
CHAPTER 14

CLEANUP OF CHEMICAL SPILLS USING AIR SPARGING

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4.1 INTRODUCTION

Air sparging is an in situ technique to remediate sites that have been contaminated with petroleum products and chlorinated solvents as a result of accidental spillage and leaking underground storage tanks. This technique was developed in the mid-1980s in Germany for the treatment of saturated soils and groundwater contaminated with volatile organic compounds (VOCs). This chapter provides an overview of the air sparging technology, including (1) air sparging technology, including applicability and advantages and disadvantages; (2) fundamental processes involved during air sparging process; (3) air sparging system design, operation, and monitoring; (4) mathematical models to describe air sparging process; (5) performance of air sparging systems in the field; (6) use of air sparging with certain modifications and/or complementing technologies; and (7) other issues, such as cost and regulatory issues.

4.2 TECHNOLOGY DESCRIPTION

4.2.1 How It Works

In a typical field system, as depicted in Fig. 14.1, compressed air is delivered to a manifold system, which in turn delivers the air to an array of air injection wells. The wells inject the air into the subsurface below the lowest known point of contamination. Due to buoyancy, the air will begin to rise toward the surface and, through a variety of mechanisms, will either remove or assist in degradation of the contamination. As the contaminant-laden air rises towards the surface, it will eventually reach the vadose zone. At this point, either the contaminated air may be collected with a soil vapor extraction (SVE) system or, if vadose zone

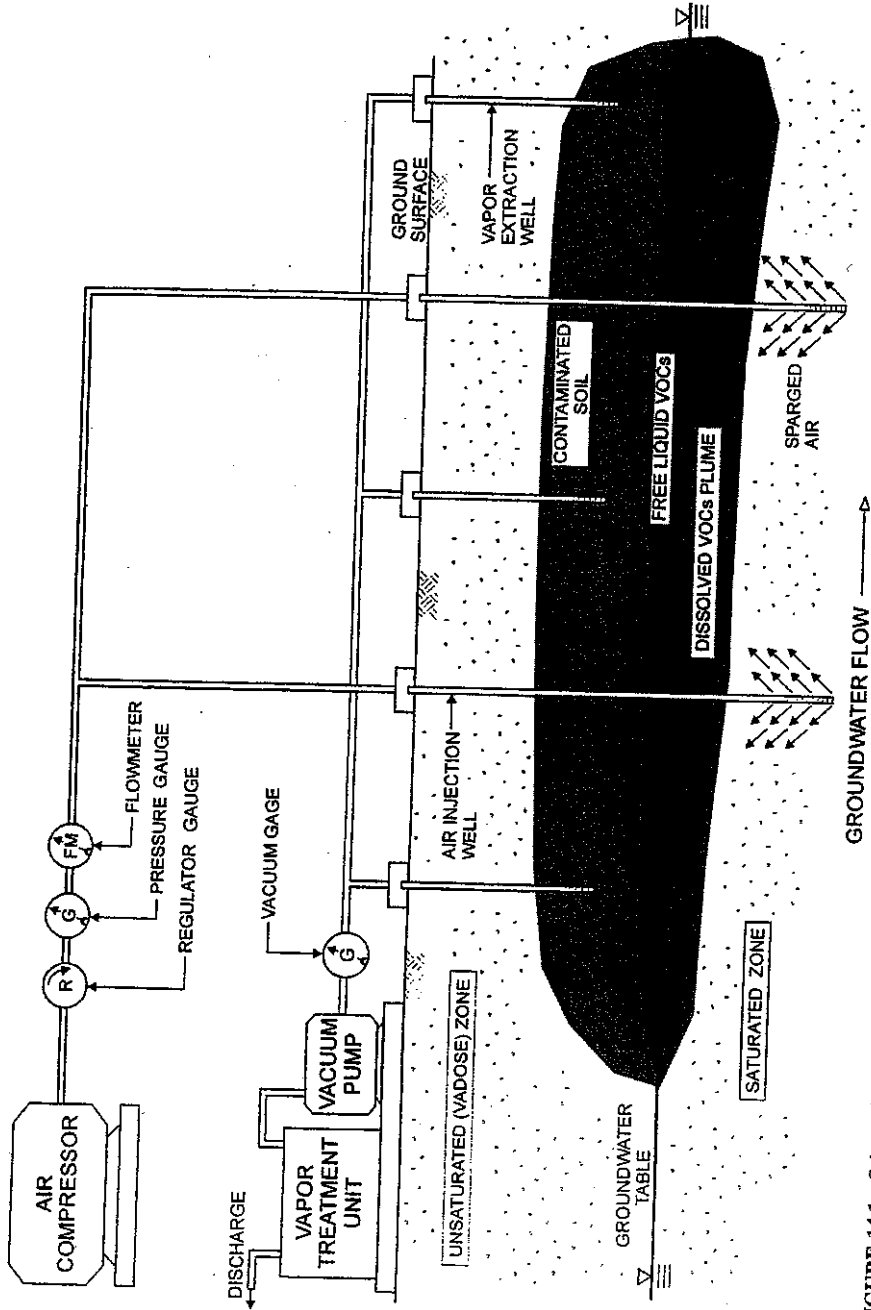


FIGURE 14.1 Schematic of air sparging field system.

conditions permit, the native subsurface microbial population may degrade the vapors into non-toxic products.

14.2.2 Applicability

Geology/Hydrogeology. Prior to the implementation of an air sparging system, a detailed geologic and hydrogeologic characterization of the contaminated site must be performed. Because the patterns of air flow resulting from air injection are controlled by the permeability of a soil, the stratigraphy of the soil profile must be assessed. The permeability of soil within each layer must be assessed to ensure that effective air flow will result; soil permeability should be at least 10^{-3} cm/s for adequate air flow to occur (Bausmith et al., 1996; Loden, 1992). Because air flow may be impacted by the presence of adjacent layers of differing permeability (Ji et al., 1993), the thickness and properties of each layer need to be determined. Additionally, lenses or inclusions of soil with different properties than the surrounding soil may impact air flow and overall remedial performance and must be delineated.

The hydrogeologic conditions of the site are also an important consideration. When applying air sparging, the depth to the water table should be at least 1.5 m (Bausmith et al., 1996), but the most successful applications are made when the depth to the water table is at least 10 ft (Miller, 1996). If depth to groundwater is less than 10 ft, the surface may be capped to prevent uncontrolled vapor migration through the surface (Miller, 1996). The properties of the aquifer material need to be assessed to determine groundwater circulation and other transport phenomena that may occur during air injection, including hydraulic conductivity and groundwater gradients that may induce groundwater flow. Additionally, the groundwater flow velocity and direction must be assessed to ensure that the air sparging system is designed to prevent down gradient contaminant migration away from the treatment zone (Reddy and Adams, 2000).

Contaminants. Air sparging is applicable to a class of contaminants known as volatile organic compounds (VOCs). Common VOCs that are the target of air sparging include petroleum products, including gasoline and its BTEX (benzene, toluene, ethylbenzene, and the xylenes) constituents, and chlorinated solvents, including trichloroethylene (TCE) and tetrachloroethylene (PCE). A compound is capable of being remediated through air sparging if it is deemed strippable; that is, if it has a Henry's constant greater than 10^{-5} atm-m³/mol and vapor pressure greater than 1 mm Hg (Bausmith et al., 1996). Bass and Brown (1997) have reported that, after a review of case studies, it appears that air sparging is more successful at chlorinated solvent sites than at petroleum sites.

Once contamination is released into the soil, it may exist in a variety of phases. It can exist as a nonaqueous or free (pure) phase liquid, dissolved in the groundwater, in vapor phase within the soil gas, bound to the organic matter of the soil, trapped within the mineral phase of the soil matrix, or within the microbial phase (Yang et al., 1995; Davis, 1997). Before it comes into contact with the water table, it will travel or reside in the vadose zone in the form of a nonaqueous phase liquid (NAPL). NAPLs fall into two categories: light (LNAPLs) and dense (DNAPLs). The distinction is simple: LNAPLs are less dense than water while DNAPLs are more dense than water. LNAPLs will spread laterally on top of the water table, while DNAPLs will continue migrating downward through the groundwater (Panday et al., 1994). During their migration through the vadose zone, NAPLs may become trapped in soil pores in the form of blobs. This transport and deposition will continue until all the NAPL becomes trapped or a low-permeability stratum is reached, preventing further migration (Powers et al., 1991). Once into the groundwater, LNAPL will be transported by water table fluctuation and ambient groundwater flow, while DNAPL will migrate to the bottom of the aquifer, where it is able to mound and spread by the resulting gradients (Panday et al., 1994; Hunt et al., 1988a). Air sparging is shown to be applicable to remove both

LNAPLs and DNAPLs existing as nonaqueous or dissolved phase (Adams and Reddy, 1999, 2000).

Advantages and Disadvantages. There are many advantages of using air sparging, including:

1. As an in situ process, it can be implemented with minimal disturbance to site operations.
2. It has been proven to be efficient—generally treatment time is less than one to three years under optimal conditions.
3. It is simple—readily available equipment can be used and installation is easy.
4. It is cost-effective—treatment cost ranges from \$20–50/ton of saturated soil, which is significantly less than other treatment technologies.
5. No removal, treatment, storage or discharge of groundwater is required.
6. It is flexible enough to address contaminants in nonaqueous and dissolved phase.
7. It can be complemented with other technologies, such as soil vapor extraction and bioremediation to increase remedial efficiency.

Although the advantages of air sparging are numerous, the following disadvantages must be kept in mind:

1. The spreading of the contaminants to the clean areas or zones due to excessive pressurization or the presence of low-permeable formations or covers above the contaminated areas
2. The uncontrolled migration of harmful vapor to undesirable receptors (e.g., residential basements, subways, utility tunnels)
3. Lack of rational design accounting for the fundamental contaminant removal processes
4. Difficulty in using conventional monitoring technologies due to transient effects of sparged air on pressures and water levels at monitoring locations

14.3 FUNDAMENTAL PROCESSES/PHENOMENA

When injected into the subsurface, air will enter into pores with lower capillary pressure (larger pore sizes) and produce a fingering pattern of preferential pathways due to low viscosity air invading the higher viscosity groundwater (Ahlfeld et al., 1994a). The mode of air migration and the zone of influence are the primary concerns during air sparging. Air sparging owes its effectiveness to a variety of mechanisms that occur during this subsurface air movement. The mechanisms can be classified into three categories: mass transfer mechanisms, mass transformation mechanisms, and mass transport mechanisms.

Mass transfer mechanisms include volatilization, dissolution, and adsorption/desorption. Biodegradation is the mass transformation that occurs during air sparging. The three mass transport mechanisms consist of advection, dispersion, and diffusion. Air sparging is a dynamic process; during different stages of a remedial program, different mechanisms will control remedial rates and efficiency. The contributions of each of the mechanisms will also vary from site to site and will ultimately determine the effectiveness of an air sparging remedial program.

The migration of air in the subsurface as well as the different mass transfer, mass transformation, and mass transport mechanisms responsible for the contaminant removal during air sparging are described in this section.

14.3.1 Air Migration

Air sparging is most effective in coarser soils because better air saturation and density will result (Baker and Benson, 1996). Unfortunately, permeability cannot be too high or else the injected air will move upwards to the surface without spreading laterally and thus will impact only a small volume of soil. Additionally, the mode of air travel within the subsurface is determined by soil permeability. In coarse soils such as gravels, the air will migrate in bubble form. Bubble form is desired because it maximizes the surface area through which mass transfer and removal is to occur. In less permeable soils, such as sands and silts, the air will migrate through a channel network formed during injection. The extent of the channel network is dependent on the permeability and the air flow being used; coarser sands and higher flow rate will lead to the development of higher channel densities.

A soil must be not only permeable but also relatively homogenous for proper air flow to occur. The air injected into the subsurface will seek the path of least resistance as it migrates away from the well. If a soil is too heterogeneous, large regions of less permeable soil will be left devoid of any air contact (Baker and Benson, 1996).

