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The use and evaluation of cleaner wicks to accelerate in situ bioremediation of organically contaminated groundwater and soil

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ABSTRACT

THE USE AND EVALUATION OF CLEANER WICKS TO ACCELERATE IN SITU BIOREMEDIATION OF ORGANICALLY CONTAMINATED GROUND WATER AND SOIL

by
Brian Michael Sielski

The adaptation of Cleaner Wicks to accelerate in situ bioremediation of organically contaminated ground water and soil can be accomplished by making minor modifications to the Cleaner Wick design.

Once these changes in the Cleaner Wick design have been made the two primary ingredients necessary for aerobic microorganisms, nutrients and oxygen, can be delivered via the Cleaner Wick to the subsurface environment both above and below the water table to stimulate microbial growth and activity. Therefore, the microbial population will be able to biodegrade the target contaminants, rendering them harmless products such as carbon dioxide and water.

An adequate understanding of the microbiological environment is necessary to achieve any type of success in bioremediation. Other factors that must be considered are subsurface temperature, pH, redox potential, site characterization, and possible inhibitory (i.e., competitive) microorganisms present.

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by
Brian Michael Sielski

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THE USE AND EVALUATION OF CLEANER WICKS TO ACCELERATE IN SITU BIOREMEDIATION OF ORGANICALLY CONTAMINATED GROUNDWATER AND SOIL

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For you, Grandpa
(Wasyl Goik, 1897 - 1992)

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

THE CLEANER WICK

1.1 Introduction

The hazardous contamination of groundwater and soil presents a major environmental challenge in its treatment. Treatment technologies for groundwater include conventional pump and treat (e.g., carbon adsorption, chemical precipitation, ion exchange, reverse osmosis), in situ (e.g., air purging, dewatering followed by vacuum extraction, chemical oxidation), and enhanced extraction (e.g., surfactant flushing, steam extraction) technologies. In situ and ex situ technologies for the treatment of soil include destruction (e.g., incineration, dechlorination, vitrification), separation (e.g., thermal desorption, soil washing, vacuum extraction), and immobilization (vitrification, solidification/stabilization).

An option to the treatment technologies listed above is the Cleaner Wick which is an effective and economical alternative in removing organic and inorganic contaminants from groundwater and soils by air stripping (discussed in this chapter) and in the emerging technology of bioremediation (chapter 2).

1.2 Design and Operation

1.2.1 Design

Over the past twenty years prefabricated vertical drain wicks have been used to achieve soil consolidation. Installed into the soil at depths of up to 100 ft, the plastic geotextile wicks serve as a vertical water migration pathways in

poor draining soils.

This existing technology was modified to adsorb groundwater contaminants. The modified wick uses the outer filter fabric and inner plastic core of any conventional drain wick (e.g., Alidrain, Hitec 8 Flodrain, Ameridrain, Flowdrain, etc.). A hollow tube is placed inside the core, or the core can be manufactured with a hollow tube in it as an integral part of the core (Fig.1). The core voids are either filled with a sorbent material (e.g., activated carbon, fly ash, ion resins, etc.) in granular form or left empty to allow oxygen circulation through the wick (1). The latter method, which acts as an in situ air stripping system for volatile organic compounds (VOCs) is preferred due to the difficulty of removing the sorbent material from an installed core after the sorbent material has been spent.

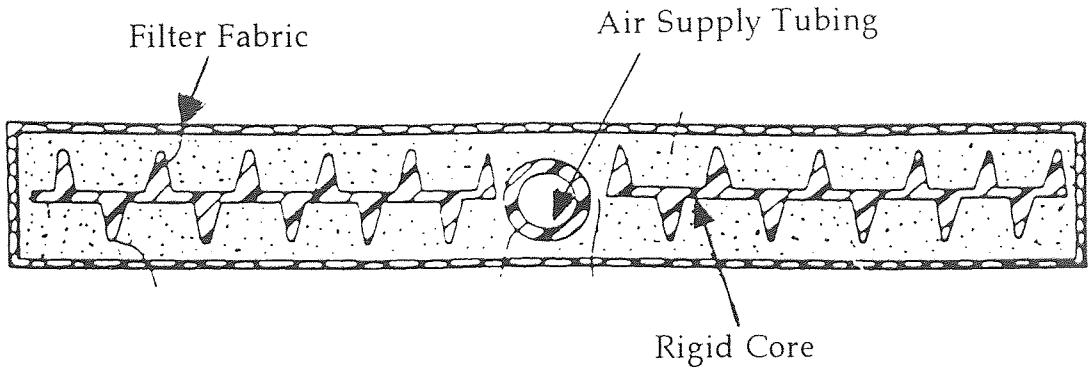

Figure 1 Cross sectional view of Cleaner Wick

The outer filter fabric of the Cleaner Wick in Figure 1 is liquid pervious so that contaminated groundwater can enter the wick. The filter fabric may have reinforcing strands added to the material to facilitate its removal (pulling out) of the wick from the soil at the conclusion of the contaminant removal operation. The rigid core within the outer fabric retains the shape

and prevents the collapse of the outer fabric. The core is made of rigid plastic formed as a planar sheet having numerous studs extending out from the core so as to retain the outer fabric in a rectangular or oval cross-sectional configuration. A studded core also has an added benefit in that the studs act as an agitator, keeping the air bubbles broken up as they rise. This allows a greater air to water surface area, thereby increasing the efficiency of the volatile stripping.

Within the rigid core center is a hollow tube that extends out the upper end, while the lower end of the hollow tube is spaced upwardly from the lower end (2).

1.2.2 Operation

The Cleaner Wick System is operated using an air lift principle to circulate the contaminated water up through the wick core. Compressed air supplied down the core tube exits at the bottom end of the tube, which is located inside the filter fabric. The air comes in contact with the contaminated groundwater which has flowed inside and filled the wick voids. The wick now acts as an air stripper, volatilizing the organics, thereby forcing them up and out (Fig. 2) of the wick. The treated groundwater circulates and exits at the top of the groundwater table. The VOCs discharged at the ground surface can be adsorbed by activated carbon filters located at the top of the wick, or collected for later surface treatment (1,3).

Conventional drain wicks can be installed to depths of 100 ft., and cleaner wicks can therefore go just as deep, but typically will be installed to depths of 40 ft. or less. Lateral spacing of individual cleaner wicks at a particular site will depend on soil permeability and would range from 3 ft. to 10 ft. centers, installed in a checkerboard pattern over the contaminated groundwater plume (3).

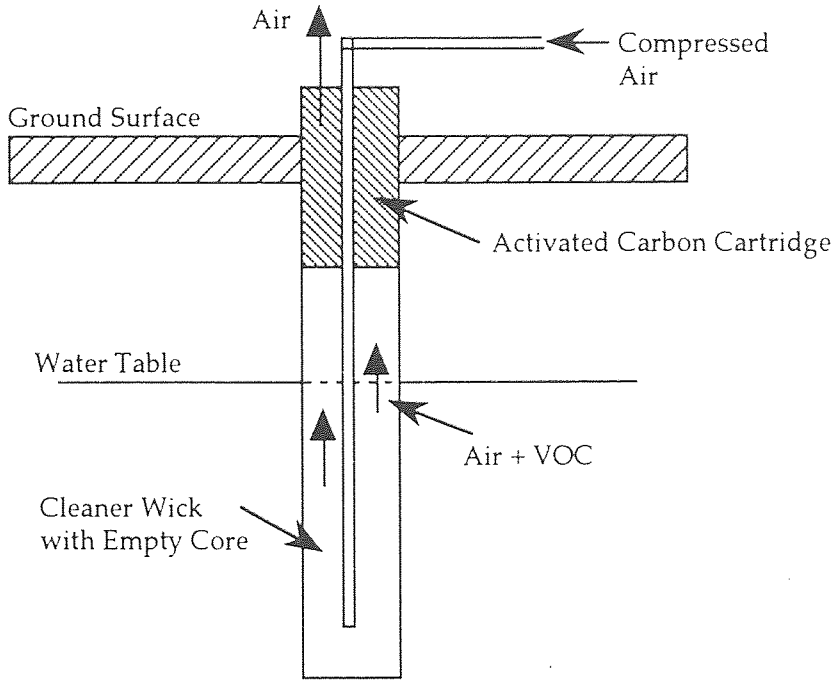

Figure 2 Cleaner Wick with activated carbon cartridge and empty core for removal of VOCs.

1.3 Air Stripping Cleaner Wick Model

The air stripping model (for VOCs) is based on the installation of 40 feet deep wicks placed 5 feet apart in 4 rows as shown in Figure 3.

The rectilinear flowing water is affected by the air lift discharge of the cleaner wicks, drawing the water toward the wick. As the water flows through the filter fabric into the core the compressed air rising through the core causes diffused aeration. The VOCs, which are now in the gas phase, rise to the surface. The now treated water flows up the core above the water table, out of the filter fabric, and back into the groundwater (see Fig. 2).

Using a model (Appendix A), it was hypothesized that 1000 ppm of trichloroethylene (TCE) in contaminated groundwater would be reduced to 126 ppm after the groundwater flows through the first row of wicks, 16 ppm after the second row, 2 ppm after the third row, and less than 1 ppm after the

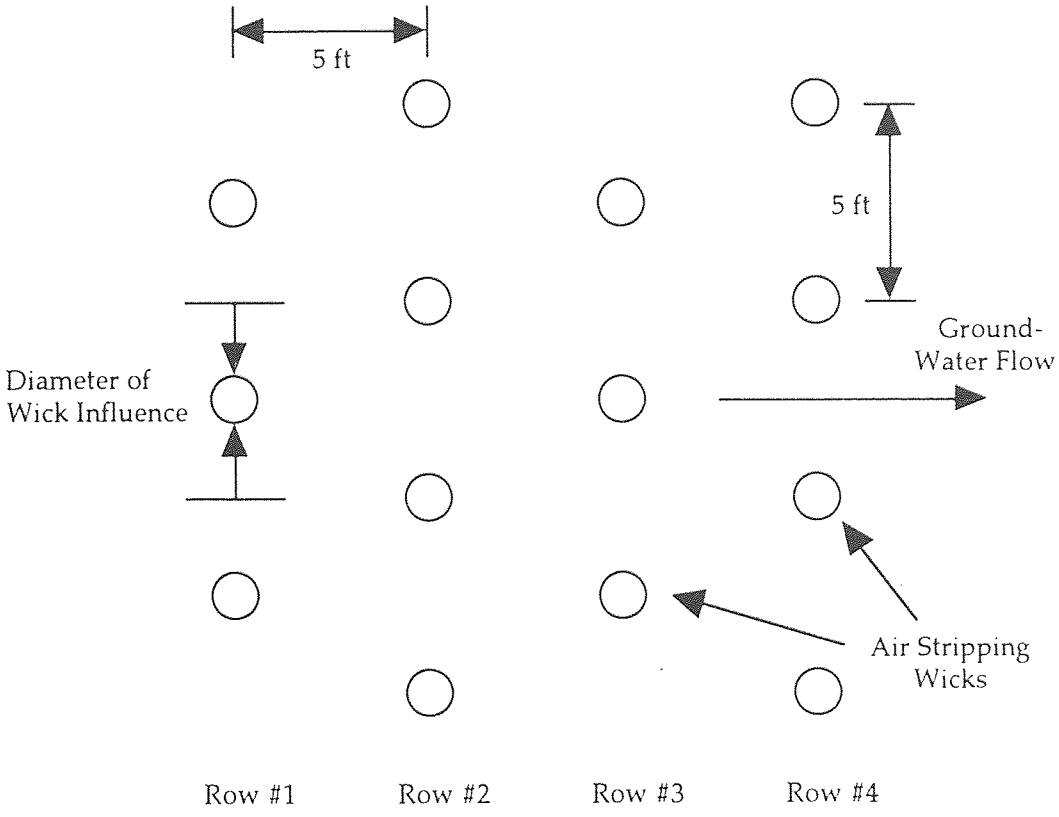

Figure 3 Plan view of air stripping Cleaner Wick system for treatment of VOCs (4).

fourth row. Carbon tetrachloride of 1000 ppm in contaminated ground water would be reduced to 31 ppm after the groundwater flows through the first row of wicks, and less than 1 ppm after just the second row of cleaner wicks (3). The results above are achieved only if the groundwater flowing through the treatment air is in fact captured by the air stripping cleaner wicks.

