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How Heat Can Enhance In-situ Soil and Aquifer Remediation: Important Chemical Properties and Guidance on Choosing the Appropriate Technique

Eva L. Davis *

Background

The EPA Regional Ground Water Forum is a group of EPA professionals representing Regional Superfund and Resource Conservation and Recovery Act (RCRA) Offices, committed to the identification and resolution of ground-water issues impacting the remediation of Superfund and RCRA sites. Innovative technologies for subsurface remediation, including in-situ techniques based on heating the subsurface to enhance the recovery of organic contaminants, are being evaluated more often for specific sites as the limitations to the conventionally-used techniques are recognized. The purpose of this Issue Paper and the three companion Issue Papers (Davis, 1997a, b, c) is to provide to those involved in assessing remediation technologies some basic information on the thermal remediation techniques. In order to understand how heat can enhance a remediation process, it is essential to understand the properties of organic contaminants that affect their recovery. Thus, this Issue Paper contains in-depth information on the properties of some common organic contaminants which can affect their movement in and recovery from the subsurface, as well as information on how these properties are affected by temperature. Then, some basic information on which of the heat-based remediation techniques may be most appropriate for the subsurface conditions and the contaminants is also provided, as well as a comparison of the heat-based techniques to other in-situ remediation techniques. The three companion Issue Papers have been written to provide an explanation of how each of the three general types of processes (steam or hot air injection, electrical heating, and hot water injection) works, as well as preliminary information on the design of a system and some estimates of the expected costs. Thus, once the ground-water remediation specialist has determined which of the thermal methods may be appropriate for a particular site, the Issue Paper on that method may be consulted for more detailed information on how the process may be applied.

Introduction

Thermal treatment is a common and proven technology for the remediation of contaminated soils (Lighty et al., 1990), but in the past thermal treatment has been applied mainly to soils that have been excavated and are then incinerated to release and/or destroy the contaminants. However, excavation of contaminated soils is not always practical and can be extremely costly when the contamination occurs at great depths or covers a large area. Excavation also increases the risk of exposure to and further dispersion of the contaminants during material handling steps (Dev et al., 1989; *Superfund Report*, August 10, 1994). Heat-based in-situ remediation methods can be used in many places where excavation is not possible, such as under and around surface structures, and around empty underground tanks and utilities (U.S. EPA, 1995d). In many instances, heat-based in-situ remediation techniques have been found to be cost effective compared to the excavation and incineration option or other remediation techniques (Dev et al., 1989; Basile and Smith, 1994; Yow et al., 1995).

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* *National Risk Management Research Laboratory, U.S. EPA*

Superfund Technology Support Center for Ground Water

National Risk Management Research Laboratory
Subsurface Protection and Remediation Division
Robert S. Kerr Environmental Research Center
Ada, Oklahoma

Technology Innovation Office
Office of Solid Waste and Emergency
Response, US EPA, Washington, DC

Walter W. Kovalick, Jr., Ph.D.
Director

The most commonly used remediation technique for the recovery of organic contaminants from ground water has been pump-and-treat, which recovers contaminants dissolved in the aqueous phase. Vacuum extraction (also called soil venting) is quickly becoming popular for removal of volatile organic contaminants from the unsaturated zone in the gaseous phase (Ho and Udell, 1992; Shah et al., 1995). Both of these techniques can, in the initial remediation phase, rapidly recover contaminants at concentrations approximately equal to the solubility limit (pump-and-treat), or the maximum gas phase concentration of the contaminant (vacuum extraction). The maximum gas phase concentration will depend on whether the contaminant is present as a free phase or as a solute in the aqueous phase. During this initial phase, large amounts of the contaminants may be removed. The second phase of the remediation, however, is characterized by rapidly declining contaminant concentration in the effluent as the rate of mass transfer into the flowing phase controls the rate of removal. The third phase of the remediation is characterized by a *tailing* in the effluent of low contaminant concentrations. However, low effluent concentrations may not be a reliable indication of low contaminant levels remaining in the subsurface. Diffusion of contaminants from less-permeable areas into the regions where flow is occurring or the slow desorption of contaminants from the soil surface may control contaminant removal during this phase, and termination of the extraction process before these processes are complete may lead to significant rebounding of the ground water and/or soil air concentrations (Mackay and Cherry, 1989).

Thus, the rate-limiting properties of the systems are different in each of the three phases of the remediation: in the first phase, the solubility of the contaminant in the aqueous phase (pump-and-treat) or its maximum gas phase concentration (vacuum extraction); in the second phase, it is the mass transfer step, i.e, dissolution into the aqueous phase (pump-and-treat), or vaporization (vacuum extraction); and, during the third phase, it is diffusion from low permeability areas or the desorption rate (Shah et al., 1995).

Instances of soil and aquifer contamination by oily contaminants such as automatic transmission fluid (Abdul et al., 1990), coal tar (Gerencher et al., 1992) and creosote (Johnson, 1994) have been documented. Contaminants such as these oils are practically insoluble in water and have essentially no vapor pressure. Thus, they will be present in the subsurface as a nonaqueous phase liquid and must be recovered as such. The recovery of these types of products is often limited by slow movement to recovery wells caused by their high viscosity and the significant residual saturation left behind. Heat-based in-situ remediation techniques which overcome or lessen the influence of each of these limitations to the recovery of organic contaminants have been developed and are being field tested.

Properties of the Contaminants

Organic contaminants in the subsurface can be present as a separate nonaqueous phase liquid, dissolved in the aqueous phase, in the vapor phase in the soil gas, partitioned into the soil organic matter, or adsorbed onto the solid mineral phase. The relative amount of the contaminant in each of these phases is determined largely by the properties of the contaminant. Generally, the most important property of the soil in determining the distribution of contaminants is the soil organic matter, which normally controls the absorption of hydrophobic compounds.

Table 1 lists some of the relevant physical properties of volatile and semivolatile organic chemicals that have been, or have the potential to be, recovered using in-situ thermal techniques. Many of these are commonly found at Superfund sites and other sites where ground-water contamination has occurred (Roberts et al., 1982; Esposito et al., 1989; Newell et al., 1995). All of the properties listed are temperature dependent. Most of these organics are essentially immiscible with water; acetone and methanol are the exceptions. Many of these compounds have low viscosities and, thus, have the potential to flow readily in the liquid phase. Approximately half of these compounds are less dense than water; the other half are more dense than water. The density of an organic liquid relative to that of water is important in determining the vertical mobility of the contaminant. Those that are less dense than water will tend to float on the ground-water table, while those that are more dense than water may move downward through the aquifer if the pressure in the organic liquid is greater than the displacement pressure of the aquifer materials. Low permeability clay layers in the aquifer may restrict the vertical movement and allow the liquids to accumulate on top of the layer.

Table 1 is set up to list the chemicals in the order of lowest to highest boiling points. Observation of the vapor pressures shows that, in general, the lower the boiling point the higher the vapor pressure at 25°C. The contaminants with the lowest boiling points also generally have a lower heat of vaporization, thus these contaminants are relatively easy to volatilize. Compounds with higher boiling points have lower vapor pressures at ambient temperatures and a higher heat of vaporization, thus more energy is required to convert them to the gaseous phase. Laboratory experiments have shown that vaporization of even highly volatile compounds can cause a measurable decrease in the temperature of the system (Lingineni and Dhir, 1992).

Henry's law constants indicate whether the compound prefers to be in the gaseous or aqueous state. Henry's law applies to dilute solutions, and can be written as: $P_A = X_A H_c$, where P_A is the partial pressure of chemical A, X_A is the mole fraction of chemical A in solution, and H_c is a constant, commonly called the Henry's law constant. Thus, the Henry's law constants are a function of the aqueous solubility and vapor pressure of a compound, and the greater the Henry's law constant, the greater the extent to which the compound partitions to the air phase (Atkins, 1986). The constants given in the table are expressed in the dimensionless form, which is a ratio of the concentrations, C_{air}/C_{water}, where both concentrations are in mol/m^3. Due to difficulties involved in determining solubilities and vapor pressures, reported values of Henry's law constants sometimes vary by two orders of magnitude or more depending on the source of the data. Mackay and Shiu (1981) performed a critical review of the available data, and determined recommended values for many chemicals of environmental interest, and a standard deviation of the reported

Table 1. Properties of some organic chemicals that have been found at contaminated sites.

Organic Contaminant	Boiling Point °C	Density gm/cm^3	Viscosity cP 25°C	Water Solubility mg/l	Vapor Pressure mm Hg T_1, °C	Vapor Pressure mm Hg T_2, °C	Henry's Law Constant dimensionless 25°C	Octanol-Water Partition Coefficient	Diffusion Coefficient in Water cm^2/day	Diffusion Coefficient in Air cm^2/day	Heat of Vaporization[b] kJ/mol 25°C
Methylene Chloride (Dichloromethane)	40	1.3182 25°C	0.413	20,000 20°C[e]	260.9 10°C	>760 50°C	0.105 ± 0.008[n]	17.78[q]			28.82
1,2-Dichloroethylene (trans)	49	1.2444	0.317	600 20°C[e]	198.7 10°C	>760 50°C					
Acetone	56.3	0.7899	0.306	∞	121.7 10°C	622.4 50°C	0.000842[k]	1.74[e]	1.106[b,p,h] 25°C	9417.6[s] 0°C	30.99
1,1-Dichloroethane	57.4	1.17	0.464	5500 20°C[e]	125.8 10°C	608.6 50°C	0.234 ± 0.008[n]	30[d] 61.7[i]			30.62
1,2-Dichloroethylene (cis)	60	1.2649 25°C	0.445	800 20°C[e]	104.8 10°C	580.0 50°C					
Trichloromethane (Chloroform)	61.2	1.49	0.537	8000 20°C[e]	98.6 10°C	541.3 50°C	0.153 ± 0.012[n]	90[d] 79.4[i] 93.3[b] 91.2[q]		7862[s] 0°C	31.28
1-Hexene	63.5	0.675	0.252	50 20°C[e]	90.0 10°C	485.3 50°C	16.87 ± 0.40[n]	2455[r,h]		6212[h] 20°C	30.61
Methanol	64.6	0.791	0.544	∞	58.5 10°C	400 50°C		0.151 - 0.219	1.11[o] 15°C 1.6[s] 25°C 1.43[h] 25°C	14,688[g]	37.43
n-Hexane	68.7	0.659	0.300	9.5 20°C[e]	80.8 10°C	407.5 50°C	68.6 ± 10.1[n]	10,000[b] 12,883[r]		6143[h] 20°C	31.56
1,1,1-Trichloroethane	74.1	1.3303 25°C	0.793	4400 20°C	67.4 10°C	360.1 50°C	1.13 ± 0.016[n]	309[b] 300[d] 147.9[i]			32.50

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Table 1 -- Continued.