To help investigate the effect of soil permeability and heterogeneity on subsurface air flow, Ji et al. (1993) performed a series of laboratory tests. Using a two-dimensional Plexiglas tank and different sizes of glass beads to represent a saturated soil matrix, they were able to simulate a variety of subsurface conditions. When 4-mm diameter glass beads were used (representing a gravel), the injected air was seen to travel in bubble form with very little lateral spreading from the injection well. The use of 0.75-mm diameter beads yielded air flow in the form of channels, and a higher density of channels was observed with increased air flow. When 2-mm diameter glass beads were used, a transition pattern was observed. When lenses, layers, and other heterogeneous structures in the soil matrix were included, it was observed that air flow was very sensitive to such inclusions and would follow paths of lesser resistance, leaving regions in the vicinity of such inclusions untouched by the injected air. Similar conclusions were drawn based on the laboratory testing of different types of soils and sediments by Semer et al. (1996, 1998), Reddy and Adams (1999), and Peterson et al. (1999).

14.3.2 Mass Transfer Mechanisms

Volatilization. Volatilization has been shown to be the dominant removal mechanism occurring during the use of air sparging (Unger et al., 1995; Johnson, 1998). It is defined as the partitioning of a contaminant from the aqueous or nonaqueous phase into the vapor phase. During air sparging, the injected air provides both a medium and a transport network to allow for such partitioning to occur. Additionally, the injected air disturbs the equilibrium that exists between the liquid and vapor phases. When the vapor phase is pulled away from its liquid source, the resulting nonequilibrium will force additional partitioning into the vapor phase. Generally speaking, the higher the vapor pressure of a contaminant, the easier it is to remove through volatilization. For a given contaminant, however, volatilization is two orders of magnitude lower in soil than when the contaminant resides in a liquid (Davis, 1997).

Henry's Law. For a given contaminant, the vapor phase and liquid phase fractions under equilibrium conditions are determined by Henry's law, which can be written as follows:

$$P_a = C_{\text{water}} H_c \quad (14.1)$$

where P_a = partial pressure of the gas (atm)

C_{water} = aqueous-phase molar concentration of VOC (mol/m³)

H_c = Henry's law constant (atm·m³/mol)

The units of Henry's law may be altered; a dimensionless Henry's law constant may be used to relate aqueous-phase concentration (mg/L) to vapor-phase concentration (mg/L). Unfortunately, due to the difficulties of determining the solubility and vapor pressure of a variety of compounds, the Henry's coefficient has proven to be difficult to measure, with reported values often differing by two orders of magnitude or more (Davis, 1997).

For a given compound, a higher Henry's coefficient will indicate that more of the compound will exist in the vapor phase at equilibrium. Similarly, higher Henry's coefficients for a given contaminant result in more of the contaminant being accepted by rising air (Semer and Reddy, 1997). For a given compound, the Henry's law constant will increase with increasing temperature. Even though subsurface temperatures remain nearly constant year round in a majority of cases, methods such as steam injection or soil heating may offer advantages. Increasing temperatures, however, may be of little significance because most volatilization takes place during the early stages of air sparging (Sellers and Schreiber, 1992; Unger et al., 1995) and temperature increases may not help to remove contamination at later stages.

In order for Henry's law to be valid in determining the rate of volatilization for a given contaminant, a condition of equilibrium must exist. For this to occur, there must be an adequate amount of residence time for air within the groundwater. Unfortunately, short residence times, discrete channels, high velocities, and the lengths of travel paths prevent equilibrium from occurring within the subsurface (Ahlfeld et al., 1994b; Sellers and Schreiber, 1992). Therefore, Henry's law does not give a good approximation for volatilization rates, and models based on Henry's law may not provide good system approximations (Sellers and Schreiber, 1992).

Raoult's Law. When subsurface NAPL-phase contamination exists, it is rarely in the form of a single compound. Distilled petroleum products, for instance, contain a great number of constituent compounds with widely ranging properties. In order to help determine the composition of vapor from a multicomponent NAPL-phase contaminant, Raoult's law is used, which may be written as follows:

$$P_i = V_{pi} X_i \quad (14.2)$$

where P_i = partial pressure of compound i in the gas phase

V_{pi} = vapor pressure of pure compound i

X_i = mole fraction of compound i in the liquid mixture

During volatilization, the compounds with higher volatility and higher solubility will be removed first, leaving behind compounds with lower volatility and solubility (Hayden et al., 1994). Because less volatile and soluble compounds remain, a tailing effect will be observed in removal as more effort is required to remove less volatile contaminants.

Volatilization is the dominant removal mechanism in the early stages of air sparging, but its importance is diminished with increasing remedial time. When air injection begins, contaminant near a channel will be easily volatilized. If a high-density channel network exists within the subsurface, this will account for a high percentage of removal and a rapid reduction in initial contaminant levels. Eventually, as the contaminant in the vicinity of channels is removed, removal rates decrease as contamination is forced to diffuse towards a channel. Thus, volatilization and overall removal rates drop when the concentration gradient drops at the air-water interface (Ahlfeld et al., 1994a).

As a demonstration, Braida and Ong (1997) performed a laboratory study of the spatial effects of volatilization. Using a small apparatus and an Ottawa sand with D_{50} of 0.2 mm, removal rates of BTEX compounds at a variety of concentrations were analyzed. Flows ranging from 460 to 2,200 m/day were used. During the first three hours of operation, volatilization was much faster than diffusion, leading to a sharp concentration gradient at the air-water interface. After three hours, however, volatilization rates dropped as diffusion

became the controlling process. Contaminants with higher aqueous diffusivity were found to be removed easier.

Dissolution. Dissolution plays an important removal role during air sparging because it assists in the volatilization and ultimate removal of the contaminant. While volatilization controls the process during the early stages of an air sparging program, contaminant dissolution from the NAPL phase to the aqueous phase is a controlling factor in later phases (Unger et al., 1995). Solubility limits vary greatly for different contaminants, but even in the case of compounds with low solubility, maximum contaminant levels for drinking water are often at least two orders of magnitude lower than solubility limits (Miller et al., 1990). Yet the solubility limit of a contaminant can often indicate whether a specific compound may be removed in a timely fashion. Burchfield and Wilson (1993) used a model and reported that an increase in the Henry's coefficient of a given contaminant did not greatly affect its removal rate using air sparging, but an increase in the solubility of a contaminant greatly increased its rate of removal.

When a contaminant enters into a soil, it will often become trapped as a blob within a single-pore or multiple-pore spaces. Once these nonaqueous phase blobs are created, they need to dissolve out of the immiscible phase into the aqueous phase, at which time they may be transported in the aqueous phase and eventually volatilized (Marley, 1992). Until this occurs, however, an immobile NAPL blob can act as a sink/source for organic solutes, enhancing retardation and delaying removal (Brusseau, 1992). When considering trapped NAPL blobs, Malone et al. (1993) reported that they may be placed into two categories: some will exist in a fast condition during which the NAPL readily exchanges mass with the aqueous phase. This occurs when there is a high NAPL surface area-to-volume ratio. The remaining NAPL will exist in a slow condition, during which there will be a slow, reversible mass transfer between the two phases. This situation occurs when the NAPL blob features a low surface area-to-volume ratio. It is obvious that surface area is an important factor because it is across this interface that dissolution will take place.

Powers et al. (1991) presented a formula to determine the interfacial area across which mass transfer may occur. The specific interfacial area between the NAPL and aqueous phases was found to be a function of soil porosity, NAPL saturation, the surface-to-volume ratio of the NAPL blob, and the fraction of blob surface area exposed to mobile water, written as follows:

$$a_o = n S_o (A/V) f \quad (14.3)$$

where a_o = specific area between the two phases

n = soil porosity

S_o = degree of NAPL saturation

(A/V) = surface area to volume ratio for the blob

f = fraction of blob surface area exposed to mobile water

NAPL size has been shown to be an important parameter (Gomez-Lahoz et al., 1994). Hunt et al. (1988a, b) found that the maximum NAPL blob length was a function of the surface tension between the NAPL and the water, the permeability of the soil, the viscosity of water, the Darcy velocity, and the throat radius of the pore. It was found that blob size and NAPL residual saturation could only be reduced by increasing the Darcy velocity or reducing the surface tension between the two phases.

When multiple contaminants are present in the subsurface, there may be a synergistic effect allowing for increased or decreased solubility compared to when the contaminants exist alone. If gasoline contains methyl tertiary butyl ether (MTBE), solubility of the BTEX contaminants is greatly increased. Additionally, Geller and Hunt (1993) presented a dissolution relationship relating to multiple contaminants. The aqueous equilibrium concentration

of a single compound was found to be a function of its mole fraction in the contaminant mixture. As the more soluble compounds dissolve, the less soluble compounds remain, but their mole fraction within the mixture is increased, forcing dissolution. This relationship does not hold if a contaminant's aqueous solubility is less than 0.001 mole fraction.

There is a growing body of evidence that dissolution is a nonequilibrium process. Voudrias and Yeh (1994) reported that the concentrations of aqueous-phase toluene in flowing water below floating NAPL-phase toluene pools were much lower than the solubility limit. Brusseau (1992), Szatkowski et al. (1995), and Hunt et al. (1988a, b) have reported that NAPL-aqueous phase partitioning is a rate-limiting, nonequilibrium process. This is supported by discrepancies between theoretical and field-measured solubilities. Some reasons that discrepancies may occur include the rate-limited mass transfer between the NAPL and aqueous phase, physical bypassing of the aqueous phase around contaminated low-permeability regions, non-uniform flow due to soil heterogeneity, and synergistic effects between compounds (Powers et al., 1991). It is suggested that nonequilibrium descriptions are needed for high pore water velocities, hydrophobic solutes, high dispersivities, as well as small spills, large blobs, low residual saturations, and heterogeneous aquifers (Powers et al., 1991).

After air sparging has ended and the subsurface is allowed to reach equilibrium once again, additional dissolution of residual contaminants may take place, serving to increase groundwater concentrations. This effect is known as rebound. Rebound is largest in areas that were subjected to low air flux during injection (Gomez-Lahoz et al., 1994). Bass and Brown (1997) reported the following equation for rebound:

$$\text{Rebound} = \frac{\log \left(\frac{C_r}{C_f} \right)}{\log \left(\frac{C_o}{C_f} \right)} \quad (14.4)$$

where C_r = dissolved concentration during postmonitoring

C_o = initial dissolved concentration

C_f = final dissolved concentration

If the rebound is less than 0.2, permanent reductions in contaminant concentrations have been achieved, but a rebound value greater than 0.2 is regarded as substantial rebound (Bass and Brown, 1997).

Adsorption/Desorption. When contaminants are released into the subsurface, they may sorb onto the particles of the soil matrix. Adsorption may become substantial when organic soil content or clay is present. Organic contaminants will be subject to increased adsorption with increased organic content. Adsorption may be a reversible process; if driven, contaminants are able to desorb from the soil matrix and into the aqueous phase. If the ratio of adsorption to desorption is less than unity, the soil has no retention capability and adsorption indeed becomes a reversible process.

Adsorption can be a difficult process to predict accurately. Brusseau (1992) has reported that equilibrium cannot be assumed for adsorption/desorption, and differences between predicted and actual rates may differ between one and three orders of magnitude. The differences may be due to the effects of competitive sorption or to the enhancement caused by cosolutes (Brusseau, 1992). Additionally, organics may bind to organic soil matter more tightly with time (Davis, 1997).

In order to help predict adsorption, the octanol/water partition coefficient, K_{ow} , is used. It is defined as the ratio of the equilibrium concentrations of a dissolved solute in a system of octanol and water, two immiscible solvents. The partition coefficient is helpful in predicting soil adsorption; a higher K_{ow} indicates a more hydrophobic compound that will adsorb more readily to organic soil matter (Davis, 1997). This in turn has been used to estimate an

adsorption coefficient by different formulas (Fetter, 1999). One such example is (Karickhoff et al., 1979):

$$K_d = 0.6 f_{oc} K_{oc} \quad (14.5)$$

where K_d = adsorption coefficient
 f_{oc} = organic fraction in soil

For any sizable amount of adsorption to occur, the soil must contain at least 0.1% organic matter (Davis, 1997). The amount of organic matter in deep soils is low, often less than 0.1% (Perlinger and Eisenreich, 1991). Clayey soils, however, may be prevalent in deep subsurface. The amount of adsorption depends on the type of clay minerals present in the soils. Adsorption to montmorillonite clay is higher than illite clay, which in turn causes higher adsorption than kaolinite clay (Semer and Reddy, 1997). Additionally, the amount of adsorption is also dependent on the water content of the soil because the contaminant must compete with water for adsorption sites (Semer and Reddy, 1997).

