OPTIMIZATION OF CONTAMINANT REMOVAL FOR HETEROGENEOUS SYSTEMS BY SOIL VENTING

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ABSTRACT The efficiency of remediation of vadose zone organic compounds can be enhanced by refinement of methods for soil venting and bioventing in complex heterogeneous systems. This can be accomplished by a) identification of physical and chemical conditions (e.g., soil temperature, moisture content, flow rates) required for rapid contaminant removal rates, b) precise engineering control of identified parameters in the subsurface, and c) development of knowledge-based operational strategies providing greater removal efficiencies at low cost. One method with promise is to moderately heat and humidify the input/replacement air during venting. Initial calculations indicate that this strategy may be quite effective in enhancing remediation of heterogeneous systems with diffusional control of cleanup time.

KEYWORDS: soil venting, soil vapor extraction, bioventing, diffusion, remediation

INTRODUCTION

A large number of sites throughout the United States have vadose zone contamination with organic chemicals ranging from chlorinated solvents to simple gasoline. Currently, soil venting and bioventing are widely used for remediation of volatile organic compound (VOC) contaminated sites. However, the methods used to design venting systems are simplistic, mostly concerned with obtaining sufficient air flow rates through the systems.

During soil venting, many subtle but important changes are produced in the subsurface as a result of latent heat of evaporation and condensation of water vapor at different locations, volatilization of the contaminants, microbial action, and vacuum-caused evaporation. Better understanding of these processes as they vary over space and time and how they can be manipulated to enhance cleanup rates will eventually lead to faster, more cost effective cleanup.

An analogy can be made with a comparison between the engine in a Model T Ford and a modern engine. The internal combustion engine gained considerable power and fuel efficiency as more was learned about control of air/fuel ratios, compression, and valving. Likewise, current designs for soil venting and bioventing systems can be significantly enhanced by more careful consideration and control of the subsurface environment during venting.

Several techniques have been tried within the context of the Superfund Innovative Technology Program, an EPA program [1] to improve the efficiency of soil venting. The major thrust has been to heat the soil in order to increase the vapor pressure of volatile or semi-volatile organic compounds and increase biochemical reaction rates. The methods proposed for soil heating include radio frequency heating, injection of heated air, and steam injection. These methods are promising but relatively expensive and energy intensive. A major limitation is how to efficiently transport the heat energy into the soil. Methods currently proposed, such

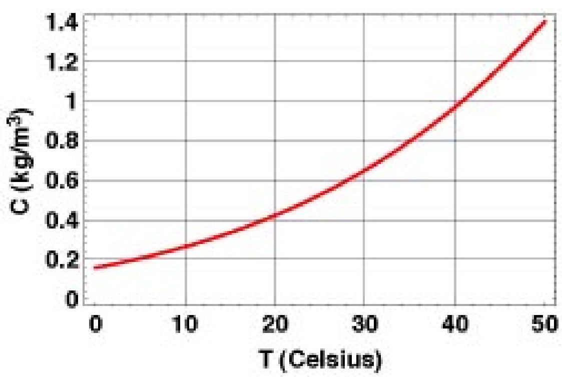

FIGURE 1. TRICHLOROETHYLENE SATURATION CONCENTRATION AS A FUNCTION OF TEMPERATURE.

as radio frequency heating, are associated with high capital equipment, energy, and environmental costs.

We have already demonstrated theoretically [2] that injection of warmed, humidified air, can efficiently transport low grade heat energy (e.g., sensible heat from the atmosphere related to diurnal and annual temperature cycles, and solar energy) into the soil, thereby greatly improving removal efficiency with only a small increase in costs. This represents a knowledge- rather than capital-based technology. By modification of system operational parameters, we take advantage of seasonal and diurnal changes in air temperature in order to warm the soil.