Organic Contaminant	Boiling Point °C	Density gm/cm^3	Viscosity cP 25°C	Water Solubility mg/l	Vapor Pressure mm Hg T_1, °C	Vapor Pressure mm Hg T_2, °C	Henry's Law Constant dimensionless 25°C	Octanol-Water Partition Coefficient	Diffusion Coefficient in Water cm^2/day	Diffusion Coefficient in Air cm^2/day	Heat of Vaporization[b] kJ/mol 25°C
Carbon Tetrachloride	76.8	1.5833 25°C	0.908	800 20°C[e]	58.3 10°C	332.8 50°C	0.807 ± 0.161[n]	676.1[b,q] 436.5[e,i]			32.43
2-Butanone (Methyl Ethyl Ketone)	79.6	0.7994 25°C	0.405	26,800	52.6 10°C	314.3 50°C	0.0010[j] 0.00112[c,k]	1.820[e]			34.76
Benzene	80.1	0.88	0.604	1770 25°C	47.8 10°C	307.8 50°C	0.22 ± 0.01[n]	134.90[b,e,h,i,l]	0.881[b,h] 20°C 0.501[h] 2°C	7460[f] 7819.2[h] 20°C 6653[s] 0°C	33.83
Cyclohexane	80.7	0.7731 25°C	0.894	58 25°C	50.5 10°C	272.3 50°C	7.27 ± 0.81[n]	2754[h]	0.726[b,h] 20°C 0.397[h] 2°C	7430.4[s] 45°C 6212[h] 20°C	33.01
1,2-Dichloroethane	84	1.257	0.779	8700 20°C	40.0 10°C	278.6 50°C	0.044 ± 0.004[n]	30.2[b,i]			35.61
Trichloroethylene	87.3	1.4578 25°C	0.545	1100 25°C[e]	37.6 10°C	256.7 50°C	0.397[f] 0.38[i] 0.372[a]	195[b] 200[d] 339[r]	0.830[f]	7030[f]	34.54
Toluene	110.6	0.8647 25°C	0.56	515 - 540 25°C	14.3 10°C	579.1 100°C	0.27 ± 0.014[n]	537[b] 490[d,e,h,i,l] 447[r]	0.734[b,h] 20°C 0.389[h] 2°C	6570[f] 7119.4[h] 20°C 6566[s] 0°C 7603[s] 30°C 7430[o] 26°C 7949[o] 59°C	38.01

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Table 1 -- Continued.

Organic Contaminant	Boiling Point °C	Density gm/cm^{3}	Viscosity cP 25°C	Water Solubility mg/l	Vapor Pressure mm Hg T_1, °C	Vapor Pressure mm Hg T_2, °C	Henry's Law Constant dimensionless 25°C	Octanol-Water Partition Coefficient	Diffusion Coefficient in Water cm^{2}/day	Diffusion Coefficient in Air cm^{2}/day	Heat of Vaporization^{b} kJ/mol 25°C
4-Methyl 2-Pentanone	116.6	0.802	0.545	19000	4.3 10°C	381.0 100°C	0.0063^{c}				40.61
Tetrachloroethylene	121.3	1.613 25°C	0.844	150 25°C	9.0 10°C	400 100°C	0.928 ± 0.161^{n}	$400^{d,e}$ 407^{q}			39.68
n-Octane	126	0.6986 25°C	0.508	0.7 20°C^{e}	6.5 10°C	368.7 100°C	121 ± 20^{n}	$104{,}700^{l}$ $151{,}356^{h,r}$		4910^{f} 5166.7^{h} 20°C 4363^{s} 0°C	41.49
Chlorobenzene	131.7	1.1007 25°C	0.753	490 25°C	6.9 10°C	323.7 100°C	0.14 ± 0.02^{n}	$691.8^{b,e,i}$ 955^{r}		6394^{o} 26°C 7776^{o} 59°C 6480^{s} 30°C	40.97
Ethylbenzene	136.2	0.8654 25°C	0.631	160 25°C	6.0 10°C	295.7 100°C	0.323 ± 0.028^{n}	$1412.5^{b,h,i}$ 1349^{r}	$0.700^{b,h}$ 20°C 0.380^{h} 2°C	6333^{h} 20°C	42.24
Xylenes	138.4 - 144.4	0.8577 - 0.8764 25°C	0.608 - 0.802	160 - 180 25°C	4.5 - 5.6 10°C	238.9 - 280.8 100°C	0.20^{f} 9400^{j} $0.202 - 0.286^{c}$ 0.214^{a}	1412 - 1585^{b} 588.8 - $1584.9^{e,h,l}$ 1349 - 1585^{r}		5980^{f} 5771.5^{h} 20°C	42.40 - 43.43
n-Decane	174.2	0.730	0.838	0.052	3.0 25°C	77.7 100°C	282.5 ± 121^{n}				51.38
Dichloro-Benzene (3 isomers)	173 - 180	1.2988 25°C (ortho isomer)	1.044 - 1.324	80 - 150 25°C	2.2 25°C	67.1 100°C	$0.048 - 0.073^{b}$	2399 - 3981^{b} 2399 - 2455^{e}			36.18 - 49.00
Dodecane	216.5	0.75	1.383	0.0034		19.5 100°C	302.7 ± 100.9^{n}	1537^{l} 13 x $10^{6\ h}$			61.51

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Table 1 -- Continued.

Organic Contaminant	Boiling Point °C	Density gm/cm^3	Viscosity cP 25°C	Water Solubility mg/l	Vapor Pressure mm Hg T_1, °C	Vapor Pressure mm Hg T_2, °C	Henry's Law Constant dimensionless 25°C	Octanol-Water Partition Coefficient	Diffusion Coefficient in Water cm^2/day	Diffusion Coefficient in Air cm^2/day	Heat of Vaporization[b] kJ/mol 25°C
Naphthalene	218	0.97		32 25°C		22.7 100°C	0.02[b,i] 0.05[m] 0.017 ± 0.002[n]	2239[b,r] 2344.2[i] 1738[l]		4432[s] 0°C	
1-Methyl naphthalene	244.8	1.020		28.5		0.043 kg/m3	0.0182 ± 0.0016[n]	7413[r]			
Hexadecane	286.9	0.773	3.032	0.0063	< 1	< 1					81.38
Phenanthrene	340	0.98		1.18			0.0016[i,m] 0.0016 ± 0.00032[n]	28,840[e,i] 37154[r]			72.50
Gasoline		0.73 0.7182[h] 20°C	0.45 0.4 - 0.6[h] 20°C	100 - 300 30 - 120[h]						6272.6[h] 20°C	

Superscripts

a - Baehr, 1987
b - Lide, 1993
c - Newell et al., 1995
d - Hunt et al., 1988
e - Verschueren, 1983
f - Ong et al., 1992
g - Thoma et al., 1992
h - Lyman et al., 1991
i - Ryan et al., 1988
j - Jury et al., 1990
k - Sanders, 1995
l - Johnson et al., 1990
m - Jury et al., 1984
n - Mackay and Shiu, 1981
o - Treybal, 1980
p - Tyn and Calus, 1975
q - Valsaraj, 1988
r - Miller et al., 1985
s - Perry and Chilton, 1973

values that were thought to be reliable. For chemicals for which their recommended values are available, they are listed in Table 1. For the other chemicals, all reported values that were located in the literature are listed to show the range in reported values. The Henry's law constants listed in the table show that at ambient temperatures, the alkanes and similar compounds, such as 1-hexene and cyclohexane, have a strong preference for the air phase rather than the aqueous phase, while the chlorinated solvents and compounds that contain a benzene ring tend to concentrate more in the aqueous phase. As the number of benzene rings in the compound increases, its preference for the aqueous phase increases. The ketones listed in Table 1 also have a very strong preference for the water phase.