Different isotherms are used to represent adsorption under different conditions (Fetter, 1999). One that is commonly used to represent non-polar organic contaminant adsorption to soil is the Freundlich isotherm (Semer and Reddy, 1997). The isotherm may be represented as:

$$C_s = K C_e^N \quad (14.6)$$

where C_s = mass of contaminant adsorbed per mass of sorbent
 K = sorption equilibrium constant
 C_e = solution concentration at equilibrium after sorption
 N = constant describing adsorption intensity

The higher the K and the N values, the greater the sorption capacity of the medium. The equation may be linearized by expressing it in logarithmic form. When this is done, N is an indicator of whether adsorption remains constant at different equilibrium concentrations (Semer and Reddy, 1997). If N is equal to one, a linear relationship exists between equilibrium concentrations and the amount of mass adsorbed; if N is less than one, adsorption decreases with increased equilibrium concentration levels; and if N is greater than one, adsorption increases with increased equilibrium concentration levels (Semer and Reddy, 1997).

Adsorption may also be modeled as a nonequilibrium process using nonequilibrium kinetic equations. In a kinetic model, the solute transport equation is linked to an appropriate equation to describe the rate that the solute is sorbed onto the solid surface and desorbed from the surface (Fetter, 1999). Depending on the nonequilibrium condition, the rate of sorption may be modeled using an irreversible first-order kinetic sorption model, a reversible linear kinetic sorption model, a reversible nonlinear kinetic sorption model, or a bilinear adsorption model (Fetter, 1999).

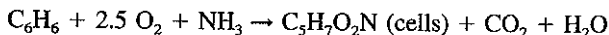
In order for air sparging to be successful, desorption must occur if organic or clayey soils are present at a given site. Although organic matter is usually confined to the upper layers of a soil stratum, clay may be present at all depths. If desorption takes place at an acceptable rate, air sparging will be successful at remediating contaminated saturated soils. If desorption does not occur, saturated soils will remain contaminated and will act as a source to further contaminate the surrounding groundwater.

14.3.3 Mass Transfer Mechanism: Biodegradation

Biodegradation is different from the other removal mechanisms that act on subsurface contamination during the air sparging process. While other mechanisms act to transfer the con-

taminant out of the subsurface, biodegradation acts to transform the contaminant into non-toxic products. Biodegradation can often account for a substantial portion of the remedial process by acting on the less volatile, more strongly adsorbed contaminants during the later stages of remediation and when dissolved concentrations have decreased (Miller, 1996; Johnson, 1998). Biodegradation becomes a significant removal mechanism when dissolved contaminant concentrations are less than 1 mg/L (Johnson, 1998). Additionally, middle distillate fuels, including diesel fuel and kerosene, are not easily volatilized and rely upon biodegradation for treatment (Hoeppel et al., 1991). Biodegradation occurs when native microbial communities within the subsurface interact with and metabolize organic contaminants. An electron acceptor (oxidizing agent) receives electrons from the electron donor (Middleton et al., 1995). The contaminant is mineralized into end products that are based both on the type of contaminant and the oxidizing agent. Biodegradation rates may be monitored in a number of ways, including the degree of consumption of electron donors, the degree of consumption of electron acceptors, and the production of metabolic byproducts (Chapelle et al., 1996). The process may involve direct mineralization or the transformation of the contaminant into intermediate compounds before mineralization is completed. Malone et al. (1993) reported that benzene, toluene, and the xylenes are degraded into intermediate compounds before they are mineralized into carbon dioxide and water.

Optimal subsurface conditions are necessary in order for biodegradation to occur successfully. While suitable microbial populations or nutrient levels may be a limiting factor to the rate of biodegradation (Widdowson and Aelion, 1991), the type of electron acceptor is often the controlling factor. The most efficient electron acceptor for biodegradation is oxygen. Aerobic biodegradation utilizes oxygen as an electron acceptor. Additionally, nutrients such as phosphorus and nitrogen necessary for cell growth and reproduction must be present if bioremediation is to be successfully implemented. During aerobic degradation of benzene, the following reaction occurs (Chiang et al., 1989):



When sufficient oxygen is lacking and anoxic conditions exist within the subsurface, biodegradation becomes less efficient. During anoxic conditions, other subsurface electron acceptors are utilized. Following oxygen as the preferred subsurface electron acceptor, in descending order of efficiency, possible electron acceptors include nitrate, ferric iron, sulfate, and carbon dioxide (Middleton et al., 1995). Despite preferences in anoxic conditions, field tests have shown that sulfate reduction is the primary electron accepting process (Chapelle et al., 1996; Thierrin et al., 1995). By adding oxygen to the subsurface through air sparging to create oxic conditions, more efficient, aerobic degradation is allowed to occur (Crocetti et al., 1992).

In some cases, oxygen is needed in order for any sufficient biodegradation to occur. While toluene has been shown to degrade using a variety of electron acceptors, benzene will not degrade to any measurable extent without the presence of oxygen (Middleton et al., 1995; Thierrin et al., 1995). Chapelle et al. (1996) reported that in field tests, benzene degradation rates were low under nitrate-amended conditions. Patterson et al. (1993) reported in another field study that benzene persisted in anoxic conditions but was easily degraded under oxygenated conditions. Thus, the presence of oxygen may be a rate-limiting factor for efficient biodegradation (Crocetti et al., 1992).

In order for aerobic biodegradation to occur, there must be an adequate level of oxygen within the soil. Miller (1996) reported that 2 to 4% oxygen by volume is needed within the subsurface for sustaining biodegradation to occur. Unfortunately, this level of subsurface oxygen may be difficult to achieve. It is estimated that between 3 to 3.5 g of oxygen are needed to completely mineralize hydrocarbons (Johnson et al., 1993). Oxygen can be supplied to the subsurface through the infiltration of precipitation, but this oxygen is quickly utilized (Chapelle et al., 1996). Groundwater may be a poor medium through which to transport oxygen; Hoeppel et al. (1991) reported that 75,000 kg of groundwater are needed

to break down 1 kg of hydrocarbons. Therefore, the delivery of oxygen to the subsurface cannot be achieved by injecting saturated groundwater, but through the use of air sparging, oxygen levels can be increased to increase the rate of biodegradation and ultimately improve remedial efficiency. When injecting air into the subsurface, oxygen levels can reach 8 to 10 mg/L, while the injection of pure oxygen can increase levels to 40 mg/L (Johnson et al., 1993). The injection of hydrogen peroxide can increase subsurface oxygen levels to 500 mg/L (Johnson et al., 1993).

Field studies have indicated successful increases of biodegradation during the use of air sparging. Covell and Thomas (1997) reported on the use of air sparging at an underground coal gasification site. Groundwater was used to help control air flow as well as deliver nutrient (ammonium phosphate) to the subsurface. After six months, over 80% of the benzene initially present at the site was removed. It was determined that volatilization was the primary initial removal mechanism; while biodegradation served as an effective polishing step.

Yaniga and Smith (1984) reported on the restoration of an aquifer that had been contaminated with gasoline-range hydrocarbons. The soils consisted of a heavy silt loam over fractured shale. A number of methods were employed at the site, including excavation of the upper soils and the inclusion of an infiltration gallery with air sparging and an air stripping tower. Even though the sparger had to be frequently cleaned due to biological fouling, a 50–85% reduction was achieved within 11 months. Because of clogging, the sparge point had trouble delivering oxygen to the subsurface. Therefore, a solution of 100 mg/L hydrogen peroxide was also injected. This served to increase oxygen delivery while reducing clogging of biological material.

While BTEX compounds can be rapidly degraded under aerobic conditions (Malone et al., 1993; Patterson et al., 1993), aerobic biodegradation of chlorinated solvents is more difficult, often requiring the presence of cosubstrates for degradation. They may, however, be degraded under anaerobic conditions, especially by methanogenic bacteria. Lombard et al. (1994) reported on the use of air sparging with the use of methane as the injected gas at the Savannah River Site in Aiken, South Carolina. Approximately 3,500,000 lb. of trichloroethylene and tetrachloroethylene were detected in the subsurface. A methane–air mixture was injected in order to stimulate the native methanotropic bacteria. Extraction was performed at a rate 20% higher than injection to control site behavior as well as prevent an explosive condition (greater than 5% methane).

Longer exposure of contaminants to the subsurface can actually sometimes help to increase the rate of biodegradation. Crocetti et al. (1992) reported that soils contaminated with heating oil had heterotrophic bacteria populations one to two orders of magnitude higher than background soils. Patterson et al. (1993) found that during a field study, degradation rates increased with time, especially in the case of toluene, possibly due to increased degradation efficiency of the resident bacteria. Jin et al. (1994) demonstrated that in three soils contaminated with toluene (sterile soil, soil preexposed to toluene, and soil not previously exposed to toluene), degradation rates increased with increased exposure time due to the buildup of an enriched microbial population.

14.3.4 Transport Mechanisms

In addition to the mass transfer and transformation mechanisms that occur during air sparging, VOC transport mechanisms play a role in ensuring remediation. The important transport mechanisms that occur during air sparging include advection, dispersion, and diffusion.

Advection and Dispersion. Advection is defined as the transport or movement of vapors or liquids in air or water due to the response to a pressure gradient (Bear, 1972; Fetter, 1999). The migration due to advection is dependent on the pressure gradient and the soil permeability. The soil permeability is dependent on soil grain size and grain size distribution, the type and structure of the soil, the soil porosity, and the water content of the soil. While

both groundwater and soil gas flow are governed by Darcy's law, mass flux due to advection in one dimension can be written as (Fetter, 1999):

$$F_v = v n_e C \quad (14.7)$$

where F_v = mass flux

v = flow velocity

n_e = effective porosity

C = contaminant mass per unit volume of solution

For one-dimensional transient conditions and uniform velocity, the advective transport equation may be written as:

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} \quad (14.8)$$

Dispersion is defined as the mixing or spreading of the contaminant in either the groundwater or soil gas due to differences in micro-scale flow velocities. Once again, soil permeability affects dispersion as pore size, path length, and pore friction create these differences in flow velocity. Dispersion that occurs along the flow path is known as longitudinal dispersion, while flow occurring perpendicular to the flow path is known as transverse dispersion. Both advection and dispersion are important mass transport mechanisms. Hein et al. (1994) reported that model simulations indicated that mass transfer/transport is dominated in part by gaseous advection and dispersion. Pepper and Stephenson (1995) reported that groundwater transport is advection-dominated, while Wilson et al. (1994a) reported that injection wells should be operated in a manner that will generate the maximum amount of dispersive mixing, a situation that can be accomplished using pulsed air injection.

Advection and dispersion act to disrupt the saturated zone by creating turbulence. The turbulence created by air injection serves to disrupt equilibrium. This action can help introduce water into dead-end pores previously occupied by NAPL ganglia as well as create groundwater flow or circulation. Such groundwater movement will aid dissolution by transporting dissolved contaminant away from NAPL sources, creating concentration gradients that will force additional dissolution. This type of behavior will also aid in desorption as concentration gradients will be established near the surface of soil particles with sorbed contaminants.

Caution should be used, however, when inducing subsurface turbulence. While this turbulence allows for desirable effects, too much movement may force unwanted migration into areas previously free of contamination. Additionally, some mechanisms, especially adsorption/desorption, are reversible, and thus advection/dispersion can act to trap contaminant in dead-end pores as well as force additional contaminant adsorption. Therefore, subsurface air flow should be carefully monitored to help minimize any negative effects of advection/dispersion.

Diffusion. Diffusion is defined as the migration of contaminant from regions of high concentration to regions of low concentration. The diffusive flux is governed by Fick's law and also depends on tortuosity, or the length of the transport path, within the soil (Bear, 1972; Fetter, 1999). Diffusion is the primary mechanism for the removal of NAPL trapped in dead-end pores. Diffusion must occur in order for movement to occur from such trapped sites into regions where other processes may occur for removal. It is also a means of transporting contaminant from source locations to air channels in order for volatilization or biodegradation to take place. Diffusion is an extremely slow process; Ahlfeld et al. (1994a) reported that in a water column with a 20-in. radius, 78 years would be required to reach a concentration of 5 parts per billion if flow took place in a 1-in.-radius channel, 1.7 years if the channel radius

were increased to 2 in., and 27 days if the channel radius was increased to 5 in. Therefore, diffusion often becomes a rate-limiting process (Ahlfeld et al., 1994a).

