AN ENVIRONMENTAL APPLICATION OF SELF POTENTIAL GEOPHYSICS

by

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Abstract

Self potential geophysics has been widely used in the area of mineral exploration and recently it has become more frequently used in environmental engineering, especially in the study of water movement. The method has great potential in the environmental field due to its ability to delineate ionic, heat, and fluid flow. This study was undertaken to determine the methods ability to map a contamination plume at the Massachusetts Military Reservation (MMR), specifically the source area of FS-12, and to try to determine the effects of the remediation systems currently in operation at the site. The MMR, which is located on Cape Cod, is a Superfund site currently listed on the National Priority List.

FS-12 was created by a leak of approximately 70,000 gallons of JP-4 jet fuel. The contaminants of concern are BTEX, which are components that are easily volatilized, strippable, and biodegradable. Hence, soil vapor extraction and air sparging are being used to remediate the site. Since these technologies create air and water movement in the subsurface, a goal was to capture this flow from the surface through the use of self potential geophysics. However, there is not conclusive results that this goal is achievable. On the other hand, the method was very successful in delineating the area of contamination through concentration gradients and/or by biodegradation processes.

Thesis Supervisor: Dale Morgan
            Title: Professor of Geophysics

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1.   Background and Site Description

1.1. Physical Characteristics

1.1.1. Location

The Massachusetts Military Reservation (MMR) is located in western Cape Cod, Massachusetts, about 60 miles south of Boston, and borders the townships of Bourne, Falmouth, Mashpee, and Sandwich (Figure 1.1 & Figure 1.2). The military reservation consists of 22,000 acres in Barnstable County and abuts the Cape Cod Canal on its northwest end. Various facilities and related operations of the Department of Defense (DOD) branches are housed at the reservation. These operations include: U.S. Coast Guard, U.S. Marine Corps, U.S. Army National Guard (ARNG [Camp Edwards]), U.S. Air Force, and U.S. Air National Guard (ANG [Otis ANG Base]). Other portions of the base are used by the Veterans Administration National Cemetery, the U.S. Department of Agriculture, and the Commonwealth of Massachusetts. The southern portion of the reservation contains most of the facilities while the northern portion consists of firing ranges and training areas for the ARNG.
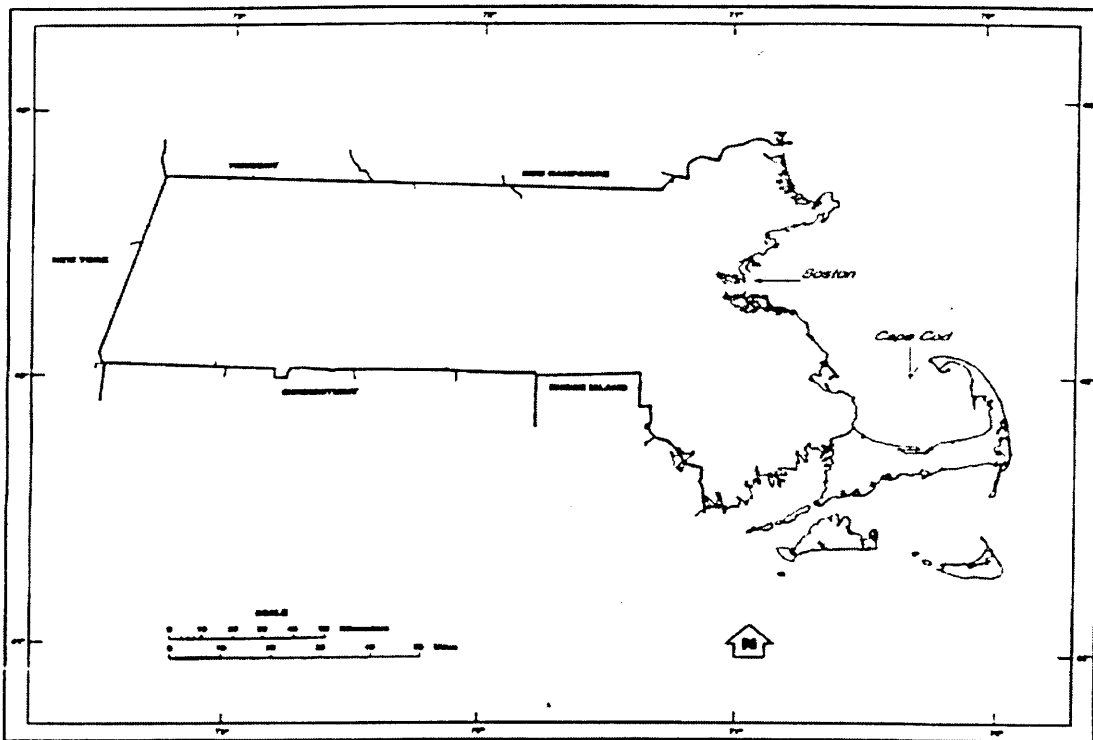
Figure 1.1: Commonwealth of Massachusetts
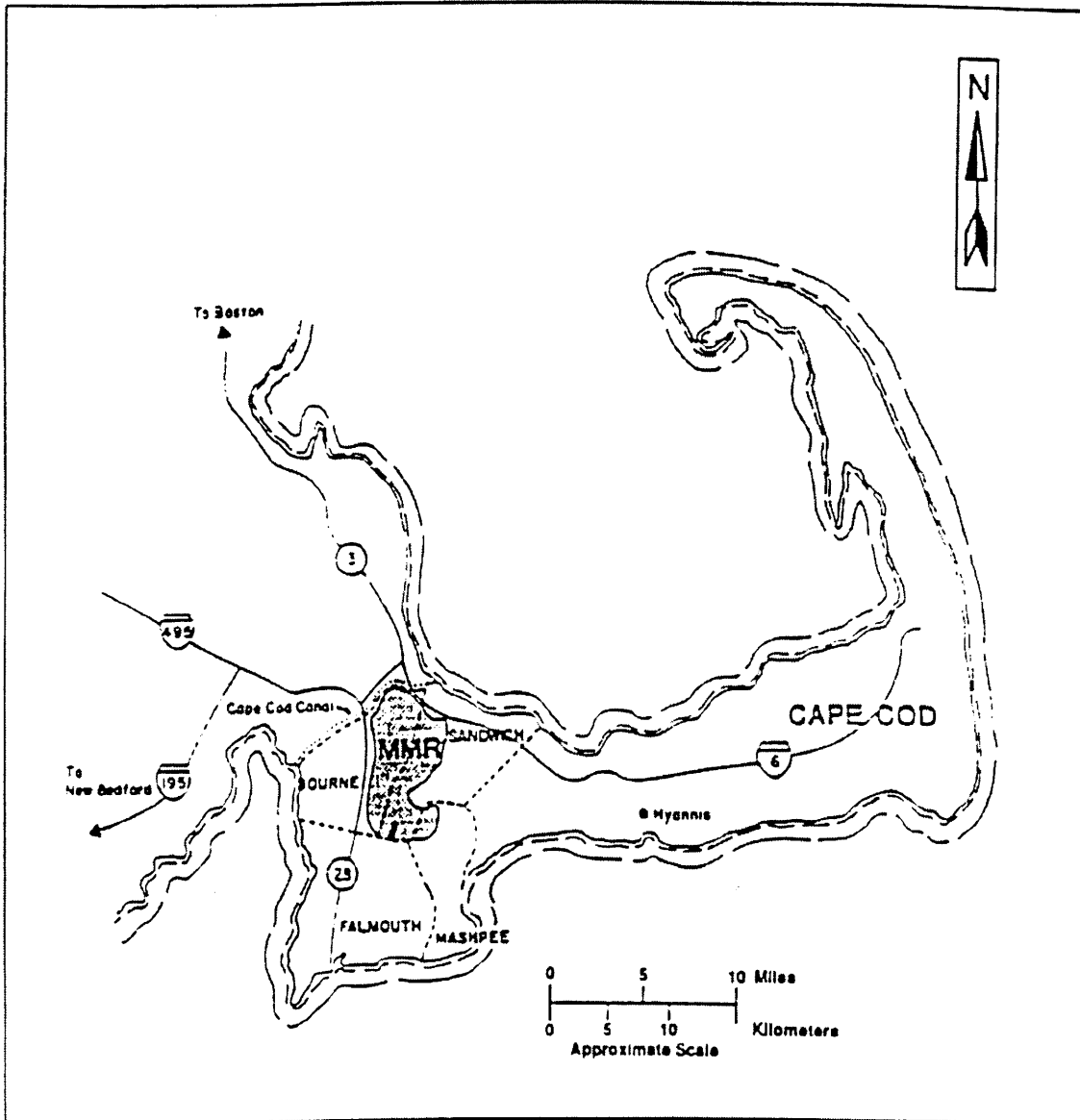
Figure 1.2: Location of MMR

1.1.2. Topography and Geology

The topography of western Cape Cod is typified by hummocky hills, broad areas of low relief, and marshy lowlands. The main southern section of the MMR is located within a broad, southward sloping glacial outwash plain, termed the Mashpee pitted plain (MPP). The MPP is characterized by low topographic relief and an abundance of kettle hole ponds and marshes. Several valleys transect the plain in a north to south direction. The plain is bounded to the north and west by terminal moraines which exhibit irregular, hilly terrain with greater topographic relief. Elevations range from a high of 306 feet, at Pine Hill in the west-central portion of the MMR, to a low of 0 feet at sea level.