A number of laboratory studies have been performed to examine the influence of temperature, pressure, and moisture content on phase partitioning and diffusion in laboratory systems. However, application of the results to the design of remediation systems is limited. Heating of the subsurface (e.g., radio frequency heating, steam injection) has been investigated but is expensive [1]. The use of dry heated air injection in soil venting [3] and in an augured soil remediation method called "mixed region vapor stripping" [4] has been investigated in laboratory and field applications. Lingineni and Dhir [3] investigated the use of hot dry air in experiments and mathematical modeling of soil venting. The results indicated that injection of hot, dry air is only sometimes effective. This agrees with the theoretical analysis given above but for different reasons. The Lingineni and Dhir study considers a VOC only system (i.e., no liquid water or water vapor) in an homogeneous material at unrealistically high flow rates. These assumptions fundamentally change the system and results from an actual field remediation site where water vapor transport is of fundamental importance and flow rates are orders of magnitude lower. The augured/mixed soil work examined the role of heated ambient air (not humidified) injected into the mixed soil [4]. The short tests (~ 4 hours) gave emissions that were controlled more by the mixing rate and essentially independent of temperature.

CONTROLLING FACTORS FOR SUBSURFACE CONTAMINANT REMOVAL

Soil temperature

Soil temperature changes compound vapor pressure, Henry's Law constant (aqueous/vapor phase partitioning), adsorption onto the solid or soil organic matter phases (K_d), the diffusion coefficient, and biological growth rates.

The vapor pressure of trichloroethylene (TCE) is shown in Figure 1. Notice that the temperature dependence is very high. Increasing soil temperature by as little as 15ºC can double vapor pressure (i.e., saturation concentration) and, thus, double the removal rate. Microbial growth rates approximately double with each 10ºC temperature rise [5]. Thus, within limits, higher temperatures also enhance bioremediation.

The influence of temperature on Henry's Law constants is variable but most compounds partition to a greater extent into the vapor phase at higher temperatures [6, 7]. Vapor phase partitioning is usually preferable, since contaminants are removed in the vapor phase; however, Wilson and others [8] have suggested that when organics are occluded by water layers, diffusion through the water layer will be slowed when Henry's Law constants lead to lower aqueous concentrations. For this reason, higher temperatures may not always be favorable, particularly when moisture content is high.

The influence of temperature on diffusion coefficients [9] is approximately the ratio of absolute temperatures to the 1.5 power. Thus, warming the soil by 15ºC will increase diffusion coefficients by about 8%. Adsorption onto the solid phase and soil organic matter is also temperature-dependent, although less information is available.

In summary, increasing soil temperature by a modest 15 to 30ºC can theoretically increase removal of TCE and other VOCs by a factor of 2 to 4 under most conditions. However, this may not be true under conditions with high soil moisture contents.

Soil moisture content

Soil moisture content has several important roles in venting:

1) high soil moisture contents lower air permeability, thereby decreasing venting air flow rates,
2) high soil moisture contents lower vapor diffusion rates in stagnant zones,
3) low soil moisture contents decrease the availability of substrate to microorganisms for biodegradation,
4) moisture content plays an important role in the partitioning of contaminants between the vapor, liquid, and solid phases in the soil.

The relationships between soil moisture content and relative vapor and liquid permeability are relatively well understood, at least for air/water (2 phase) systems [10]. Increasing soil moisture contents to near saturation lowers the vapor phase permeability, making venting of a wet soil more difficult than for a dry soil. High moisture contents also lower the diffusion of oxygen into stagnant, low permeability zones in the vented soil. Diffusion of oxygen through water-logged soils is slow because vapor phase diffusion is more rapid than liquid phase diffusion and oxygen has a limited solubility in water (~10 ppm).

On the other hand, moisture is essential for biodegradation. Skopp, *et al*. [11], developed a theoretical model to predict the optimum moisture content for degradation based upon the two controlling processes of oxygen availability (greatest at low moisture contents) and aqueous transport of substrate to the microbial colonies (greatest at high moisture contents). There is a middle point in which both oxygen availability and aqueous transport of the substrate is optimum. Studies in soils have indicated that maximum degradation rates occur in the range of 40 to 60% saturation [12, 13].