While diffusion rates in gas can be calculated to a reasonable degree of accuracy, it is more difficult to do so in liquids than in gas (Peterson et al., 1994). Additionally, diffusion was determined to be affected by porous media (Davis, 1997), and diffusion rates in porous media will decrease with increased saturation (Peterson et al., 1994). Davis (1997) reported that soil gas diffusion can be approximated as follows:

$$\frac{D_s}{D_a} = \frac{a^2}{n^{2/3}} \quad (14.9)$$

where D_s = soil diffusion

D_a = air diffusion

a = volumetric air content for soil

n = soil porosity

Diffusion of gas within soil is important as it will help determine any type of air or vapor movement. Additionally, trapped gas may also be removed through diffusion (Fry et al., 1995).

14.4 SYSTEM DESIGN AND IMPLEMENTATION

When designing an air sparging system, a number of site-specific and operator-controlled parameters must be addressed. A flowchart summarizing air sparging design process is shown in Fig. 14.2. The soil profile needs to be explored in order to determine what soils exist. The hydrologic conditions at the site also need to be analyzed. Questions need to be answered regarding site contamination, including contaminant type and properties, concentrations, and locations. If the contaminants present at the site are conducive to removal using air sparging, then system parameters such as the number, spacing, and depth of air injection wells need to be determined. Flow rates and pressures need to be determined, as well as the details of the soil vapor-extraction system. Once the system is designed, the performance of the system needs to be monitored to ensure adequate performance. If the system is not performing well, changes need to be made and performance reevaluated. This iterative design process continues until the air sparging system is performing to expectations.

14.4.1 Equipment

A major advantage of air sparging is that it requires only simple materials to construct a field system. No special equipment needs to be designed; and all equipment used is easily obtained. Equipment required for the air injection system and soil vapor extraction system is summarized in this section.

Injection System. An air compressor is used to force air into the air injection wells. The compressor must be capable of injecting air at a proper flow rate under suitable air pressure. The number of wells that are fed by a given compressor also dictates the size of the air compressor. Typically, reciprocating or rotary screw compressors are used during field application (Marley et al., 1992a). Regardless of what type is used, the compressor must be oil-free in order to prevent the delivery of additional contamination to the subsurface (Johnson et al., 1993).

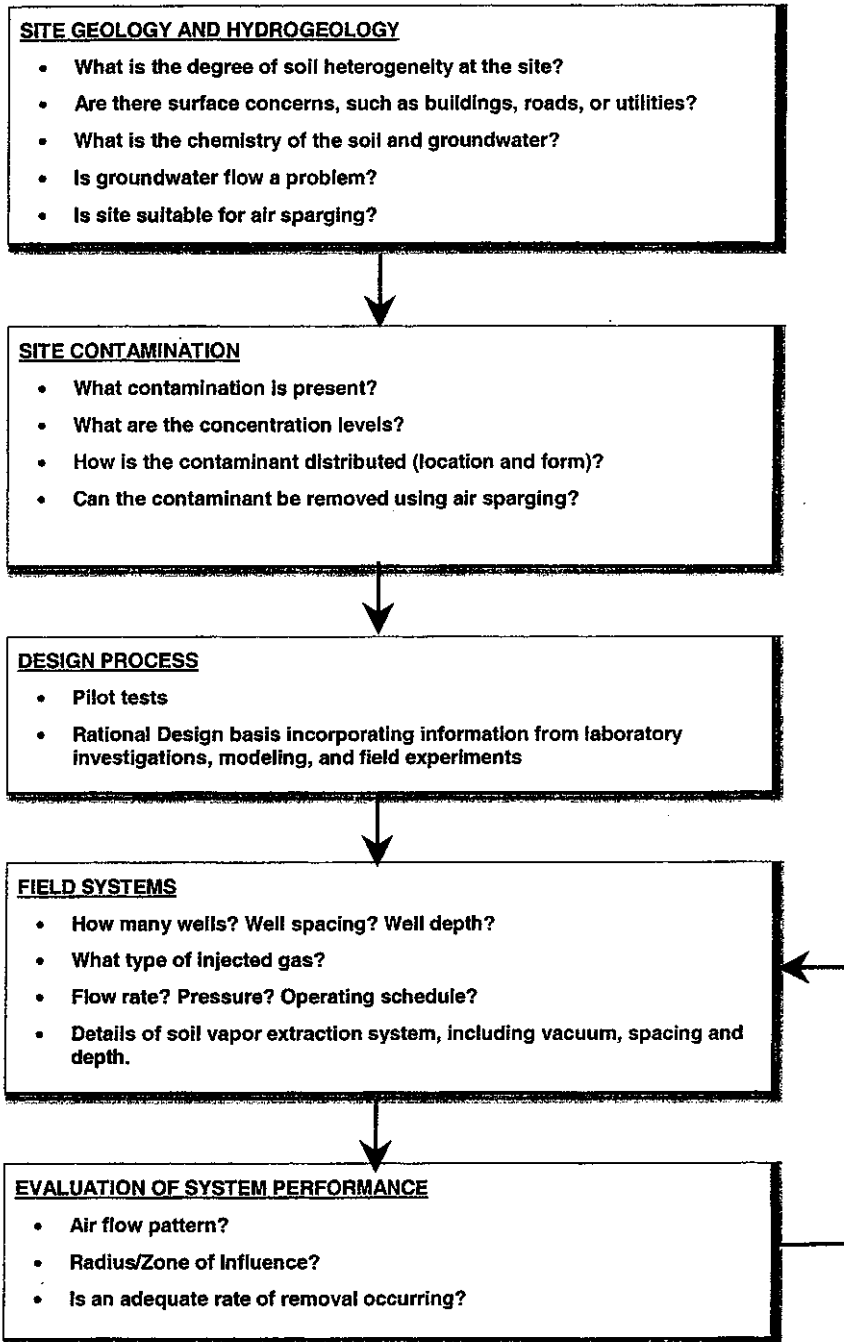


FIGURE 14.2 Design process for air sparging systems.

The air leaves the compressor at a flow rate and pressure that is controlled through the use of regulators. It passes into a manifold system used for delivery to the injection wells. Because the air leaving the compressor may be high in temperature, rubber hose or metal pipes are often used in the manifold system (Marley et al., 1992a). Valves are included in the manifold system to ensure that the desired amount of air is delivered to each well. The injection well usually consists of 1- to 4-in.-diameter PVC pipe, although stainless steel may be used if steam or heated air is to be injected (Johnson et al., 1993). One- to 2-in. in diameter PVC pipe is often used because it is cheaper to install (Johnson et al., 1993). A borehole for well placement is often drilled, but the use of direct push methods for well placement may provide significant cost savings (Joiner and O'Keefe, 1996). The well screen is placed below the lowest known point of contamination to ensure that the entire plume is addressed.

Nyer and Suthersan (1993) stated that injection should be at least 1 to 2 ft below the lowest point of contamination, but typical injection points during field applications are 10 ft below the lowest point of contamination (Bruell et al. 1997). Loden (1992) reports that wells are effective in delivering air to a depth of 150 ft, but if depths are below 40 ft, a series of nested wells should be used (Nyer and Suthersan, 1993). The well screen is usually 1 to 3 ft long (Marley et al., 1992a). The screens help minimize any effects of clogging as well as provide for even air distribution. The well is backfilled with 6 in. to 2 ft of sand or gravel to act as a filter and is then sealed with a bentonite seal to prevent air from short-circuiting to the surface. The remaining annulus is grouted to the surface to assist in providing a seal (Loden, 1992).

Soil Vapor Extraction System. Once the air is injected into the saturated subsurface, it will migrate toward the surface due to the effect of buoyancy. Eventually the contaminated injected air will enter the vadose zone. At this point, a soil vapor extraction (SVE) system may be implemented. Soil vapor extraction applies a vacuum to the vadose zone to assist in collecting vapors. The vacuum will help vapor collection as well as assist in preventing unwanted off-site migration. Equipment used in a soil vapor extraction system is similar to that used in an air sparging system, except that a vacuum pump is used instead of an air compressor. Additionally, if the vapors being collected by the soil vapor extraction system are moist, a dewatering system may be employed (Johnson et al., 1993).

The extraction flow rate is very important in order to control air and contaminant vapor migration. Simply stated, the extraction rates must be higher than the injection rates in order to prevent soil pressure buildup. Loden (1992) reported that the ratio of extraction to injection commonly used during field application are between 4:1 and 5:1. Johnson et al. (1990) reported that typical extraction rates are between 100 and 1,000 standard cubic feet per minute (scfm).

14.4.2 Operational Controls

In addition to proper system design and layout, proper choices regarding the operating parameters of an air sparging system are essential to the success of the remediation program.

Injection Media. The first choice that must be made is the type of gas to be injected into the subsurface. The choice of gas is especially important in ensuring the delivery of oxygen to the subsurface in order to stimulate biodegradation. Air is the gas most commonly used in remedial programs. Air is low in cost and not explosive or flammable. When air is injected into the subsurface, dissolved oxygen levels may be raised from typical concentrations of about 2 mg/L to between 9 and 10 mg/L, thereby providing suitable oxygen levels for biodegradation (Johnson et al., 1993).

If higher levels of dissolved oxygen are desired, pure oxygen or air enriched with oxygen may be used. When pure oxygen is injected into the subsurface, dissolved oxygen levels

may reach 40 mg/L (Johnson et al., 1993). Even if the reported oxygen levels can be delivered to the subsurface, Bausmith et al. (1996) reported that high levels of oxygen could stimulate such rapid biological growth that injection wells may become clogged with biomass. Additionally, the elevated levels of oxygen can force soluble manganese or iron present in the groundwater to precipitate into insoluble manganese dioxide (MnO_2) or ferric hydroxide ($Fe(OH)_3$). Calcium may precipitate as insoluble calcium carbonate ($CaCO_3$) in the presence of carbon dioxide (Bausmith et al., 1996). If chlorinated solvents are present at a site, aerobic degradation becomes difficult. These solvents, however, may be anaerobically degraded, especially by methanotropic bacteria. In such situations, methane can be injected into the subsurface to stimulate methanogenic degradation (Leonard et al., 1994).

Another alternative is the use of ozone for injection, a method that is being increasingly adopted for treating both contaminated soils and groundwater. The injection of ozone allows subsurface ozonation to occur. Ozonation is an advanced chemical oxidation process that may be used to break complex organic contaminants into less persistent or less toxic molecules (Nelson and Brown, 1994). The ozone accomplishes this by assisting in the degradation of double-bonded organics (Leonard et al., 1994).

Steam may be used in place of air or oxygen for injection into the subsurface. The injection of steam increases the temperature of the subsurface, helping to improve the removal efficiency of semivolatile organic compounds (SVOCs) as well as stimulating microbial activity in colder soils and climates (Leonard et al., 1994). Steam has been used for years by the oil industry to recover crude oil from the subsurface. By 1979, 20% of the oil produced in California had been extracted from the subsurface using steam injection (Falta et al., 1992). During the use of steam injection, contaminant mass transport occurs by advection in all three phases and by multicomponent diffusion in the gas phase (Falta et al., 1992). Heat transfer to the subsurface occurs due to conduction, multiphase convection, and gaseous diffusion (Falta et al., 1992).

To study the performance of steam injection, Hunt et al. (1988b) performed laboratory tests in a 91-cm Pyrex horizontal glass column. Ottawa sand was contaminated with trichloroethylene, benzene, and toluene and then subjected to both water (pump-and-treat) injection and steam injection. The water injection proved to be ineffective, even when flow rates of up to 15 m³/day were used. When steam was injected, the contaminant was displaced as a slug just ahead of the steam front at flow velocities of up to 1.5 m/day. It was demonstrated that only one pore volume of fluid was needed to achieve cleanup using steam. Additionally, the use of steam allowed for the possibility of actual NAPL recovery.

Flow Rate/Mode of Injection. Once the type of gas to be injected is determined, the flow rate and mode of injection must be determined. Loden (1992) reported that flow rates of 2 to 16.5 scfm are typical for field application. Nyer and Suthersan (1993) reported that when soil vapor extraction systems are used at a site, injection flow rates between 4 and 10 scfm are used. It has been reported that any flow rates beyond contaminant diffusion kinetics are a waste of effort (Roberts and Wilson, 1993; Reddy and Adams, 1999; Adams and Reddy, 1999). Additionally, Rutherford and Johnson (1996) found that oxygen transfer into groundwater may actually be impeded by an injection flow rate that is high because the air will act to push the groundwater away from the point of injection, decreasing interfacial transfer area and oxygen transfer.