The glacial outwash plain, which comprises most of the area of the MMR, consists of highly permeable sand and gravel, and locally occurring lenses of lower permeability, fine grained silt and clay. These sands and gravels are commonly poorly graded, medium to coarse grained sand with well graded gravel. The predominant sediments are quartz and feldspar with surface coatings of iron oxide and occasionally manganese oxide (Knoll et al., 1991). The well graded deposits of the Sandwich Moraine to the north and the Buzzards Bay Moraine to the west were deposited at the terminus of two adjacent glacial lobes during the last glacial advance and retreat. The sediments of these moraines are mixtures of till, sand, silt, clay, and gravel to boulder size clasts.

1.1.3. Regional Climate

Cape Cod has a temperate climate with an average temperature ranging from 19 to 81 degrees Fahrenheit. Temperatures remain fairly moderate due to the proximity to the Atlantic Ocean and the accompanying Gulf Stream. Wind speeds typically vary from 9 to 12 miles per hour with stronger storm velocities of 40 to 100 mph. Annual precipitation averages 48 inches with a somewhat higher portion in winter than summer. Annual groundwater recharge is 26 inches/year.

1.1.4. Ecosystems

The coastal plain ponds, formed in the glacial kettles of Cape Cod, are considered unique and sensitive natural communities by the Massachusetts Division of Fisheries and Wildlife. The rare ecosystem that develops on the shores of these ponds is highly sensitive to water level, temperature, and pH changes.

1.2. Demographics and Socio-Economic Impacts

Fuel Spill-12 is located on the Upper Cape, near the top of the Sagamore lens. Being the sole-source water-supply aquifer for western Cape Cod, the lens is of vital importance to the four towns adjacent to the MMR - Falmouth, Mashpee, Sandwich, and Bourne.

The MMR has a year round population of approximately 2,000 people with an additional 800 nonresident employees. The population of the four surrounding towns fluctuates greatly between winter (29,000) and summer (70,000) due to a strong tourism industry. Between 1980 and 1990, the Upper Cape population grew 35%. As a reference, the population growth of Massachusetts declined 5% over the same period (Bosch et al. 1996).

In the Upper Cape, 80% of the population uses public water supply systems. This amounts to an average off-season demand of 8 million gallons per day (MGD) with a peak 16

MGD during the summer. The remaining 20% of the population relies entirely on private wells for their water supply (Bosch et al. 1996).

1.3. Historical Site Activity

1.3.1. Military Activity

The MMR has been in existence since 1912 and was a major facility for the U.S. Air Force from 1948 to 1973. Since 1973, the MMR has been used primarily by the Massachusetts National Guard and the U.S. Coast Guard. In 1986, the National Guard Bureau's Installation Restoration Program (IRP) was initiated to investigate suspected contaminant plumes at the MMR (Masterson et al. 1996).

1.3.2. Regulation

The MMR was listed as a Superfund site on the National Priority List on November 21, 1989. The National Guard Bureau (NGB) and the U.S. Coast Guard entered into an Interagency Agreement (IAG) with the EPA in July 1991. As a result, any site investigation and remedial action is subject to the requirements and regulations of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). The Department of Defense (DOD) formulated and organized the IRP to address the investigation and remediation efforts at DOD facilities. Through the Air Force Engineering Service Center, the NGB entered into an IAG with the U.S. Department of Energy (DOE). The NGB, with support of DOE, analyzed the extent of contamination and potential site contamination at the MMR (Bosch et al. 1996).

1.3.3. Contamination History

The source area of Fuel Spill-12, is at the intersection of Greenway Road and the western entrance of the L-firing range, about 3,000 ft north of Snake Pond. Leakage from an underground fuel pipeline during 1972 resulted in the FS-12 plume. The pipeline was constructed in the early 1960s; its main purpose was to transport aviation fuel from the Cape Cod Canal to the National Guard flight line. Both aviation gasoline and JP-4 jet fuel were carried in the pipeline. The IRP has estimated a spill volume of approximately 70,000 gallons. The contaminants of greatest concern are benzene and ethylene dibromide (EDB) since they are the ones with potential health hazards. The direction of the plume movement is south-southeastward.

Table 1.1: Break Down of Major Components of JP-4 Jet Fuel

Component	Concentration (g/L)
n-butane	4.92
iso-pentane	2.6
n-pentane	2.07
2-methylpentane	7.43
3-methylpentane	6.48
n-hexane	17.9
methylcyclopentane	11.6
benzene	7.82
cyclohexane	9.63
2-methylhexane	28
3-methylhexane	27.1
dimethylhexane	6.21
n-heptane	33.1
methylcyclohexane	22
toluene	10.7
2-methylheptane	16.5
3-methlyheptane	12.4
n-octane	21.3
ethylbenzene	9.89
m- and p-xylene	12.5
o-xylene	2.04
n-nonane	1.54
n-decane	5.22
n-undecane	2.68
napthalene	ND
n-dodecane	ND
n-tridecane	ND
n-tetradeane	ND

2.   Fuel Spill 12 Description

2.1. Location

The FS-12 source area crosses Greenway Road at the L-firing range and the leading edge of the plume is near J. Braden Thompson Road.
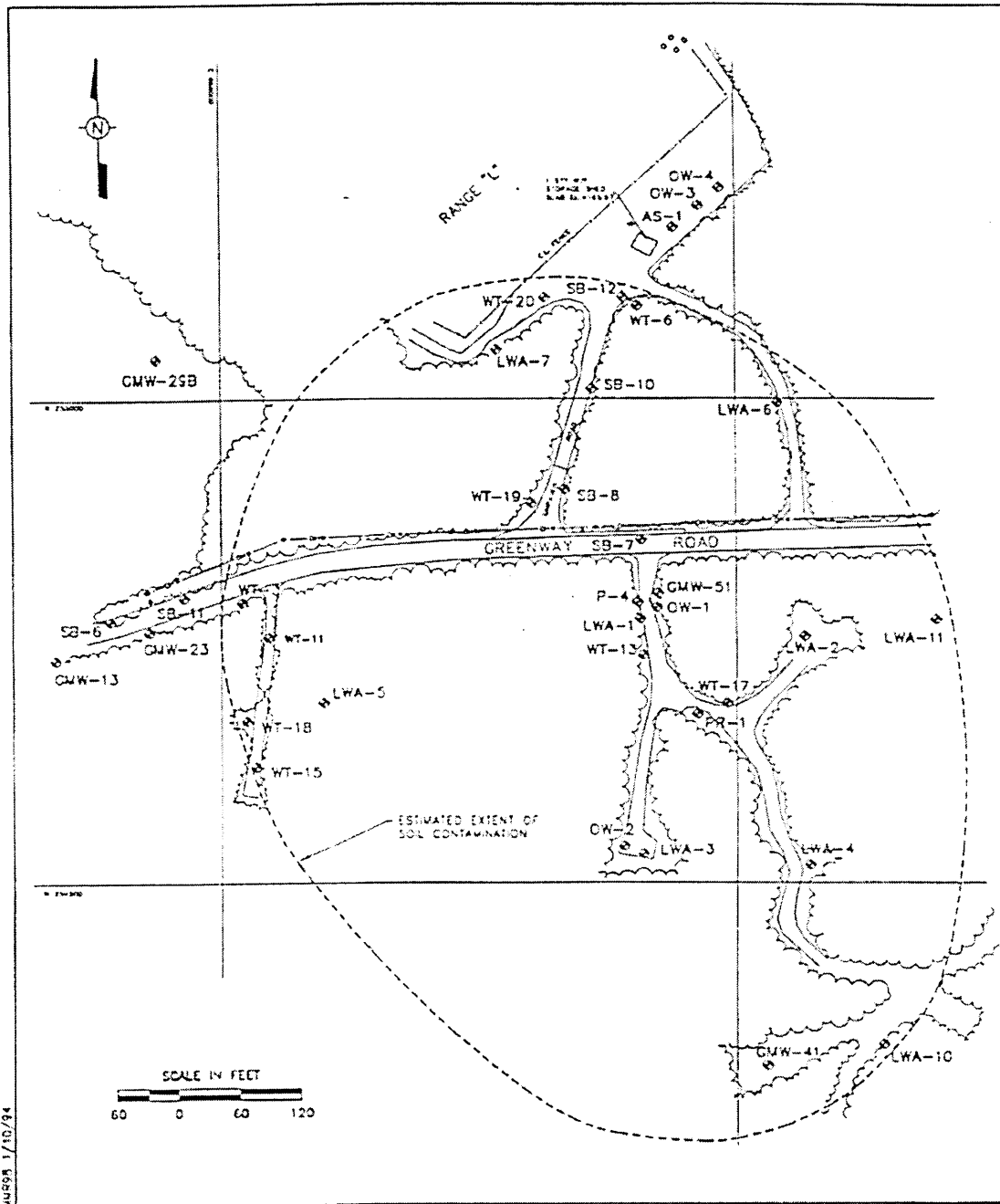
Figure 2.1: FS-12 Source Area

2.2. Physical Characteristics

2.2.1. Geology

The FS-12 site is located entirely in the Mashpee Pitted Plain (MPP). Data indicates that the substrata consist of outwash sands and gravels with discontinuous lenses of fine sand, silt, and clay down to at least a depth of 130 feet below the water table. The bottom of the aquifer has not been drilled, so there are only guesses as to the nature of the confining layer. There are two views in this regard: (1) The majority of the aquifer is confined by a deep clay layer, (2) The confining layer is bedrock. The bedrock has been mapped by using geophysical seismic surveys that produced data which appears to point to bedrock as the confining layer (Masterson, et al.,1996).