Soil moisture content is also important in bioventing. At low moisture content (the normal case for arid climates), biodegradation of simple hydrocarbons is frequently limited by moisture content rather than nutrient or oxygen supply. Our calculations indicate that desiccated soil conditions tend to occur near the extraction well in some venting operations as a result of vacuum related evaporation of water. Additional concerns are oxygen flux through the system and carbon dioxide as it influences the pH of soil moisture.

Soil moisture content is as important as temperature in influencing physical removal efficiency. At high soil moisture content, air permeability and vapor diffusion from stagnant zones are lowered, potentially lowering mass transfer rates. At low soil moisture content, partitioning of organic compounds between the solid, nonaqueous phase liquid (NAPL), aqueous, and gas phases is influenced by vapor adsorption on the mineral surfaces. Low relative humidity can occur in soils in arid climates and/or near extraction wells where the pressure drop near the well causes desiccation of the soil. Peterson, *et al.* [14], for example, reported that linear partition coefficients for binding of TCE vapor under a range of unsaturated conditions were 1 to 4 orders of magnitude greater than for a water saturated system. Pennell, *et al.* [15], stated that "Antecedent moisture content or relative humidity is arguably the most important factor influencing vapor-phase sorption in the unsaturated zone. In the absence of water, soils and clay minerals exhibit a sizable capacity to adsorb p-xylene vapors, which is governed primarily by adsorption on mineral surfaces." Culver, *et al*. [16], in a modeling study of the importance of vapor sorption found that, in arid climates, vapor sorption can be a significant source of retardation for VOC migration. A special area of concern is near extraction wells since our current venting models indicate that vacuum-induced desiccation may occur near extraction wells.

Pressure

Soil air pressure changes caused by venting can lead to secondary effects of potential importance. The diffusion coefficient is inversely related to pressure [9]. When air pressure is reduced by 10%, diffusion rates increase by 10% leading to higher removal of contaminants near extraction wells. A second and related effect is that pressure drops in the soil tend to "stretch" air parcels as they travel through the soil, allowing them to hold greater quantities of moisture and volatile organics. However, the situation is complicated by secondary effects. At lower pressure, vacuum drying and associated cooling of the soil near the extraction well occur. The localized cooling can lower contaminant vapor pressures and, therefore, removal rates.

Heterogeneities

Almost all geological systems are heterogeneous. The ubiquitous presence of heterogeneities contrasts with most computer models where a uniform layer-cake geology is assumed. Heterogeneities may include such diverse parameters as: fast flow zones, where the majority of flow occurs; low permeability zones (vertical, inclined and horizontal); and regions with high moisture contents, and/or complex, subtle geological interlayering and interfingering (Figure 2). In many circumstances, the presence of heterogeneities causes the cleanup rate to be diffusionally limited.

To quote from a recent *Ground Water* editorial [17], "After 20 years of feverish activity and billions of Dollars….We have achieved widespread characterization of contaminated aquifers, but minuscule progress in restoring them.…The failure is not a lack of effort....It is a growing consensus among the research community to

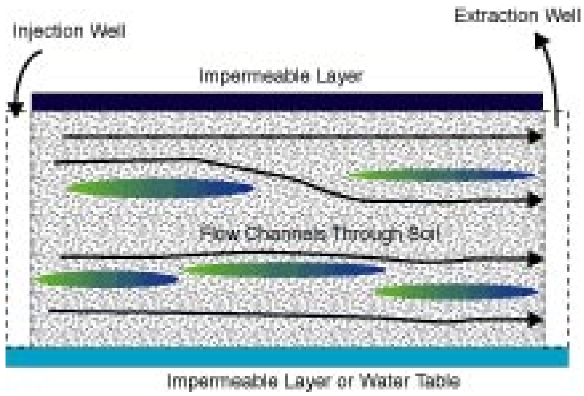

FIGURE 2. SCHEMATIC OF SIMPLE VENTING SYSTEM.

