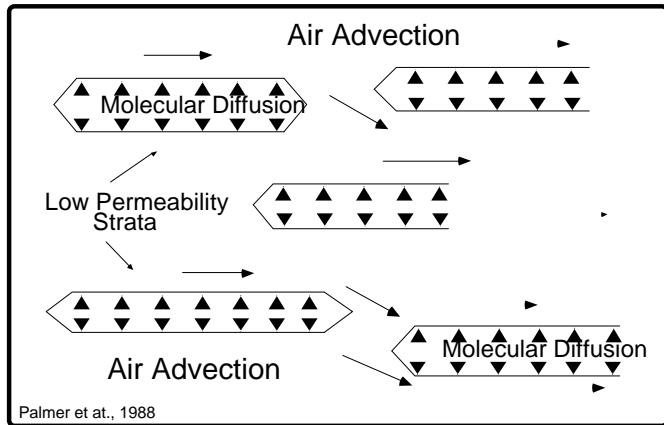


Figure 5. Effect of Low Permeability Lenses.

determined from laboratory column tests and are then used for model input to determine required remediation times. While this method does indirectly account for mass transport limitations, problems may arise when one attempts to quantitatively describe several processes with lumped parameters. The primary concern is whether the lumped parameter is suitable for use only under the laboratory conditions from which it was determined, or whether it can be transferred for modeling use in the field. Perhaps the most direct method of accounting for mass transport limitations would be to incorporate diffusive transfer directly into convective-dispersive vapor transport models.

Enhanced Aerobic Biodegradation

With the exception of a few field research projects, soil vacuum extraction has been applied primarily for removal of volatile organic compounds from the vadose zone. However, circulation of air in soils can be expected to enhance the aerobic biodegradation of both volatile and semivolatile organic compounds. One of the most promising uses of this technology is in manipulating subsurface oxygen levels to maximize in-situ biodegradation. Bioventing can reduce vapor treatment costs and can result in the remediation of

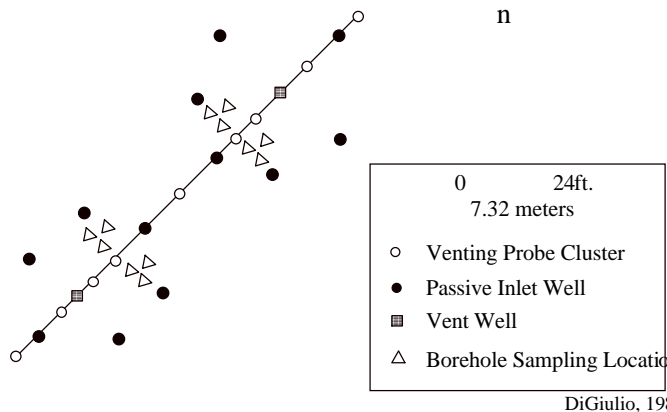


Figure 6. Proposed Pilot Test Design.

semivolatile organic compounds which cannot be removed by physical stripping alone.

Venting circulates air in soils at depths much greater than are possible by tilling, and oxygen transport via the gas phase is much more effective than injecting or flooding soils with oxygen saturated liquid solutions.

Hinchee (1989) described the use of soil vacuum extraction at Hill AFB, Utah for oxygenation of the subsurface and the enhancement of biodegradation of petroleum hydrocarbons in soils contaminated with JP-4 jet fuel. Figures 7 and 8 illustrate subsurface oxygen profiles at the Hill site prior to and during venting. It is evident that soil oxygen levels dramatically increased following one week of venting. Soil vapor samples collected from observation wells during periodic vent system shutdown revealed rapid decreases in oxygen concentration and corresponding CO₂ production suggesting that aerobic biodegradation was occurring at the site. Laboratory treatability studies using soils from the site demonstrated increased carbon-dioxide evolution with increasing moisture content when enriched with nutrients. It is worthwhile to note that soils at Hill AFB were relatively dry at commencement of field vacuum extraction indicating, that the addition of moisture could perhaps stimulate aerobic biodegradation even further under field operating conditions.