A zone of surface soil and weathered residuum of approximately two to five feet is common in the study area. The interval typically consists of silty clay or clayey silt, with variable mixtures of fine sand and/or organic matter. Underlying this layer is the upper sand and gravel outwash deposits of the MPP. The substrata are unconsolidated and typically consist of sand with minor amounts of gravel. The sand is dominantly weathered quartz with some feldspar, the grains are typically poorly graded, mostly medium grained, and sub-angular to sub-rounded. The gravel component typically ranges between 0 to 25 percent of the lithology. The gravel is well graded, with clasts ranging in size from fine gravel to cobbles and boulders. The clasts are dominantly weathered granite. Locally, an abundance of coarse gravel is common in the uppermost 30 ft. The primary source bedrock for the outwash sediment appears to be granite. Below the uppermost 130 ft of the sand and gravel deposits, intervals of fine grained sediments have been noted, particularly at depths ranging between 130 ft to 215 ft. Most intervals have not been penetrated, therefore thickness data is limited. The few borings that have penetrated these sediments of fine sand and silt show dense deposits with an approximate thickness of 20 to 25 feet. These sediments typically consists of silty to sandy clay, clayey silt and sand, or silty sand. See Appendix-A for stratigraphic cross sections.

2.2.2. Hydrogeology

The FS-12 area is underlain by the Cape Cod Aquifer. These sands and gravels serve as a primary water source for municipal and residential water supply wells. The total thickness of the saturated zone is estimated to be in excess of 200 ft, with an average depth to water of 70 ft for the unconfined aquifer. The water table is exposed at the surface in Snake Pond, the southwestern boundary of the FS-12 area. Data indicate horizontal gradients in the range of 0.0003 to 0.00067 ft/ft to the south-southeast. This range is one order of magnitude lower than

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gradients in adjacent areas of the MMR. The area has an estimated horizontal hydraulic conductivity of 151 ft/day, an estimated porosity of 30 percent, and a horizontal ground water flow velocity of 100 ft/yr at the source and 333.33 ft/yr downgradient. The variation in horizontal flow velocity is due to the proximity of the groundwater divide to Greenway Road, where the velocity is zero.

2.3. Remedial Activities

There are two distinct remediation objectives: plume containment and source remediation. A proposed pump and treat (P&T) system, due to operate in the summer of 1997 is designed to contain the plume. Air sparging (AS), in conjunction with soil vapor extraction (SVE), is currently being used to remediate the source.

2.3.1. Plume Containment

The primary focus of plume containment will be to avoid impacts to Snake Pond. A P&T system has been designed based on a model of groundwater flow in the region of interest. An extraction and injection well fence system will be employed. Thirty preliminary extraction and injection wells are currently being installed. Data obtained from these wells will be used to refine and calibrate the model. The refined model will be used to decide the quantity and location of additional extraction and injection wells, and corresponding flow rates. The entire process is expected to take one-half to two years.

2.3.2. Source Remediation

An air sparging and soil vapor extraction system is currently in operation to remove fuel at the source area of FS-12. The SVE system couples vapor extraction wells with vacuum pumps to remove contaminants from zones permeable to vapor flow, thereby enhancing the volatilization and efficiency of removal of contaminants from the subsurface. The components of the system include vacuum pumps and controls, control valves to adjust air flow, pressure gauges and flow meters at well heads, air-liquid separator for removing moisture from the extracted gases, vapor treatment unit, air treatment using catalytic and carbon adsorbers. Air sparging, a more recent innovation, extends the application of SVE to water saturated soils. AS is accomplished by injecting air under pressure below the water table. It is expected that contaminants located within air flow pathways will volatilize or biodegrade and there is the potential that dissolved phase contaminants that contact the air flow field could also be volatilized or biodegraded. There are two theories that have been advanced which explain the effect of air sparging: injected air strips contaminants from the soil and groundwater into vapor flow; and injected air increases the

oxygen content of the groundwater, resulting in increased aerobic biodegradation. It is most likely that both contribute to remediation. The SVE system began operation October 23, 1995. The AS system began operation February 21, 1996. As of February 22, 1997, an estimated 19,147 kilograms of product had been removed from the site of the 186,220 kilograms of estimated residual.

2.3.3. Extent of Contamination

The extent of benzene contamination is shown in Figure 2.2. The greatest level of contamination in the source area is 2000 ppb and at a depth of 100 feet and in the downgradient plume greatest contamination is 2400 ppb and at a depth of 150 feet.
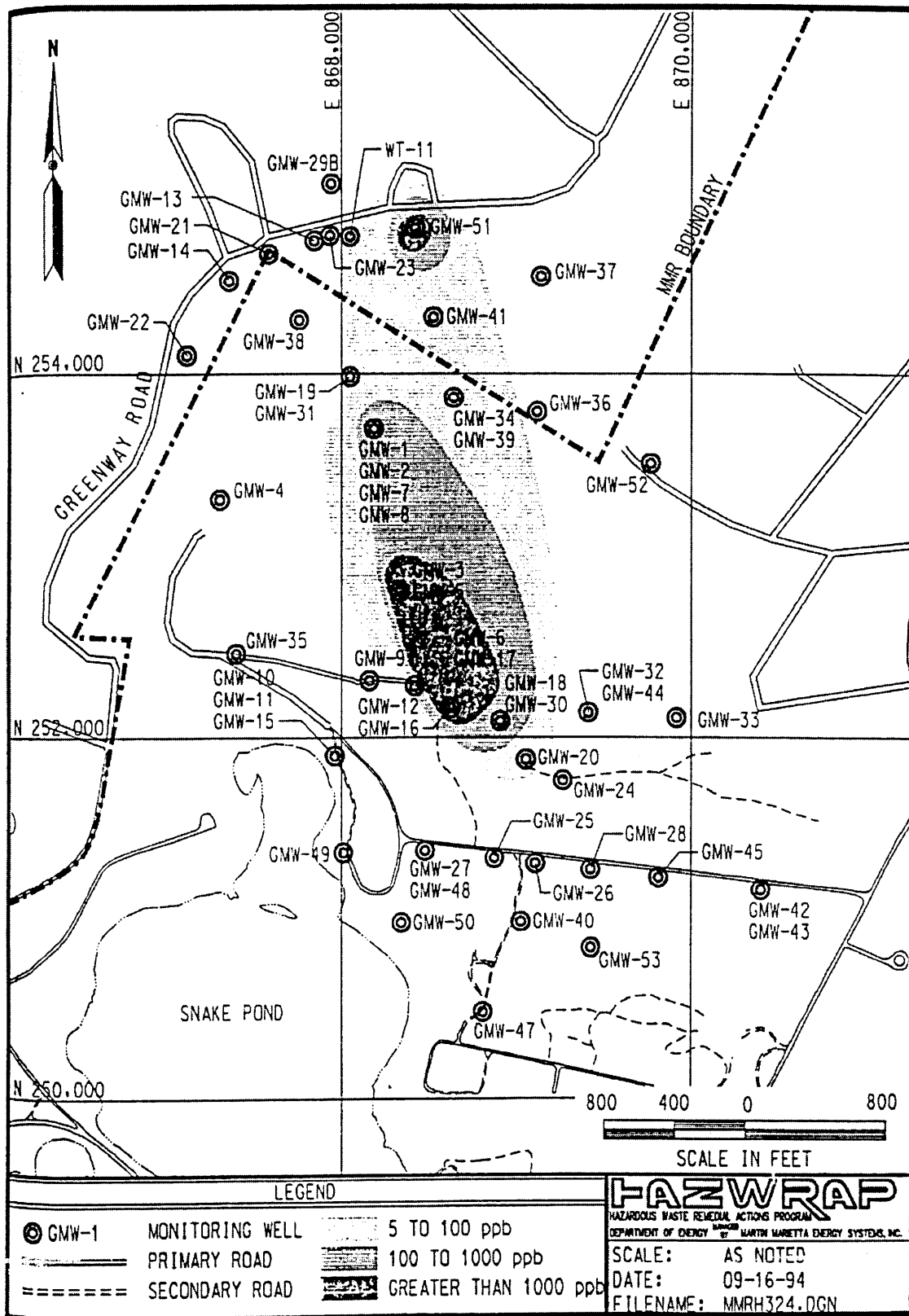
Figure 2.2: Extent of Benzene Contamination

3. FS-12 Source Remediation: Soil Vapor Extraction

3.1. Introduction

Vapor extraction technologies induce air flow in the subsurface using an above ground vacuum blower/pump system. Adequate air movement within the contaminated zones is of primary importance to the success of soil vapor extraction. The induced air flow brings clean air in contact with the contaminated soil, non-aqueous phase liquid (NAPL), and soil moisture. The contaminated soil gas is drawn off by the SVE and the air in the soil matrix becomes recharged with new vapor phase contamination as the soil/pore water/soil gas/NAPL partitioning is re-established.