1.4 Installation and Cost

The Cleaner Wick may be installed by employing either vibratory or static pile driving methods. The vibratory method is used in the event that the subgrade were a stiffer soil, while the static method is used when the subgrade does not pose any difficulties while installing, such as fine sand.

The Cleaner Wick is enclosed in a tubular steel mandrel of small cross-sectional area. A small steel anchor plate is attached to the Cleaner Wick at the bottom of the mandrel. The mandrel is then driven into the soil either with a static or vibratory rig. When the depth is reached, the mandrel is extracted. The anchor plate retains the wick in the soil. When the mandrel is fully extracted, the Cleaner Wick is cut off, a new anchor plate is installed, and the process begins again.

A cost feasibility for various sites was previously investigated (5). For a 100 by 100 Class D Hazardous Site with wicks 5 ft. on center, 40 ft. deep, totaling 441 wicks (17,640 total linear feet of wick installed), it was estimated that the wick material costs would amount to $0.65/ft., and wick installation would amount to $0.80/ft. For a higher class hazardous site, the cost per foot could be 1.5 to 2 times as much. Also, the cost per foot will decrease with an increase in the amount wick to be installed, as well as the cost increasing if a smaller amount of wick is installed.

1.5 Summary

Further testing is required to determine the operational parameters, i.e., air flow, on/off cycle, etc., for given groundwater contaminants and soil conditions.

The Cleaner Wick has two advantages over existing technology. First, in a non flow situation and the soil has a low permeability (i.e., find sand), the Cleaner Wick provides a less expensive alternative to treatment over existing pump and treat technology. In such soils, the circle of influence around each pump is small, therefore requiring many pumps to treat the groundwater, increasing the cost of treatment proportionally. Inexpensive Cleaner Wicks can be used to treat the same area instead.

The second advantage, again over pump and treat, is that when using

Cleaner Wicks to treat groundwater, there is no draw down in the water table. In some situations, it may be advantageous to treat the groundwater without creating a draw down. Treating the leachate adjacent to a landfill using pump and treat could create a large diameter cone of depression in the ground water table and therefore increase the rate of flow out of the landfill. By using Cleaner Wicks with a relatively small diameter of influence, the rate of flow from the landfill will remain constant.

CHAPTER 2

BIOREMEDIATION AND THE CLEANER WICK

2.1 Introduction

The most promising new technology for solving hazardous waste problems involves the use of bioremediation. Bioremediation is a process that relies on microorganisms (i.e., bacteria or fungi) to transform hazardous chemicals into less toxic or nontoxic compounds. In situ bioremediation usually consists of modifying the environment of an aquifer by the addition of oxygen and other inorganic nutrients in order to enhance the activity of native microbial populations in degrading contaminants. The microorganisms have the ability to metabolize many different types of compounds in different media (i.e., contaminated aquifers or soils) by using the microorganisms in the treatment system that breaks down the pollutants.

Bioremediation has many advantages over current technologies. The first is that it is an attractive option due to it being a natural process and the residues from the biological processes (such as carbon dioxide and water) are usually geochemically cycled in the environment as harmless products. The bioremediation process is carefully monitored to ensure that the product or process is not more toxic than the original pollutant. Another advantage of biological treatment, especially in situ treatment of soils and ground water, is that it is less expensive and less disruptive compared to existing options, such as excavation followed by incineration and/or landfilling. Finally, instead of transferring contaminants from one medium to another, biological treatment can degrade the target chemical or pollutant (6).

Bioremediation consists of utilizing techniques to enhance the development of large populations of microorganisms which will be able to transform the pollutants of interest. It should also ensure that these large populations of microorganisms are in contact with the pollutants. It is important to realize though that in almost all cases bioremediation depends on communities of microorganism species, rather than just one or two species.

2.1.1 Microbial Metabolism

Microbial metabolism refers to all the chemical processes taking place within a cell; the ability to organize molecules and systematic sequences, and the ability of the microorganism to replicate itself. The two major factors in microbial metabolism are: 1) the general nutritional requirements of the microorganisms encountered in the soil environment, and 2) the nature of microbial metabolism based on the need for molecular oxygen.

2.1.1.1 Nutritional Requirements for Microbial Growth. In order to reproduce and continue to function properly, an organism must have a source of energy, carbon for the synthesis of new cellular material, and inorganic nutrients (7).

Microorganisms obtain energy from light or chemical reactions. In the soil environment, biogeochemical cycling plays an important role in the metabolism of microorganisms. Biogeochemical cycling is discussed later in this chapter.

Carbon sources for cell synthesis are either carbon dioxide or organic carbon. Microorganisms that use carbon dioxide are called autotrophs while those that use organic carbon are called heterotrophs.

The principal inorganic nutrients that are required by microorganisms for

cell synthesis and growth are nitrogen, sulfur, potassium, magnesium, calcium, iron, sodium, and chlorine. Minor nutrients of importance are zinc, manganese, molybdenum, selenium, cobalt, copper, nickel, vanadium, and tungsten (7, 8).

2.1.1.2 Types of Microbial Metabolism. Significant attention is to be made to chemoheterotrophic microorganisms due to their ubiquity in the soil environment. Chemoheterotrophs usually obtain their energy from the oxidation of organic compounds, as opposed to phototrophic organisms which use light as an energy source.

Chemoheterotrophic microorganisms are grouped according to their metabolic type and molecular oxygen requirement. Microorganisms are said to have respiratory metabolism if they generate energy by enzyme-mediated electron transport from an electron donor to an external electron acceptor. If the process does not involve an external electron acceptor, it is said to be fermentative metabolism.

If molecular oxygen is used as the electron acceptor in respiratory metabolism, the process is known as aerobic respiration. The microorganisms that use aerobic respiration are said to be obligately aerobic if they can only exist if molecular oxygen is present in the environment. In contrast, anoxic organisms can use other oxidized inorganic compounds as electron acceptors, such as nitrate and nitrite.

The microorganisms that use fermentative metabolism are said to be obligately anaerobic if they can only exist in an environment that is devoid of oxygen. If the microorganism can grow with or without molecular oxygen, they are said to be facultative anaerobes. Facultative anaerobes can shift from fermentative to respirative metabolism depending on the presence of

molecular oxygen. Aerotolerant anaerobes are strictly fermentative, but can exist in the presence of molecular oxygen (7).

2.1.2 Biogeochemical Cycling

Microorganisms are usually only considered as laboratory entities or in their relationships to humans and disease. But it is important to consider microorganisms in soil, water and other environments and to consider how these microorganisms act to chemically change their environments. The term environment refers to everything surrounding a living organism: the chemical, physical, and biological factors and forces that act on a living organism. Microorganisms are part of organismal communities called ecosystems interacting with its surroundings, and sometimes greatly modifying the characteristics of the ecosystem.

Elements tend to circulate in characteristic paths or cycles between the biotic and abiotic portions of the environment. The term "biogeochemical cycling" describes the conversion and movement of materials by biochemical forces through the environment. An element undergoes changes in oxidation state as it moves through the ecosystem. The energy that drives the biogeochemical cycle enters ecosystems mainly in the form of radiant energy of the sun and is used by phototrophic organisms to synthesize new organic matter. The organic matter not only contains carbon, but also nitrogen, sulfur, phosphorus, iron, and many other elements (9). The biogeochemical cycles involve physical and chemical transformations of materials, which in turn leads to the spatial transportation of materials (e.g., from water to soil to the atmosphere). Since all living organisms participate in one way or another in the biogeochemical cycling of materials, it is apparent that microorganisms play a major role, because microorganisms are abundant, have diverse metabolic capabilities, and high enzymatic activity.

The cycling rates of elements vary greatly. The major elemental components of living organisms, the organic matter, (i.e., carbon, oxygen, hydrogen, nitrogen, sulfur, and phosphorus) are cycled the most intensively. The minor elements (i.e., magnesium, potassium, sodium, and the halogens) and the trace elements (i.e., aluminum, boron, colbolt, chromium, etc.) are cycled less intensively. Iron, manganese, calcium, and silicon are exceptions to this (10). Important biogeochemical cycles are discussed in Appendix B.

2.1.3 Aerobic and Anaerobic Bioremediation

Most subsurface bioremediation processes rely on aerobic (i.e., molecular oxygen-containing) microbial metabolism. The oxygen that serves as a terminal electron acceptor for the microorganisms and can be supplied as compressed air, liquid oxygen, hydrogen peroxide, or ozone. Without an adequate supply of oxygen, the aerobic microorganisms can not exist. Oxidized inorganic compounds such as nitrate, sulfate, and carbon dioxide can function as electron acceptors for some respiratory organisms in the absence of molecular oxygen (Table 1).

Table 1 Electron acceptors in microbial processes (13).

Environment	Electron Acceptor	Process	Order of Preference
Aerobic	O_2	Aerobic metabolism	1
	NO_3^-	Denitrification	2
Anaerobic	SO_4^{2-}	Sulfate reduction	3
	CO_2	Methanogenesis	4

Microorganisms that generate energy by fermentation (i.e., not involving the participation of an external electron acceptor) and that can exist only in an environment that is devoid of oxygen are anaerobic. Anaerobic

bioremediation remains relatively unexplored to date. This may be attributed to the difficulties associated with research on anaerobic microorganisms or the misconceptions about the numbers and activities of microorganisms in the subsurface. Many questions about anaerobic metabolism remain, including: 1) What types of contaminants are susceptible to anaerobic decay and which are not? 2) What structural features of the contaminants favor its bioconversion under anaerobic conditions? 3) Are pollutants mineralized or only partially transformed? 4) What rates of transformation can be expected? 5) How do such transformations impact predictions of the transport and fate characteristics of contaminants? (11)

2.1.4 Microorganisms and Bioremediation

The microorganisms that carry out bioremediation are mostly bacteria, although research has shown in some cases fungi may be used, especially with halogenated compounds (12). The bioremediation of pollutants requires large populations of the microorganisms to be in contact with the pollutant. To do this efficiently, necessary provisions for microbial growth and reproduction must be maintained. These critical factors are listed in Table 2.

Most microorganisms that are active in the bioremediation process must live in water. If the environment is too dry, or even if the water in the microorganism's environment contains high amounts of solutes, the microorganism cannot maintain the proper amount of water internally due to the fact that they are sensitive to the osmotic potential of their environment. Microbial activity subjected to sudden changes in osmotic potential result in lysis (disintegration of cell walls) (9). If the change is gradual though, the microorganism can usually adapt to the environmental change.

Soil water also serves as the transport medium through which many nutrients reach the microbial cell. It affects soil aeration status, amount of soluble materials, and the pH of the soil.

Table 2 Critical environmental factors for microbial activity (13).