When injecting air, either continuous or pulsed air flow may be used. Pulsed flow involves using a cycle that consists of injection followed by a time of cessation. After the period of cessation has elapsed, air is once again injected and the cycle is repeated. Wilson et al. (1994a, b) reported that pulsing helps improve removal efficiency by inducing mixing. McKay and Acomb (1996) stated that frequent pulsing is needed to optimize oxygen distribution within the subsurface. Reddy and Adams (1998) and Adams and Reddy (1999) found that pulsed air injection improves removal efficiency in finer soils, whereas it does not affect the removal in coarser soils.

Injection Pressure. When air sparging is performed, air must be injected under proper pressure. If air is injected under pressure that is too low, it will be unable to enter into the subsurface. If air is injected at pressure that is too high, the contaminant plume may be forced to migrate into previously uncontaminated areas. Additionally, soil heaving or fracturing may result within the subsurface if injection pressure is too high. The necessary pressure needed for air to enter into the subsurface is the sum of hydrostatic pressure at the injection point, friction due to exiting from the well, and the capillary pressure due to the interface of two fluids within the porous media (Johnson et al., 1993; Ahlfeld et al., 1994a; Bausmith et al., 1996). One pound per square inch of pressure is needed to overcome every 2.3 ft of static water above the injection point (Bausmith et al., 1996). The capillary or air entry pressures that must be overcome may range between a few centimeters of pressure head in coarse, sandy soils to several meters in low-permeability clay (Johnson et al., 1993). Wehrle (1990) reported that additional air pressure will be needed to overcome capillary pressure when the D_{50} of a soil is smaller than 0.8 mm.

Vapor Treatment. When soil vapor extraction is used, the contaminated vapors that have been collected must be addressed. The simplest solution is to release the contaminated vapors directly to the atmosphere. Using this option, the effluent gases are passed through a diffuser stack and released into the air. This is applicable only when local regulations allow and compliance with air emission standards can be ensured. When vapor treatment is needed, a popular option is the use of carbon adsorption. The vapors are passed through an activated carbon matrix, effectively removing contaminated vapors from the effluent gas. Either virgin or recharged carbon may be used during application (Loden, 1992). Thermal incineration is another option. Temperatures between 1,000 and 1,400°F are used to destroy the contaminants, providing contaminant destruction rates of 95–100% (Loden, 1992). Care must be taken not to exceed the explosive limit; this can be avoided by diluting and mixing the vapors with fresh air (Loden, 1992). Lower temperatures may be used with the use of catalytic oxidation. Because a catalyst is employed, temperatures may be lowered to values of 600–800°F. Such a process allows for contaminant destruction efficiencies of up to 85% (Loden, 1992). Additionally, if off-vapors provide proper conditions, internal combustion engines may be used to provide power while treating the vapors.

14.5 PREDICTIVE MODELING

Mathematical models for predicting air sparging performance will eliminate a great deal of the guesswork involved in system component design and layout. Several researchers have developed mathematical models to simulate air sparging performance (Marley et al., 1992b; Sellers and Schreiber, 1992; Wilson, 1992; Burchfield and Wilson, 1993; Roberts and Wilson, 1993; Gomez-Lahoz et al., 1994; Reddy et al., 1995a, b; Reddy and Zhou, 1996; Lundegard and Andersen, 1996; McCray and Falta, 1997; Wilson et al., 1994a, b; Wilson and Norris, 1997; Rabideau and Blayden, 1998; and van Dijke and van der Zee, 1998).

Simple models may be used to study specific mass transfer, transformation, or transport processes, or more rigorous models may be used to study macroscale performance. Unfortunately, because air sparging creates dynamic, nonequilibrium processes, models based on simplifying assumptions may provide misleading results. Additionally, many models have yet to be validated with controlled laboratory test data and field data.

14.6 PERFORMANCE ASSESSMENT

Monitoring of air sparging systems installed at different sites provided valuable information on the air sparging process, particularly the radius or zone of influence and contaminant

removal behavior, which are briefly explained in this section (Bruell et al., 1997; Bass and Brown, 1997).

14.6.1 Radius of Influence / Zone of Influence

Arguably the most important factor related to air sparging is the radius of influence (ROI), defined as the lateral distance from the center of the sparge well to the edge of the region that is impacted by the injected air. The region of soil that is delineated by the ROI is known as the zone of influence (ZOI); it is the actual volume of soil that is impacted by the injected air. Both the radius and the zone of influence are of the utmost importance for the successful design and implementation of an air sparging system. Since the radius and zone indicate the footprint of treatment that a given well creates, it assists in the proper spacing and layout of wells. If the design radius of influence is underestimated, the wells will be spaced closer together than necessary, leading to an overdesigned and overpriced remedial system. If the radius of influence used for design is overestimated, the wells will be spaced too far apart, leaving regions of the contaminated soil profile untreated.

The radius and zone of influence are heavily dependent on soil permeability. The injected air rises towards the surface due to buoyancy, but the conical zone is established because of lateral air migration. The lateral air migration takes place because of differences between the horizontal and vertical permeability. Because horizontal permeability may be 10–1,000 times greater than vertical permeability (Nyer and Suthersan, 1993), the vertical resistance is high enough to overcome buoyancy and force some lateral movement. Overall soil permeability also dictates the size of the radius/zone of influence; the less permeable a soil, the larger the radius/zone of influence. Nyer and Suthersan (1993) reported that the angle of the zone tangent with the vertical ranges from 15° for coarse gravels to 60° for silty sands. Zumwalt et al. (1997) performed laboratory tests with homogenous, isotropic sands and measured an angle of 26.5°.

Since the radius of influence is so important in the design of a field system, its accurate measurement is also crucial to ensure proper performance during operation. Several different methods are available to facilitate field measurement of the radius/zone of influence. Water table mounding is defined as the increase in the height of the water table due to the additional pressure caused by the injection of air. It can be measured rather easily through the use of monitoring wells. Unfortunately, the increase in water table height is a transient situation; the increase in table height creates a hydraulic gradient within the table that will eventually level out the table, creating a steady-state condition. At a remedial site in Florence, Oregon, Lundegard and LaBrecque (1995) measured a radius of influence of 63 ft 30 minutes after injection began, but the increase in water table elevation had disappeared within 3 to 4 hours.

A similar method that may be employed is the observation of air bubbles within groundwater monitoring wells. The bubbles are the result of the intersection of an air channel or flowing bubbles with the wall of the well. The bubbles provide direct evidence that air flow is occurring within the subsurface of the well. In a related application, Kraus et al. (1997) reported on the progress of remediation at a field site. The remedial site was at a lower elevation than the surrounding area and often became submerged with surface runoff following summer rainstorms. While the site was submerged, the effluent air was observed exiting the soil profile because it bubbled through the water lying above. Radii of influence measuring between 4.5 and 12 m were observed during injection.

The mounding of groundwater is essentially the measure of water table encroachment into the vadose zone. Other measures of the radius/zone of influence are possible, including the measurement of VOC vapors in the vadose zone, the increase of dissolved oxygen, the extent of tracer gases that may have been included in the air injection process, and the increase of overall soil gas pressure within the vadose zone. Caution should be exercised, however, when using vadose detection methods because differences exist between the permeabilities of the saturated zone and the vadose zone. Any type of measurement that requires

measurement of gas within the vadose zone may be skewed by the migration patterns that occur and may not be representative of conditions within the saturated zone (Javanmardian and Kremesec, 1995). McCray and Falta (1997) used a model known as T2VOC to analyze a subsurface flow pattern occurring during air injection. They found that positive pressure measurements made below the water table closely corresponded to subsurface gas distribution and the zone of influence, showing that soil gas pressure measurement is an easily implemented technique that is a good monitor of the radius/zone of influence.

Other gas measurements may be made within the saturated zone. Using monitoring devices placed directly in the saturated zone, increases in dissolved oxygen or carbon dioxide caused by the sparging process may be measured. The injected air will cause volatilization of the subsurface contaminants to occur; therefore, measurements of contaminant vapors within the subsurface may help determine the extent of the zone of influence. During injection, tracer gases may be sparged into the groundwater. One such gas that has been widely used is sulfur hexafluoride (SF_6). Sulfur hexafluoride is virtually nonreactive, has very similar dissolution characteristics to those of oxygen, and is detectable at very low concentrations (Javanmardian and Kremesec, 1995). The changes in soil gas composition may also be indirectly determined through the measurement of major consumers/producers of soil gas, the native microbial population.

Some of the above techniques, including measurements of water table mounding, soil gas pressure, and tracer gases are indirect indicators of subsurface air flow and the radius/zone of influence; caution should be exercised when using such methods (Lundegard and LaBrecque, 1995). Newer, more innovative techniques for measuring subsurface air flow are being increasingly used. Goldflam et al. (1997) implemented radar at a remedial site. They used a RAMAC 60 MHz center borehole radar to determine both the extent of air flow and the zone of influence. This system provided definition on the scale of 10 cm due to the spacing of the rays. Another innovative technique that has been widely used recently is electrical resistivity tomography (ERT). During implementation, an electrode pair is placed within the subsurface, and a current is passed between the two electrodes. Air insulates electricity, but groundwater is a conductor of electricity (Schima et al., 1996). Subsurface electrical resistance is a function of saturation, porosity, and clay content. The resistance to current flow is measured, with regions of high resistance indicating regions of air flow. During measurement, a resistivity distribution is created, and a finite element mesh is generated for analysis.

Lundegard and LaBrecque (1995) performed an extensive field test in order to compare several methods for radius of influence measurement with electrical resistivity tomography. The field site (Florence, Oregon) consisted of a sandy, isotropic, homogenous aquifer that had been contaminated with hydrocarbons, especially gasoline. The water table was located at a depth of 17 ft below the ground surface, and a groundwater flow gradient of 0.006 ft/ft was measured. The permeability of the aquifer soils was approximately 2×10^{-2} cm/s. Air was injected into the subsurface using a 2-in. diameter PVC well that was screened for 2 ft beginning at a depth of 14 ft below the water table. In addition to the use of the measurement of groundwater mounding previously mentioned, dissolved oxygen levels and increases in soil gas pressure (at least 0.01 inches of water) were measured, as well as the use of ERT. The ERT system, which had a definition on the scale of 1 to 2 ft, revealed a zone of influence parabolic in shape with a radius of influence of approximately 8 ft. Because rather large changes in resistance were measured, it was determined that a high-density air flow channel network had been established. It was also observed that air was entering the soil at the bentonite seal. When comparing all of the methods used during the test, it was determined that the radius of influence determined using ERT was two to eight times smaller than with the other methods, indicating that the other methods may seriously overestimate the radius of influence of a given well.

Johnson et al. (1995) also performed a comparative study to determine how different measurement techniques may offer different values for the radius of influence. A sparge well was screened at 6 ft below ground surface. Direct push methods were used for the monitoring

of the radius/zone of influence. A neutron probe revealed a radius of influence of 3 m with highly scattered air flow. Electrical resistivity tomography was applied, revealing the same result. The use of sulfur hexafluoride as a tracer gas also gave a radius of influence of 3 m, but the zone of influence appeared to be skewed in shape. Dissolved oxygen levels within the groundwater were monitored, and a radius of influence of between 6 and 9 m was determined. Because of induced groundwater circulation, groundwater that had come into contact with the injected air may have flowed away from the well, being detected at further distances and providing a larger radius of influence than that determined with the other methods.

14.6.2 Contaminant Removal

A number of methods can be employed to monitor remedial progress, including the use of monitoring wells, groundwater analysis, and effluent vapor analysis. Selected case studies are summarized in Table 14.1 and in this section to provide information on expected contaminant removal using air sparging systems.

Ardito and Billings (1990) utilized a subsurface volatilization and ventilation system (SVVS), which featured a nested well pair consisting of a sparge well and an extraction well. Three site applications were reported. At Isleta, New Mexico, a 90% cost reduction per percent benzene reduction was realized. At Bernanillo, New Mexico, between 12,000 and 13,000 gallons were remediated to nondetectable levels. At Arneal, New Mexico, concentrations of 23,000 to 43,000 ppb benzene dropped to 730 to 6,300 ppb after application of SVVS and free-product skimming.

Brown et al. (1991) reported on the remediation of a former dry cleaning facility that was contaminated by a combination of PCE, TCE, DCE, and heating oil. After pilot tests were run, a design radius of influence of 50 ft was used. Injection was performed at 16 standard cubic feet per minute under a pressure of 10 in water column. Within the first six weeks, 900 lb of PCE and TCE were removed, and a 98% reduction was achieved in 125 days.