Vapor extraction is performed to volatilize the hydrocarbon constituents in situ. Compounds that are volatile move with the air, and compounds that are degradable have an increased rate of degradation.

Figure 3.1 shows the basic components of a vapor extraction system. Subsurface vapors are withdrawn through an extraction well that may be vertically or laterally constructed. Recovered vapors are routed to an above ground vapor treatment unit, if required. The key to a successful design is to place the wells and equipment so that when the system is in operation an air flow pattern is created across the entire section of the unsaturated zone that is contaminated. The design must also be careful that the air does not move through a small percentage of the area due to porous geology.
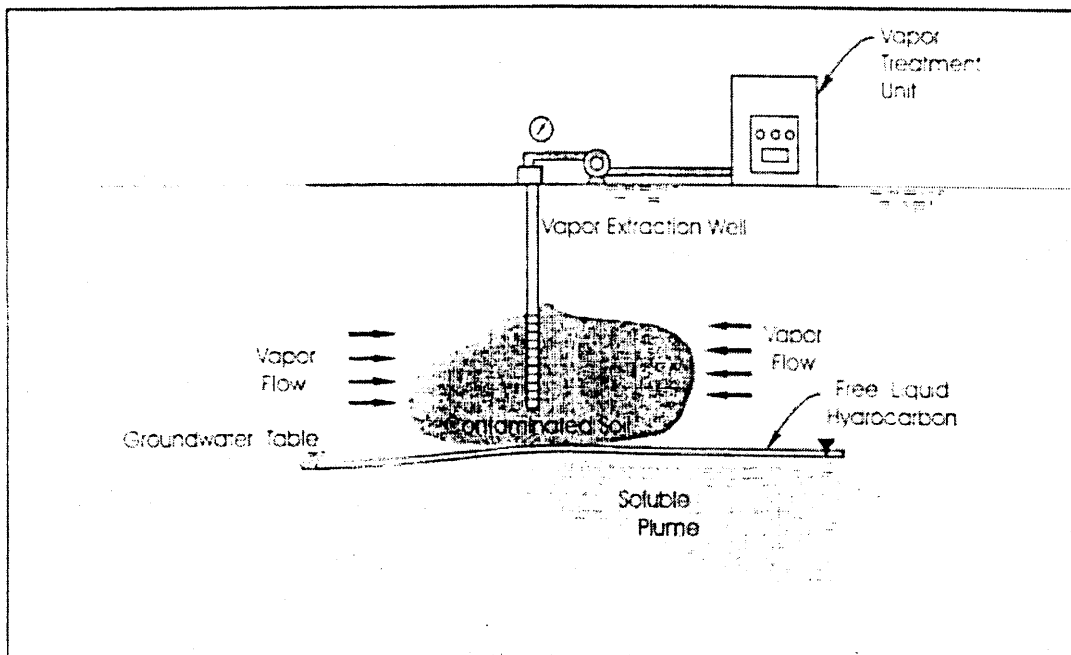
Figure 3.1: A Typical Soil Vapor Extraction System

A vacuum pump or blower is the tool that is used to create subsurface air flow, Figure 3.1. The vacuum created at the extraction well head is an indication of the subsurface soil resistance to air flow. If the subsurface is very porous (sand/gravel) there will be very little vacuum at the extraction well head regardless of vacuum pump that is utilized. If there is little resistance, there will be little resultant vacuum. If one increases the flow from a given well, more vacuum application will be required because of the increased subsurface resistance created by the higher flow. Vacuum is an indication of subsurface resistance to flow and is not the variable that is critical to SVE success. Sufficient air flow is the critical variable. The vacuum application is a system operational parameter that allows creation of the desired air flow.

3.2. Contaminant Partitioning

Contaminants that are released to the environment will be distributed in the subsurface in a manner consistent with their physical properties. This subsurface distribution (in pore water, adsorbed to soil, or in pure NAPL) is termed partitioning. Partitioning is related to properties of the soil as well as the contaminants.

Transfer of the contaminants between phases is affected by the relative affinity of the contaminant to each phase. These affinities can be evaluated using the constituent partitioning coefficients to the various phases. The inter-phase partitioning coefficients can be expressed as the concentration ratios of the constituents in each phase, and this ratio is dictated by the equilibrium relations in the subsurface. Since, to a large extent, the inter-phase transfer is governed by these equilibrium partitioning relationships, the most effective remediation will create the subsurface conditions that will drive the inter-phase transfer towards the phase(s) that allow for the most efficient mass removal. Site remediation, therefore, can be viewed as implementing changes or perturbations to the subsurface that will drive chemical and biological processes toward the site remediation goals (Sims, 1990). The subsurface change that is affected during vapor extraction is replenishment of the subsurface soil vapor, therefore driving the contamination to the vapor phase where it is collected for above ground treatment.

When a volatile NAPL is present in the soil, the bulk of the mass removal by SVE will come first from direct volatilization of the NAPL. Research work (Hoag et al., 1989) has shown that the bulk (over 95%) of the NAPL can be removed within passage of several hundred pore volumes of air through the experimental soil columns. In field application, where air flow is usually over the NAPL rather than through it, SVE still often recovers the bulk of the NAPL within several hundred pore volumes (Sims, 1990). Under conditions of NAPL presence, mass

removal rates are often correlated with air flow rates. When NAPL is not present in the subsurface, air flow requirements become very different and are often governed by non-equilibrium rate limiting conditions.
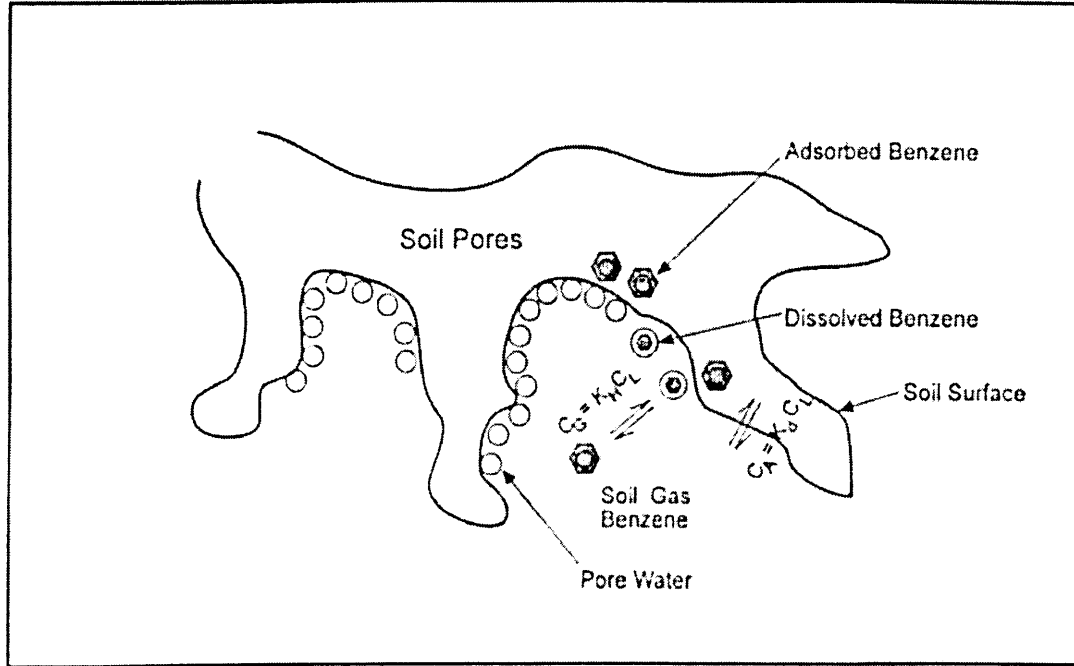
Figure 3.2: Vadose Zone Partitioning

Under moist soil conditions, contaminant partitioning in the vadose zone can be described by the following equation (1) Figure 3.2 is an illustration of the equation:

$$C_T = p_b\, C_A + \theta_L\, C_L + \theta_G\, C_G \qquad (3-1)$$

where

C_T = total quantity of chemical per unit soil volume,

C_A = adsorbed chemical concentration,

C_L = dissolved chemical concentration,

C_G = vapor concentration,

p_b = soil bulk density,

θ_L = volumetric water content,

θ_G = volumetric air content.