Environmental Factor	Optimum Levels
Available soil water	25-85% of water holding capacity; -0.01 MPa
Oxygen	Aerobic metabolism: Greater than 0.2 mg/l DO, minimum air-filled pore space of 10% by volume; Anaerobic metabolism: O_2 concentrations less than 1% by volume
Redox potential	Aerobes: greater than 50 millivolts Anaerobes: less than 50 millivolts
Nutrients	Sufficient nitrogen, phosphorus, and other nutrients so not to limit microbial growth (suggested C:N:P ratio of 120:10:1)
Temperature	0-20 °C (Psychrophiles) 15-45 °C (Mesophiles) >40 °C (Thermophiles)
pH	5.5 - 8.5

Microbial respiration, plant respiration, and other organism respiration all deplete oxygen from the soil environment and enrich it with carbon dioxide. The oxygen from the air diffuses into the soil, and the gases in the soil environment diffuse into the air. Due to the depletion of oxygen in the soil from the various respirations, the oxygen concentration may be much less than in air while carbon dioxide concentrations may be many times that of air (13). Oxygen is important because a large portion of the microbial population depends on it as the terminal acceptor in metabolism. If oxygen is

facing 15

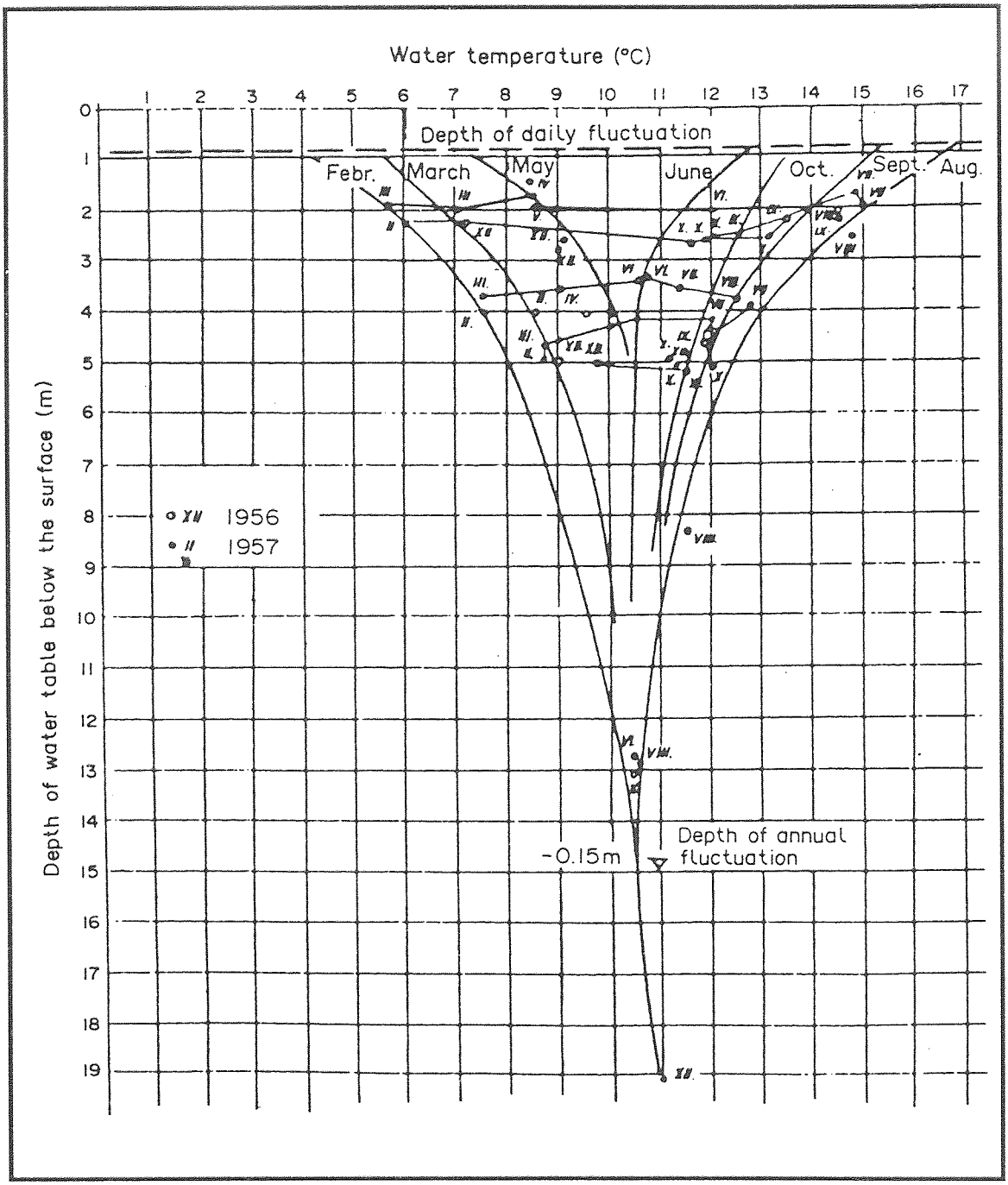

Figure 4 Development of the temperature of ground water at the water table as a function of the depth of the latter. Kovács, G. and Associates: Subterranean Hydrogeology, Water Resources Publications, Littleton, Col. 1981. p. 421 (14).

consumed faster than it is replaced by diffusion from the atmosphere, the soil may become anaerobic. When oxygen is no longer present in sufficient quantities to act as an electron acceptor, there is a marked changed in the soil microbial population. Facultative anaerobic microorganisms, those that can switch between oxygen and nitrate or sulfate as electron acceptors freely, and obligate anaerobic microorganisms, those that can exist in an environment devoid of oxygen, become the dominant populations (7).

Redox potential is a measurement of the oxidation-reduction potential of the soil. It provides a measurement of the electron density of the system. As the target pollutants are reduced, oxygen is depleted in the soil environment and then other substances are used as electron acceptors. There is an increase in electron density, increasing the negative potential. Redox potential is measured as E_h, expressed in millivolts.

In addition to oxygen, other nutrients may limit microbial metabolism and growth. Inorganic nutrients such as nitrogen and phosphorus may be limiting the ratios of carbon to nitrogen or carbon to phosphorus. If the pollutant is high in carbonaceous materials, the soil may become depleted of available nitrogen and phosphorus required for microbial growth. Fertilization with nitrogen and phosphorus may be required at some point during the bioremediation of a site.

Temperature is known to have a profound effect on the microbial metabolism of subsurface pollutants. The temperature of the upper 10 m of the subsurface varies seasonally while that between 9 to 18 m is approximately equal to the mean air temperature of the particular region (between 3 and 25 °C in the U.S.) (14, 15). For example, figure 4 shows the development of temperature of groundwater at the water table as a function of the depth of the latter for a temperate climate. Biodegradation has been shown to essentially stop at a temperature of 0 °C (16). Psychrophiles'

optimal temperature for growth is 15 °C, and that for mesophiles is even higher at 40 °C. Bioremediation of the subsurface pollutants may be limited in winter months in the northern, colder climate of the U.S where an average temperature of 5 °C can be expected, does not even approach the psychrophiles' optimal growth temperature. By controlling the temperature of the ground water, it will be possible to sustain microbial activity year round and biodegrade the pollutants.

Soil pH also affects the activity and growth of microorganisms in the soil. Each microorganism has a well defined optimum pH range where growth is possible. Natural environments usually have a pH range of 5 to 9, and most organisms within this range are also the most common. The few organisms that are able to live at a pH of 2 or lower are called acidophiles. The few that can live in a pH of 10-11 are called alkalinophilic. Fungi are generally more acid-tolerant than bacteria, and grow optimally at a pH of 5 or lower (16).

2.2 Bioremediation with the Cleaner Wick

The Cleaner Wicks discussed in Chapter 1 can easily be modified to provide the oxygen and nutrients (carbon, nitrogen, and phosphorus) needed by microorganisms. Both air (oxygen) and nutrients can be pumped down the Cleaner Wick into the subsurface soil environment. Nutrients in aqueous solution could be pumped and regulated in order to maintain an adequate ratio of C:N:P. Temperature can also be regulated at 15 to 45 °C by pumping the aqueous solution or water into the subsurface at moderate temperatures.

2.2.1 Site Characterization

A thorough site investigation is necessary to determine the constraints or opportunities to use the Cleaner Wick. An adequate site characterization should include surface soil characteristics, subsurface aquifer characteristics,

subsurface hydrogeology, types of contaminants, and the extent of contamination.

Determining the extent of contamination at a site provides important information in order to select the Cleaner Wick as a viable bioremediation option. For example, if the contamination is widespread and in low concentration, the Cleaner Wick might be of use. On the other hand, a high concentration of contaminants in the vadose zone might require soil excavation instead in order to halt the contaminants infiltrating into the ground water.

Subsurface aquifer characteristics help determine if the specific site environment is satisfactory for the biodegradative process Aquifer characteristics also provide information required for hydraulic design and operation of the system. Table 3 provides important site and soil characteristics important to in situ treatment.

2.2.2 Microbiological Characterization

The microbiological characterization of a contaminated site is required in order to determine that a viable community of microorganisms is present which can degrade the contaminants of concern. Approaches for characterizing the kinds, numbers, and metabolic activities include 1) determination of the form arrangement and biomass of microorganisms in soil, 2) isolation and characterization of subgroups and species, and 3) detection and measurement of metabolic processes (10). Many methods are available including direct light and epifluorescence microscopy, viable counts(i.e., plate counts, most probable number counts, and enrichment culture procedures), and biochemical indicators of metabolic activity such as ATP, GTP, phospholipid, and muramic acid (17). Nonuniform distribution

Table 3 Site and soil characteristics important for in situ treatment (16).

Site location/topography and slope
Soil type, and extent
Soil profile properties boundary characteristics depth texture* amount and type of coarse fragments structure* color degree of mottling bulk density* clay content type of clay cation exchange capacity* organic matter content* pH* Eh* aeration status*
Hydraulic properties and conditions soil water characteristic curve field capacity/permanent wilting point water holding capacity* permeability* (under saturated and a range of unsaturated conditions) infiltration rates* depth to impermeable layer or bedrock depth to groundwater*, including seasonal variations flooding frequency runoff potential*
Geological and hydrogeological factors subsurface geological features groundwater flow patterns and characteristics
Meteorological and climatological data wind velocity and direction temperature precipitation water budget
* Factors that may be managed to enhance soil treatment

of microorganisms in the subsurface indicate micro-environments which is conducive to microbial growth.

2.2.3 Basic Design and Operation

There are no major differences in the design and operation of the Cleaner Wick used for bioremediation below the water table and the Cleaner Wick used for air stripping discussed in Chapter 1. The only changes in operation are the addition of nutrients, as well as a rigorous soil monitoring program.

A nutrient feeding system must be installed with the Cleaner Wick. It has the ability to regulate the amounts of carbon, nitrogen, phosphorus, and oxygen, independent of each other. As stated earlier, microbial metabolism and growth requires adequate amounts of nutrients in a suitable form, appropriate concentrations, and proper ratios. For example, if the contaminants in the subsurface are high in carbonaceous materials but low in nitrogen and phosphorus, then the subsurface can become depleted of the available nitrogen and phosphorus required for microbial metabolism.

By monitoring this at the site, the Cleaner Wick can be used to deliver the required amounts of nitrogen and phosphorus (C:N:P ratio of 120:10:1 on a weight basis). If later it was determined that too much of one nutrient (or not enough) was added, the Cleaner Wick can regulate the addition of the other nutrients needed to obtain the proper C:N:P ratio.

Along with monitoring the nutritional requirements, the oxygen profile must be monitored as well. The removal of oxygen from the soil environment due to microbial respiration, plant root respiration, and respiration from other soil organisms enriches it with carbon dioxide. The oxygen is consumed faster than it can be replaced by diffusion between the atmosphere and soil surface, leading to an anaerobic environment.

By using the Cleaner Wick system to inject oxygen back into the

subsurface environment, an aerobic condition will exist, allowing the aerobic microorganisms to use the oxygen as the terminal electron acceptor. Figure 5 represents a schematic of Cleaner Wick operation for contaminants below the water table. In this operation oxygen is supplied directly to the Cleaner Wick, which will infiltrate to the surrounding subsurface environment and also establish a water flow circulation pattern near the wick. Note that due to the continued air flow up the Cleaner Wick, it is likely that the operation will still remove VOCs (if present) by air stripping. Due to this duality, the activated carbon cartridge is still necessary.

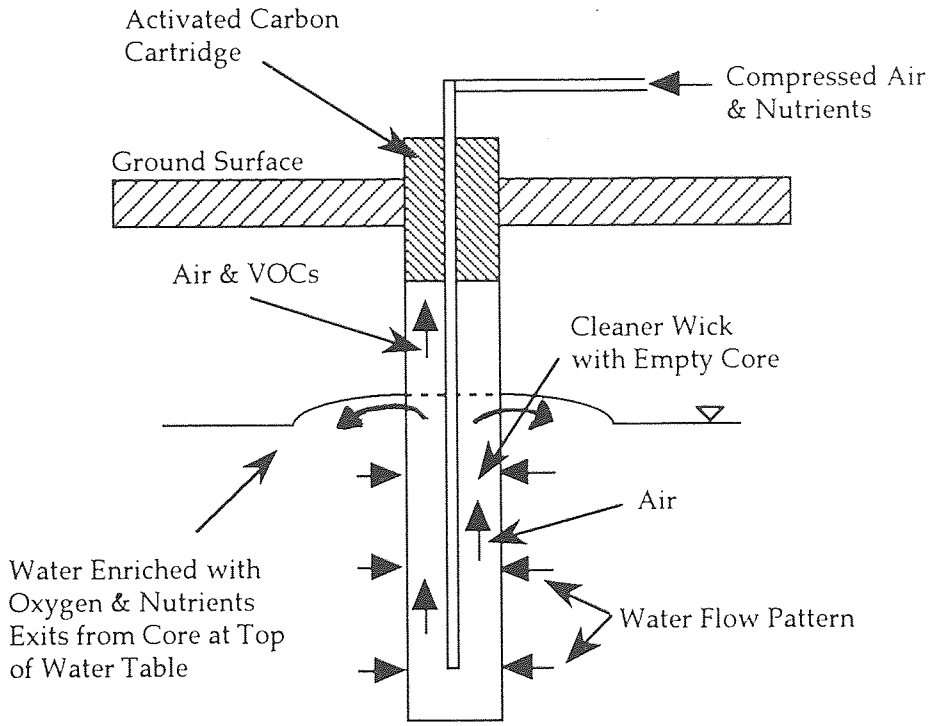

Figure 5 Cleaner Wick with empty core for delivery of nutrients and oxygen to the subsurface environment below the water table.