Marley (1992) reported on the use of air sparging at a BTEX-contaminated site. Coarse sand extended to 20 ft below ground surface, which in turn was underlain by denser sand. The water table was between 15.5 and 16 ft below ground surface. A pilot test determined no appreciable benefit from pulsed air injection, but a full-scale system was installed featuring pulsed air injection due to operating concerns. Shallow wells were run with three hours injection followed by nine hours of down time, while the deep wells were operated with a regime of six hours on, six hours off. In 60 days, 5 to 10 lb of hydrocarbon were removed.

Leonard and Brown (1992) reported on the use of air sparging applied to a site contaminated with toluene and chlorinated solvents. It was found that 75% of the contaminant resided in the saturated zone. A sparge well was placed at 14.5 ft below ground surface (8.5 ft below the water table). Within three months, 7% of the contaminant was removed.

Deaver and Tworowski (1994) reported on a remedial program at an adhesives manufacturing facility. The site consisted of 56,000 $\mu\text{g}/\text{L}$ of 1,1,1-TCA and 4,000 $\mu\text{g}/\text{L}$ of 1,1,1-DCE. SVE was shown to clean the vadose zone, but it did not address the saturated zone. A single well was placed in the spill area, leading to a drop from 2,000 $\mu\text{g}/\text{L}$ to 200 $\mu\text{g}/\text{L}$.

Damera et al. (1997) used air sparging at a site contaminated by a multiple fuel spill. The site consisted of 3 to 10 ft of silty clay over fine to medium sand, with the water table at 29 ft. Within a year and a half, 57,000 lb of hydrocarbons were removed from the site due to biodegradation and volatilization. An analysis was performed, determining that 61% was removed due to volatilization.

TABLE 14.1 Selected Air Sparging Case Studies

Author	Contaminant	Soil	Number of wells/ depth	Operation	Results
Marley et al., 1992	TCE	Fine/very fine sand, silts	7 wells 15 ft B.W.T.	30 days 3 to 10 scfm	4 lb removed
Marley et al., 1992	BTEX 20,000 to 30,000 µg/L	Sand/gravel over fine sand	7 wells 6 ft B.W.T. 6 deep wells	60 days 2 to 6.5 scfm	5 to 10 lb removed 600 µg/L in groundwater 50% reduction
Basinet and Wollenberg, 1997	Gasoline	Fine sand, silty clays	1 A.S. well 18 ft B.G.S.	1 year	80% benzene reduction
Covell and Thomas, 1997	Benzene	0-10 ft clay/silt 10-20 ft silty sandstone 28-31 ft coal seam	5 A.S. wells 4 SVE wells	3.5 months on 1 month off 2.5 months on	BTEX non-detect. at 9 mos. MTBE 2450 µg/L Benzene 98% reduction BTEX 99.3% reduction
Damera et al., 1997	BTEX 1 to 2 mg/L MTBE 7010 µg/L	Silty clay 3-10 ft sand, clay, gravel water table at 29 ft	3 SVE, A.S. clusters	1.5 years	BTEX non-detect. at 9 mos. MTBE 2450 µg/L Benzene 98% reduction BTEX 99.3% reduction
Klemm et al., 1997	Gasoline	12-15 ft sand/gravel over slate water at 1 ft	63 wells at 15 ft B.G.S.	2 years	1100 lb removed, most solvents at non-detectable levels
Gordon, 1998	Chlorinated solvents	Medium to coarse sand, sandy clay	134 A.S. wells, 58 SVE wells	450 days	

14.7 MODIFIED/RELATED TECHNOLOGIES

Even though traditional air sparging (vertical well, injection of air) has proven to be successful in a wide variety of field applications, alternative strategies exist that can make air sparging applicable to other conditions. Sometimes other remedial technologies such as pump and treat and bioremediation are used in conjunction with the air sparging technology to address site-specific contaminant conditions.

14.7.1 Horizontal Wells

Horizontal wells may be implemented under a wide range of field applications, but they are especially useful in treating long, shallow spills, such as those that may occur under leaking above-ground or in-ground pipelines (Bausmith et al., 1996). There are four proven methods for horizontal well placement: directional drilling, trenching, boring, and backhoe excavation. These placements and subsequent improvements have made the use of horizontal wells an attractive option with many benefits over the use of vertical wells (Plummer et al. 1997). One horizontal well can replace several vertical wells, leading to a reduction in operating expense that can help offset the additional placement costs. Because of the continuous nature of a horizontal well, the injected air is able to interact with the subsurface contaminant over a larger surface area, accelerating removal. The continuous nature of a horizontal well also allows for easier interception of a migrating contaminant plume (Mast and Koerner, 1996). Additionally, the flexibility of directional drilling allows for the placement of injection wells in locations that may be difficult or impossible with the use of vertical wells, especially in cases of surface or subsurface obstructions caused by roads, buildings, or utilities.

Despite the possible advantages that the use of horizontal wells offers, horizontal wells do have drawbacks that must be dealt with during design and operation (Mast and Koerner, 1996). The placement of horizontal wells becomes impractical with increasing depth, especially when techniques other than directional drillings are used. Their use may become cost-prohibitive when placement depths greater than 15 ft are required. Therefore, when contamination is detected at great depths, vertical wells should be used. In a horizontal well, it is often hard to provide for even air injection and flow over the length of a well, leading to uneven air coverage within the subsurface. Even though horizontal wells may provide a large area of coverage, the use of a vertical well in lower permeability soils provides a sizeable zone of treatment, making the use of a horizontal well unnecessary. Wilson et al. (1994b) analyzed the performance of horizontal versus vertical wells using a computer model and found that vertical wells actually performed better because the groundwater circulation path that a horizontal well created spread the contaminant out too far to be remediated efficiently.

To analyze the performance difference between horizontal and vertical wells, Plummer et al. (1997) performed laboratory tests in both saturated beach sand and glass beads to analyze the air flow created by both types of wells. Their apparatus consisted of a two-dimensional Lexan tank topped by a manifold/flowmeter system designed to measure regional effluent gas flow rates. They found that under the same air injection pressure, a horizontal well allowed for one and a half to two times higher air flow than a vertical well. Additionally, more groundwater was displaced during the use of a horizontal well, indicating the existence of more extensive air flow.

Past work in the field using horizontal wells has demonstrated successful implementation. Ghandehari et al. (1994) reported on the use of a horizontal well at a remedial site in Charlotte, North Carolina. The site, consisting of clayey silts with a shallow water table (7 to 15 ft below ground surface), was contaminated with BTEX constituents and methyl tertiary butyl ether (MTBE). A 2-in. diameter PVC vapor extraction measuring 230 ft in length was placed 4 to 5 ft below ground surface. A 2-in. diameter PVC injection well measuring 310 ft in length was placed 40 ft below grade. The injection well was screened over 130 ft of

its length. The radius of influence was measured in a variety of ways, including soil air pressure, dissolved oxygen, groundwater mounding, and native bacterial populations, and was found to measure approximately 40 ft. Within one year, BTEX concentrations dropped from 65 to 100 ppb to non-detectable levels. Reductions in MTBE concentrations were also seen.

14.7.2 Sparge Trenches

Sparge trenches or curtains may be used instead of horizontal and/or vertical wells. Trenches and curtains are especially useful when the contaminant plume is migrating in a region of high groundwater flow or where the prevention of off-site migration is of the utmost concern. The typical volume flux into a trench is on the order of 0.015 to 0.5 m³/m² per day (Pankow et al., 1993). After digging, the trench is shored up with sheet piling and may be left open or backfilled with soil. The backfill must be of equal or higher permeability in order to prevent the flowing groundwater from circumventing the treatment zone. Additionally, cutoff wells are often used to ensure the groundwater is flowing in the proper direction. Along the wall, 5 to 20% needs to consist of gates to prevent groundwater from building up, which could possibly cause flow in undesired directions (Pankow et al., 1993). Larger dimensions actually do not lead to greater efficiency, only to increased volumes of water to be treated. The parameters that have the greatest effect on efficiency include the Henry's constant(s) of the contaminant(s) and the gas sparge rate (Pankow et al., 1993).

Marley et al. (1994) reported on the typical field application of a trench. The site consisted of clayey silts with an unconfined, perched aquifer with the water table residing 2 ft below ground surface. The trench used was built in 40-ft segments for a total of 360 ft. The trench measured 1 meter in width, and air was injected at a rate of 0.005 m³/s per meter of trench. Volatile VOCs were emitted directly to the atmosphere. Bittner and Hoffman (1996) reported on the use of an aeration curtain at a site in Utah. The subsurface was contaminated with trichloroethylene with concentrations as high as 1,000 µg/L. Air was injected into the trench 21.7 L/s. Approximately 90% of the initial concentrations were removed within 48 hours of operations, and 99% was removed within 8 days.

14.7.3 Biosparging

Biosparging is an alternative to the use of an air sparging/soil vapor extraction system. During the implementation of biosparging, lower injection flow rates are used to prevent the buildup of excess soil gas pressure. The injected air increases the concentration of dissolved oxygen within the groundwater, stimulating aerobic biodegradation of subsurface by the native microbial population. To prevent the buildup of pressure, flow rates of approximately 1 scfm are used (Nyer and Suthersan, 1993). The viability of biosparging is dependent on subsurface conditions; in addition to the introduction of dissolved oxygen to serve as an electron acceptor, a suitable microbial population as well as essential microbial nutrients must be present in sufficient quantity. When the subsurface conditions are favorable, the contamination may be degraded and mineralized into harmless by-products such as carbon dioxide and water, depending on the specific metabolic reaction occurring.

14.7.4 Related/Complementary Technologies

Air sparging may be combined with other technologies such as pump and treat and bioremediation to address certain site-specific conditions, including the type and distribution of the contaminants as well as site hydrogeologic conditions.

14.8 SUMMARY

Air sparging has proven to be an effective technique for the remediation of VOC-contaminated saturated soils and groundwater. Due to its use of readily available equipment and its overall remedial efficiency, air sparging can offer significant cost savings compared to other remedial technologies. The operator-controlled parameters allow for flexible implementation, and an air sparging system may be combined with a soil vapor extraction system or used for biosparging. To ensure efficient performance, a detailed geologic and hydrogeologic characterization must be performed before system implementation. The site characterization will also provide important information regarding the relative contribution of critical mass transfer, transport, and transformation parameters that occur during the use of air sparging.

Several air sparging systems have been designed, operated, and monitored in the field under different contaminant and hydrogeologic conditions. The performance data from these sites have helped in understanding the advantages and limitations of the technique as well as provided a database to use as guidance for future air sparging systems. Air sparging is being used increasingly because of its low cost and significantly reduced treatment time compared to the very high cost and long treatment time associated with conventional remediation technologies. In general, acceptance of the air sparging technology by the regulatory agencies has been high.

Air sparging is still a relatively new technology, and much more needs to be learned about how it works and how it can best be applied. Most of the laboratory work performed has included simplifications that may restrict the applicability of the results to field situations. Often, field studies have not been monitored and documented enough to understand the processes of air sparging. Many models developed to date include unrealistic simplifications or have not been validated with laboratory or field investigations. Therefore, in order to advance the state of the art regarding air sparging, controlled laboratory tests studying a wide range of operator-controlled and site-specific parameters and a careful assessment of field systems need to be performed to develop realistic mathematical models that will adequately describe and predict behavior during the implementation of air sparging.