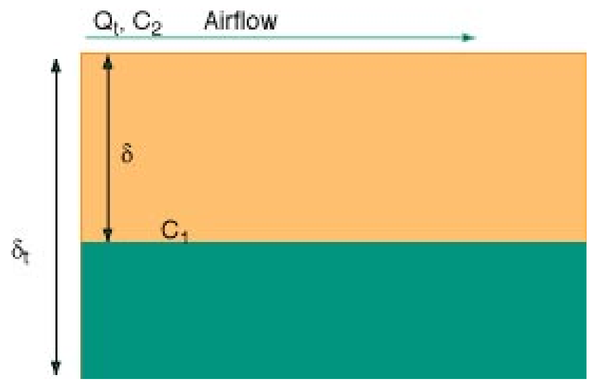

FIGURE 3. GEOMETRY DEFINITION.

recognize the role of diffusion in the (remediation) process." When contaminant transport is diffusionally controlled, faster pumping and additional wells do little to enhance remediation. An important question is: What low cost methods can be used to enhance remediation rates of occluded zones where molecular diffusion is the dominant transport mechanism?

Diffusional removal from stagnant zones

A conceptualization of the subsurface environment at an opposite pole from the homogeneous, isotropic situation is an heterogeneous soil with a series of macropores, where air flow is channeled, separated by stagnant zones with diffusion only transport. The following mathematical exercise takes the viewpoint of a highly heterogeneous system. The zone of contaminated soil (Figure 3) is assumed to be remediated by diffusional mass transport from the zone of residual contamination out to the macropores.

ENERGY AND MOISTURE RELATIONSHIPS IN SOIL VENTING

The above observations suggest that soil venting and bioventing could be improved significantly by more precise and knowledgeable control of subsurface temperature, moisture content, and biostimulant supply. This requires a) improved fundamental understanding of optimal conditions for mass transport in heterogeneous systems and b) improved fundamental understanding of how the optimal conditions can be produced or engineered using cost effective technologies.

Soil venting leads to temperature and moisture content changes in the subsurface. The changes can be either inadvertent or purposeful. Figure 4 gives the amount of heat energy imparted to the soil for each cubic meter of air passed through the soil using equations from Walton and Anker [2]. The energy is broken into latent heat of condensation, sensible heat, and total heat. The calculation assumes that the input air is at 100% relative humidity and the soil is at a temperature of 10ºC. Notice that the latent heat of condensation generally dominates the energy balance.

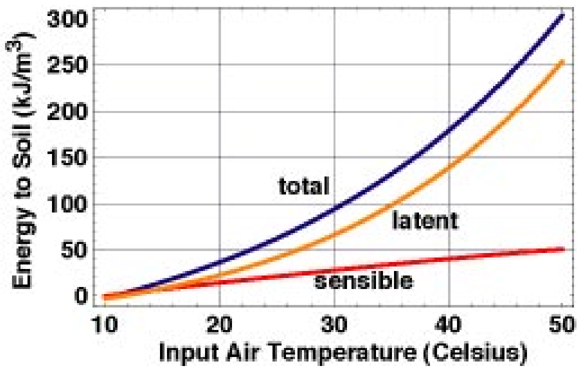

FIGURE 4. ENERGY CONTENT OF SATURATED AIR AT GIVEN TEMPERATURE CONTACTING 10ºC SOIL.

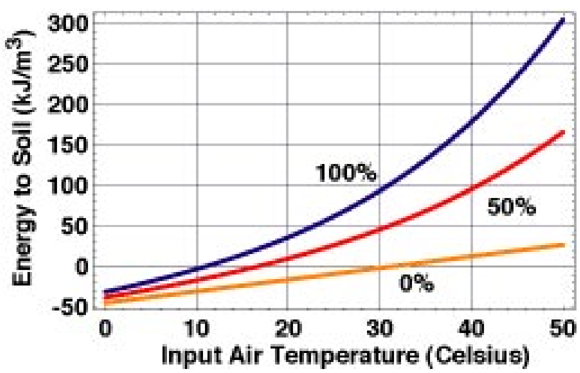

FIGURE 5. ENERGY CONTENT OF SATURATED AIR AT GIVEN TEMPERATURE CONTACTING 10ºC SOIL.