2.2.3.1 Design and Operation for Contaminants above the Water Table. If the target population of microorganisms is above the water table, oxygen delivered by the Cleaner Wick should again be provided by air (since air is less viscous than water). The only change in the Cleaner Wick is the activated carbon filter is replaced with a seal or cap. This will provide the necessary buildup of pressure to force the oxygen into the surrounding soil environment. Nutrients will be provided in an aqueous solution which will fill the wick voids, and then infiltrate into the surrounding soil. Figure 6 shows a schematic for operation above the water table.

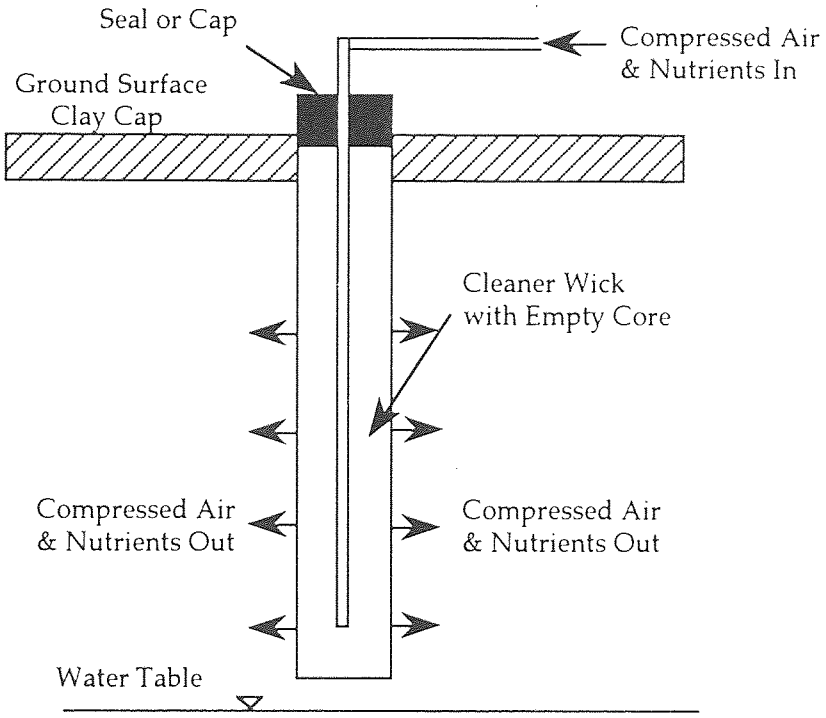

Figure 6 Capped Cleaner Wick with empty core for delivery of nutrients and oxygen to the subsurface environment above the water table.

High oxygen concentrations in air provide a large driving force for diffusions of oxygen into less permeable areas within a soil formation. Oxygen diffuses through air 10,000 times faster than it does through water (10). Air has greater potential than water for delivering oxygen to soil on a weight-to-weight and volume-to-volume basis. An important parameter then is conductivity of air which can be determined if the intrinsic permeability of the soil is known. The common relationship between hydraulic conductivity and intrinsic permeability is (18):

$$K = K_i(\gamma/\mu)$$

or

$$K = K_i(\rho g/\mu)$$

where K is the hydraulic conductivity, K_i is the intrinsic permeability, g is the acceleration of gravity, ρ is the density, and γ and μ are properties of the fluid. Therefore, the intrinsic permeability of the soil is:

$$K_{i(soil)} = K_{water} (\mu/\gamma)_{water}$$

then the conductivity of air is:

$$K_{air} = K_{i(soil)} (\gamma/\mu)_{air}$$

For example, fine to coarse gravels have a hydraulic conductivity of

approximately K = 10^4 m/day. At 15 °C, water has a viscosity of 1.139×10^{-3} Pa•s and specific weight of 9.798 kN/m^3. A conversion factor of 1 day = 86,400 seconds is used also.

$$K_{i(soil)} = 10^4 \, (1.139 \times 10^{-3}) \, / \, 9798$$

$$K_{i(soil)} = 1.35 \times 10^{-8} \, m^2$$

then, the conductivity of air in fine to coarse gravel is calculated. The viscosity of air is 1.789×10^{-5} Pa•s and has at specific weight of 12.01 N/m^3 at 15 °C.

$$K_{air} = 1.35 \times 10^{-8} \, (12.01) \, / \, 1.789 \times 10^{-5}$$

$$K_{air} = 780 \text{ m/day}$$

Table 4 and Figure 7 lists conductivities of air for other soils based on the above calculation. In Table 4, the hydraulic conductivities used for the different soil types represent average values due to the variance of hydraulic conductivities within particular soil types. Examination of the data obtained in Table 4 suggests that a formula for direct calculation to obtain the conductivity of air can be found, if the hydraulic conductivity at a site is known. This equation can be expressed as:

$$K_{air} = K_{water} \, (\mu/\gamma)_{water} \, (\gamma/\mu)_{air}$$

or

$$K_{air} = K_{water} \, C$$

where C is a constant equal to 7.804×10^{-2} at 15°C.

Figure 7 was developed to show the range of values for conductivity of air. Typical hydraulic conductivity values were obtained from reference 18, page 75.

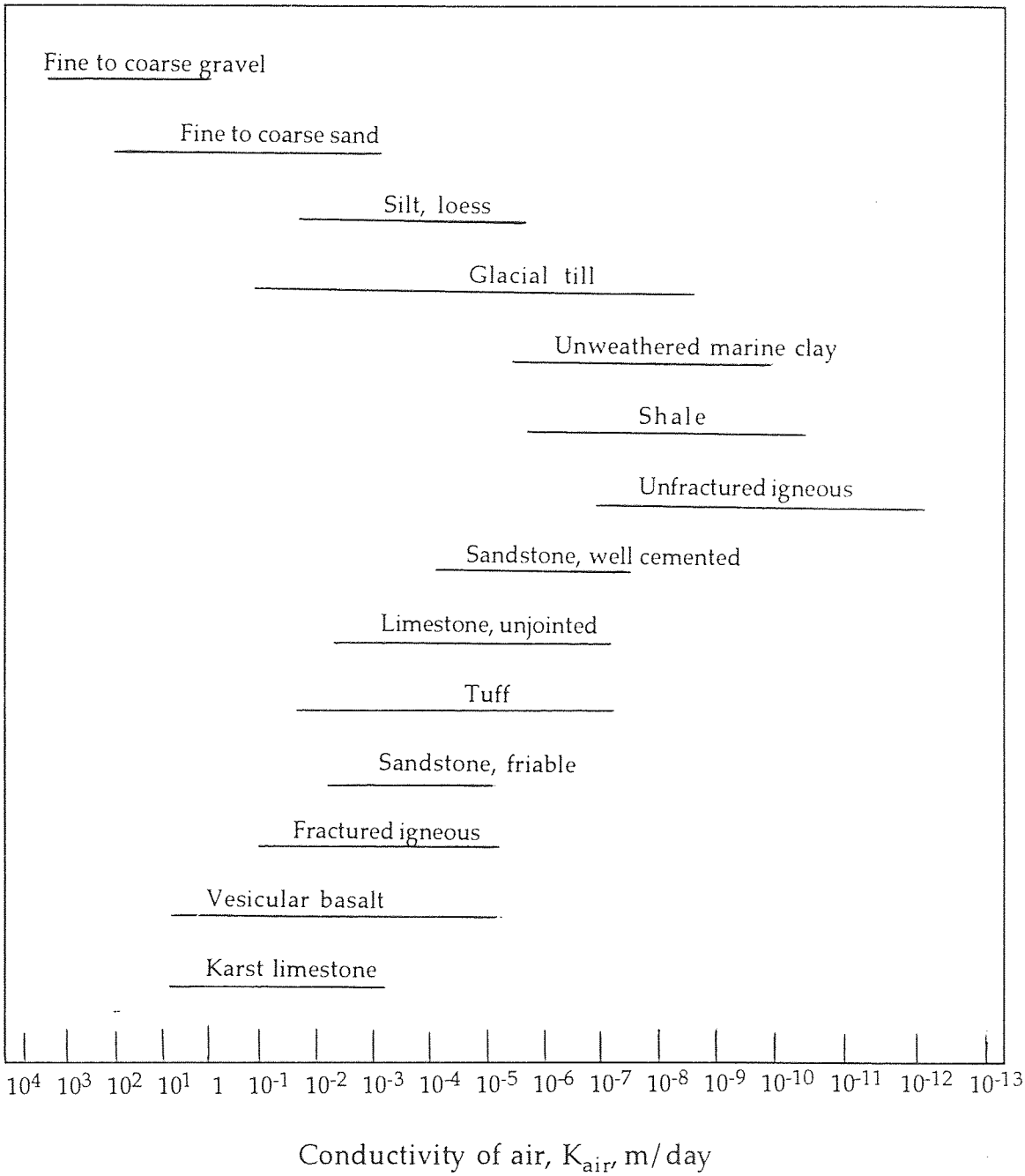

Figure 7 Typical K_{air} values for some different soil types.

Table 4 Average K_{air} values for various soil types.

Soil Type	Average Hydraulic Conductivity, K_{water}, m/day	Average Intrinsic Permeability of Soil, $K_{i(soil)}$, m^2	Conductivity of Air, K_{air}, m/day
Fine to coarse gravel	10^4	1.35×10^{-8}	7.80×10^2
Fine to coarse sand	10^1	1.35×10^{-11}	7.80×10^{-1}
silt, loess	10^{-2}	1.35×10^{-14}	7.80×10^{-4}
Glacial till	10^{-3}	1.35×10^{-15}	7.80×10^{-5}
Unweathered marine clay	10^{-5}	1.35×10^{-17}	7.80×10^{-7}
Shale	10^{-6}	1.35×10^{-18}	7.80×10^{-8}
Unfractured igneous and metamorphic rocks	10^{-7}	1.35×10^{-19}	7.80×10^{-9}
Sandstone, well cemented, unjointed	10^{-4}	1.35×10^{-16}	7.80×10^{-6}
Limestone, unjointed crystalline	10^{-3}	1.35×10^{-15}	7.80×10^{-5}
Tuff	10^{-2}	1.35×10^{-14}	7.80×10^{-4}
Sandstone, friable	10^{-1}	1.35×10^{-13}	7.80×10^{-3}
Fractured igneous and metamorphic rocks	10^{-1}	1.35×10^{-13}	7.80×10^{-3}
Vesicular basalt	1	1.35×10^{-12}	7.80×10^{-2}
Karst limestone	10^1	1.35×10^{-11}	7.80×10^{-1}

2.2.3.2 Alternate Oxygen Sources. Depending upon the temperature of the ground water, between 8 to 12 mg/l of dissolved oxygen is achieved by air sparging (19). A higher concentration of 40 to 50 mg/l of dissolved oxygen can be achieved by using pure oxygen. The disadvantage of using pure oxygen is that it is expensive, extremely explosive if handled carelessly, and may bubble out of solution before the microorganisms can use it as a terminal electron acceptor (20). Other sources of oxygen are hydrogen peroxide and ozone.

Hydrogen peroxide decomposes to form two molecules of water and one

molecule of oxygen, represented by the net result reaction (21),

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

the most important aspect being the liberation of one mole of oxygen. Stoichiometry shows that by weight, 47.1% of the decomposed hydrogen peroxide is pure oxygen.

The hydrogen peroxide may also be toxic to the microorganisms that are indigenous to the soil environment. Before using hydrogen peroxide, the tolerance range of the microorganisms should be determined by laboratory experiment.