When conducting site characterization and field studies, it is recommended that CO₂ and O₂ levels be monitored in soil vapor probes and extraction well offgas to allow the assessment of basal soil respiration and the effects of site management on subsurface biological activity. These measurements are simple and inexpensive to conduct and can yield a wealth of information regarding:

1. The mass of VOCs and semivolatiles which have undergone biodegradation versus volatilization. This information is crucial if subsurface conditions (e.g., moisture content) are to be manipulated to enhance biodegradation to reduce VOC offgas treatment costs and maximize semivolatile removal.
2. Factors limiting biodegradation. If O₂ and CO₂ monitoring

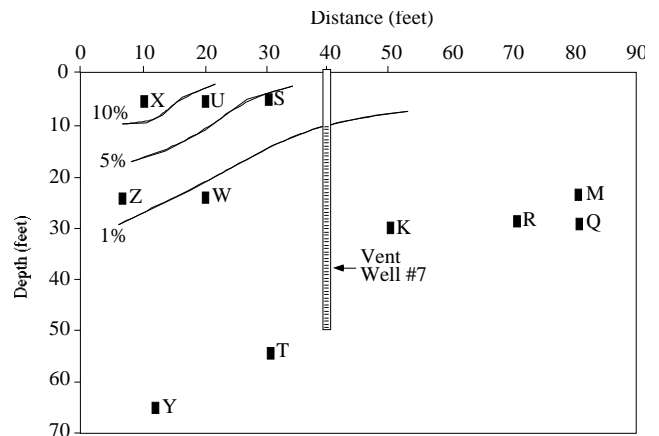


Figure 7. Oxygen concentration in vadose zone before venting.

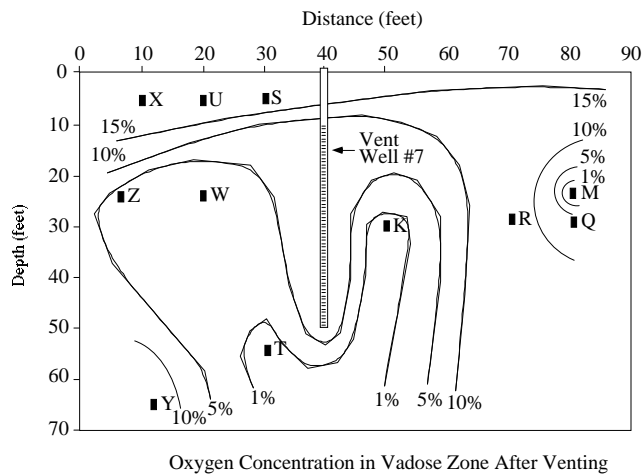


Figure 8. Oxygen concentration in vadose zone after venting.

reveals low O_2 consumption and CO_2 generation while readily biodegradable compounds persist in soils, further characterization studies could be conducted to determine if biodegradation is being limited by insufficient moisture content, toxicity (e.g. metals), or nutrients.

3. Subsurface air flow characteristics. Observation wells which indicate persistent, low O_2 levels may indicate an insufficient supply of oxygenated air at that location suggesting the need for air injection, higher extraction well vacuum, additional extraction wells, or additional soils characterization which may indicate high moisture content or the presence of immiscible fluids impeding the flow of air.

Location and Number of Vapor Extraction Wells

One of the primary objectives in conducting a venting field test is to evaluate the initial placement of extraction wells to optimize VOC removal from soil. Placement of extraction wells and selected applied vacuum is largely an iterative process requiring continual re-evaluation as additional data are collected during remediation. Vacuum extraction wells produce complex three-dimensional reduced pressure zones in affected soils. The size and configuration of this affected volume depends on the applied vacuum, venting geometry (e.g., depth to water table), soil heterogeneity, and intrinsic (e.g., permeability) and dynamic (e.g., moisture content) properties of the soil. The lateral extent of this reduced pressure zone (beyond which static vacuum is no longer detected) is often termed the radius or zone of influence (ROI). Highly permeable sandy soils typically exhibit large zones of influence and high air flow rates whereas less permeable soils, such as silts and clays, exhibit smaller zones of influence and low air flows.