The partition coefficient is defined as the ratio of the equilibrium concentration C of a dissolved substance in a system containing two largely immiscible solvents. Thus, the octanol-water partition coefficient is defined as $K_{ow} = C_{octanol}/C_{water}$. The octanol-water partition coefficient has proven useful as a means to predict soil absorption as well as biological uptake and biomagnification and related phenomenon (Verschueren, 1983). In general, the more hydrophobic a compound is, the greater its octanol-water partition coefficient and the greater its absorption onto soil organic matter (Karickhoff et al., 1979). However, this generalization is limited to hydrophobic organic compounds and soils which contain significant amounts of organic matter, on the order of at least 0.1 percent (Schwarzenbach and Westall, 1981; Weber et al., 1991). Most of the organic compounds listed in Table 1 are at least moderately hydrophobic, thus the octanol/water partition coefficient might be expected to indicate the degree of absorption of these compounds in surface soils or other soils with high organic carbon contents. It can be seen in Table 1 that there are also some large differences in the reported values for the octanol/water partition coefficients for a given organic compound depending on the source of the data. Despite these differences, the reported values show that most of the compounds listed have a strong preference for organic matter rather than the water phase, with the exception being the ketones and methanol. The absorption of contaminants into the soil organic matter will tend to limit the rate at which they can be recovered in either the aqueous or gaseous phase.

To illustrate what the Henry's law constants and octanol-water partition coefficients indicate about the distribution of an organic chemical in the subsurface, a few calculations were carried out using the equations given by Feenstra et al. (1991). The results of these calculations are shown in Table 2. A surface soil of loam texture with a bulk density of 1.28 gm/cm^3, a porosity of 0.30, a water saturation of 50 percent, and an organic matter content of 2 percent was assumed. Karickhoff et al.'s (1979) relationship between the octanol-water partition coefficient and the adsorption coefficient, K_d, was assumed to be valid: $K_d \;\; 0.6f_{oc}K_{ow}$, where f_{oc} is the fraction of organic matter in the soil. In order to demonstrate the effect of soil properties on the distribution of an organic chemical, calculations were also done for the same chemicals for a sandy soil of bulk density 1.86 gm/cm^3, porosity 0.30, and organic matter 0.1 percent. Again, a 50 percent water saturation was assumed.

Table 2 shows that in soils with high organic carbon content, organic compounds may be highly associated with the solid material. Calculations for 1,1,1-trichloroethane (TCA) were carried out using the range of values that have been reported for K_{ow} for this chemical to illustrate the difference this can make in the calculated distributions. For soils with high organic matter content there is very little difference as most of the chemical is still associated with the solids. For low organic matter conditions the difference in the distribution is significant, and the lower K_{ow} value means that more of the chemical is recoverable in the water or air phase. Trichloroethylene (TCE) and TCA have similar K_{ow} values at ambient temperatures, but TCA has a Henry's law constant that is greater than that of TCE at temperatures around 20°C and, thus, much more of the TCA will be in the air phase. TCE is a volatile organic compound but, at 20°C, significantly more of its mass will be in the aqueous phase rather than in the gas phase; a very significant proportion of it will be associated with the solids. Acetone is highly volatile with a boiling point of 56°C, but its extremely low K_{ow} and H_c concentrate it in the aqueous phase. Because acetone is miscible with water and is a good solvent for many organic chemicals, acetone may significantly increase the transport of less soluble organic chemicals in ground water (Huling, 1989; Udell and Stewart, 1989).

The diffusion coefficient measures the rate at which molecules spread down a concentration gradient, and is dependent on the chemical nature of the system and the concentration, as well as the temperature and pressure. As can be seen from the coefficients listed in Table 1, diffusion in gases is much greater than diffusion in liquids, which is due to the considerably higher molecular concentration of liquids. When experimental data is not available, the diffusion coefficient for gases can be estimated fairly accurately by equations that have been developed based on the kinetic theory of gases. For liquids, diffusion coefficients cannot be estimated with the same degree of accuracy because a sound theory of the structure of liquids has not been developed. However, empirical correlations have been developed and can be used in the absence of laboratory data (Treybal, 1980). Observation of the values in the table shows that most of the organic compounds for which values could be located fall in the range of 5000 to 8000 cm^2/day for diffusion in air; methanol and acetone are again the exceptions with larger coefficients. All of the water diffusion coefficients, also, fall in a rather narrow range from 0.7 to 1.6 cm^2/day.

The properties listed in Table 1 are for pure chemicals, and do not consider the effects of a porous solid on the properties and behavior of the chemical. The vapor pressure, the diffusion coefficient in both air and water, and perhaps the viscosity, are all significantly affected by the presence of the chemical in porous media and the properties of that media. The partial pressure of a liquid is dependent on the curvature of the interface between the liquid and gaseous phases, and the values contained in Table 1 are for a flat interface. When the interface is curved, the partial pressure of the liquid is reduced. Although this effect is very small in sandy soils with a less than one percent reduction in vapor pressure, it becomes important in clay soils when the pore sizes are less than approximately 10^{-6} cm,

Table 2. Distribution of chemicals in low and high organic matter content soils.

	High Organic Matter			Low Organic Matter		
	Air	Water	Solids	Air	Water	Solids
1,1,1-Trichloroethane $P_{oct} = 300$	5%	5%	90%	26%	23%	51%
1,1,1-Trichloroethane $P_{oct} = 147.9$	6%	6%	88%	35%	31%	34%
Trichloroethylene 20°C	1.6%	4.6%	93.8%	14%	35%	52%
Trichloroethylene 90°C	30%	7%	63%	73%	16%	11%
Acetone	0.07%	85%	15%	0.08%	99%	1%

causing a decrease in vapor pressure of approximately 40 percent (Wilson et al., 1988). This effect can also be important when the medium is dry and the remaining liquid has receded into the smallest pores (Bear and Gilman, 1995). These capillarity effects will determine the level of cleanup that can be achieved by a venting process at a given temperature (Lingineni and Dhir, 1992).

Adsorption of the organic onto the solid phase or partitioning into the soil organic matter can also have the effect of lowering the partial pressure of an organic compound. Adsorption can occur from the liquid onto the solid and, when the water content is very low, from the vapor phase onto the soil surface (Lighty et al, 1990; Tognotti et al., 1991). Fares et al. (1995) have studied desorption of TCE from soils, and their data shows that the equilibrium vapor pressure of TCE as it desorbs from a soil is approximately an order of magnitude lower than the partial vapor pressure of TCE when no soil is present. Experiments performed by Arthurs et al. (1995) showed that the rate of volatilization of the liquid in the presence of a soil is about two orders of magnitude slower than from the pure liquid, and that the vaporization rate increases as the vapor pressure of the compound increases. Fares et al. (1995) and Keyes and Silcox (1994) found that the rate of desorption was linearly correlated with the inverse of the soil particle diameter. Hatzinger and Alexander (1995) found that organic compounds may become more tightly bound to the soil or organic matter with time, which reduces their desorption. Thus, the equilibrium partial pressure of a volatile contaminant in the pore space and mass transfer from the aqueous liquid or adsorbed phase will depend on the properties of the chemical and the soil environment in which it resides.

The diffusion coefficients listed in the table are for bulk air or water. In the pore spaces of a soil, diffusion in both the air and water phase is reduced because of the reduced cross-sectional area and increased path length caused by the presence of solid and liquid obstacles (Millington, 1959). Diffusion coefficients in porous media are a function of both the porosity of the soil and the water (or air) content of the pores. At low water contents, diffusivity in the water is also limited by the continuity of the water phase. For diffusion in water in porous media, Porter et al. (1960) found a nearly linear increase in effective diffusion as the water content increased, ranging from 4 to 30 percent of its diffusion in bulk water. Jin and Jury (1996) recommended the use of a second model developed by Millington (1959) for predicting gas phase diffusion in disturbed porous media: $D_s/D_a = a^2/n^{2/3}$, where D_s is the diffusion coefficient of a gas through soil, D_a is the diffusion coefficient in free air, a is the volumetric air content of the pores, and n is the porosity. They did not find a unique relationship for gaseous diffusion in undisturbed soils due to their heterogeneous nature. Measured gas phase diffusion in undisturbed soils is both higher and lower than predicted by this theory, but is not generally greater than about 40 percent of the diffusion in air, and the diffusion drops off rapidly as the air-filled porosity decreases.

Adsorption of water onto solid surfaces, particularly onto the reactive surfaces of clays, will increase the viscosity of the water in the layers immediately adjacent to the clay surface. Theoretical and experimental results of Kemper (1961a, 1961b) indicated that the first layer of water on the surface of a clay may have a viscosity on the order of 10 times that of the bulk water, and the viscosity of each adjacent layer of water then decreases rapidly to the viscosity of the bulk water. How much effect this has on bulk flow in soils depends on the thickness of the water films in proportion to the pore sizes. Neutral organic species will generally not be adsorbed to the surface of the soil as strongly as water. Therefore, neutral organics may have a smaller effective viscosity relative to that of water in porous media, allowing them to flow more readily. For clays that are highly reactive and swell in the presence of water, research has shown that the presence of organic chemicals may shrink the clay. Cracks may form which allow a much greater flow of the organic chemical than was possible with water (Anderson et al., 1985; Brown and Thomas, 1987; Fernandez and Quigley, 1988).

Table 3 lists a few of the viscous oils that have been found contaminating the subsurface. These oils are essentially nonvolatile and are not soluble to an appreciable degree in water. Thus, they remain a separate liquid phase in the subsurface. All of these oils are mixtures of many different hydrocarbons. Coal tar and creosote also contain polycyclic aromatic hydrocarbons. When oils such as these are spilled to the subsurface and are exposed to air and water, "weathering" will occur, as the more volatile hydrocarbons volatilize to the pore air, and the more soluble hydrocarbons dissolve in the pore water. Water and air moving past these oils while they are trapped in the subsurface will enhance the weathering process. The loss of the “light” hydrocarbons by the weathering process will increase the specific gravity and viscosity of the remaining oil, and lower the surface and interfacial tensions. Measurements made in the author’s laboratory, Robert S. Kerr Environmental Research Center, showed that a significant proportion of the crude oil was volatilized at room temperature, causing a 7-fold increase in viscosity. Creosote was found to contain few volatiles at room temperature, and weathering did not change its viscosity significantly. The specific gravity of both oils increased, and the surface and interfacial tensions decreased by approximately 5 to 10 dynes/cm by the weathering. Mungan (1964, 1966) has found that decreasing the interfacial tension in an immiscible displacement will increase recovery of the oil. Although decreases in interfacial tension will favor recovery of these oils, that may be offset by a decrease in mobility caused by the higher viscosities.