2.2.3.3 Estimate of Oxygen Demand Case Study. As far as is known, in situ bioremediation has only been applied to hydrocarbon contaminated sites. The contamination at the U.S. Coast Guard Air Station at Traverse City, Michigan, was produced by a spill of aviation gasoline. In order to initiate hydrocarbon oxidation, microbial populations utilized oxygen. As a result of the contamination, the subsurface is anaerobic, i.e., very low concentrations of oxygen. Therefore, oxygen must be supplied for in situ bioremediation. Oxygen demand for microbial respiration of total fuel hydrocarbons was estimated assuming the following stoichiometry (22):

$$CH_{2.2} + 1.55O_2 \longrightarrow CO_2 + H_{2.2}O_{1.1}$$

The oxygen demand of alkylbenzene fraction alone was estimated by:

$$CH_{1.1} + 1.28O_2 \longrightarrow CO_2 + 0.55H_2O$$

The theoretical oxygen demand for aviation gasoline is 3.5 mg/mg and for the alkylbenzene fraction is 3.1 mg/mg.

Determining the oxygen demand in a segment of a flow path, the hydrocarbon content (mg hydrocarbon/kg aquifer) is multiplied by the bulk density of the sediment and then divided by the porosity of the aquifer. This determines the quantity of hydrocarbons exposed to each liter of pore water in the segment. This quantity of hydrocarbon is then multiplied by its oxygen demand to estimate the quantity of oxygen that must be delivered to each liter of pore water in the segment (22).

2.2.4 Iron and Iron Bacteria

Iron clogging problems frequently encountered in wells could pose a potential problem to the application of the Cleaner Wicks as well. The determination of Fe concentration becomes extremely important because high concentrations of iron can cause precipitation under aerobic conditions, caused by the infiltration of oxygen during the biorestoration process. Common concentrations of ferrous iron in the U.S. are in the range of 1 to 5 mg/l. Problems exist when iron concentrations range from 2 to 10 mg/l. In ground waters of neutral pH and no oxygen, ferrous ion concentrations can reach up to 50 mg/l (18). The concentrations above where problems occur should be considered guidelines only. Speaking to experts in the field of pumping and air stripping from OHM Remediation Service Corp., it was discussed that higher iron concentrations are more common in south New Jersey, and that remediation techniques used by OHM have little problem with less than 10 mg/l iron concentrations. Anything greater than 10 mg/l to 25 mg/l poses problems.

The maximum rate of iron oxidation will occur when oxygen pumping is stopped and the water closest to the Cleaner Wick gradually becomes

oxygenated after exposure to O_2. When oxygen (or nutrients) are being pumped into the subsurface, the rate of iron oxidation will be at a minimum due to the circulation of ground water nearest to the wick.

The kinetics of ferrous iron, Fe^{+2}, oxidation to amorphous ferric hydroxide, $Fe(OH)_3$, is a three step process, the first of which is the electron transfer of the ferrous ion:

$$4Fe^{+2} + 4H + O_2 \longrightarrow 4Fe^{+3} + 2H_2O$$

This is a rapid reaction at neutral pH, and is immediately followed by the formation of ferric hydroxide

$$Fe^{+3} + 3OH^- \longrightarrow Fe(OH)^0_3 + 3H^+$$

As the oxidation continues, the $Fe(OH)^0_3$ concentration increases. The water becomes supersaturated with respect to amorphous $Fe(OH)_3$ which facilitates its nucleation and growth (23).

$$Fe(OH)^0_3 = Fe(OH)_3 \text{ (am)}$$

It has been shown that the half-time for oxidation can be represented by (23):

$$t_{1/2} = 0.693/(kP_{O2}[OH\text{-}]^2)$$

where k is the rate constant in $M^{-2}\ atm^{-1}\ min^{-1}$, P_{O2} is the partial pressure of oxygen in atmospheres, and $[OH\text{-}]^2$ is the hydroxyl ion concentration. The rate constants determined by different researchers generally are in the range

of 1-6 $\times 10^{13}$ M^{-2} atm^{-2} min^{-2}. Evaluation of available data by Davidson and Seed (1983) suggest an average value of 2 $\times 10^{13}$ M^{-2} atm^{-2} min^{-2} for natural fresh waters at pH 6.5-7.4 (23).

It can easily be seen how ferrous iron oxidation rates increase with the rise in pH. The half-time, $t_{1/2}$, is inversely proportional to $[OH^-]^2$. With an increase in pH, the half-time decreases by two orders of magnitude. The pH is the governing factor, as opposed to O_2 addition, in increasing the oxidation rates.

The radial distance, r, at which oxidation of Fe^{+2} occurs can also be estimated for a Cleaner Wick installed below the water table. It has been shown for wells that for a homogeneous, isotropic aquifer, the radial distance from the well is given by (23):

$$r = (V / \Phi \Pi L)^{1/2}$$

where V is the volume of water pumped from the well, Φ is the sediment porosity, and L is the saturated thickness of the sediment.

This equation can theoretically be applied to the Cleaner Wick to determine the radial distance where iron oxidation starts to occur. It follows that where oxidation occurs, oxygen is present and available to act as an electron acceptor for microorganisms, including iron bacteria, necessary for microbial activity and growth.

It was experimentally determined in sand that the Cleaner Wick lifts a water flow volume equal to approximately 3% of the air flow volume supplied (3). Therefore V for the equation above can be computed by multiplying the calculated rate of flow of water in the Cleaner Wick times the half-time for oxidation.

The half-time for oxidation can either be computed directly from the half-time for oxidation equation mentioned above, or by using Figure 8.

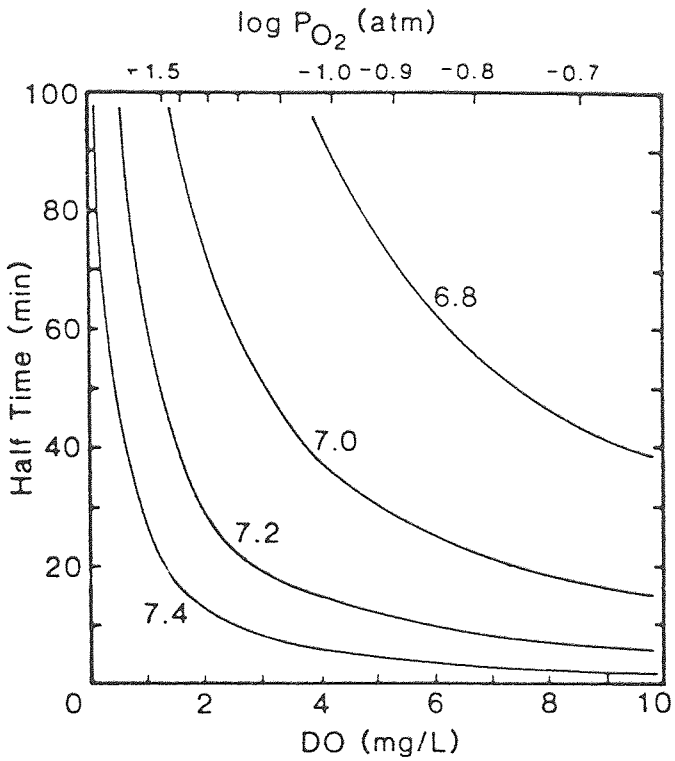

Figure 8 Half-times for oxidation of Fe^{+2} to Fe^{+3} as a function of dissolved oxygen for pH 6.8-7.4 computed from the equation for half-time oxidation (23).

For example, Cleaner Wicks installed to a depth of 10m at a site (sand soil type) is supplied with an air flow of 0.1 m^3/min (3.5 ft^3/min), providing a water flow equal to 0.003 m^3/min (0.8 gpm). Using an average DO content of 2.0 mg/l and average pH of 7.0, Figure 8 predicts a half-time for oxidation of about 74 min. The volume lifted is then 0.003 m^3/min times 74 min which is equal to 0.222 m^3.

Sand has a sediment porosity of approximately 0.30 and assume a saturated thickness of L = 5 m, then

$$r = (V / \Phi \Pi L)^{1/2}$$

$$= (0.222 / 0.30\ \Pi\ 5)^{1/2}$$

$$r = 0.21 \text{ m}$$

The distance seems rather small but it can be manipulated. For instance, if air flow is increased by a factor of 10 to 1 m^3/min (35 ft^3/min) the radius is r = 0.69. To obtain 1.5 m (5 ft) centers, the air flow must be increased to 1.25 m^3/min (44 ft^3/min). See Appendix C. It can be seen also that as L, the saturated thickness increases, the radius of available oxygen will decrease. By increasing the air flow to the Cleaner Wick as the saturated thickness increases, the 1.5 m centers can be maintained.

Disappointing filtration rates can also be related to excessive growth of microorganisms, especially iron bacteria. Iron bacteria compound the problem further by increasing the rate of iron oxidation. Due to the small amount of energy (-71.2 kJ/reaction) available from the aerobic oxidation of Fe^{+2} to Fe^{+3}, large amounts or iron are needed in order for the iron bacteria to grow. For example, *Gallionella* thrive in iron concentrations ranging from 1 to 25 mg/l.

Generally iron bacteria grow at acid pHs of 2 to 6, although *Gallionella* has a pH range of 6 to 7.6. The best known iron oxidizing bacterium is *Thiobacillus ferrooxidans*, common in acid-polluted environments. Another bacterium is *Sulfolobus acidocaldarius* found in hot acid springs at temperatures that can reach the boiling point of water. *Thiobacillus ferrooxidans* and *Sulfolobus acidocaldarius* exist at the high temperatures of 15.6 to 85 °C. Yet, *Gallionella* prefer temperatures much lower, 4.4 to 15.6 °C.

Gallionella also are characteristic in waters low in oxygen, in the 0.1 to 1.0 mg/l range. Others have a wide range of oxygen tolerances and will grow in water with 0.3 to 9.0 mg/l dissolved oxygen (18, 24, 25).

Acid or neutral pH, high or low temperatures, with or without oxygen, iron bacteria will be difficult to control their growth, and if not outright impossible, definitely taxing. When iron is present, these bacteria can plug the Cleaner Wick by enzymatically catalyzing the oxidation of iron. Then, the energy bacteria obtain by oxidizing ferrous ions to ferric ions is used to promote the growth of slimes and accumulate large amounts of ferric hydroxide in the slime.

Some of the methods used to control iron bacteria are listed in Table 5, with preference in field use given to chemical methods of control.

Table 5 Methods to control iron bacteria (18).

Chemical	Physical
Oxidizing agents such as chlorine	Heat
pH adjusters such as acids	Ultrasonics
Quaternary ammonium compounds	Radiation
	Anoxic blocks

2.3 Mathematical Models

As discussed, the bioremediation of a contaminated plume may involve adding nutrients such as nitrogen and/or phosphorus or air, dissolved oxygen or hydrogen peroxide in order to degrade a particular waste. In order for the Cleaner Wick process to be successful, it may be necessary to minimize the migration of the plume during in situ treatment. In order to evaluate a site's potential for use of the Cleaner Wick, the transport rate of the contaminants are compared to the rate of degradation.

2.3.1 Rate of Transport

The rate of transport can be described by predicting its retardation factor as it migrates through the soil. The retardation factor is the relative velocity of the contaminant compared to the velocity of the water through the soil:

$$R = V_w / V_c$$

where R = retardation factor, V_w = average water velocity, and V_c = average contaminant velocity. If the retardation factor is less than one, then the contaminants are moving faster than the water through the soil and therefore the contaminants must be managed or contained in order to stop further spread of the pollutant.

A common method of calculating R is by the relation (13):

$$R = 1 + (\rho K_d / \theta)$$

where ρ = the bulk density, K_d = the partition coefficient in grams of contaminant adsorbed per gram aquifer, and θ = the aquifer porosity or volumetric moisture content. By controlling these parameters, such as changing the bulk density or porosity, the contamination can be managed to remain within the Cleaner Wick system, allowing for the required time to complete the bioremediation process.

2.3.2 The Rate of Degradation

The rate of degradation can be expressed as a function of the concentration of the contaminant being degraded. In general, the rate depends on 1) the concentration of the pollutants (or reactants), 2) the concentration of one or

more products, and 3) other species not involved in the stoichiometry. This is defined as the order of reaction. In environmental applications, zero or first order reactions are used most.

The zero order reaction is when the rate of degradation of the contaminant is not affected by the change in the contaminant concentration. The reaction rate is determined by some other factor rather than contaminant concentration. The rate of change is defined as (16):

$$dC/dt = -k$$

using integration to solve:

$$dC = -k\,dt$$

$$\int_{C_o}^{C_t} dC = -k\int_{o}^{t} dt$$

$$C\Big|_{C_o}^{C_t} = -k\,t\Big|_{o}^{t}$$

$$C_t - C_0 = -kt$$

$$C_t = C_0 - kt$$

where C_t = the concentration of the contaminant remaining after time t, C_0 = the initial concentration of the contaminant, t = time, and k =the zero order rate constant.