The equilibrium relationship between vapor concentration (C_G) and the associated pore water concentration (C_L) is given by Henry's Law:

$$C_G = K_H C_L \qquad\qquad (3 - 2)$$

where K_H = Henry's Law constant.

Henry's Law is often associated with air stripping, where air removes dissolved volatile organic compounds (VOCs) from the water stream. The efficiency of this removal is related to the Henry's Law constant of the compound. Under moist soil conditions, the extracted vapors during vapor extraction similarly remove VOCs from water.

The relationship between equilibrium solution concentration and adsorbed concentration is given by:

$$C_A = K_d C_L \qquad\qquad (3 - 3)$$

where K_d (L/m) is the distribution coefficient expressed as $K_d = f_{OC} K_{OC}$, where f_{OC} is the mass fraction of organic carbon, and K_{OC} is the organic carbon partitioning coefficient.

Equation (3) is considered to be valid for soils with high organic content ($f_{oc} > 0.1\%$ solids). For soils with lower organic content sorption to mineral grains may be dominant.

3.3. Air Flow

The need to understand and predict the subsurface mass transfer relationships relates to the practical need to deliver the required air flow to achieve the remedial goals. In instances where NAPL is present in pockets, pools, or as a layer atop the ground water, mass removal often is linear or semilinearly rated to the air flow. This does not imply that if NAPL is present, high air flow is required, since often the NAPL is removed rapidly, leading to site conditions that may not require further high air flow. Air flow generation capability (air flow that can be generated based upon soil conditions) and the air flow requirements to achieve remediation must be met in order to appropriately install a SVE system.

Delivering the required air flow to achieve the cleanup criteria is the basic design goal for SVE installation. This basic goal, however, remains the most difficult to predict due to the limited understanding of subsurface conditions. The most distant location from the extraction well should receive sufficient air flow to achieve remediation. The most distant location from the extraction well is termed the radius of influence. Sufficient wells are spaced in the contaminated area to deliver the minimally acceptable air flows across the entire site.

3.4. SVE Applicability

Vapor extraction system efficiency is affected by parameters related to the contaminants to be removed and by variables related to the site to be remediated. Contaminant properties that effect SVE are vapor pressure, solubility, Henry's Law constant, biodegradibility and other molecular properties. Vapor pressure is the most important chemical parameter affecting SVE

performance. Soil properties that affect SVE performance include soil porosity, soil adsorption, soil moisture, site topography, depth to water table and site homogeneity. Of the soil properties, permeability is the most critical parameter related to system success.

3.5. Contaminant Properties

3.5.1.   Vapor Pressure

Vapor pressure is the parameter that can be used to estimate the tendency of a compound to volatilize and partition into the gaseous state. The vapor pressure of a compound is defined as the pressure exerted by the vapor at equilibrium with the liquid phase (NAPL) of the compound in the system at a given temperature (Anderson, 1993). Table 3.1 provides a listing of relevant parameters for some common environmental contaminants.

Table 3.1: Compound Properties

Contaminant	Strippability	Volatility	Aerobic Biodegradation	Solubility
Benzene	High (H = 5.5 X 10^{-3})	High (VP = 95.2)	High ($t_{1/2}$ = 240)	1750 mg/L
Ethyl Benzene	High (H = 8.7 X 10^{-3})	High (VP = 9.5)	High ($t_{1/2}$ = 144)	152 mg/L
Toulene	High (H = 6.6 X 10^{-3})	High (VP = 28.4)	High ($t_{1/2}$ = 168)	535 mg/L
Xylenes	High (H = 5.1 X 10^{-3})	High (VP = 6.6)	High ($t_{1/2}$ = 336)	175 mg/L
Trichloroethylene (TCE)	High (H = 10.0 X 10^{-3})	High (VP = 60)	Very Low ($t_{1/2}$ = 7704)	1100 mg/L
Perchloroethylene (PCE)	High (H = 8.3 X 10^{-3})	High (VP = 14.3)	Very Low ($t_{1/2}$ = 8640)	150 mg/L

H = Henry's Law constant (atm-m^3/mol)

VP = Vapor pressure (mmHg) at 20 °C

$t_{1/2}$ = Half-life during aerobic biodegradation, hours

When chemicals exist in pure form (NAPL), the vapor pressure of the contaminant is very important to its removal efficiency by SVE. The higher the vapor pressure, the more it is amenable to vapor extraction. The lower the vapor pressure, the less likely the contaminant will volatilize and the greater reliance on biodegradation for successful remediation. For mixtures of

compounds, the composition of the mixture also has a bearing on the vapor pressure according to the following relationship:

$$P_i = X_i \, A_i \, P_i^{\,o} \qquad\qquad (3 - 4)$$

where

P_i = equilibrium partial pressure of component i in the organic mixture

X_i = mole fraction of component i in the organic compound mixture

A_i = activity coefficient of component i in the organic compound mixture

$P_i^{\,o}$ = vapor pressure of component i as a pure compound

If NAPL is not present in the soil, vapor pressure becomes a less accurate predictor of SVE efficiency since other relationships become more important in governing system success such as adsorption to soil and moisture content. However, even under conditions of no NAPL presence, a compound must be volatile to be removed by SVE. Sufficiently high vapor pressure can therefore be viewed as a prerequisite for successful vapor extraction. Although the definition of sufficiently high vapor pressure is rather subjective, 1 to 2 mmHg should be used as a guideline (Norris, 1994). Compounds with lower vapor pressures will likely be removed more slowly and greater reliance will be required on in situ biological breakdown of the compounds.

3.5.2. Solubility

Aqueous solubility is one of the most important parameters governing the partitioning, transport, fate, and ultimate remediation of site contaminants. Solubility can be defined as the maximum amount of a constituent that will dissolve in pure water at a specified temperature (Anderson, 1993). For organic mixtures solubility is additionally a function of the mole fraction of each individual constituent in the mixture according to Equation (3 - 5).

$$C_i = X_i \, A_i \, C_i^{\,o} \qquad\qquad (3 - 5)$$

where

C_i = equilibrium concentration of component i in the organic mixture

X_i = mole fraction of component i in the compound mixture

A_i = activity coefficient of component i in the organic compound mixture

$C_i^{\,o}$ = equilibrium solute concentration of component i as a pure compound

Under most vapor extraction conditions, the vadose zone is relatively moist and contaminants are generally dissolved in the soil pore water. Solubility is also a critical factor for biodegradation of contaminants since it is enhanced if the contaminants are more available for

microbial uptake by being dissolved in the pore water. A soil moisture of 12% by weight is generally required for adequate biodegradation (Norris, 1994).

3.5.3. Henry's Law

The interaction of solubility and vapor pressure produces a behavioral modification that renders the additive effects of solubility and vapor pressure nonlinear. This interaction has particular impact on volatilization of organics from water. Henry's Law constant is functionally defined as the ratio of saturated vapor density to chemical solubility for a given compound:

$$H = C_v / C_w \qquad\qquad (3 - 6)$$

where:

H = Henry's Law constant

C_v = concentration in the vapor phase at the water/vapor inter-phase

C_w = concentration in the water phase at the water/vapor inter-phase

In moist soil conditions SVE efficiency is Henry's Law dependent. SVE also has a temperature dependence similar to air stripping. The temperature relationship is more complex for SVE due to the existence of multiple system variables such as biodegradation, adsorption, etc. (Anderson, 1993). In general, higher temperatures in the vadose zone enhance volatilization, which improves operations of SVE systems. Increased temperature also enhances biodegradation, increases the rate of desorption, and weakens the adsorption binding.

3.5.4. Molecular Properties

There are several other molecular properties of the contaminant that influence the success of vapor extraction. These properties are not as significant as vapor pressure, solubility, and Henry's Law and hence they are considered secondary. These properties often may be the rate-limiting criteria to site remediation. Compound size, molecular weight, electronegativity, and polarity affect adsorption of the contaminant to soil particles and its travel through the soil micropores. Larger, bulkier (branched molecules) travel more slowly within soil micropores and tend to adsorb more strongly to soil surfaces. Once the majority of the more accessible (from large pores, and not directly adsorbed to soil) contamination is removed, the final portion of removal becomes rate limiting. Polarity and electronegativity relate to the effective charge of a compound and its interaction with the surface charge of the soil.