Measured or anticipated radii of influence are often used to space extraction wells. For instance, if a ROI is measured at 10 feet, extraction wells are placed 20 feet apart. However, this strategy is questionable since vacuum propagation and air velocity decrease substantially with distance from an

extraction well. Thus, only a limited volume of soil near an extraction well will be effectively ventilated regardless of the ROI. Johnson (J.J., 1988) describes how the addition of 13 extraction wells within the ROI of other extraction wells increased blower VOC concentration by 4000 ppmv and mass removal by 40 kg/day. They concluded that the radius of influence was not an effective parameter for locating extraction wells and that operation costs could be reduced by increasing the number of extraction wells as opposed to pumping at higher rates with fewer wells.

Determining the propagation of induced vacuum requires conducting pneumatic pump tests in which variation in static vacuum is measured in vapor observation wells at depth and distance from extraction wells. Locating extraction and observation wells along transects as illustrated in Figure 4 minimizes the number of observation wells necessary to evaluate vacuum propagation at linear distances from extraction wells. Pressure differential can be observed at greater distances than would otherwise be possible in other configurations.

Propagation of vacuum in soils as a function of applied vacuum can be determined by conducting pneumatic pump tests with incrementally increasing flow or applied vacuum. Vacuum is increased after steady state conditions (relatively constant static vacuum measurements in observation wells) exist in soils from the previously applied vacuum. A step pump test will indicate a significant increase in static vacuum or air velocity with increasing applied vacuum near an extraction well. However, at distance from an extraction well, a significant increase in static vacuum will not be observed with an increase in applied vacuum. Pneumatic pump tests allow determination of radial distances from extraction wells in which air velocity is sufficient to ensure remediation.

After the initial placement of extraction wells has been established based on the physics of air flow, an initial applied vacuum must be selected to ensure optimal VOC removal. In regard to mass transfer considerations, the vent rate should be increased if a significant corresponding mass flux is observed. Even though an increased venting rate may not substantially increase the propagation of vacuum with distance, air velocity will increase near the extraction well. If most contaminants are in more permeable deposits, an increase in applied vacuum will increase mass removal eventually to a point of diminishing returns or until the system is limited by diffusion. Note that this strategy is for optimization of volatilization not biodegradation. Optimizing in-situ biodegradation often necessitates reducing air velocity in soil. As a result, vapor treatment costs are minimized but overall mass flux decreases. Thus, in-situ biodegradation of VOCs minimizes overall costs but may extend venting operation time.

During a field test, it is desirable to operate until mass transport limitations are realized in order to evaluate the long term performance of the technology. This can be achieved by isolating small selected areas of a site by the use of passive air inlet wells. When attempting to evaluate diffusion limited mass removal in isolated areas, applied vacuum should remain high and the distance between passive inlet and extraction wells should be minimized. Too often, venting field tests are conducted for relatively short periods of time (e.g.,

2 - 21 days) which only results in assessment of air permeability and initial mass removal. Longer field studies (e.g., 6 months - 12 months) enable better insight into mass transfer limitations which eventually govern venting effectiveness.

Screened Interval

The screened interval of extraction wells will play a significant role in directing air flow through contaminated soils. Minimum depths are recommended by some practitioners for venting operation to avoid short-circuiting of air flow. However, the application of venting need not be limited by depth to water table since horizontal vents can be used in lieu of vertically screened extraction wells to remediate soils with shallow contamination. Often, it is desirable to dewater contaminated shallow aquifer sediments for venting application. For remediation of more permeable soils with deep contamination, an extraction well should be screened at the maximum depth of contamination or to the seasonal low water table, whichever is shallowest, to direct air flow and reduce short-circuiting. For less permeable soils, or for more continuous vertical contamination, a higher and longer screened interval may be useful. In stratified systems, such as in the presence of clay layers between more permeable deposits, more than one well will be required, each venting a distinct strata. Screening an extraction well over two strata of significantly different permeability will result in most air flow being directed only in the strata of greater permeability. It is important to screen extraction wells over the interval of highest soil contamination to avoid extracting higher volumes of air at lower vapor concentration.