The rate constant must be determined experimentally. Just as in biological treatment of wastewaters where determination of kinetic coefficients are done using bench-scale reactors or pilot-scale systems, similar types of modeling will need to be done with the Cleaner Wick as well to determine the rate constant k. Also, actual site results can and should be collected and used to increase the amount of data available for determination.

The rate constant k is determined by using the solution $C_t = C_0 - kt$ which can be graphed as a straight line equation ($y = mx + b$), given that the initial concentration and final concentrations are known, and the time it took to reach the final concentration. Figure 9 shows an example graph.

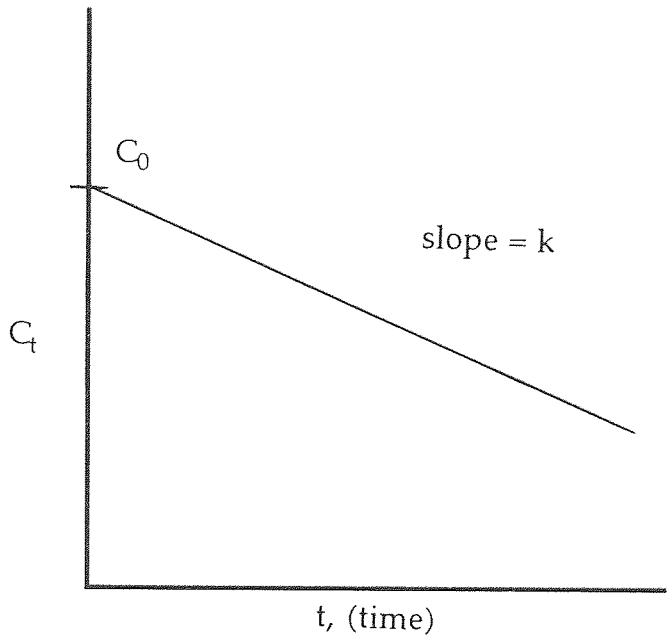

Figure 9 Example graph of a zero order reaction to determine the rate constant k.

The rate constant k is simply the slope of the line. It should be noted that there will be different rate constants with each different contaminant, bacteria, temperature, soil, etc., that determination of k should be done over a wide range of concentrations for each of the different parameters listed.

A useful term used in reaction kinetics is called the half-time, which is the time it takes to transform 50% of the original contaminant. If $C_t = C_0/2$, then the half-time, $t_{1/2}$ can be solved for directly:

$$t_{1/2} = C_0/2k$$

If the graph of the zero order reaction fails to exhibit a straight line, then the rate of degradation is not zero order, but another order reaction, most likely first order. In the first order reaction, the rate of degradation of the contaminant is proportional to the contaminant concentration (16):

$$dC/dt = -kC$$

where C = contaminant concentration and k = the first order rate constant. Integrating:

$$\ln(C_t/C_0) = -kt$$

or,

$$C_t = C_0 e^{-kt}$$

where C_t = the concentration of the contaminant remaining after time t, C_0 = the initial concentration of the contaminant, t = time, and k = the first order rate constant (1/time). The first order rate constant is determined the same way as for a zero order. The equation $\ln(C_t) = \ln(C_0) - kt$ can also be graphed as a straight line, the slope of which is k. The half-time can be determined by substituting $C_t = C_0/2$ into the equation above, giving:

$$\ln((C_o/2)/C_o) = -kt_{1/2}$$

Solving for the half-time, $t_{1/2}$:

$$t_{1/2} = 0.693/k$$

With the ability to predict the rate of transport and the rate of degradation, the time it takes to degrade potentially harmful contaminants can be determined. A judgment can then be made on the feasibility of using bioremediation and the Cleaner Wick at a site.

CHAPTER 3

CONCLUSIONS

When ground water contamination occurs, there are several remedial techniques that can be used to treat the pollutant. In situ bioremediation is a relatively new technology that has seen increased attention as a remedial alternative recently. Several subsurface environments have already been shown to biodegrade some organic pollutants, mostly petroleum hydrocarbons (6, 22). Under the right conditions, the contaminants can be completely degraded to harmless products. Under other conditions, however, the contaminants can be transformed to new substances that are more mobile or even more toxic than the original target contaminant. Researchers are investigating this bioremediation further to determine when and how natural biodegradation occurs, the stage it is in, and whether enhancement of the biodegrative process is possible or desirable. The Cleaner Wick can potentially be used in this area.

3.1 Design

The decision for application of in situ bioremediation of a site can only be taken after a comprehensive site, soil, and waste characterization.

The limiting factor most of the time is the lack of oxygen or necessary redox conditions. Air, hydrogen peroxide, ozone, pure oxygen, and nitrate (as electron acceptor) can be used as an oxygen source. The choice of source will ultimately be based on cost efficiency, contaminant loading, and ease of use.

Nutrient addition is dependent upon the original available nutrients in

the soil and the uptake by the microorganisms. Addition of nitrogen, phosphorus, and trace minerals stimulates the microorganisms to aerobically degrade the subsurface contaminants. By sampling, the proper ratio of nutrients (C:N:P) needed can be determined.

Temperature plays in important role in microbial activity and growth. Since practically all microbial activity stops at 0 °C, it can be expected that in the northern winter climates here in North America, biorestoration will slow down remarkably. This can be circumvented by maintaining higher temperatures in the subsurface environment. It is recommended that the optimal growth temperatures be maintained for psychrophiles (15 °C) and mesophiles (40 °C). It is further recommended that whenever possible, mesophiles be considered the organism of choice. Mesophiles have a growth rate of approximately 2.5 generations/hr, while that of psychrophiles is less than 1 generation/hr. By using mesophiles, the biorestoration process will be more than 2.5 times faster.

Addition of microorganisms to the subsurface environment is an option available to either further enhance biodegradation, or stimulate biodegradation where microbial activity is low. Introduction of microorganisms into the soil environment is suspect and faces many challenges. Research in this area is still limited and very few companies supply the needed microorganisms. Cost-benefit calculations are lacking. In addition, introduced microorganisms failure to metabolize in the subsurface environment may be due to a low contaminant concentration. The subsurface environment may also contain some substance or organisms that inhibit growth. It is therefore recommended to use existing microorganisms in the soil environment whenever possible.

3.2 System Design

The simplicity of the Cleaner Wick design lends itself to act as an excellent delivery system of required nutrients necessary for subsurface microbial growth and activity. The radial distances for the penetration of oxygen into the soil environment indicate that subsurface micro-environments can obtain the necessary nutrients when the Cleaner Wick provides the necessary flow volume lift.

The Cleaner Wick should not be considered as a "stand alone" technology which can limit its use in the filed. A combination of chemical and physical treatments above and/or below ground along with the in situ biological treatment expands the application, especially to compounds which are more difficult to break down biologically (such as polycyclic aromatic hydrocarbons) yet easily biodegraded once the oxidation process has started.

Bioventing the VOCs in the unsaturated zone presents a viable opportunity to use the Cleaner Wick. Soil microorganisms tend to adsorb onto soil particles in the unsaturated zone. Moisture must be present or provided though to allow microorganisms to maintain the proper amount of water internally for metabolism. Bioventing with the Cleaner Wick calls for further investigation.

3.3 Specific Problems

The Cleaner Wick can be subject to the problem of clogging in the subsoil which will result in poor filtration rates. It can be caused by different factors, including permeability as well as excessive growth of microorganisms such as iron bacteria and high concentrations of iron (or manganese). Various methods of control were discussed, and are existing and proven technologies. An interesting option that has not been explored yet is to use anerobic bacteria in high iron concentration ground waters. Iron oxidation will be at a

minimum, since only nutrients are being supplied, and not oxygen.

Modeling of biodegradation is still lacking. Few subsurface models currently exist and most information is based still on case studies and experimentation. Time of contaminant clean up is an important factor in selecting any remedial option, and all data to date suggests that bioremediation has a significantly faster clean up time than current technologies, such as pump and treat. It is believed that implementation of the Cleaner Wick used in biorestoration will correlate itself to that data.

3.4 Recommendations

The Cleaner Wick can be a viable bioremedial alternative if clogging can be controlled and limited, such as by monitoring pH and managing it. More importantly, a radius of influence about each Cleaner Wick in different soil types, recirculation rate and flow, as well as the extent of oxygen and nutrient infiltration into the surrounding soil and aquifer environment must be determined. The kinetic models presented should provide an estimation of clean up times when rate constants are determined. Further experimentation and field testing are required.

APPENDIX A

AIR STRIPPING CLEANER WICK MODEL FOR REMOVAL OF VOCs FROM GROUNDWATER (3)

The air stripping cleaner wick model for in situ treatment of VOCs uses the following assumptions:

1. Hydraulic conductivity of soil, $K = 2.36 \times 10^{-2}$ cm/s = 500 gpd/ft^2,
2. Hydraulic gradient = 1%,
3. Air flow, $Q = 1$ ft^3/min/wick,
4. 5 ft. center between Cleaner Wick,
5. Maximum wick depth, D = 40 ft,
6. Groundwater temperature, T = 20 - 24 °C,
7. Four rows of wicks each 5 ft apart (see Fig. 3, pg. 5),
8. All groundwater flowing 2.5 ft to the top and bottom of the wick of (Fig. 3) will pass through the wick due to the action of the air lift.

An air stripping performance based equation was developed by Clark, Eilers, and Goodrich (26), which is

$$AW = 74.6RM^{12.44}\, SL^{0.37}\, V^{-0.45}\, ML^{-0.18}\, (0.33)^{S}$$

in which AW = air-to-water ratio; RM = removal as a decimal; V = vapor pressure; SL = solubility; ML = molecular weight; and S = saturation state: S = 1 for saturated compounds, S = 0 for unsaturated compounds (26).

To determine the removal efficiency of the air stripping cleaner wick

system, the air-to-water ratio is the response variable, and can be determined for the system. In that way, RM can be calculated with all the other variable known. For example:

To calculate the air-to-water ratio, AW, we know

$$AW = Q_a / Q_w$$

where Q_w is the flow of water through the wick, and Q_a is the flow of air through the wick. Q_a is given to be 1 cfm (1440 ft^3/day) and Q_w can be calculated from

$$Q_w = Kia$$

$$= (500\ gpd/ft^2)(0.01)[(5\ ft.)(40\ ft.)]$$

$$Q_w = 133.6\ ft^3/day, \text{ therefore}$$

$$AW = 10.778$$

For trichloroethylene,

S = 0 (unsaturated compound),

ML = 131.5,

V = 74 mm Hg at 24 °C,

SL = 1000 mg/l at 24 °C, and

AW = 10.778

then,

$$AW = 74.6RM^{12.44}\ SL^{0.37}\ V^{-0.45}\ ML^{-0.18}\ (0.33)^S$$

substituting,

$10.778 = 74.6RM^{12.44} (1000)^{0.37} (74)^{-0.45} (131.5)^{-0.18} (0.33)^{0}$

and solving for RM,

RM = 0.874 or 87.4% for one row of wicks.

For the four rows of wicks in the model, assume an influent concentration of 1000 ppm TCE. The influent and effluent concentrations of TCE after each row of wicks is listed in the table below.

Table 6 Influent and effluent concentrations of TCE after passing through four rows of Cleaner Wicks.

	Row #1	Row #2	Row #3	Row #4
Influent (ppm)	1000	126	16	2
87.4% removal	874	110	14	1.75
Effluent (ppm)	126	16	2	0.25

Similarly for carbon tetrachloride,

S = 1 (saturated compound),

ML = 153.82,

V = 133 mm HG at 25 °C,

SL = 1,160 mg/l at 25 °C, and

AW = 10.778

then,

$AW = 74.6RM^{12.44} SL^{0.37} V^{-0.45} ML^{-0.18} (0.33)^{S}$

substituting,

$10.778 = 74.6RM^{12.44} (1160)^{0.37} (113)^{-0.45} (153.82)^{-0.18} (0.33)^{1}$

and solving for RM,

RM = 0.969 or 96.9% for one row of wicks.