Research in the author’s laboratory has shown that oils such as the crude oil listed in Table 3 flows more readily through some silica sands than would be predicted based on the intrinsic permeability of the sand measured with water and the density and viscosity of the crude oil. This is likely due to the nonpolar nature of these hydrocarbons which limits their adsorption to soil surfaces. The greater mobility of the crude oil would give it a greater tendency to spread as it enters the subsurface, but also should aid in its recovery by a displacement process such as hot water injection.

Mechanisms for Enhanced Recovery

In general, when an organic chemical is heated, its density is reduced, its vapor pressure is increased, its adsorption onto solid phases or absorption into soil organic matter is decreased, and its molecular diffusion in the aqueous and gaseous phase is increased (Isherwood et al., 1992). The viscosity of a liquid will decrease as the temperature is increased, but the viscosity of gases increases with temperature. Which of these effects of heat is important for the enhanced recovery of a particular contaminant depends mostly on the properties of the contaminant and the mechanism limiting the removal rate of the contaminant in the particular circumstance.

Available data on the expansion of organic chemicals such as those listed in Table 1 with temperature shows that these chemicals expand approximately 0.1 percent per degree Celsius. Thus, increasing the temperature by 100°C will increase the liquid volume by approximately 10 percent. Since the volume of a gas is directly proportional to temperature given in Kelvin, a 100°C increase in temperature will cause approximately a 30 percent increase in the gas volume. These changes are small compared to the volume change that occurs when a liquid is converted to a gas; water at 100°C has approximately a 1600-fold increase in volume when it is converted from a liquid to a vapor.

The expansion of liquids with temperature causes a reduction in the interaction between molecules, and thus a reduction in its viscosity. For the organic chemicals listed in Table 1, generally there is about a one percent change in viscosity per degree Celsius. Thus, the higher the viscosity of the liquid at ambient temperatures, the greater the reduction in viscosity as the temperature is increased. The viscosity of gases at ambient temperatures is approximately one to two orders of magnitude lower than the viscosity of liquids. However, the increase in the velocity of gas molecules with temperature is such that it causes greater interaction between molecules as the temperature increases, causing an increase in viscosity with temperature. This increase is proportional to the temperature in degrees Kelvin, so that a 100°C increase in temperature will increase the viscosity of a gas by about 30 percent.

The effect of temperature on solubility is dependent on the chemical. Increasing temperature will reduce the water-water, water-solute, and solute-solute interactions, so the net effect of temperature on solubility will depend on which interactions are affected to the greatest extent (Yalkowsky and Banerjee, 1992). Thus, some chemicals show increasing solubility with temperature while others show decreasing solubility with temperature. Maximum or minimum solubilities with temperature have also been found for some chemicals; many organic liquids exhibit minima in solubility at about room temperature (Yalkowsky and Banerjee, 1992). Measurements by Stephenson (1992) and the data compiled by Horvath (1982) show that the solubility of the organic chemicals listed in Table 1 often decreases in the temperature range of 0°C to 90°C, but the change in solubility in this temperature range is generally less than a factor of two.

Vapor pressures always increase with temperature. For the organics listed that have a boiling point of less than 100°C, the vapor pressure increases by a factor of 5 to 7 as the temperature increases from 10°C to 50°C. For those compounds that have a boiling point greater than 100°C, their vapor pressure generally increases by a factor of 40 to 50 by raising the temperature from 10°C to 100°C. Limited data on the desorption of organics from

Table 3. Properties of some oily contaminants.

	Boiling Range	Specific Gravity	Viscosity cp	Water Solubility mg/l	Vapor Pressure mm Hg	Surface Tension dynes/cm	Interfacial Tension dynes/cm
Automatic Transmission Fluid[a]	> 350°C	0.875		< 50	$< 2 \times 10^{-4}$	33.7	
		20°C		20°C			
Coal Tar[b]		25°C 0.9744	25°C 41.4				
		60°C 0.9469	60°C 1.65				
		85°C 0.9263	85°C 1.16				
Coal Tar[c]	50% can be distilled at 270°C	7°C 1.028	7°C 18.98			28.8	22
		15°C 1.017	50°C 5.04				22°C
		38°C 0.991	60°C 3.89				
		60°C 0.985					
Creosote[d]	45 to 65% can be distilled at 315°C[e]	10°C 1.1060	10°C 35.7			10°C 32.4	9.65 10°C
		20°C 1.1027	20°C 19.8			20°C 33.5	7.83 20°C
		30°C 1.0957	30°C 12.4			30°C 29.0	6.16 30°C
		40°C 1.0893	40°C 8.57			40°C 25.0	5.31 40°C
		50°C 1.0816	50°C 6.17			50°C 26.8	5.90 50°C
Crude Oil[d]		10°C 0.8953	10°C 160.2			10°C 26.2	22.0 10°C
		20°C 0.8883	20°C 63.0			20°C 24.5	21.0 20°C
		30°C 0.8820	30°C 34.8			30°C 23.2	20.5 30°C
		40°C 0.8760	40°C 23.2			40°C 23.3	20.2 40°C
		50°C 0.8680	50°C 16.4			50°C 22.8	21.4 50°C

a - Abdul et al., 1990 b - Johnson and Guffey, 1990 c - Villaume et al., 1983 d - unpublished data from the author's lab
e - American Wood Preservers' Association Standards

soils shows that the exponential increase in the vapor pressure with temperature also holds when the organic chemical is in the presence of soils (Fares et al., 1995).

The combination of only small changes in solubility with temperature but large increases in vapor pressure results in increases in Henry's constant as a function of temperature. However, very few measurements of Henry's constants for chemicals of environmental concern as a function of temperature have been made, and most of these measurements are over a limited temperature range. Heron et al. (1996) calculated and measured H_c values for TCE as a function of temperature and found an order of magnitude increase when the temperature was raised from 20°C to 90°C. For the more soluble compounds such as dichloromethane or 2-butanone, and the water-miscible compounds such as acetone and methanol, H_c may not be influenced significantly by temperature.

Few measurements of K_{ow} and/or K_d have been made as a function of temperature, and most of the measurements that have been made are over very small temperature ranges. Although it has been shown for some systems that adsorption may increase with temperature over narrow temperature ranges (Weber et al., 1983), adsorption is, in general, an exothermic process and, thus, will decrease as the temperature increases. The magnitude of the effect of temperature is dependent on the particular chemical, the soil, and the water content, as these factors will determine the mechanism causing the adsorption (Cancela et al., 1992; Piatt et al., 1996). Heron et al. (1996) showed theoretically, based on heats of sorption, that adsorption from the aqueous phase onto soils can be expected to decrease by a factor of approximately 2.2 as the temperature is increased from 20°C to 90°C. Adsorption from the vapor phase onto dry soils generally has a larger heat of sorption, which leads to a greater influence of temperature on the adsorption process. For TCE, Heron et al. (1996) found approximately an order of magnitude decrease in adsorption onto dry soil as the temperature was increased from 20°C to 90°C. For high molecular weight organics such as PCBs, a large fraction of the organic may remain adsorbed to the soil at ambient temperatures, and significantly higher temperatures (300°C to 400°C) may be required for desorption to occur (Uzgiris et al., 1995).

Measured data has shown that the diffusion coefficient in liquids is proportional to temperature in degrees Kelvin. Increasing the temperature from 10°C to 100°C will increase the diffusion of a solute in the aqueous phase by approximately 30 percent (Treybal, 1980). The diffusion coefficient for gases is also dependent on temperature. Observation of the theoretical equation for diffusivity in the gas phase developed for mixtures of nonpolar gases or of a polar with a nonpolar gas shows that the diffusivity varies almost as $T^{3/2}$ (Treybal, 1980). Increasing the temperature from 10°C to 100°C will increase diffusion in the air phase by approximately 50 percent, while a temperature increase from 10°C to 300°C will increase diffusion by approximately 200 percent.

Essentially all of these changes with temperature can aid in the recovery of contaminants from the subsurface. The thermal expansion of a liquid with its accompanying decrease in viscosity will allow the heated liquid to flow more readily. For gases, the expansion with temperature will be largely offset by the increase in viscosity. However, since the viscosity of gases is approximately two orders of magnitude lower than the viscosity of liquids, conversion of a liquid to a gas will greatly increase its mobility. The act of expansion itself will aid in moving the fluids out of the pore space, with the greatest effects coming from the vaporization of a liquid to a gas. The increased diffusion of contaminants as the temperature increases in both the aqueous and gaseous phases will help to move contaminants from areas of low permeability to areas of high permeability and speed their recovery.

To demonstrate the effects of temperature on the distribution of organic contaminants between the phases in the subsurface, calculations were carried out using the data of Heron et al. (1996) for TCE at 90°C. The results are shown in Table 2. It can be seen that raising the temperature to 90°C significantly increases the concentration in the air phase under both the high and low soil organic matter conditions, while significantly decreasing the amount that is associated with the solids. Only small amounts remain in the liquid phase. Thus, as the temperature is increased, significantly more of the TCE can be recovered in the vapor phase. If the high organic matter content soil is considered under water saturated conditions, the amount of TCE in the water would approximately double as the temperature was increased from 20°C to 90°C, but 82 percent of the TCE would remain adsorbed to the solids. Under the low organic matter/water saturated conditions, there would be approximately a 30 percent increase in the amount of TCE in the water phase when the temperature is increased from 20°C to 90°C, leaving approximately 25 percent adsorbed to the solids.