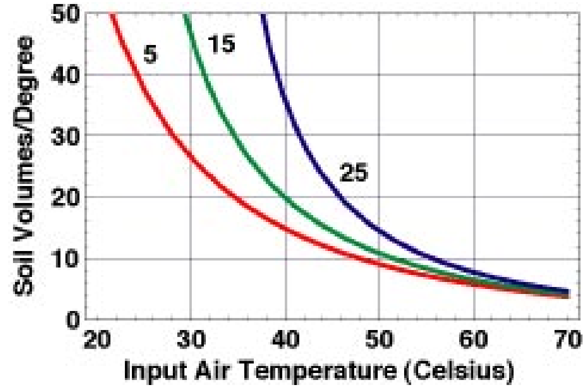

FIGURE 6. SOIL VOLUMES OF AIR PASSED THROUGH SYSTEM FOR EACH DEGREE RISE IN SOIL TEMPERATURE. THE THREE LINES REPRESENT SOIL TEMPERATURE.

Figure 5 gives the total energy imparted to the soil when the input air is at 0%, 50%, and 100% relative humidity. The soil is assumed to have a temperature of 10ºC. The humidified air is much more effective at warming the soil because the latent heat of vaporization dominates the enthalpy balance equations. Notice that at less than 100% relative humidity, the energy balance can be negative (i.e., the soil is cooled) even when the air is warmer than the soil. For completely dry air (0% relative humidity), the air temperature must be above 30ºC (i.e., 20ºC warmer than the soil) before the energy balance becomes negative. Dry air input causes the soil to act like an evaporative cooler. For this reason, injection of warm, dry air is generally ineffective in warming the subsurface.

An important question is what flow rates are required to significantly change soil temperatures. If very high flow rates are required, warming through the input air will not be feasible in most systems. Figure 6 examines the rate of temperature change in the soil as a function of injection air temperature and soil temperature. The results are given in terms of the number of soil volumes of air passed through the system required to change soil temperature by 1ºC. The input air is assumed to be at 75% relative humidity, the same as the simulations shown below. Typical venting rates are in the range of 0.1-10 soil volumes per day.

The temperature on each line is the assumed soil temperature and the input air is at 75% relative humidity. Notice that when input air is slightly heated and humidified, significant changes in subsurface temperature can be obtained even at low flow rates. Contrary to intuitive expectations, average soil moisture content is not changed significantly by injection of warm, humidified air. Because of the high value of the latent heat of vaporization/condensation of water, the soil volumetric moisture content increases by only about 10^{-3} (0.1%) per degree increase in soil temperature caused by moisture condensation. Increasing the soil temperature by 10ºC with warm humidified air increases soil moisture content by <1%, a relatively small change.

MASS TRANSPORT THROUGH HETEROGENEOUS SYSTEMS

Many processes may limit removal rates from soil. In this model, we assume that most airflow occurs through fast transport pathways (macropores or other high permeability zones). Contaminant removal from the remainder of the system is assumed to occur by diffusion from the residual NAPL out to the fast transport pathways where transport is by advection. The entire system is assumed to be initially contaminated with an input initial saturation of contaminant (θ_c). The surface area available for diffusion to the macropores is

$$A = V/\delta_t \,. \tag{1}$$

The concentration in the macropores is

$$C_2 = \frac{F}{Q_t} \tag{2}$$

with the diffusional flux (F) given by Fick's Law,

$$F = \frac{DA(C_1 - C_2)}{\delta}. \tag{3}$$

The diffusion coefficient is estimated with the Millington-Quirk formulation [18] to account for changes in soil moisture content and porosity and is corrected for volumetric water content, porosity, temperature, and pressure:

$$D = D_0 \frac{(\phi-\theta)^{10/3}}{\phi^2}\left(\frac{P_{ref}}{P}\right)\left(\frac{273.15+T}{273.15+25}\right)^{3/2}. \tag{4}$$