For the four rows of wicks in the model, assume an influent concentration of 1000 ppm carbon tetrachloride. The influent and effluent concentrations of carbon tetrachloride after each row of wicks is listed in the table below.

Table 7 Influent and effluent concentrations of carbon tetrachloride after passing through four rows of Cleaner Wicks.

	Row #1	Row #2	Row #3	Row #4
Influent (ppm)	1000	31	0.961	0.030
96.9% removal	969	30.039	0.931	0.029
Effluent (ppm)	31	0.961	0.030	0.001

APPENDIX B

BIOGEOCHEMICAL CYCLES

B.1 The Nitrogen Cycle

One of the most important biogeochemical cycles in water and soil environments are those involving nitrogen compounds. They are summarized in the nitrogen cycle shown in Figure 10.

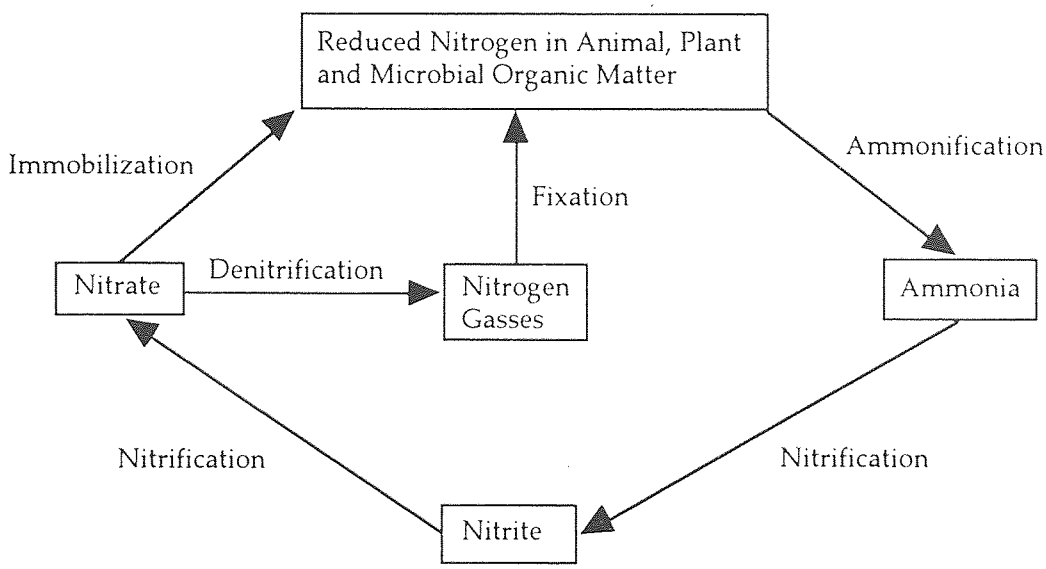

Figure 10 The nitrogen cycle (27).

The biogeochemical transformations in the nitrogen cycle are nitrogen fixation, whereby molecular nitrogen is fixed as organic nitrogen; nitrification, the process of oxidizing ammonia to nitrate; nitrite reduction, the process by which nitrogen in chemical compounds is reduced to lower oxidation states; ammonification, in which ammonia is produced during the

decomposition of organic nitrogen compounds; and denitrification, the reduction of nitrate and nitrite to gaseous nitrogen compounds (24).

B.2 The Sulfur Cycle

Sulfur transformations are more complex than nitrogen transformations due to the variety of oxidation states of sulfur and that some of the sulfur transformations occur at high rates chemically as well as biologically. The sulfur cycle is summarized in Figure 11.

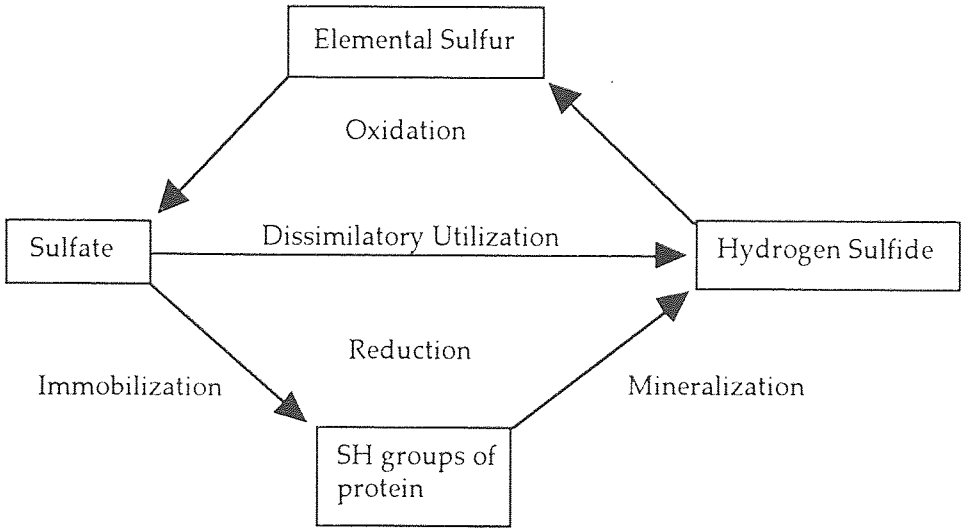

Figure 11 The sulfur cycle.

The biogeochemical transformations of the sulfur are mineralization, where heterotrophic microorganisms decompose sulfur containing organic matter; immobilization, whereby sulfur, often as sulfate, may be assimilated by microorganisms to produce sulfur amino acids (SH groups of protein); reduction, in which oxygen deficient soil have microorganisms which use oxidized forms of sulfur as electron acceptors; and oxidation, where the final product is sulfate (SO_4^{2-}) and the total number of electrons involved between

H_2S (oxidation state, -2) and sulfate (oxidation state, +6) is 8 (9). The variety of oxidation-reduction states (Figure 12) means that there is a wide range of chemical and enzymic systems involved in the biogeochemical transformation of sulfur.

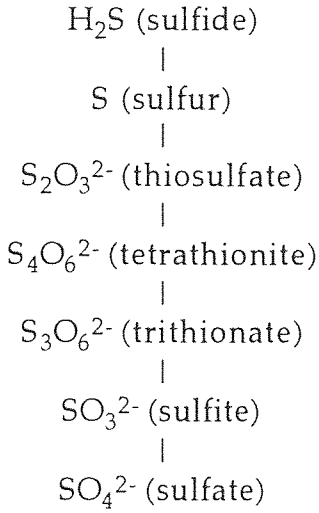

Figure 12 Oxidation-reduction states of sulfur.

The microorganisms catalyzing these changes fall into four categories.

The first is the *Thiobacillus* species which is most commonly involved in elemental sulfur oxidation. The bacteria attach to the sulfur crystals (elemental sulfur is very insoluble), oxidizing it and form sulfate and hydrogen ions. The sulfur oxidation results in a lowering of the pH. Second are heterotrophs, whereby a variety of heterotrophic bacteria, fungi, and actinomcetes will oxidize elemental sulfur or thiosulfate in the presence of an organic substrate (27). The third group will oxidize hydrogen sulfide and deposit elemental sulfur and are called trichome formers. Examples of such bacteria are *Beggiatoa*, *Thiothrix*, *Thioplaca*, and *Sphaerotilus* (27). The last group is photosynthetic sulfur bacteria, which perform the anaerobic oxidation of sulfur.

Overall, microorganisms play a very important part in the oxidation-reduction of the sulfur cycle. Sulfur-oxidizing and sulfide-oxidizing bacteria produce sulfate, usually in sulfuric acid form, which acidifies the environment. The sulfate-reducing bacteria in turn use this sulfate as an electron acceptor in anaerobic respiration producing hydrogen sulfide. Due to the toxicity of hydrogen sulfide, sulfate reduction is an important biochemical process (9).

B.3 The Iron Cycle

The biogeochemical transformation in the iron cycle is oxidation. Iron exists in two oxygen states, ferrous (+2) and ferric (+3). Due to the high electrode potential of 0.76 V for the Fe^{+3}/Fe^{+2} couple, the only electron acceptor able to oxidize ferrous iron is oxygen (8). At neutral pH, ferrous iron oxidizes with air to ferric iron. In turn, highly insoluble precipitates of ferric hydroxide and ferric oxides are formed (9).

The bacteria *Ferrobacillus* and *Gallionella* utilize iron to catalyze the oxidation of Fe^{+2} to Fe^{+3} by molecular oxygen (24). The overall reaction of ferrous iron oxidation is as follows:

$$4Fe^{+2} + 4H^{+} + O_2 \longrightarrow 4Fe^{+3} + 2H_20$$

$$Fe^{+3} + 3OH^{-} \longrightarrow Fe(OH)_3 \text{ precipitates}$$

In the initial oxidation of the ferrous iron, the hydrogen ions are consumed which leads to a rise in pH of the medium. The hydrolysis of Fe^{+3}, and the formation of $Fe(OH)_3$ consumes the hydroxyl ions and leads to the acidification of the medium. This is an example of how iron oxidation leads to acidification in the environment.

APPENDIX C

DETERMINATION OF RADIAL DISTANCE OF OXIDATION OCCURRENCE FROM CLEANER WICK FOR EXPERIMENTALLY DETERMINED FLOW RATES

Prior testing of the Cleaner Wick determined the water flow up the wick (3). With the rate of water flow known, the radius from the Cleaner Wick where oxidation of iron occurs can be calculated.

Two series of tests were originally conducted on the Cleaner Wick. The first series of tests placed a Cleaner Wick into a water tank and measured water flow up and out the wick. The second series of tests placed the Cleaner Wick in a water tank which was also filled with sand. The results of the water flow test for a Cleaner Wick in sand are in Table 8.

Table 8 Results of wick flow test in sand (3)

Air Flow Pressure (psi)	Air Flow Volume (ft^3/min)	Air Flow Volume (l/min)	Water Flow Volume (ft^3/min)	Water Flow Volume (l/min)	Water to Air Flow (%)
5	1.06	30	0.04	1.1	3.7
10	1.94	55	0.05	1.4	2.6
15	2.47	70	0.06	1.7	2.4

The results of the test show that in sand, the Cleaner Wick captured and lifted a volume of water equal to approximately 3% of the air flow volume supplied.

With a half-time of oxidation $t_{1/2} = 74$ min (from Chapter 2), a V = 1.50 l/min is lifted when 50 l/min air flow is supplied (the approximate average

air flow used during testing). The porosity of sand is 0.30 and the laboratory test used a sediment thickness L = 1.42m (the actual length of the Cleaner Wick in contact with the water), then

$$r = (V / \Phi \Pi L)^{1/2}$$

$$= (1.50 / 0.30 \, \Pi \, 1.42)^{1/2}$$

$$r = 0.29 \text{ m}$$

As expected, the radial distance in the laboratory test is larger than in the example in Chapter 2. This is due to the fact that at relatively the same pressure, the effect of sediment thickness plays an important role in determining radial distance. The larger the thickness, the smaller the radius. Conversely, with the sediment thickness constant, a lower air flow and the resulting water flow will give a smaller radius.

It is also of interest to develop a table of increasing air flow, and determining the corresponding radius, as in Table 9. Note that a doubling of airflow and corresponding water flow do not double the radius.

Table 9 Determination of radial distances of oxidation with increasing pressure.

Air Flow (l/min)	Water Flow (l/min)	radius (m)
100	3	0.41
150	4.5	0.50
200	6	0.58
300	9	0.71
400	12	0.81
500	15	0.91
1000	30	1.29

APPENDIX D

PARTIAL PREPROPOSAL IN RESPONSE TO RFP SITE E08

D.1 Technical Description

Cleaner Wick technology is a patented approach for introducing air (or other gases) into groundwater and soil (2). One major advantage of Cleaner Wick technology is that it is essentially both an in situ conduit for gases and aqueous materials and an in-ground reactor system. Thus treatment of contaminants can occur without expensive excavation or pumping and use of above ground reactors.

The Cleaner Wick system was developed and tested through the support of the Hazardous Substance Management Research Center during 1988, 1989, and 1991 (3). A schematic of the system is shown in Figure 13.