This small effect of temperature on the concentration in the aqueous phase shows that raising the temperature would have a limited effect on the recovery in a pump-and-treat system. For the volatile and semivolatile organic compounds, such as those listed in Table 1, the enhanced vapor pressure and rate of vaporization are generally the most important mechanisms for enhanced recovery using the in-situ heat based remediation techniques. Some of the most volatile compounds, which includes TCE, benzene, and toluene, can be removed fairly efficiently from sandy soils by vacuum extraction alone (Ho and Udell, 1992; Gauglitz et al., 1994; Shah et al., 1995), and laboratory experiments on vacuum extraction have shown that the addition of heat had little effect on the vaporization of the less volatile compounds. For the higher boiling point compounds and when clays are present in the subsurface, the addition of heat as part of the remediation process will significantly increase volatilization and enhance the vacuum extraction process (Lingineni and Dhir, 1992). Recovery of most of these chemicals from the subsurface will be enhanced by either steam or hot air injection or by electrical heating processes.

For the volatile and semivolatile contaminants, steam stripping and steam distillation can also be important recovery mechanisms (Dev et al., 1989; Stewart and Udell, 1988). Steam distillation occurs when an immiscible liquid is present along with water, as the mixture of immiscible liquids will boil when the total pressure reaches one atmosphere, rather than when the pressure of the individual component reaches one atmosphere. Because both liquids are contributing to the vapor pressure, the vapor pressure reaches one atmosphere at a lower temperature than either of the individual components would (Atkins, 1986). Steam stripping enhances volatilization of a volatile organic compound by removing the vapor phase from contact with the aqueous phase, thus preventing the liquid and vapor phases from reaching equilibrium and allowing volatilization to continue. Steam stripping becomes important when an immiscible phase is not present (Dev et al., 1989).

For the types of contaminants listed in Table 3, the greatest enhancement effect coming from the addition of heat is likely to be a reduction in the viscosity of the oil phase. Highly viscous oils will generally show a substantial decrease in viscosity with only a moderate temperature increase above ambient temperatures (Herbeck et al., 1976), and the rate of decrease with temperature then drops off rapidly with continuing increases in temperature. Edmondson (1965) found that the greater the dependence of viscosity of the oil on temperature, the greater the increase in its recovery by a hot water displacement as the temperature increased. Other mechanisms for the increased recovery of oils by hot water include the thermal swelling of liquids (Willman et al., 1961), shifts in the relative permeabilities to oil and water with temperature, and decreases in the residual oil saturation (Edmondson, 1965; Davidson, 1969; Poston et al., 1970; Davis and Lien, 1993). Decreases in the interfacial tension with temperature for contaminants such as creosote may also aid in its recovery from the subsurface. Different researchers have found shifts of varying magnitudes and directions in relative permeability curves, but in all cases the increase in oil recovery as the temperature increases always appears to be greater than would be predicted based on the viscosity reduction alone. Capillary pressure-saturation curves measured for two phase water/oil systems have shown substantial decreases in the residual oil phase as the temperature increased (Davis, 1994), and thus, a greater portion of the oil may be recoverable as the temperature is increased.

Heat-based In-situ Remediation Techniques

There are three general methods that can be used to inject or apply heat to the subsurface to enhance remediation: injection in the form of hot gases such as steam or air, electromagnetic energy heating, and hot water injection. Another thermal remediation technique that relies on thermal conduction of soil to heat the subsurface is also under development (Iben et al., 1996), but will not be discussed here. All of these methods were first developed by the petroleum industry for enhanced oil recovery, and have more recently been adapted to soil and aquifer remediation applications. The two applications have significantly different objectives. In oil recovery operations, the reservoir initially has a large oil saturation, and the objective is to recover as much as possible economically. In these operations, a large residual oil saturation of as much as 50 percent or more may be acceptable. In contamination remediation applications, the initial saturation of the contaminant may be anywhere from essentially fully saturated to less than residual saturation, and the objective is to reduce the contaminant concentration to very low levels. The techniques of steam injection, electrical energy application, and hot water injection have been the subject of extensive research and development, and it has been established that these techniques are effective for the remediation of organic contaminants when they are appropriately applied (Fulton et al., 1991; Davis and Lien, 1993; U.S. EPA, 1995a; Newmark and Aines, 1995).

Injection of hot air has been tried in the laboratory and found to enhance the removal of contaminants from one-dimensional soil columns (Lingineni and Dhir, 1992; Shah et al., 1995). However, the use of hot air in the field is limited by the very low heat capacity of air (approximately 1 kJ/kg °C) (Ramey, 1967). Steam, with a heat capacity that is approximately four times that of air (approximately 4 kJ/kg °C), and heat of evaporation of more than 2000 kJ/kg, has been used successfully to heat soils, aquifers and reservoirs to enhance the recovery of contaminants and oils. However, the injection of steam will always leave behind a residual water saturation (Stewart and Udell, 1988), and contaminants that have a significant solubility in water may remain at high concentrations in this residual water or may even appear to increase in concentration (Udell and Stewart, 1989; U.S. EPA, 1991). For these situations, recovery of the contaminants may require that the soil be dried, and hot air injection may be applicable (Farrington, 1996).

Steam, hot air and hot water injection rely on contact between the injected fluid and the contaminant for the transfer of heat to and recovery of the contaminant. Steam injection will displace mobile contaminants in front of the steam as well as vaporize volatile residual contaminants, and therefore can recover volatile contaminants in both the liquid or vapor phase. Hot air injection has been used to recover contaminants only in the vapor phase. Hot water injection generally recovers contaminants only in the liquid phase. Thus, steam injection is applicable to volatile and semivolatile organic compounds that are immiscible with water, hot air is applicable to volatile and semivolatile organics that are water soluble, and hot water injection is applicable for the oils that have low volatility and very low solubility in water. The main mechanism for enhanced recovery using hot water is generally a reduction in the viscosity. Changes in relative permeability and reductions in residual saturation are likely to also aid in the recovery of nonvolatile oils. Hot water injection is most likely effective only when the nonaqueous phase is present in quantities greater than the residual saturation, as the main recovery mechanism is the physical displacement of the nonaqueous phase. Hot water injection may be most effective for light oils that are floating on top of the water table, as the lower-density hot water has a tendency to rise if injected below the water table. For oils that are more dense than water at ambient temperatures but less dense than water at the displacement temperature, heating of the subsurface by hot water injection may help to float these oils, which may aid in their recovery (Johnson and Guffey, 1990). Steam injection has a definite advantage over hot water injection when the contaminants have a low boiling point and are present as an immiscible phase, and thus can be steam distilled at the temperatures achieved by steam injection (Willman et al., 1961). Field trials have shown that steam injection can be carried out above or below the water table (Udell and Stewart, 1989; U.S. EPA, 1991; Aines et al., 1992).

There are limitations on the pressures that can be used for steam and hot water displacement processes, and this limits the viscosity of the fluid that can be displaced from a media with a certain permeability. However, volatilization processes using steam or hot air may still be possible in low permeability media (Farrington, 1996), and for highly viscous oil, it may be possible to heat the oil and lower its viscosity sufficiently to recover at least a portion of the oil by either a displacement process or gravity drainage (Hall and Bowman, 1973; Vogel, 1992).

Electrical energy has been applied to the soil in the low frequency range used for electrical power (called electromagnetic (EM), alternating current (AC), or resistivity heating) as well as in the radio frequency (RF) range. When EM heating is used, the water in the pore spaces of the soil absorbs essentially all the applied energy, so the evaporation of water limits the transport of energy in the soil and, therefore, limits the heating process. Thus, for the low frequency methods, the boiling point of water is the highest temperature that can be achieved. For semivolatile organic contaminants, the vapor pressure at 100°C may not be adequate to effectively recover the contaminants. For this reason, researchers have also developed the use of RF energy for soil heating. RF energy can be absorbed by the soil itself, and thus is not limited by a lack of water in the pore space. Using RF energy, the upper temperature limit of the technique is 300°C to 400°C (Dev, 1993; Sresty, 1994). For electrical heating, the electrical properties of the soil and the presence of water are important in determining the efficiency of the heating process (Dev et al., 1989; Marley et al., 1993). The electrical heating techniques are recommended for the removal of organic contaminants which exhibit a vapor pressure of at least 10 mm Hg in the treatment temperature range (Sresty, 1994). There is some evidence that high molecular weight organics, such as organopesticides, can be broken down to simpler organics such as acetone, benzene and toluene, at the temperatures and conditions that can be achieved by RF heating (U.S. EPA, 1995b&c; Swanstrom and Besmer, 1995). Electrical heating has been proven effective in sandy media (Dev, 1986), and also has a greater potential than steam or hot water injection to be effective in less permeable media such as clays. The higher water content generally found in the clay will aid in directing the electromagnetic energy to the clay and allow a faster heating rate and higher temperatures to be achieved. RF heating, however, is limited to the unsaturated zone. For contaminants trapped below the water table, dewatering would have to be done prior to electrical heating (U.S. EPA, 1995b).