During venting, the reduced pressure in the soil will cause an upwelling of the water table. The change in water table elevation can be determined from the predicted radial pressure distribution. Johnson et al. (1988) indicated that upwelling can be significant under typical venting conditions. Water table rise will cause contaminated soil lying above the water table to become saturated, resulting in decreased mass removal rates. Ground water upwelling due to venting system operation can be minimized with concurrent water table dewatering.

Placement of Observation Wells

Observation wells are essential in determining whether contaminated soils are being effectively ventilated and in the evaluation of interactions among extraction wells. The more homogeneous and isotropic the unsaturated medium, the fewer the number of vapor monitoring probes required. To adequately describe vacuum propagation during a field test, usually at least three observation well clusters are needed within the ROI of an extraction well. At least one of these clusters should be placed near an extraction well because of the logarithmic decrease in vacuum with distance. The depth and number of vapor probes within a cluster depends on the screened intervals of extraction wells and soil stratigraphy. However, vertical placement of vapor probes might logically be near the soil-water table interface, soil horizon interfaces, and near the soil surface. As previously mentioned, the use of air flow modeling can assist in optimizing the depth and placement of vapor observation wells and in the interpretation of data collected from these monitoring points.

When constructing observation wells it is desirable to minimize vapor storage volume in the screened interval and sample transfer line. This will minimize purging volumes and ensure a representative vapor sample in the vicinity of each observation well. Analysis of soil gas in an on-site field laboratory is preferred to provide real time data for implementation of engineering controls and process modifications. It is recommended that steel canisters, sorbent tubes, or direct GC injection be used in lieu of Tedlar bags when possible because of potential VOC loss through bag leakage or diffusion within the teflon material itself. This problem may lead to erroneous analytical results and the potential of a false negative indication of soil remediation at low soil gas concentrations.

Summary/Conclusions

While the application of soil vacuum extraction is conceptually simple, its success depends on understanding complex subsurface physical, chemical, and biological processes which provide insight into factors limiting venting performance. Optimizing venting performance is critical when attempting to meet stipulated soil-based clean-up levels required by regulators. The first step in evaluating a venting application is to assess contaminant volatility. Volatility is a function of a contaminant's soil-water partition coefficient and Henry's constant if present in a three-phase system, and a contaminant's vapor pressure and mole fraction in an immiscible fluid, if present in a four phase system. Volatility is greatly decreased when soils are extremely dry. As vacuum extraction proceeds, lower molecular weight organic compounds preferentially volatilize and biodegrade. Decreasing mole fractions of lighter compounds and increasing mole fractions of heavier compounds affect observed offgas concentrations. Understanding contaminant volatility is necessary when attempting to utilize offgas vapor concentrations as an indication of venting progress.

The significance of mass transport limitations should be evaluated during venting field tests. Long term performance of venting will most likely be limited by diffusion from soil regions of lesser permeability which are not exposed to direct airflow. Mass transport limitations can be assessed by isolating a small area of a site and aggressively applying vacuum extraction. Simplistic methods to evaluate remediation time should be avoided. One of the most promising uses of vacuum extraction is in manipulating subsurface oxygen levels to enhance biodegradation. When conducting field studies, it is recommended that CO₂ and O₂ levels be monitored in vapor probes to evaluate the feasibility of VOC and semivolatiles contaminant biodegradation.

Air permeability in soil is a function of a soil's intrinsic permeability and liquid content. Relative permeability of air can be estimated using relationships developed by Brooks and Corey (1964) and Van Genuchten (1980). The most effective method of measuring air permeability is by conducting pneumatic pump tests. Information gained from pneumatic pump tests can be used to determine site-specific design considerations such as the spacing of extraction wells. Measured or anticipated zones of influence are not particularly useful in spacing extraction wells. Extraction wells should be located to maximize air velocity in contaminated soils.

Pneumatic pump tests with increasing applied vacuum may be useful in determining radial distances from extraction wells in which air velocity is sufficient to ensure remediation. Screened intervals should be located at or below the depth of contamination. In stratified soils, more than one well is necessary to ventilate each strata. At least three observation well clusters are usually necessary to observe vacuum propagation within the radius of influence of an extraction well. Logical vertical placement of vapor probes might be near the soil-water table interface, soil horizon interfaces, and near the soil surface.

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