The equation shows that diffusion increases with increases in soil porosity and temperature and decreases with increases in soil volumetric moisture content and pressure. In order to increase diffusional mass transport, we should increase soil temperature, lower the pressure, and (within limits) dry out the soil.

Substitution gives

$$F = \frac{DA\left(C_1 - \frac{F}{Q_t}\right)}{\delta} = \frac{DAC_1}{\delta} - \frac{DAF}{\delta Q_t}, \tag{5}$$

$$F\left(1+\frac{DA}{\delta Q_t}\right) = \frac{DAC_1}{\delta}, \tag{6}$$

$$F = \frac{DAC_1}{\delta\left(1+\frac{DA}{\delta Q_t}\right)} = \frac{DAC_1}{\left(\delta+\frac{DA}{Q_t}\right)}. \tag{7}$$

The rate of migration of the front is

$$\frac{d\delta}{dt} = \frac{F}{A\rho_c\theta_c} = \frac{DC_1}{\rho_c\theta_c\left(\delta+\frac{DA}{Q_t}\right)}. \tag{8}$$

Integration, at constant flow rate and temperature, gives

$$\frac{\delta_t^2}{2} + \frac{DA\delta_t}{Q_t} = \frac{DC_1}{\rho_c\theta_c} t; \tag{9}$$

$$t = \left(\frac{\delta_t^2}{2} + \frac{AD\delta_t}{Q_t}\right)\frac{\rho_c\theta_c}{DC_1} = \left(\frac{\delta_t^2}{2} + \frac{VD}{Q_t}\right)\frac{\rho_c\theta_c}{DC_1}. \tag{10}$$

Variable definitions are given in the nomenclature section and shown in Figure 2. Note that cleanup time is linear with respect to the concentration (or vapor pressure since

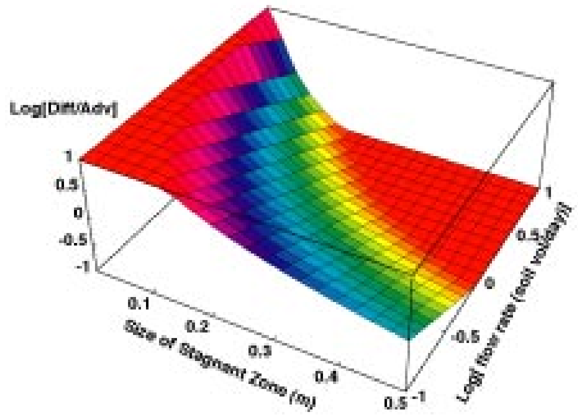

FIGURE 7. INFLUENCE OF SIZE OF HETEROGENEITIES AND AIR FLOW RATE ON DIMENSIONLESS GROUP COMPARING REMEDIATION BY DIFFUSION AND ADVECTION.

$C = MP/RT$) of the compound, so a doubling of vapor pressure halves the cleanup time. This is true for both the advective- and diffusionally-limited special cases shown below. When the flow rate is high, or

$$\frac{2VD}{\delta_t^2 Q_t} << 1, \tag{11}$$

the cleanup time simplifies to:

$$t = \frac{\delta_t^2}{2}\frac{\rho_c \theta_c}{DC_1}. \tag{12}$$

In this situation, the cleanup rate is diffusionally limited and independent of the flow rate. Alternatively, when the flow rate is low, or

$$\frac{2VD}{\delta_t^2 Q_t} >> 1, \tag{13}$$

the cleanup time becomes:

$$t = \frac{V}{Q_t}\frac{\rho_c \theta_c}{C_1} \tag{14}$$

which is independent of macropore spacing and diffusion coefficient (advectively-controlled release). Figure 7 shows the dimensionless group, $(2VD)/(\delta_t^2 Q_t)$, controlling cleanup of trichloroethylene (TCE) from a heterogeneous system. Volumetric moisture content is 0.1, porosity is 0.2, and temperature is 25ºC.