Because steam injection (at least in its initial stages) and hot water injection are displacement processes, they can also recover nonvolatile contaminants dissolved in the aqueous phase, such as salts (Vaughan et al., 1993), but heat does not necessarily enhance the recovery of this type of inorganic contaminant. Metals, with the exception of mercury, cannot be recovered from soils by thermal means. Mercury has a significant vapor pressure at ambient temperatures, and it increases as the temperature increases. Adsorption onto soils and other materials can reduce its partial vapor pressure significantly, and it was found that drying soil samples to 100°C did not recover measurable amounts of mercury. At temperatures of 200°C and greater, significant amounts of mercury can be recovered from soils, reducing the residual remaining in the soil to as little as 1 part per million at 400°C (Dewing and Schluter, 1994).

Each of these thermal methods is generally applicable only to certain types of contaminated sites, and it is important that the appropriate heat-based remediation technique is chosen for a given site. The choice of technique must be based on both the characteristics of the subsurface and of the contaminants to be recovered. Steam or hot air injection or the electrical heating techniques are generally applicable for the types of chemicals that are listed in Table 1, while hot water injection is generally applicable for the nonvolatile oils listed in Table 3. The permeability of the media, the amount and type of heterogeneity, the amount of adsorption, and the solubility of the contaminant must all be considered when choosing between the technologies. Electrical heating may be favored in low permeable media and when there is significant heterogeneity. For highly soluble contaminants, drying the soil may be necessary and, thus, hot air or RF heating may be more applicable. Because desorption can be a slow process, higher temperatures and/or longer remediation times may be necessary when adsorption is significant.

Figure 1 can be used as a quick guide to determine which of the techniques would likely be applicable for a given situation; in some cases, more than one technique may be applicable. The principle that has been applied in developing this figure is to recommend the least severe technique, in terms of temperature and pressure requirements, that is likely to be able to recover the contaminants. For example, although hot water and steam injection may both be able to recover a nonvolatile, viscous oil, hot water injection is recommended because it will generally recover the same amount of this type of oil (Willman et al., 1961) at a lower temperature. Equipment and facilities for generating and handling hot water are relatively simple and inexpensive (Harmsen, 1971), but the generation and transport of steam involves more complex and expensive systems. Higher operating temperatures also mean greater safety risks (Herbeck et al., 1976). The Issue Paper specific to that technique can then be consulted for further information.

Comparison to Other In-situ Techniques

The one significant advantage of heat-based remediation techniques over other in-situ remediation techniques is that these methods do not require that chemicals of any sort be injected into the subsurface as part of the remediation effort. This is a very significant advantage over the surfactant and cosolvent techniques because surfactants and cosolvents may themselves have toxic properties, and it may not be possible to recover all of the injected chemicals. Also, when surfactants or cosolvents are used, the technique may be limited by a lack of contact between the injected chemical and the contaminants, which can be caused by low permeability layers within the media or by reductions in relative permeability to one phase because of the presence in the pores of another phase (Peters et al., 1991). With the in-situ heating techniques discussed in these Issue Papers, heating of the entire area to be treated has generally been accomplished (Aines et al., 1992; Gauglitz et al., 1994).

These heating techniques can be used with a technique such as vacuum extraction, with benefits that may be significantly greater than for either process used separately (Udell and Stewart, 1989; Jarosch et al., 1994). Also, these processes are applicable in heavily contaminated soils, the “hot spots” of contaminated sites, which generally are very important to clean up in order to stop the spread of the contamination, and where biological treatment may not be effective (Johnson and Guffey, 1990; Aines et al., 1992).

These thermal techniques initially may be limited by subsurface heterogeneities, which affects all other in-situ remediation techniques. When low permeability clay lenses are present in an aquifer, the injected fluids often bypass these low permeability areas and, therefore, do not contact the contaminants contained within them. With time, however, the heat will be conducted into the lower permeability areas. Also, the Dynamic Underground Stripping Process, developed by the Lawrence Livermore National Laboratory, circumvented this problem for the case where relatively thick clay layers are interbeded with sandy layers by combining both steam injection and electromagnetic heating with vacuum extraction (Newmark and Aines, 1995; Yow et al., 1995).

Research has shown that complete desorption of chemicals from clay soils, or soils containing a significant amount of natural organic material, may require extreme temperature conditions (Lighty et al., 1988; Tognotti et al., 1991), which may not be achievable in-situ. Thus, in many cases, a secondary or polishing step may be required to achieve very low contaminant concentrations (Yow et al., 1995). Hot water injection or shallow steam injection applications where low temperature and pressures are used may leave the subsurface system amenable to bioremediation. In fact, raising the temperature above ambient temperatures may, in many instances, enhance naturally occurring biodegradation of contaminants (Isherwood et al., 1992). However, if steam is injected into the deeper subsurface at high temperatures and pressures, or if the soil is heated to high temperatures using RF heating, the soil will likely require cooling

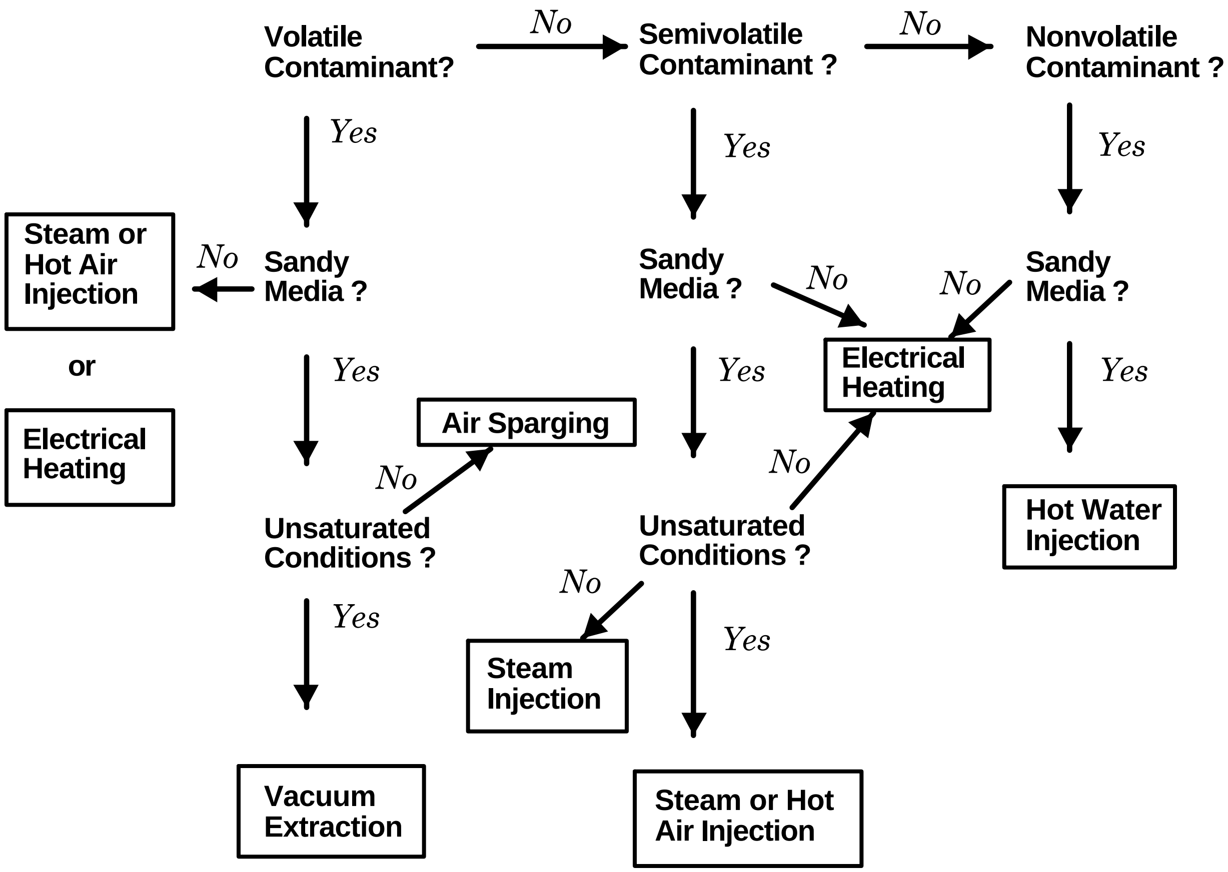

Figure 1. Flow Chart to indicate which of the thermal techniques may be applicable for a particular site.

before reestablishment of the microbial population can take place (U.S. EPA, 1991).

Notice

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References

Abdul, A. S., T. L. Gibson, and D. N. Rai, Selection of surfactants for the removal of petroleum products from shallow sandy aquifers, Ground Water, 28(6):920-926, 1990.

Aines, R., R. Newmark, W. McConachie, K. Udell, D. Rice, A. Ramirez, W. Siegel, M. Buettner, W. Daily, P. Krauter, E. Folsom, A. Boegel, D. Bishop, Dynamic underground stripping project, UCRL-JC-109902, Waste Management Symposium, Tucson, Arizona, March 1-5, 1992.

Anderson, D. C., K. W. Brown, and J. C. Thomas, Conductivity of compacted clay soils to water and organic liquids, Waste Manag. Res., 3:339-349, 1985.

Arthurs, P., W. H. Stiver, and R. G. Zytner, Passive volatilization of gasoline from soil, J. Soil Contamin., 4(2):123-135, 1995.

Atkins, P. W., *Physical Chemistry*, Third Edition, W. H. Freeman, New York, 1986.

Basile, A. J., and G. Smith, Innovative treatment combination rings bell for AT&T, Hazmat World, 52-53, March 1994.