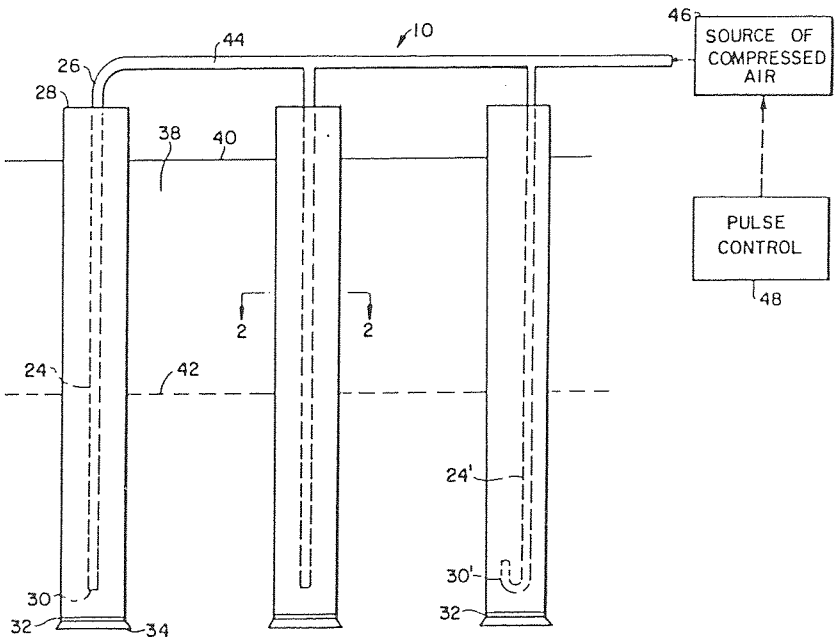

Figure 13 Schematic of Cleaner Wick system.

Individual Cleaner Wicks consist of hollow flexible plastic tubes installed in the center of a conventional drain wick core. Air under pressure is forced down the tube and exits at the bottom within the wick core void. The air mixes with the contaminated groundwater and forces water up through the core. The Cleaner Wicks can be economically installed to depths of up to 100 ft by conventional drain wick installation equipment. The lateral spacing of individual Cleaner Wicks depends on site characteristics and project goals.

The Cleaner Wick system attracts, lifts, aerates, and circulates significant amounts of ground water. To date, through modeling and laboratory testing, it has been found that contaminant removal efficiency of the Cleaner Wick system depends on the effectiveness of air to water ratios. The appropriate air to water ratio can be obtained by varying the number and spacing of the individual wicks and by controlling the air flow rate. Optimization of the system depends on the physical/chemical characteristics of the site and the specific properties of the target contaminants (solubility, volatility, partition coefficients, etc.).

The Cleaner Wick system can also deliver under pressure down the tube and discharge through ports along the tube inside the wick core, the necessary oxygen and nutrients needed to stimulate microbial activity and growth in order to degrade the contaminants. For ground water treatment, the air and nutrients would mix with ground water that enters the core void through the filter fabric that surrounds the core. An upward movement of liquids would result thereby promoting additional ground water flow toward the wick. The Cleaner Wick would therefore serve as a system for delivering nutrients and a method of inducing localized ground water circulation. Target contaminants for microbial degradation are not limited to, but include such organics as petroleum hydrocarbons (LNAPLs) such as gasoline, heating oil, kerosene, jet fuel, and aviation gas, and chlorinated hydrocarbons

(DNAPLs) including 1,1,1-trichloroethene, carbon tetrachloride, chlorophenols, chlorobenzenes, tetrachloroethylene, PCBs, and creosote.

D.2 Summary of Data and Results to Date

Testing and modeling have concentrated on the Cleaner Wick as an air stripping system to remove VOCs. Results to date have been encouraging showing that the Cleaner Wick can be used for air stripping volatile organic compounds from ground water. The purpose of this project is to evaluate the feasibility of adapting the Cleaner Wick technology for use in facilitating in situ bioremediation by providing an air and nutrient delivery system for aerobic applications and a nutrient and electron acceptor delivery system for alternative types of bioremediation such as methanotrophic, denitrification, or anaerobic systems. The project will involve comprehensive laboratory scale testing of the ability of the Cleaner Wick system to enhance the rate of bioremediation for various types of soil conditions and to further investigate a group of target contaminants.

D.3 Description of Proposed Project

The objective of this project is to test the effectiveness of using Cleaner Wicks in tandem with bioremediation for treatment of organically contaminated ground water and soil and to identify site and contaminant conditions for which this approach is best suited. The overall goal is to develop laboratory simulations of the Cleaner Wick system to test its effectiveness in accelerating bioremediation.

The first phase of the project will involve designing, constructing, and testing the laboratory systems to be used in this study. The lab scale system will involve installation of Cleaner Wicks into soil columns that can accommodate different types of soils and can be operated in a static or flow

through mode. Each test system will be equipped with multiple sample ports and will be connected to computer data acquisition systems to provide on-line monitoring of selected parameters. The operational parameters of the test systems will be optimized including flow characteristics at various gas pressures for different soil types.

The second phase involves developing analytical methodologies for conduct of the biological component of the project. A set of candidate contaminants will be selected based on known ground water and soil contamination problems that represent an array of physical/chemical properties (solubilities, volatility, degradability, partition coefficients, etc.). Soil types will be selected based on prevalent soil conditions at contaminated sites. Because quantification of contaminants bound to soils (particularly clays) can be difficult, a comprehensive laboratory program will be undertaken to ensure adequate recovery of contaminants. Standard Operating Procedures (SOPs) will be developed for extraction and analysis of the contaminants of interest and a detailed quality assurance/control program will be developed. Methods for monitoring microbial activity will be an integral part of the test program. All laboratory studies will be designed with an effort towards waste minimization and pollution prevention.

The third phase will involve a detailed program for testing the ability of the Cleaner Wick system to facilitate bioremediation. For the initial tests, soil containing contaminants that have been proven to biodegrade will be used. Each set of tests will involve an abiological control reactor in which nonbiological removal can be quantified. The abiological reactor will contain sterilized soil and will be maintained under conditions that prevent biological growth. The biological test reactors will be operated by applying air or nutrients through the Cleaner Wicks to stimulate growth of native soil microorganisms. In some cases, additional sources of acclimated

microorganisms will be used to inoculate the soil and minimize the start-up time. The tests will be conducted under controlled conditions and efforts will be made to conduct comprehensive mass balances of contaminants and to track the transformations that occur using the SOPs developed previously. Initial tests will focus on aerobic systems treating volatile and nonvolatile organic contaminants individually or in mixtures. The soils to be tested include sand and clays.

Initially, the reactors will be filled with soil and the Cleaner Wicks will be inserted. For ground water test systems, the soil will be saturated with water and allowed to equilibrate. For soil remediation systems, the soil will be maintained in an unsaturated state. Monitoring will be conducted through the depth and width of the reactor to evaluate the spatial distribution of pollutants and microbial activity. All gases released from the test system will be monitored for the presence of volatile components and for gas composition. After completion of the initial testing, the use of chemical pretreatment, the addition of co-metabolic substrates, and the use of surfactants and enzymes will be recommended.

D.4 Value of the Treatment Technology to the Superfund Program

The Cleaner Wick is a promising new technology for solving hazardous waste problems using bioremediation. With the ability of microorganisms to metabolize different chemicals, the Cleaner Wick can be tailored to the contaminants in the subsurface environment by using microorganisms that break down a particular contaminate. Because bioremediation is a natural process, it is favorable than other existing options (such as pump and treat, soil excavation, etc.). The residues of biological processes (i.e., water and carbon dioxide) are usually geochemically cycled in the environment as harmless products. Because the Cleaner Wick system is a in situ process, it

can be less expensive than the existing options. Finally, bioremediation does not just transfer contaminants from one medium to another, rather it degrades the target chemical.

REFERENCES

1. Konon, W. "Field Testing of Air Stripping Wicks." Final Report, Project: PHYS-13, Hazardous Substance Management Research Center, NJIT, December 1989.

2. Konon, W. "System For Removing Contaminants From Groundwater." United States Patent, Patent Number 4,883,589, November 28, 1989.

3. Konon, W. "Field Testing of Air Stripping Wicks." Final Report, Project: SITE-24, Hazardous Substance Management Research Center, NJIT, January 1992.

4. Konon, W. "Air-Stripping Wicks Remove VOCs From Ground Water." The Hazardous Waste Consultant, September/October 1992, 1.1-1.2.

5. Brian D. Charters. "Feasibility Cost Estimate of Initial Setup for Various Wick Installations Used in Soil Remediation." Master's Project, NJIT. May 1993.

6. U.S. EPA. 1992. U.S. Environmental Protection Agency. Bioremediation of Hazardous Wastes. Office of Research and Development, Washington, DC. EPA/600/R-92/126. August.

7. George Tchobanoglous, Franklin L. Burton. Wastewater Engineering, Treatment, Disposal, and Reuse. New York: McGraw-Hill, Inc., 1991.

8. Clair N. Sawyer, Perry L. McCarty. Chemistry for Environmental Engineering. New York: McGraw-Hill, Inc., 1978,

9. Thomas D. Brock, Michael T. Madigan. Biology of Microorganisms. Englewood Cliffs, NJ: Prentice Hall, 1991.

10 U.S. EPA. 1993. U.S. Environmental Protection Agency. Bioremediation of Hazardous Wastes Sites: Practical Approaches to Implementation. Office of Research and Development, Washington, DC. EPA/600/K-93/002. April.

11. U.S. EPA. 1991. U.S. Environmental Protection Agency. Anaerobic Biotransformation of Contaminants in the Subsurface: Environmental Research Brief. Robert S. Kerr Environmental Research Laboratory, Ada, OK. EPA/600/M-90/024. February.

12. U.S. EPA. 1993. U.S. Environmental Protection Agency. Bioremediation Using the Land Treatment Concept. Office of Research and Development, Washington, DC. EPA/600/R-93/164. August.

13. Judith L. Sims, Ronald C. Sims, John E. Matthews. "Approach to Bioremediation of Contaminated Soil." Hazardous Waste and Hazardous Materials, Vol. 7, No. 2, 1990.

14. László Alföldi. "Groundwater Microbiology: Problems and Biological Treatment — State-of-the-Art Report." Water Science Technology, Vol. 20, No. 3, 1988.

15. J.F. McNabb, W.J. Dunlap. "Subsurface Biological Activity in Relation to Ground Water Pollution." Ground Water, 13, 33, 1975.

16. U.S. EPA. 1989. U.S. Environmental Protection Agency. Bioremediation of Contaminated Surface Soils. Robert S. Kerr Environmental Research Laboratory, Ada, OK. EPA/600/9-89/073. August.

17. U.S. EPA. 1992. U.S. Environmental Protection Agency. In Situ Bioremediation of Contaminated Ground Water. Office of Research and Development, Washington, D.C. EPA/540/S-92/0003. February.

18. F.G. Driscoll. Groundwater and Wells. St. Paul, Minnesota: Johnson Division, 1986.

19. M.D. Lee, J.M. Thomas, R.C. Borden, P.B. Bedient, J.T. Wilson, C.H. Ward. "Biorestoration of Aquifers Contaminated with Organic Compounds." National Center for Ground Water Research, Vol. 18, No.1, 1988.

20. R.A. Brown, R.D. Norris, R.L. Raymond. "Oxygen Transport in Contaminated Aquifers." NWWA Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration, 421, 1984.

21. U.S. EPA. 1990. U.S. Environmental Protection Agency. Enhanced Bioremediation Utilizing Hydrogen Peroxide as a Supplemental Source of Oxygen. Robert S. Kerr Environmental Research Laboratory, Ada, OK. EPA/600/2-90/006. February.

22. U.S. EPA. 1989. U.S. Environmental Protection Agency. In Situ Bioremediation of Spills from Underground Storage Tanks: New Approaches for Site Characterization, Project Design, and Evaluation of Performance. Robert S. Kerr Environmental Research Laboratory, Ada, OK. EPA/600/2-89/042. July.

23. K.R. Applin, N. Zhao. "The Kinetics of Fe(II) Oxidation and Well Screen Encrustation." Ground Water, Vol.27, No. 2, March-April 1989.

24. Stanley E. Manahan. Environmental Chemistry. Chelsea, MI: Lewis Publishers, INC., 1991.

25. M.D. Campbell, J.H. Lehr. Water Well Technology. New York, New York: MaGraw-Hill, 1973.

26. Robert M. Clark, Richard G. Eilers, James A. Goodrich. "VOCs in Drinking Water. Cost of Removal." Journal of Environmental Engineering, Vol.110, No. 6, December 1984.

27. I.J. Higgins, R.G. Burns. The Chemistry and Microbiology of Pollution. New York: Academic Press, 1975.