The dimensionless group is qualitatively the ratio of diffusional transport out of the stagnant areas to advective transport in the macropores or other high permeability areas. It should be noted that contaminant transport through the system as a whole is a combination of both processes, similar to two pipes in series. The result depends on the slower process. When the diffusion term dominates, $2VD/\delta_t^2 Q_t >> 1$, cleanup time is controlled by the airflow (pumping) rate, or smaller advective term. This is the upper flat zone in Figure 7 that occurs when the pumping rate is low and/or when the characteristic size of the stagnant zone is small. Conversely, the lower flat zone corresponds to the case where cleanup time is diffusionally controlled, or the advection term dominates (i.e., $2VD/\delta_t^2 Q_t << 1$). Diffusional control occurs when pumping is rapid and/or when heterogeneities are large.

The simple mathematical exercise illustrates that cleanup of heterogeneous systems by venting can be enhanced by a) increasing the saturation concentration (i.e., the vapor pressure) of the contaminant and b) by increasing the diffusion coefficient. Increasing the diffusion rate into stagnant zones also assists bioventing since diffusion of biostimulants (e.g., oxygen, methane) into stagnant zones is exactly analogous to diffusion of contaminants out of the zones. Low-cost methods for enhancing diffusional mass transport are discussed following.

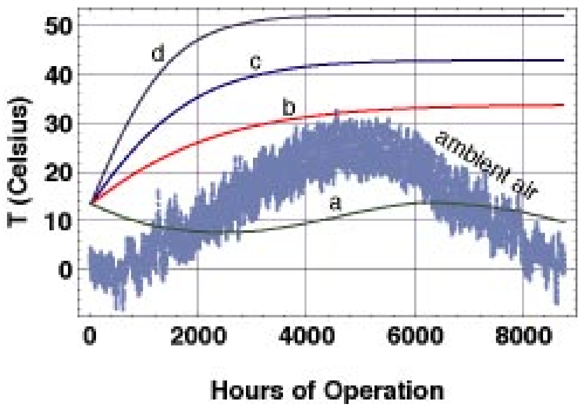

FIGURE 8. PREDICTED CHANGE IN SOIL TEMPERATURE AND ACTUAL AMBIENT AIR TEMPERATURE FOR FOUR ALTERNATIVE REMEDIATION STRATEGIES.

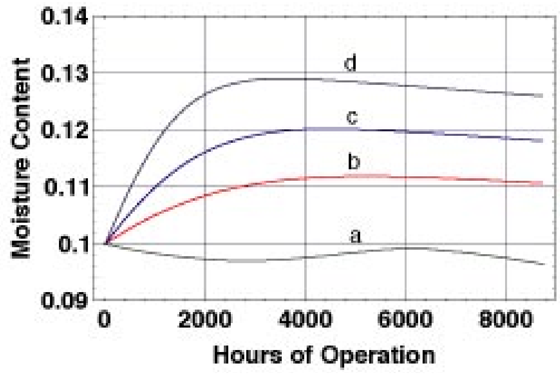

FIGURE 9. PREDICTED CHANGE IN SOIL VOLUMETRIC MOISTURE CONTENT FOR FOUR ALTERNATIVE REMEDIATION STRATEGIES.