Baehr, A. L., Selective transport of hydrocarbons in the unsaturated zone due to aqueous and vapor partitioning, Water Resour. Res., 23(10):1926-1938, 1987.

Bear, J., and A. Gilman, Migration of salts in the unsaturated zone caused by heating, Trans. Porous Media, 19(2):139-156, 1995.

Brown, K. W., and J. C. Thomas, A mechanism by which organic liquids increase the hydraulic conductivity of compacted clay materials, Soil Sci. Soc. Am. J., 51:1451-1459, 1987.

Cancela, G. D., E. R. Taboada, and F. Sanchez-Rasero, Carbendazim adsorption on montmorillonite, peat, and soils, J. Soil Sci., 43:99-111, 1992.

Davidson, L. B., The effect of temperature on the permeability ratio of different fluid pairs in two-phase systems, J. Petrol. Tech., 1037-1046, August 1969.

Davis, E. L., Effect of temperature and pore size on the hydraulic properties and flow of a hydrocarbon oil in the subsurface, J. Contamin. Hydrol., 16:55-86, 1994.

Davis, E. L., Steam injection for soil and aquifer remediation, Ground Water Issue Paper, in preparation, 1997a.

Davis, E. L., Electrical heating of the subsurface for soil and aquifer remediation, Ground Water Issue Paper, in preparation, 1997b.

Davis, E. L., Hot water enhanced remediation of soils and aquifers, Ground Water Issue Paper, in preparation, 1997c.

Davis, E. L., and B. K. Lien, Laboratory study on the use of hot water to recover light oily wastes from sands, EPA/600/R-93/021, R. S. Kerr Environmental Research Laboratory, Ada, Oklahoma, February 1993.

Dev, H., Radio frequency enhanced in-situ decontamination of soils contaminated with halogenated hydrocarbons, EPA/600/9-86/022, Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Wastes, Proceedings of Twelfth Annual Research Symposium at Cincinnati, Ohio, April 21-23, 1986.

Dev, H., Management Plan: Demonstration testing and evaluation of in situ soil heating, DOE Contract Number DE-AC05-930R22160, IITRI Project C06787, 1993.

Dev, H., J. Bridges, G. Sresty, J. Enk, N. Mshaiel, and M. Love, Radio frequency enhanced decontamination of soils contaminated with halogenated hydrocarbons, U.S. EPA, Cincinnati, Ohio, EPA/600/2-89/008, February 1989.

Dewing, H. H., and R. B. Schluter, Characterization and recovery of mercury from electrical manufacturing wastes by thermal desorption, U. S. Department of the Interior, Report of Investigations 9513, 1994.

Edmondson, T. A., Effect of temperature on waterflooding, J. Can. Petrol. Technol., 236-242, October 1965.

Esposito, P., J. Hessling, B. B. Locke, M. Taylor, M. Szabo, R. Thumau, C. Rogers, R. Traver, and E. Barth, Results of treatment evaluations of a contaminated synthetic soil, J. Air Pollut. Control Assoc., 39:294-304, 1989.

Fares, A., B. Kindt, R. Lapuma, and G. P. Perram, Desorption kinetics of trichloroethylene from powdered soils, Environ. Sci. Technol., 29(6):1564-1568, 1995.

Farrington, P., Groundwater Technologies Inc., Norwood, Mass., Personal Communication, July 22, 1996.

Feenstra, S., D. M. Mackay, and J. A. Cherry, A method for assessing residual NAPL based on organic chemical concentrations in soil samples, Ground Water Monit. Rev., 128-136, Spring, 1991.

Fernandez, F., and R. M. Quigley, Viscosity and dielectric constant controls on the hydraulic conductivity of clayey soils permeated with water-soluble organics, Can. Geotech. J., 25:582-589, 1988.

Fulton, D. E., G. J. Reuter, and T. E. Buscheck, Hot water enhanced recovery of phase separated lubricating oil, Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration Conference and Exposition, 143-156, November 20-22, 1991.

Gauglitz, P. A., T. M. Bergsman, S. M. Caley, W. O. Heath, M. C. Miller, R. W. Moss, J. S. Roberts, R. Schalla, M. H. Schlender, T. R. Jarosch, C. A. Eddy-Dilek, and B. B. Looney, Six-phase soil heating for enhanced removal of contaminants: Volatile organic compounds in non-arid soil integrated demonstration, Savannah River Site, Prepared for the U.S. Office of Technology Development, U.S. Department of Energy, Contract DE-AC-06-76RLO 1830, October 1994.

Gerencher, E. H., D. E. Konasewich, and K. A. Morin, Hydrogeological investigation of coal tar contamination at a former coal gasification facility, Subsurface contamination by immiscible fluids, Balkema Rotterdam, 1992.

Hall, A. L., and R. W. Bowman, Operation and performance of the Slocum thermal recovery project, J. Petrol. Tech., 402-408, April 1973.

Harmsen, G. J., Oil recovery by hot-water and steam injection, Eighth World Petroleum Congress, 3:243-251, 1971.

Hatzinger, P. B., and M. Alexander, Effect of aging chemicals in soil on their biodegradability and extractability, Environ. Sci. Technol., 29(2):537-545, 1995.

Herbeck, E. F., R. C. Heintz, and J. R. Hastings, Fundamentals of tertiary oil recovery Part 8 - Thermal recovery by hot fluid injection, Petrol. Eng., 24-34, August 1976.

Heron, G., T. H. Christensen, and C. G. Enfield, Temperature effects on the distribution of organics in soils and groundwater and implications for thermally enhanced in-situ remediation, submitted for publication in Environ. Sci. Technol., December 1996.

Ho, C. K., and K. S. Udell, An experimental investigation of air venting of volatile liquid hydrocarbon mixtures from homogeneous and heterogeneous porous media, J. Contamin. Hydrol., 11:291-316, 1992.

Horvath, A. L., *Halogenated Hydrocarbons*, Marcel Dekker, New York, 1982.

Huling, S. G., Facilitated transport, Superfund Ground Water Issue Paper, EPA/540/4-89/003, August 1989.

Hunt, J. R., N. Sitar, and K. S. Udell, Nonaqueous phase liquid transport and cleanup, 2. Experimental studies, Water Resour. Res., 24(8):1259-1267, 1988.

Iben, I. E., W. A. Edelstein, R. B. Sheldon, A. P. Shapiro, E. E. Uzgiris, C. R. Scatena, S. R. Blaha, W. B. Silverstein, G. R. Brown, G. L. Stegemeier, and H. J. Vinegar, Thermal blanket for in-situ remediation of surficial contamination: A pilot study, Environ. Sci. Technol., 30(11):3144-3154, 1996.

Isherwood, W. F., J. Ziagos, E. Nichols, P. Krauter, and D. Rice, Jr, Enhancing aquifer cleanup with reinjection, National Ground Water Association Meeting, Houston, Texas, November 4-6, 1992.

Jarosch, T. R., R. J. Beleski, and D. Faust, Final Report: In Situ Radio Frequency Heating Demonstration, WSRC-TR-93-673, U. S. Department of Energy Contract No. DE-AC09-89SR18035, 1994.

Jin, Y., and W. A. Jury, Characterizing the dependence of gas diffusion coefficient on soil properties, Soil Sci. Soc. Am. J., 60:66-71, 1996.

Johnson, Jr., L. A., Development of the CROW^{TM} Process, Topical Report, DOE/MC/11076-3847, May 1994.

Johnson, Jr., L. A., and F. D. Guffey, Contained Recovery of Oily Wastes (CROW), Work performed under Assistance Agreement CR-815333, U. S. EPA, Risk Reduction Engineering Laboratory, Cincinnati, Ohio, August 1990.

Johnson, P. C., C. C. Stanley, M. W. Kemblowski, D. L. Byers, and J. D. Colthart, A practical approach to the design, operation, and monitoring of in situ soil-venting systems, Ground Water Monit. Rev., 159-178, Spring, 1990.

Jury, W. A., D. Russo, G. Streile, and H. El Abd, Evaluation of volatilization by organic chemicals residing below the soil surface, Water Resour. Res., 26(1):13-20, 1990.

Karickhoff, S. W., D. S. Brown, and T. A. Scott, Sorption of hydrophobic pollutants on natural sediments, Water Res., 13:241-248, 1979.

Kemper, W. D., Movement of water as effected by free energy and pressure gradients: I. Application of classic equations for viscous and diffusive movements to the liquid phase in finely porous media, Soil Sci. Soc. Am. Proc., 25(4):255-260, 1961a.

Kemper, W. D., Movement of water as affected by free energy and pressure gradients: II. Experimental analysis of porous systems in which free energy and pressure gradients act in opposite directions, Soil Sci. Soc. Am. Proc., 25(4):260-265, 1961b.

Keyes, B. R., and G. D. Silcox, Fundamental study of the thermal desorption of toluene from montmorillonite clay particles, Environ. Sci. Technol., 28:840-849, 1994.

Lide, D. R., ed., *CRC Handbook of Chemistry and Physics*, 74th Edition, CRC Press, Boca Raton, 1993.

Lighty, J. S., D. W. Persing, V. A. Cundy, and D. G. Linz, Characterization of thermal desorption phenomena for the cleanup of contaminated soil, Nucl. Chem. Waste Manage., 8:225-237, 1988.

Lighty, J. S., G. D. Silcox, D. W. Persing, V. A. Cundy, and D. G. Linz, Fundamentals for the thermal remediation of contaminated soils. Particle and bed desorption models, Environ. Sci. Technol., 24(5):750-757, 1990.