14.9 REFERENCES

- Adams, J. A., and K. R. Reddy. 1999. "Laboratory Study of Air Sparging of TCE-Contaminated Saturated Soils and Groundwater," *Ground Water Monitoring and Remediation*, vol. 19, no. 3, pp. 182-190.
- Adams, J. A., and K. R. Reddy. 2000. "Removal of Dissolved and Free-Phase Benzene Pools from Groundwater Using In Situ Air Sparging," *Journal of Environmental Engineering*, vol. 125, no. 8, pp. 697-707.
- Ahlfeld, D. P., A. Dahmani, and W. Ji. 1994a. "A Conceptual Model of Field Behavior of Air Sparging and its Implications for Application," *Ground Water Monitoring Review*, vol. 14, no. 4, pp. 132-139.
- Ahlfeld, D., A. Dahmani, G. Hoag, M. Farrell, and W. Ji. 1994b. "Field Measurements of Air Sparging in a Connecticut Site: Results and Comments," in *Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*, Houston, pp. 175-190.
- Ardito, C. P., and J. F. Billings. 1990. "Alternative Remediation Strategies: The Subsurface Volatilization and Ventilation System," in *Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*, pp. 281-296.
- Baker, D. M., and C. H. Benson. 1996. "Review of Factors Affecting In-Situ Air Sparging," in *Proceedings of 1996 ASCE Specialty Conference*, Washington, DC, pp. 292-310.
- Basinet, R., and J. Wollenberg. 1997. "Petroleum Hydrocarbon Clean-up Using Soil Vapor Extraction and Air Sparging Via Horizontal Wells at a Commercial Navy Site in San Diego, CA," in *Proceedings*

- of the *Fourth International Symposium on In-Situ and On-Site Bioremediation*, Batelle Press, Columbus, OH, vol. 1, pp. 205–208.
- Bass, D. H., and R. A. Brown. 1997. "Performance of Air Sparging Systems—A Review of Case Studies," in *Proceedings of the Fourth International Symposium on In-Situ and On-Site Bioremediation*, Batelle Press, Columbus, OH, vol. 1, pp. 117–122.
- Bausmith, D. S., D. J. Campbell, and R. D. Vidic. 1996. "In Situ Air Stripping: Using Air Sparging and Other In Situ Methods Calls for Critical Judgments," *Water Environment and Technology*, February, pp. 45–51.
- Bear, J. 1972. *Dynamics of Fluids in Porous Media*, American Elsevier, New York.
- Bittner, P. R., and D. A. Hoffman. 1996. "Non-aqueous Phase Liquids (NAPLs) in Subsurface Environment: Assessment and Remediation," in *Proceedings of 1996 ASCE Specialty Conference*, Washington, DC, pp. 776–787.
- Braida, W. J., and S. K. Ong. 1997. "Factors Affecting Air Sparging Remediation Technologies," in *Proceedings of the Fourth International Symposium on In-Situ and On-Site Bioremediation*, Batelle Press, Columbus, OH, vol. 1, pp. 187–192.
- Brown, R., C. Herman, and E. Henry. 1991. "The Use of Aeration in Environmental Cleanups," in *Proceedings of the Haztech International Pittsburgh Waste Conference*, Pittsburgh, pp. 2A.1–2A.42.
- Bruell, C. J., M. C. Marley, and H. H. Hopkins. 1997. "American Petroleum Institute Air Sparging Database," *Journal of Soil Contamination*, vol. 6, no. 2, pp. 169–185.
- Brusseau, M. L. 1992. "Rate-Limited Mass Transfer and Transport of Organic Solutes in Porous Media that Contain Immobile Immiscible Organic Liquid," *Water Resources Research*, vol. 28, no. 1, pp. 33–45.
- Burchfield, S. D., and D. J. Wilson. 1993. "Groundwater Cleanup by In-situ Air Sparging. IV. Removal of Dense Non aqueous Phase Liquid by Sparging Pipes," *Separation Science and Technology*, vol. 28, nos. 17/18, pp. 2529–2551.
- Chapelle, F., P. Bradley, D. Lovley, and D. Vroblesky. 1996. "Measuring Rates of Biodegradation in a Contaminated Aquifer Using Field and Laboratory Methods," *Ground Water*, vol. 34, no. 4, pp. 691–698.
- Chiang, C. Y., J. P. Salanitro, E. Y. Chai, J. D. Colthart, and C. L. Klein. 1989. "Aerobic Biodegradation of Benzene, Toluene, and Xylene in a Sandy Aquifer Data Analysis and Computer Modeling," *Ground Water*, vol. 27, no. 6, pp. 823–834.
- Covell, J. R., and M. H. Thomas. 1997. "Air Sparge and Bioremediation Demonstration at an Underground Coal Gasification Site," in *Proceedings of the Fourth International Symposium on In-Situ and On-Site Bioremediation*, Batelle Press, Columbus, OH, vol. 1, pp. 173–178.
- Crocetti, C. A., C. L. Head, and A. J. Ricciardelli. 1992. "Aeration-Enhanced Bioremediation of Oil-Contaminated Soils: A Laboratory Treatment Study," in *Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*, NGWA, Dublin, OH, pp. 427–440.
- Damera, R., M. R. Hill, D. Murali, and R. McDermott. 1997. "Rapid Clean-up of a Multiple Fuel Spill," in *Proceedings of the Fourth International Symposium on In-Situ and On-Site Bioremediation*, Batelle Press, Columbus, OH, vol. 1, pp. 109–204.
- Davis, E. L. 1997. *How Heat Can Enhance In-Situ Soil and Aquifer Remediation: Important Chemical Properties and Guidance on Choosing the Appropriate Technique*, EPA/540/S-97/502. Washington, DC.
- Deaver, G. H., and R. J. Tworkowski. 1994. "Application of Air Sparging to 1,1,1-trichloroethane Contaminated Soil—A Success Story," in *Proceedings of 1st International Congress on Environmental Geotechnics*, BiTech, Richmond, VA, pp. 201–208.
- Falta, R. W., K. Pruess, I. Javandel, and P. A. Witherspoon. 1992. "Numerical Modeling of Steam Injection for the Removal of Non aqueous Phase Liquids from the Subsurface I. Numerical Formulation," *Water Resources Research*, vol. 28, no. 2, pp. 433–449.
- Fetter, C. W. 1999. *Contaminant Hydrology*, Prentice-Hall, Upper Saddle River, NJ.
- Fry, V. A., J. D. Istok, L. Semprini, K. T. O'Reilly, and T. E. Buscheck. 1995. "Retardation of Dissolved Oxygen due to a Trapped Gas Phase in Porous Media," *Ground Water*, vol. 33, no. 3, pp. 391–398.
- Geller, J. T., and J. R. Hunt. 1993. "Mass Transfer from Non aqueous Phase Organic Liquids in Water-saturated Porous Media," *Water Resources Research*, vol. 29, no. 4, pp. 833–845.

- Ghandehari, M., B. Kelly, A. Holt, S. Hines, and J. Doesburg. 1994. "In Situ Remediation of Groundwater using Horizontal Well Air Injection," in *Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*, NGWA, Dublin, OH, pp. 221-235.
- Goldflam, R., M. Van Benthem, and A. G. Finci. 1997. "Use of Borehole Radar for Air Sparging Operations Monitoring," in *Proceedings of the Fourth International Symposium on In-Situ and On-Site Bioremediation*, Batelle Press, Columbus, OH, vol. 1, pp. 259-264.
- Gomez-Lahoz, C., J. M. Rodriguez-Maroto, and D. J. Wilson. 1994. Groundwater Cleanup by In-Situ Air Sparging. VII. Volatile Organic Compounds Concentration Rebound Caused by Diffusion after Shutdown," *Separation Science and Technology*, vol. 29, no. 12, pp. 1509-1528.
- Gordon, M. J. 1998. "Case History of a Large-Scale Air Sparging Soil Vapor Extraction System for Remediation of Chlorinated Volatile Organic Compounds in Ground Water," *Groundwater Monitoring and Remediation*, vol. 18, no. 2, pp. 137-149.
- Hayden, N. J., T. C. Voice, M. D. Annable, and R. B. Wallace. 1994. "Change in Gasoline Constituent Mass Transfer during Soil Venting," *Journal of Environmental Engineering*, vol. 120, no. 6, pp. 1598-1615.
- Hein, G. L., N. J. Hutzler, and J. S. Gierke. 1994. "Quantification of the Mechanisms Controlling the Removal Rate of Volatile Contaminants by Air Sparging," in *Proceedings of the National Conference on Environmental Engineering*, Boulder, CO, pp. 556-563.
- Hoepfel, R. E., R. E. Hincee, and M. F. Arthur. 1991. "Bioventing Soils Contaminated with Petroleum Hydrocarbons," *Journal of Industrial Microbiology*, vol. 8, pp. 141-146.
- Hunt, J. R., N. Sitar, and K. S. Udell. 1988a. "Nonaqueous Phase Liquid Transport and Cleanup 1. Analysis of Mechanisms," *Water Resources Research*, vol. 24, no. 8, pp. 1247-1258.
- Hunt, J. R., N. Sitar, and K. S. Udell. 1988b. "Nonaqueous Phase Liquid Transport and Cleanup 2. Experimental Studies," *Water Resources Research*, vol. 24, no. 8, pp. 1259-1269.
- Javanmardian, M., and V. J. Kremesec. 1995. *Air Sparging/Biosparging Pilot Test and Design Guidance*, Amoco Corporation, July.
- Ji, W., A. Dahmani, D. P. Ahlfeld, J. D. Lin, and E. Hill, III. 1993. "Laboratory Study of Air Sparging: Air Flow Visualization," *Ground Water Monitoring Review*, vol. 13, no. 4, pp. 115-126.
- Jin, Y., T. Streck, and W. A. Jury. 1994. "Transport and Biodegradation of Toluene in Unsaturated Soil," *Journal of Contaminant Hydrology*, vol. 17, pp. 111-127.
- Johnson, P. C. 1998. "Assessment of the Contributions of Volatilization and Biodegradation to In-situ Air Sparging Performance," *Environmental Science Technology*, vol. 32, no. 2, pp. 276-281.
- Johnson, P. C., C. C. Stanley, M. W. Kemblowski, D. L. Byers, and J. D. Colthart, 1990. "A Practical Approach to the Design, Operation, and Monitoring of In situ Soil-venting Systems," *Ground Water Monitoring Review*, vol. 10, no. 2, pp. 159-178.
- Johnson, R. L., P. C. Johnson, D. B. McWhorter, R. E. Hincee, and I. Goodman. 1993. "An Overview of In Situ Air Sparging," *Ground Water Monitoring Review*, vol. 13, no. 4.
- Johnson, P. C., R. L. Johnson, C. Neaville, E. E. Hansen, S. M. Stearns, and I. J. Dortch. 1995. "An Assessment of Conventional In Situ Air Sparging Tests," *Ground Water*, vol. 35, no. 5, pp. 765-774.
- Joiner, D. P., and T. L. O'Keefe. 1996. "Direct Push Technology in Air Sparging Pilot Studies for Groundwater Remediation," *Iron and Steel Engineer*, vol. 73, no. 12, pp. 53-58.
- Karickhoff, S. W., D. S. Brown, and T. A. Scott. 1979. "Sorption of Hydrophobic Pollutants on Natural Sediments," *Water Resources*, vol. 13, pp. 241-248.
- Klemm, D. E., S. Lummus, and S. Eaton. 1997. "Air Sparging in Various Lithologies: 3 Case Studies," in *Proceedings of the Fourth International Symposium on In-Situ and On-Site Bioremediation*, Batelle Press, Columbus, OH, vol. 1, pp. 193-198.
- Kraus, J., S. Nelson, P. Boersma, and A. Maciey. 1997. "Comparison of Pre/post-sparging VOC Concentrations in Soil and Groundwater," in *Proceedings of the Fourth International Symposium on In-Situ and On-Site Bioremediation*, Batelle Press, Columbus, OH, vol. 1, pp. 123-128.
- Leonard, W. C., and R. A. Brown. 1992. "Air Sparging: An Optimal Solution," in *Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*, Houston.
- Leonard, W. C., S. R. Thompson, and R. A. Brown. 1994. "Air Sparging Reduces Solvent Contamination," *Environmental Solutions*, June, pp. 69-71.