3.6. Soil Properties

3.6.1. Porosity

Decreasing soil permeability generally reduces the efficiency of SVE because the diffusive transport from the soil matrix to the soil surface and in turn to the soil gas reduced due to the increased path length (path to convective air flow) and a decrease in cross-sectional area for air flow. Another influence of decreasing porosity is the increase in the soil surface areas available for contaminant binding.

3.6.2. Soil Adsorption

There are two methods by which the soil can adsorb the organic contaminant. The soil organic content and its mineral adsorptive surface sites are both capable of contaminant adsorption. The adsorption of contaminants to the soil organic or mineral clay surfaces tends to increase the immobile fraction of the contaminant (adsorbed to the soil) and to decrease the vacuum extraction system efficiency. Soil adsorptive interactions become particularly important (rate limiting) under drier soil moisture conditions.

Soil total organic carbon (TOC) matter is strongly correlated with the binding capacity for organic chemicals. The soil adsorption correlation coefficient is likely to be highest when the soil organic content is high. A relationship describing the binding capacity of the soil to organics was defined in equation (3 - 3). Most organic contaminants are more easily adsorbed to the soil than they are desorbed. It therefore takes much longer and requires more energy to remove the contaminants from the subsurface than it does to spill them.

3.6.3. Soil Moisture

Soil moisture is a very important parameter for SVE success. High soil moisture content limits air advection travel pathways by occupying void space. Since movement of VOCs is much faster in the gas phase than in the liquid phase, it would be expected that VOC removal by vacuum extraction would be enhanced by decreasing soil moisture. This trend is not always observed, the lack of soil moisture allows contaminant adsorption to soil surfaces to play a more prominent role in mass transfer as the water particles are removed from the surface (Anderson, 1993). If the soil adsorptive capacities are strong, the benefits of soil dewatering (increased air travel pathways) may be partially offset by this increased soil binding capacity. The moisture content at which a decrease in vapor concentration during SVE operation is termed the critical moisture content and is empirically defined as one monolayer of water molecules coating the soil surface (Norris, 1994).

3.6.4. Site Surface Topography

Site topography can greatly influence the success of SVE. Ideally the site should be covered by an impermeable surface such as pavement or concrete. The covered surface serves two functions. First, it minimizes the infiltration of rainwater to the vadose soils and consequently allows some control over soil moisture. Second, the covered surface eliminates the possibility of extraction well short circuiting (Figure 3.3), where the majority of the extracted volume of air is coming from near the ground surface, and locations more distant from the extraction wells receive minimal air flow (Anderson, 1993).
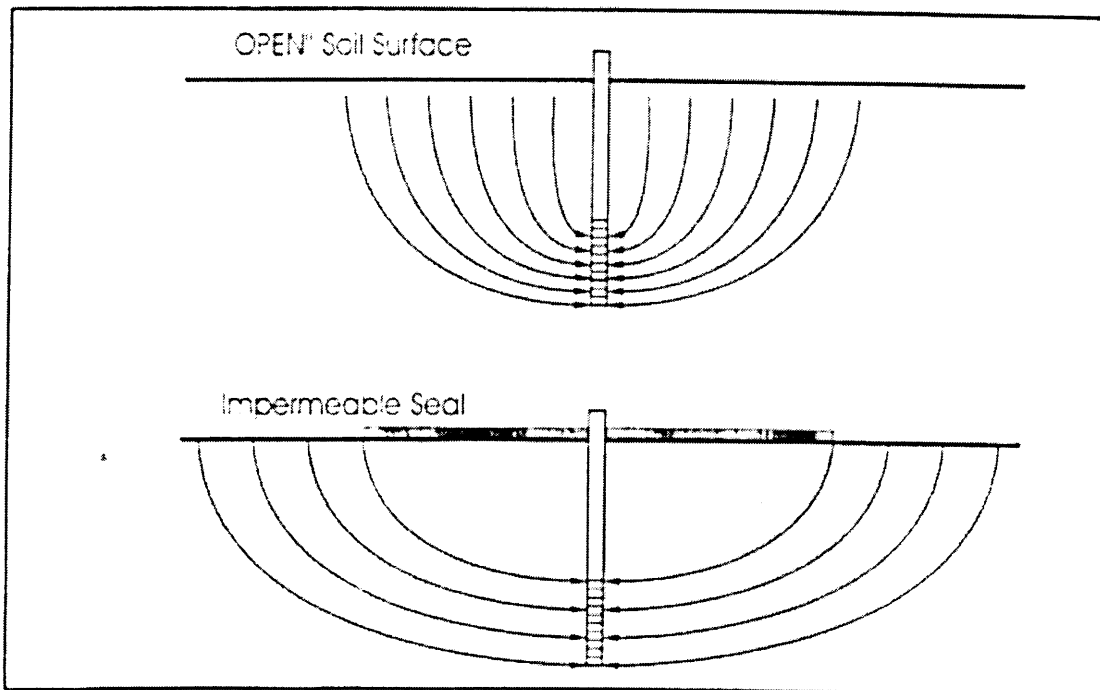
Figure 3.3: SVE Short Circuiting

3.6.5. Site Homogeneity

Site homogeneity is very important to ensuring that air flow reaches all areas requiring remediation. The air carrier must flow past the contaminants if they are to be removed. Transport of the contaminants by the carrier air flow minimizes diffusion requirements for mass removal. The is reduces the travel path length to remediation and expedites the cleanup.

3.7. SVE System Design

The goal in designing vapor extraction based processes is to specify system components and operating conditions that will meet the remedial goals (cleanup level and specified duration), while operating within constraints (costs, emissions limits, etc.) Because of uncertainties and

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inherent limitations arising from natural heterogeneities, site characterization data, and predictive capabilities, even well reasoned goals cannot realistically be expected to be met with a high degree of confidence (Anderson, 1993). The design of SVE systems continues even after the initial system is installed and started. System performance should be monitored, the results interpreted, and system modifications made accordingly.

The following components are typically specified in a soil vapor extraction system design: number of extraction wells, number of air injection wells, well locations, well construction (depth, screened interval, materials, etc.), extraction blowers or vacuum pumps, vapor treatment units, equipment manifolding & piping, instrumentation & controls (flow meters, sampling ports, vapor concentration monitoring, control valves, pressure or vacuum relief valves, etc.).

3.8. Design Approach

3.8.1. Empirical Approach

In the empirical approach, the most simplistic of the design approaches, the number of wells, well locations, and blower, vapor treatment requirements are specified based on previous experience, general guidelines, and intuition. The only essential information is a baseline geologic/hydrogeologic assessment indicating the general location of contaminant impacted soils. This design process can be easily and quickly performed. It requires a minimum level of skill in design and little understanding of vapor extraction processes. The performance of the resulting system may be problematic and may even cause detrimental effects. (Anderson, 1993).

3.8.2. Matching System Design to Equipment

In this approach, the use of existing equipment is maximized in order to minimize capital expenses. In the extreme case, a portable skid-mounted vapor extraction system is connected to existing ground water monitoring wells, and the only cost is that of connecting the system. The only advantage of this approach is the minimizing of installation costs. Although these savings are likely to be offset by the increased operating costs of an inefficient system.

3.8.3. Radius of Influence

Radius of influence approaches are currently the most frequently used. The number of wells and their spacing is based solely on the pressure distribution measured during a pilot test (Anderson, 1993.) Once the radius of influence has been determined, circles with this radius are drawn on a site map locating wells such that areas are circumscribed by the circles overlap the

zone to be remediated. After well locations have been specified, extraction pumps and a vapor treatment unit is selected.

This approach is widely practiced because it is simple, graphical, and closely imitates common ground water recovery design systems. Unfortunately, at best, this approach merely assures containment of contaminant vapors and does not provide for estimation of performance or long term costs (Anderson, 1993).

3.8.4. Screening Level Model

The major limitation of the simplistic design approaches is their failure to consider probable system performance factors or constraints. In order to incorporate these factors, a predictive model needs to be applied that facilitates estimation of system performance as a function of a wide range of parameters, such as geologic conditions, contaminant type, and number of wells (Anderson, 1993). The data requirements for these screening models such as HyperVentilate are the following:

- extraction flow rate as a function of applied vacuum for conceptual well design
- estimate of average residual soil concentration and volume of impacted soil
- remedial goals - cleanup level and remediation time
- minimum volume of vapor to achieve required cleanup
- steady state pressure distribution from the well
- effluent vapor concentration data from pilot test
- geological cross-section map with contaminant distribution
- constraints - cost, regulatory requirements, etc.

The following equation provides a relationship for some of the relevant parameters:

$$N = [\, V \, C \, \alpha \rho] \, / \, [\, Q \, t \,] \qquad\qquad (3 - 7)$$

where

N = number of wells

V = volume of contaminant containing soil

C = average soil contaminant concentration

α = minimum volume of vapor required to achieve cleanup per unit mass of contaminant

ρ = density of soil

Q = flow rate of single well

t = target remediation time

The number of wells predicted by equation (3 - 7) is a minimum estimate of wells required, as any real system performs less efficiently than an ideal system. The equation provides a screening level toll relating number of wells, cleanup objectives, and operating conditions.