A SPECIFIC EXAMPLE OF ENHANCED VENTING—INPUT OF WARMED, HUMIDIFIED AIR USING INDUSTRIAL WASTE HEAT

Four scenarios are simulated for a one-year period for a hypothetical site located at Lexington, KY. The pumping rate is five soil volumes per day. Governing equations for enthalpy balance are given in Walton and Anker [2, 19]. The contaminant transport is found by numerical integration of the equations for an heterogeneous system given above. Scenario **a** (the default or control) assumes that input air into the soil is at ambient temperature, and moisture content as shown by the gray dots. The ambient conditions (ambient air) are represented by a 10-year average of hourly airport data for temperature and humidity. Scenarios **b**, **c**, and **d** assume input air is humidified to 75% relative humidity and warmed to 40ºC, 50ºC, and 60ºC, respectively, prior to injection.

Normal or default venting with ambient air (**a**) tends to cool and dry the soil slightly over a one-year period (Figure 8). The net drying and cooling are caused by vacuum evaporation of soil moisture in response to the pressure drop. The warmed and humidified air scenarios result in higher soil temperatures, thereby increasing the vapor pressure of volatile or semi-volatile organics and diffusion coefficients. The energy for warming the input air can come from solar heating or low grade waste heat from industrial processes.

Projected soil volumetric moisture content is given for the four venting scenarios in Figure 9. Humidified and heated input air (75% relative humidity) results in only a small change in soil moisture content. Note that the scale on the graph has been expanded to illustrate the changes in soil moisture content. In every case, the change in moisture content is very small.

Cleanup time for a TCE spill is shown for the four options in Figure 10. The simulation assumes that removal is from a heterogeneous medium with 50 cm deep stagnant soil zones where the contaminant must be removed by diffusion out to the fast air flow channels. TCE is removed in approximately one-half of the time for the heated soil cases. The model accounts for the latent heat of vaporization for the contaminant and the influence of changes in

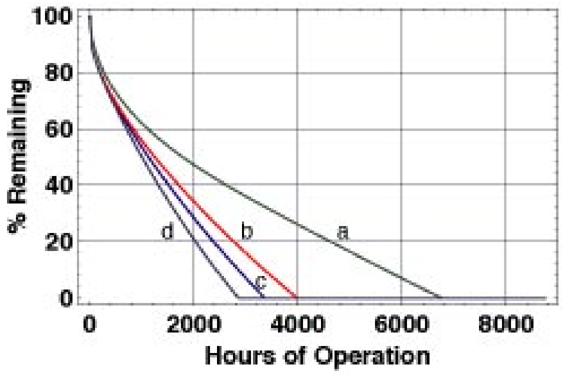

FIGURE 10. PREDICTED REMEDIATION RATES FOR THE FOUR ALTERNATIVE REMEDIATION STRATEGIES.

soil moisture content on vapor diffusion. Other alternative venting options, including solar heating, are explored in Walton and Anker [2].

DISCUSSION

A number of system properties important to remediation may change during soil venting operations. The changes may be inadvertent or intentional and may slow or enhance remediation. Initial investigations indicate that soil temperature, soil moisture content, and air pressure can be modified using low-cost methods to enhance remediation. Initial simulations have investigated the potential for injection of slightly warmed, humidified air into the subsurface. Nomogram-type charts were presented to allow estimation of anticipated rate of temperature change in soils as a function of air flow rate, input air temperature, and input air humidity.

This preliminary work has demonstrated in principle that inputs and outputs to a soil venting operation can be managed using low-cost methods in a manner to enhance remediation. Additional work is required to determine optimal remediation designs and operational strategies. Our long-term goals are to better understand how to enhance soil venting operations and eventually apply the concepts at an actual field site.

Nomenclature

A	surface area of residual NAPL soil (m^2)
ϕ	soil porosity
θ	volumetric water content
θ_c	volumetric contaminant content
ρ_c	contaminant density
δ_t	initial half spacing between macropores (m)
δ	diffusional path length (m)
F	diffusional flux of contaminant (kg/s)
C_1	vapor saturation concentration (kg/m^3)
t	cleanup time (s)
C_2	concentration in macropores (kg/m^3)
V	volume of contaminated soil = $A\delta_t$

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