Lingineni, S., and V. K. Dhir, An experimental and theoretical study of remediation of multicomponent organic contaminants in the unsaturated soil by venting, Fundamentals of Heat Transfer in Porous Media, HTD-VOl. 193, ASME, 99-107, 1992.

Lyman, W. J., P. J. Reidy, and B. Levy, Assessing UST corrective action technology, A scientific evaluation of the mobility and degradability of organic contaminants in the subsurface environments, U.S. EPA Report, EPA/600/2-91/053, September 1991.

Mackay, D. M., and J. A Cherry, Groundwater contamination: Pump-and-Treat remediation, Environ. Sci. Technol., 23(6):630-636, 1989.

Mackay, D. M., and W. J. Shiu, Critical review of Henry's law constants for chemicals of environmental interest, J. Phys. Chem. Ref. Data, 10(4):1175-1199, 1981.

Marley, M. C., R. S. Kasevich, and S. L. Price, Enhancing site remediation through radio frequency heating, AIChE Annual Meeting, St. Louis, Missouri, November 7-12, 1993.

Miller, M. M., S. P. Wasik, G.-L. Huang, W.-Y. Shiu, and D. Mackay, Relationship between octanol-water partition coefficient and aqueous solubility, Environ. Sci. Technol., 19(6):522-529, 1985.

Millington, R. J., Gas diffusion in porous media, Science, 130:100-102, 1959.

Mungan, N., Role of wettability and interfacial tension in water flooding, Soc. Petrol. Eng. J., 115-123, June 1964.

Mungan, N., Interfacial effects in immiscible liquid-liquid displacement in porous media, Soc. Petrol. Eng. J., 217-253, 1966.

Newell, C., S. D. Acree, R. R. Ross and S. G. Huling, Light nonaqueous phase liquids, Ground Water Issue Paper, EPA/540/S-95/500, July 1995.

Newmark, R. L., and R. D. Aines, Summary of the LLNL gasoline spill demonstration - Dynamic Underground Stripping Project, Lawrence Livermore National Laboratory, Berkeley Environmental Restoration Center, UCRL-ID-120416, April 3, 1995.

Ong, S. K., T. B. Culver, L. W. Lion, and C. A. Shoemaker, Effects of soil moisture and physical-chemical properties of organic pollutants on vapor-phase transport in the vadose zone, J. Contamin. Hydrol., 11:273-290, 1992.

Perry, R. H., and C. H. Chilton, Chemical Engineers' Handbook, 5th ed., McGraw-Hill, New York, 1973.

Peters, R. W., C. D. Montemango, L. Shem, and B. G. Lewis, Surfactant Flooding of Diesel-Fuel-Contaminated Soil, ANL\CP—73805, 1991.

Piatt, J. J., D. A. Backhus, P. D. Capel, and S. J. Eisenreich, Temperature-dependent sorption of naphthalene, phenanthrene, and pyrene to low organic carbon aquifer sediments, Environ. Sci. Technol., 30(3):751-760, 1996.

Porter, L. K., W. D. Kemper, R. D. Jackson, and B. A. Stewart, Chloride diffusion in soils as influenced by moisture content, Soil Sci. Soc. Am. Proc., 24:460-463, 1960.

Poston, S. W., S. Ysrael, A. K. M. S. Hossain, E. F. Montgomery, and H. J. Ramey, Jr., The effect of temperature on irreducible water saturation and relative permeability of unconsolidated sands, Trans. Soc. Petrol. Eng., 249:171-180, 1970.

Ramey Jr., H. J., A current review of oil recovery by steam injection, Seventh World Petroleum Congress Proceedings, 3:471-476, 1967.

Roberts, P. V., J. Schreiner, and G. D. Hopkins, Field study of organic water quality changes during groundwater recharge in the Palo Alto Baylands, Water Res., 16:1025-1035, 1982.

Ryan, J. A., R. M. Bell, J. M. Davidson, and G. A. O'Connor, Plant uptake of non-ionic organic chemicals from soils, Chemosphere, 17(12):2299-2323, 1988.

Sanders, P. F., Calculation of soil cleanup criteria for volatile organic compounds as controlled by the soil-to-groundwater pathway: Comparison of four unsaturated soil zone leaching models, J. Soil Contamin., 4(1):1-24, 1995.

Schwarzenbach, R. P., and J. Westall, Transport of nonpolar organic compounds from surface waters to groundwater. Laboratory sorption studies, Environ. Sci. Technol., 15:1360-1367, 1981.

Shah, F. H., H. A. Hadim, and G. P. Korfiatis, Laboratory studies of air stripping of VOC-contaminated soils, J. Soil Contamin., 4(1):93-109, 1995.

Sresty, G. C., Treatability study work plan, Demonstration testing and evaluation of in situ soil heating, U. S. DOE Contract DE-AC05-930R22160, December 30, 1994.

Stephenson, R. M., Mutual solubilities: Water-ketones, water-ethers, and water-gasoline-alcohols, J. Chem. Eng. Data, 37:80-95, 1992.

Stewart, L. D., and K. S. Udell, Mechanism of residual oil displacement by steam injection, SPE Reservoir Engineering, 1233-1242, November 1988.

Swanstrom, C. P., and M. Besmer, Bench- and pilot-scale thermal desorption treatability studies on pesticide-contaminated soils from Rocky Mountain Arsenal, Presented at Seventh Annual Gulf Coast Environmental Conference, Houston, Texas, March 9, 1995.

Thoma, G. J., G. Hildebrandt, K. T. Valsaraj, L. J. Thibodeaux, and C. Springer, Transport of chemical vapors through soil: A landfill cover simulation experiment, J. Hazard. Mat., 30:333-342, 1992.

Tognotti, L., M. Flytzani-Stephanopoulos, A. F. Sarofim, H. Kopsinis, and M. Stoukides, Study of adsorption-desorption of contaminants on single soil particles using the electrodynamic thermogravimetric analyzer, Environ. Sci. Technol., 25(1):104-109, 1991.

Treybal, R. E., *Mass-Transfer Operations*, 3rd. ed., McGraw-Hill, New York, 1980.

Tyn, M. T., and W. F. Calus, Temperature and concentration dependence of mutual diffusion coefficients of some binary liquid systems, J. Chem. Eng. Data, 20(3):310-316, 1975.

Udell, K. S., and L. D. Stewart, Jr., Field study of in situ steam injection and vacuum extraction for recovery of volatile organic solvents, Dept. of Mechanical Engineering, University of California, June 1989.

U.S. Environmental Protection Agency, Toxic Treatments, In situ steam/hot-air stripping technology, Applications Analysis Report, EPA/540/A5-90/008, Risk Reduction Engineering Laboratory, Cincinnati, Ohio, March 1991.

U.S. Environmental Protection Agency, SITE Technology Capsule, KAI radio frequency heating technology, EPA 540/R-94/528a, Cincinnati, Ohio, 1995a.

U.S. Environmental Protection Agency, IITRI radio frequency heating technology, Innovative Technology Evaluation Report, EPA/540/R-94/527, June 1995b.

U.S. Environmental Protection Agency, Low temperature thermal aeration (LTTA) process Canonie Environmental Services, Inc., Applications Analysis Report, EPA/540/AR-93/504, July 1995c.

U.S. Environmental Protection Agency, In situ steam enhanced recovery process, Hughes Environmental Systems, Inc., Innovative Technology Evaluation Report, EPA/540/R-94/510, July 1995d.

Uzgiris, E. E., W. A. Edelstein, H. R. Philipp, and I. E. T. Iben, Complex thermal desorption of PCBs from soil, Chemosphere, 30(2):377-387,1995.

Valsaraj, K. T., On the physico-chemical aspects of partitioning of non-polar hydrophobic organics at the air-water interface, Chemosphere, 17(5):875-887, 1988.

Vaughan P. J., K. S. Udell, and M. J. Wilt, The effects of steam injection on the electrical conductivity of an unconsolidated sand saturated with a salt solution, J. Geophys. Res., 98(B1):509-518, 1993.

Verschueren, K., *Handbook of Environmental Data on Organic Chemicals,* 2nd ed., Van Nostrand Reinhold, New York, 1983.

Villaume, J. F., P. C. Lowe, and D. F. Unites, Recovery of coal gasification wastes: An innovative approach, Proceedings of the Third National Symposium on Aquifer Restoration and Ground-Water Monitoring, OCLC #9983271, 434-445, 1983.

Vogel, J. V., Gravity drainage vital factor for understanding steam floods, Oil Gas J., 90(48):42-47, 1992.

Weber, W. J., Jr., T. C. Voice, M. Pirbazari, G. E. Hunt, and D. M. Ulanoff, Sorption of hydrophobic compounds by sediments, soils and suspended solids - II. Sorbent evaluation studies, Water Res., 17(10):1443-1452, 1983.

Weber, W. J., Jr., P. M. McGinley, and L. E. Katz, Sorption phenomena in subsurface systems: Concepts, models and effects on contaminant fate and transport, Water Res., 25:499-528, 1991.

Willman, B. T., V. Valleroy, G. Runberg, A. Cornelius, L. Powers, Laboratory studies of oil recovery by steam injection, Petrol. Trans., AIME, July 1961.

Wilson, D. J., A. N. Clarke, and J. H. Clarke, Soil clean up by in-situ aeration. I. Mathematical modeling, Separation Sci. Technol., 23(10&11):991-1037, 1988.

Yalkowsky, S. H., and S. Banerjee, *Aqueous Solubility Methods of Estimation for Organic Compounds*, Marcel Dekker, New York, 1992.

Yow, J. L., R. D. Aines, and R. L. Newmark, Demolishing NAPLs, Civil Eng., 65(8):57-59, August 1995.