3.8.5. Numerical Modeling and Optimization

The screening level approach can be extended through the use of more complex mathematical models. Such models usually require more data than is readily available; however there are sites for which the projected cost of remediation warrants the expense of acquiring the needed data. To be used most effectively, complex modeling must be performed iteratively. The predictive model must be continuously refined, calibrated, and updated based on performance data collected from system operation. (Anderson, 1993)

3.8.6. SVE Implemented Design

The SVE design implemented at FS-12 was based primarily on a pilot study and a MODFLOW model whose results where used as input parameters for the Venting software program which calculates remediation time. The main objective of the pilot test was to determine radius of influence (ROI) for a single extraction well. A pressure change of 0.1 in of water was used to determine the ROI. The pressure drops are plotted on a semi-log plot from which the ROI is interpreted. The test showed a ROI of 160 ft for a 0.1 in HO pressure drop and an ROI of 260 for no pressure change. A ROI of 120 feet was used for the full scale design to provide a factor of safety to ensure that the entire area is affected by the SVE system and that all vapors from the AS system are captured.
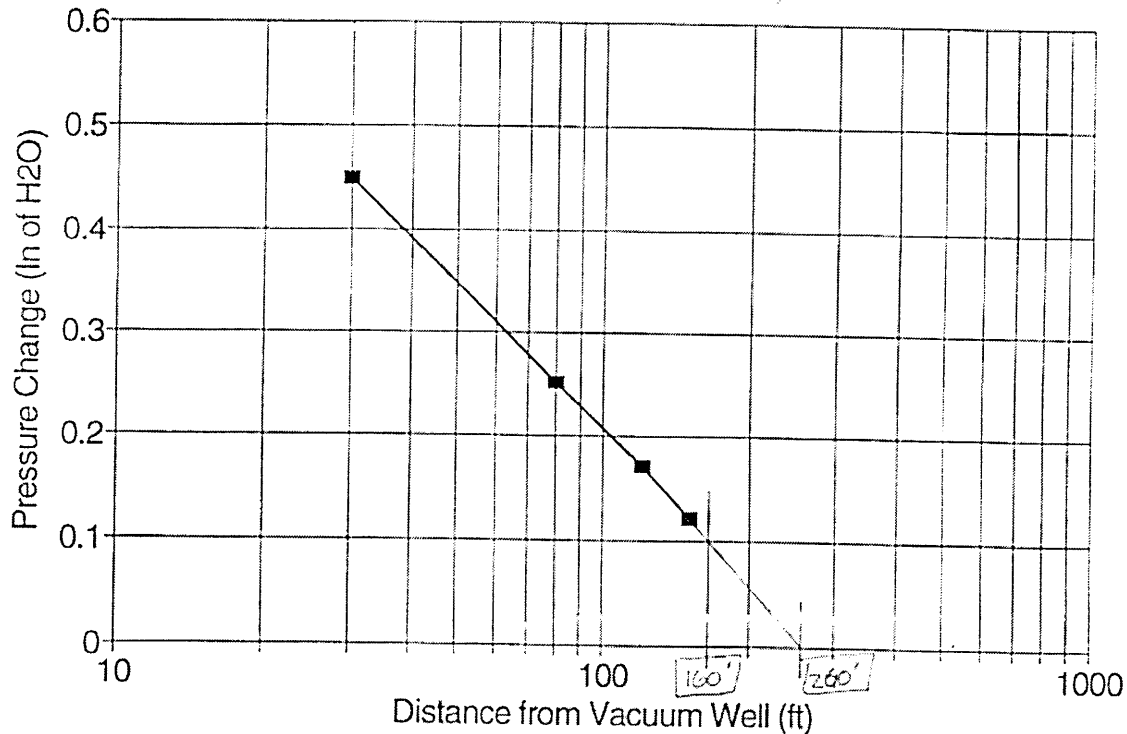
Figure 3.4: Radius of Influence

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Well layout was determined by a review of the site and of the differences of radius of influences between air sparging and soil vapor extraction concluded that the 75 ft radius of influence of air sparging would be the controlling factor in spacing wells. The air sparging wells were laid out at the site on a 150 ft by 150 ft grid and the soil vapor extraction wells were laid out in 150 ft by 180 ft grid, the grids were solely determined on a geometric basis. The layout requires a total of 21 SVE wells and 22 AS wells, Figure 3.5 & Figure 4.5. This layout was then used as input to the computer program Modflow to ensure that as the air sparging was cycled through the site that all the "dead spots" between the wells would receive adequate ventilation and that all of the vapors created by air sparging would be captured by the SVE system. (Advanced Sciences, 1994) The typical operational flow rate for each SVE well is 145 cfm and the depth of extraction of 80 feet below ground surface (Atlantic, Nov-Dec 1996).
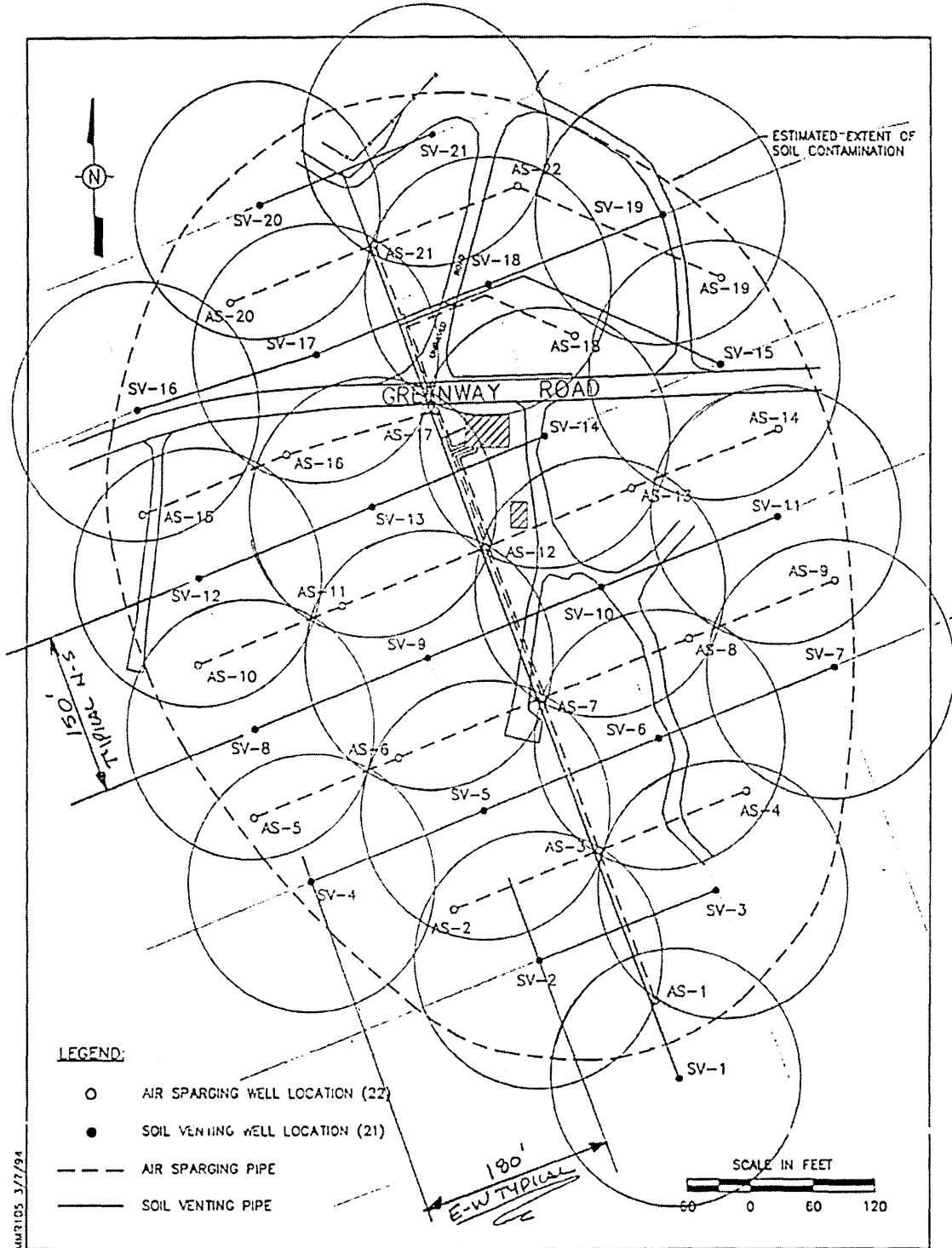
Figure 3.5: SVE Well Layout

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4. FS-12 Source Remediation: Air Sparging