- Loden, M. E. 1992. *A Technology Assessment of Soil Vapor Extraction and Air Sparging*, EPA/600/R-92/173, Cincinnati, OH.
- Lombard, K. H., J. W. Borthen, and T. C. Hazen. 1994. "The Design and Management of System Components for In situ Methanotrophic Bioremediation of Chlorinated Hydrocarbons at the Savannah River Site," in *Air Sparging for Site Remediation*, ed. R. H. Hinchee, Lewis, Ann Arbor, MI, pp. 81-96.
- Lundegard, P. D., and G. Andersen. 1996. "Multiphase Numerical Simulation of Air Sparging Performance," *Ground Water*, vol. 34, no. 3, pp. 451-460.
- Lundegard, P. D., and D. LaBrecque. 1995. "Air Sparging in a Sandy Aquifer (Florence, Oregon, U.S.A.): Actual and Apparent Radius of Influence," *Journal of Contaminant Hydrology*, vol. 19, pp. 1-27.
- Malone, D. R., C. M. Kao, and R. C. Borden. 1993. "Dissolution and Bioremediation of Nonaqueous Phase Hydrocarbons: Model Development and Laboratory Evaluation," *Water Resources Research*, vol. 29, no. 7, pp. 2203-2213.
- Marley, M. C. 1992. "Air Sparging in Conjunction with Soil Vapor Extraction for Source Removal at VOC Spill Sites," in *Proceedings of 5th Annual Conference on Hydrocarbon-Contaminated Soils*, Lewis, Chelsea, MI, pp. 579-590.
- Marley, M. C., D. J. Hazebrouck, and M. T. Walsh. 1992a. "The Application of In situ Air Sparging as an Innovative Soils and Ground Water Remediation Technology," *Ground Water Monitoring Review*, vol. 12, no. 2, pp. 137-145.
- Marley, M. C., F. Li, and S. Magee. 1992b. "The Application of a 3-D Model in the Design of Air Sparging Systems," in *Proceedings of Focus on Eastern Ground Water Issues*, pp. 377-392.
- Marley, M., F. Li, E. Droste, and R. Cody. 1994. "The Design of an In-situ Sparging Trench," in *Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*, NGWA, Dublin, OH, pp. 579-590.
- Mast, V., and K. Koerner. 1996. "Horizontal vs. Vertical Wells: Which to Use and When," *Soil and Groundwater Cleanup*, April, pp. 10-16.
- McCray, J. E., and R. W. Falta. 1997. "Numerical Simulation of Air Sparging for Remediation of NAPL Contamination," *Ground Water*, vol. 35, no. 1, pp. 99-100.
- McKay, D. J., and L. J. Acomb. 1996. "Neutron Moisture Probe Measurements of Fluid Displacement during In-situ Air Sparging," *Ground Water Monitoring Review*, vol. 16, no. 4, pp. 86-94.
- Middleton, A. C., A. W. Lawrence, D. J. Morgan, M. G. Less, and T. D. Hayes. 1995. "Biosparging Strategies for Contaminant and Remediation of Organic Contaminant Groundwater Plumes at E & P Sites Using Either Vertical or Horizontal Sparge Wells," Institute of Gas Technology, Des Plaines, IL.
- Miller, C. T., M. M. Poirier-McNeill, and A. S. Mayer. 1990. "Dissolution of Trapped Nonaqueous Phase Liquids: Mass Transfer Characteristics," *Water Resources Research*, vol. 26, no. 11, pp. 2783-2796.
- Miller, R. R. 1996. *Air Sparging*, Groundwater Remediation Technologies Analysis Center, Pittsburgh.
- Nelson, C. H., and R. A. Brown. 1994. "Adapting Ozonation for Soil and Groundwater Cleanup," *Environmental Engineering*, November.
- Nyer, E. K., and S. S. Suthersan. 1993. "Air Sparging: Savior of Ground Water Remediation or Just Blowing Bubbles in the Bathtub?" *Ground Water Monitoring Review*, vol. 13, no. 4, pp. 87-91.
- Panday, S., Y. S. Wu, P. S. Huyakorn, and E. P. Springer. 1994. "A Three-dimensional Multiphase Flow Model for Assessing NAPL Contamination in Porous and Fractured Media, 2. Porous Medium Simulation Examples," *Journal of Contaminant Hydrology*, vol. 16, pp. 131-156.
- Pankow, J. F., R. L. Johnson, and J. A. Cherry. 1993. "Air Sparging in Gate Wells in Cutoff Wells and Trenches for Control of Plumes of Volatile Organic Compounds (VOCs)," *Ground Water*, vol. 31, no. 4, pp. 654-663.
- Patterson, B. M., F. Pribac, C. Barber, G. B. Davis, and R. Gibbs. 1993. "Biodegradation and Retardation of PCE and BTEX Compounds in Aquifer Material from Western Australia Using Large-Scale Columns," *Journal of Contaminant Hydrology*, vol. 14, pp. 261-278.
- Pepper, D. W., and D. E. Stephenson. 1995. "An Adaptive Finite-Element Model for Calculating Sub-surface Transport of Contaminant," *Ground Water*, vol. 33, no. 3, pp. 486-496.
- Perlinger, J. A., and S. J. Eisenreich. 1991. "Sorption of Alkyl Benzene to Mineral Oxides," in *Organic Substances and Sediments in Waters*, ed. R. A. Baker, Lewis, Chelsea, MI, pp. 49-78.

- Petersen, L. W., D. E. Rolston, P. Moldrup, and T. Yamaguchi. 1994. "Volatile Organic Vapor Diffusion and Adsorption in Soils," *Journal of Environmental Quality*, vol. 23, pp. 799–805.
- Peterson, J. W., P. A. Lepczyk, and K. L. Lake. 1999. "Effect of Sediment Size on Area of Influence During Groundwater Remediation by Air Sparging: A Laboratory Approach," *Environmental Geology*, vol. 38, pp. 1–6.
- Plummer, C. R., J. D. Nelson, and G. S. Zumwalt. 1997. "Horizontal and Vertical Well Comparison for In-situ Air Sparging," *Ground Water Monitoring Review*, vol. 17, no. 1, pp. 91–96.
- Powers, S. E., C. O. Loureiro, L. M. Abriola, and W. J. Weber, Jr. 1991. "Theoretical Study of the Significance of Nonequilibrium Dissolution of Nonaqueous Phase Liquids in Subsurface Systems," *Water Resources Research*, vol. 27, no. 4, pp. 463–477.
- Rabideau, A. J., and J. M. Blyden. 1998. "Analytical Model for Contaminant Mass Removal by Air Sparging," *Ground Water Monitoring and Remediation*, vol. 18, no. 4, pp. 120–130.
- Reddy, K. R., and J. A. Adams. 1999. "System Effects on Benzene Removal from Saturated Soils and Groundwater Using Air Sparging," *Journal of Environmental Engineering*, vol. 124, no. 3, pp. 288–299.
- Reddy, K. R., and J. A. Adams. 2000. "Effects of Groundwater Flow on Remediation of Dissolved Phase VOC Contamination Using Air Sparging," *Journal of Hazardous Materials*, vol. 72, nos. 2/3, pp. 147–165.
- Reddy, K. R., and J. Zhou. 1996. "Finite Element Modeling of In-situ Air Sparging for Groundwater Remediation," in *Proceedings of the 2nd International Congress on Environmental Geotechnics*, Balkema, Rotterdam, pp. 299–304.
- Reddy, K. R., S. Kosgi, and J. Zhou. 1995a. "A Review of In-situ Air Sparging for the Remediation of VOC-Contaminated Saturated Soils and Groundwater," *Hazardous Waste and Hazardous Materials*, vol. 12, no. 2, pp. 97–118.
- Reddy, K. R., J. Zhou, and S. Kosgi. 1995b. "New Model to Simulate Air Sparging for Groundwater Remediation," in *Proceedings of 5th WERC Development Conference*, Las Cruces, NM, pp. 299–308.
- Reddy, K. R., R. Semer, and J. A. Adams. 1999. "Air Flow Optimization and Surfactant Enhancement to Remediate Toluene-Contaminated Saturated Soils Using Air Sparging," *Environmental Management & Health*, vol. 10, no. 1, pp. 52–63.
- Roberts, L. A., and D. J. Wilson. 1993. "Groundwater Cleanup by In-situ Air Sparging. III. Modeling of Dense Nonaqueous Phase Liquid Droplet Removal," *Separation Science and Technology*, vol. 28, no. 5, pp. 1127–1143.
- Rutherford, K. W., and P. C. Johnson. 1996. "Effects of Process Control Changes on Aquifer Oxygenation Rates during In-situ Air Sparging in Homogenous Aquifers," *Ground Water Monitoring Review*, vol. 16, no. 4, pp. 132–141.
- Schima, S., D. J. LaBrecque, and P. D. Lundegard. 1996. "Monitoring Air Sparging Using Resistivity Tomography," *Ground Water Monitoring Review*, vol. 16, no. 2, pp. 131–138.
- Sellers, K. L., and R. P. Schreiber. 1992. "Air Sparging Model for Predicting Groundwater Cleanup Rate," in *Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*, Houston.
- Semer, R., and K. R. Reddy. 1997. "Mechanisms Controlling Toluene Removal from Saturated Soils during In Situ Air Sparging," *Journal of Hazardous Materials*, vol. 57, nos. 1–3, pp. 209–230.
- Semer, R., J. A. Adams, and K. R. Reddy. 1996. "Surfactant Enhanced Air Sparging for Groundwater Remediation: Preliminary Results," in *Proceedings of the Fourth Great Lakes Geotechnical/Geoenvironmental Conference on In-Situ Remediation of Contaminated Sites*, Chicago, pp. 197–213.
- Semer, R., J. A. Adams, and K. R. Reddy. 1998. "An Experimental Investigation of Air Flow Patterns in Saturated Soils during Air Sparging," *Geotechnical and Geological Engineering Journal*, vol. 16, no. 1, pp. 59–75.
- Szatkowski, A., P. T. Imhoff, and C. T. Miller. 1995. "Development of a Correlation for Aqueous-Vapor Phase Mass Transfer in Porous Media," *Journal of Contaminant Hydrology*, vol. 18, no. 85–106.
- Thierrin, J., G. B. Davis, and C. Barber. 1995. "A Ground-water Tracer Test with Deuterated Compounds for Monitoring In Situ Biodegradation and Retardation of Aromatic Hydrocarbons," *Ground Water*, vol. 33, no. 3, pp. 469–475.
- Unger, A. J. A., E. A. Sudicky, and P. A. Forsyth. 1995. "Mechanisms Controlling Vacuum Extraction Coupled with Air Sparging for Remediation of Heterogeneous Formations Contaminated by Dense Nonaqueous Phase Liquids," *Water Resources Research*, vol. 31, no. 8, pp. 1913–1925.

- Van Dijke, M. I. J., and S. E. A. T. M. van der Zee. 1998. "Modeling of Air Sparging in a Layered Soil: Numerical and Analytical Approximations," *Journal of Geophysical Research*, vol. 34, no. 3, pp. 341-353.
- Voudrias, E. A., and M. F. Yeh. 1994. "Dissolution of a Toluene Pool under Constant and Variable Hydraulic Gradients with Implications for Aquifer Remediation," *Ground Water*, vol. 32, no. 2, pp. 305-311.
- Wehrle, K. 1990. "In-situ Cleaning of CHC Contaminated Sites: Model-Scale Experiments Using the Air Injection (In-Situ Air Stripping) Method in Granular Soils," in *Proceedings of Contaminated Soil*, ed. F. Arendt, M. Hinsenveld, and W. J. van den Brink, Kluwer, Dordrecht, pp. 1061-1062.
- Widdowson, M. A., and C. M. Aelion. 1991. "Application of a Numerical Model to the Performance and Analysis of an In Situ Bioremediation Project," *In Situ Bioremediation*, ed. R. E. Hinchee and R. F. Olfenbuttel, Butterworth-Heinemann, Boston, pp. 227-244.
- Wilson, D. J. 1992. "Groundwater Cleanup by In-situ Air Sparging. II. Modeling of Dissolved Volatile Organic Compound Removal," *Separation Science and Technology*, vol. 27, no. 13, pp. 1675-1690.
- Wilson, D. J., and R. D. Norris. 1997. "Sparging and Biosparging: Insights through Mathematical Modeling," in *Proceedings of the Fourth International Symposium on In-Situ and On-Site Bioremediation*, Batelle Press, Columbus, OH, vol. 1, pp. 147-152.
- Wilson, D. J., C. Gomez-Lahoz, and J. M. Rodriguez-Maroto. 1994a. "Groundwater Cleanup by In-situ Air Sparging. VIII. Effect of Air Channeling on Dissolved Volatile Organic Compounds Removal Efficiency," *Separation Science and Technology*, vol. 29, no. 18, pp. 2387-2418.
- Wilson, D. J., J. M. Rodriguez-Maroto, and C. Gomez-Lahoz. 1994b. "Groundwater Cleanup by In-situ Air Sparging. VI. A Solution/Distributed Diffusion Model for Nonaqueous Phase Liquid Removal," *Separation Science and Technology*, vol. 29, no. 11, pp. 1401-1432.
- Yang, X., L. E. Erickson, and L. T. Fan. 1995. "A Study of the Dissolution Rate-Limited Bioremediation of Soils Contaminated by Residual Hydrocarbons," *Journal of Hazardous Materials*, vol. 41, pp. 299-313.
- Yaniga, P. M., and W. Smith. 1984. *Aquifer Restoration via Accelerated In-Situ Biodegradation of Organic Contaminants*, Ground Water Technology, Chadds Ford, PA.
- Zumwalt, G. S., A. P. Krishna, and J. D. Nelson. 1997. "Air Distribution within a Sparging Cone of Influence," in *Proceedings of the Fourth International Symposium on In-Situ and On-Site Bioremediation*, Batelle Press, Columbus, OH, vol. 1, pp. 141-146.