4.1. Introduction

An inherent limitation of soil vapor extraction is that it will not remove contaminants that are beneath the unsaturated zone. In many cases, contaminants are released into the subsurface at such large quantities that the liquid migrates down to the saturated zone. Contaminant migration through the vadose zone and toward ground water occurs in several mechanisms. Above the capillary fringe, the soil is only partially saturated with water and contaminants migrate principally by vapor diffusion, pure phase infiltration, and infiltration in aqueous phase. The majority of contaminant mass migrates in pure phase, but mass migrating by this mechanism is impeded in soil that is nearly saturated. This may occur in any wet zone in the vadose zone, but always becomes the case within the capillary fringe, which depending on the soil and its capillary characteristics may extend less than a meter to several meters above the water table. Within the capillary fringe the pure phase accumulates in the non-saturated pores. Monitoring well within the zone typically show a layer of pure LNAPL floating on the water table, but the actual transition from LNAPL to ground water is more gradual, with the capillary fringe representing a zone of partial water and partial LNAPL saturation (Norris, 1993). When the water table fluctuates the contaminant becomes smeared or immobilized below the water table.
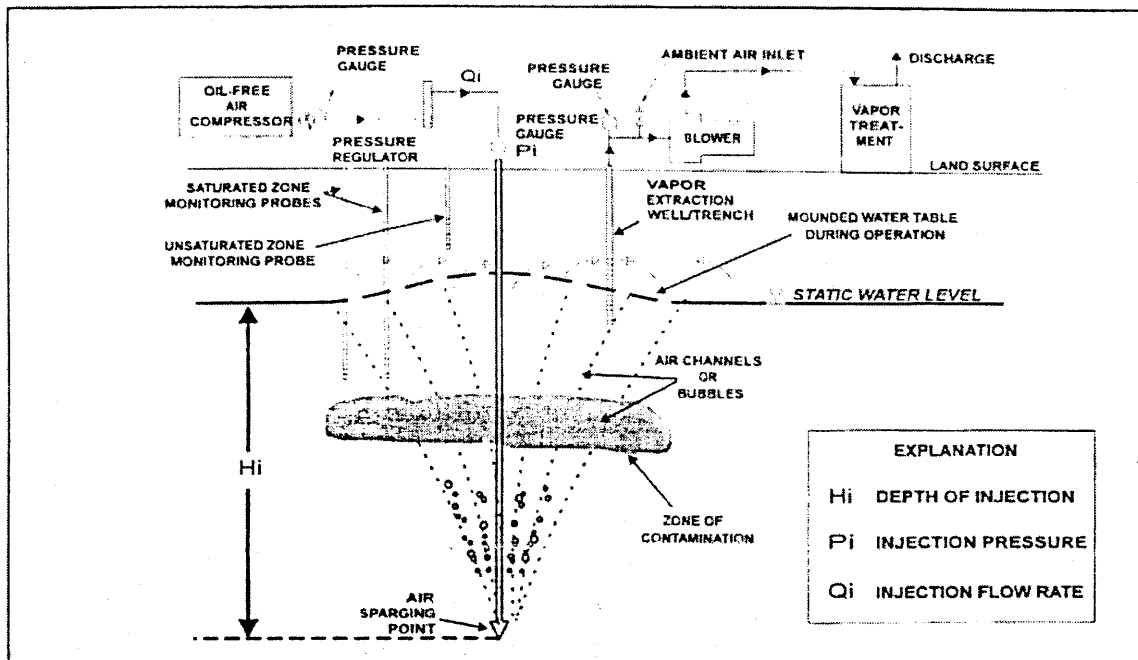
Figure 4.1: Air Sparging

Air sparging is able to extend the utility of soil vapor extraction to water saturated soils. Air is injected under pressure below the water table (Figure 4.1) It is commonly envisioned that injected air in the form of bubbles travels up through the saturated zone, thereby transferring the hydrocarbons from the soil and ground water phase into the vapor phase. It is more realistic, however, to expect continuous air channels to direct air flow in the saturated zone (Ahlfeld, 1994). In addition to volatilization, it is postulated that the injected air increases the oxygen re-supply rate to the ground water, resulting in increased aerobic biodegradation rates.

Once air is injected into the saturated zone, its advective flow is governed largely by the applied pressure, buoyant forces, vertical and horizontal permeability distributions in the saturated zone, immiscible fluid displacement phenomena, and capillary properties of the soils. Depending on the size of the pores within the media, either air bubbles (extremely coarse materials) or continuous air channels (fine subsurface materials) form, providing a pathway for the injected air to the vadose zone. Significant channeling of the injected air may result from relatively minor heterogeneities in the saturated zone. It is expected that contaminants located within air-flow pathways will volatilize, and the potential exists for the stripping of dissolved phase contaminants that contact the air flow field. It is intended that air be injected to flow primarily through the area of contamination in the saturated zone, however, due to the complex phenomena governing the air flow field and the limited ability to characterize soil heterogeneities, there is a large degree of uncertainty as to the true behavior of any air sparging system design (Ahlfeld, 1994).

4.2. Governing Concepts

In situ air sparging is potentially applicable when volatile or easily aerobically biodegradable organic contaminants are present in water saturates zones, under relatively permeable conditions. The AS process can be defined as injection of compressed air at controlled pressures and volumes into water saturated soils (Norris, 1994). The three main removal mechanisms that occur during the operation of AS systems include: in situ stripping of dissolved VOCs, volatilization of trapped and sorbed phase contamination present below the water table and in the capillary fringe, and aerobic biodegradation of both dissolved and sorbed phase contaminants resulting from the delivery of oxygen.

4.2.1. In Situ Air Stripping

Among the above contaminant removal mechanisms, stripping may be the dominant process for some dissolved contaminants. The strippability of any contaminant is a function of its Henry's Law constant. Compounds such as benzene, toulene, xylene, ethylbenzene, and tri & tetrachloroethylene are considered to be very easily strippable. During air sparging, dissolved

compounds are transferred into the vapor phase and will be captured by a vapor extraction system once they migrate into the vadose zone.

The basic assumption made in analyzing the air stripping process during AS is that Henry's Law applies to the volatile contaminants and to all the contaminated water encountered by the injected air. In depth evaluation of these assumptions exposes the shortcomings and complexities of inter-phase mass transfer during air sparging (Anderson, 1993).

Due to the removal of contaminants in the immediate vicinity of the air channels, it is safer to assume that the contaminant concentration is going to be lower around the channels. To replenish the mass lost from the water around the air channel, mass transfer by diffusion and convection must occur from water away from the air channels. Hence, the density of air channels will play a significant role in mass transfer efficiencies by minimizing the distances required for a contaminant molecule to encounter an air channel. This may prevent AS from reaching final cleanup criteria.

In situ air sparging also helps to increase the rate of dissolution of the sorbed phase contamination and eventual stripping below the water table. This is due to the enhanced dissolution caused by increased mixing and the higher concentration gradient between the sorbed and dissolved phases under sparging conditions (Norris, 1994).

4.2.2. Direct Volatilization

The primary mass removal mechanism for VOCs in the saturated zone is by direct volatilization of the sorbed and trapped contaminants which is enhanced in the zones where air flow takes place. The volatile compounds do not have to transfer through the water to reach the air. If an air channel intersects pure compound, direct volatilization can occur. Direct volatilization of any compound is governed by its vapor pressure. Most volatile organic compounds are easily removed through volatilization.

Where significant levels of residual contamination of VOCs or NAPLs is present in the saturated zone, direct volatilization into the vapor phase may become the dominant mechanism for mass removal. The high level of mass that air can carry combined with the fast exchange of pore volumes results in a process that can remove significant pounds of contaminants in a relatively short period of time (Anderson, 1993).

4.2.3. Biodegradation

In natural conditions aerobic biodegradation of biodegradable compounds in the saturated zone is limited by the availability of oxygen. Biodegradability of any compound under aerobic

conditions is dependent on its chemical structure and the environmental parameters such as pH and temperature. Some of the VOCs are considered to be easily biodegradable under aerobic conditions (benzene, toulene, acetone, etc.) and some are not (trichloroethylene and tetrachloroethylene).

Typical dissolved oxygen (DO) concentrations in uncontaminated ground water is less than 4.0 milligrams per liter (mg/L), and under anaerobic conditions induced by natural degradation of contaminants, is often less than 0.5 mg/L (Norris, 1994). DO can be raised by air sparging up to 6 to 10 mg/L in equilibrium conditions. This potential increase in DO levels is a contributor to enhanced rates of aerobic biodegradation in the saturated zone. This method of introducing oxygen to increase the dissolved oxygen levels to enhance biodegradation rate is an inherent advantage of in situ air sparging.

Organisms generally derive energy from oxidation-reduction (redox) reactions. An enzyme-mediated oxidation/reduction reaction is the transfer of electrons from electron donors to acceptors. Energy is derived from these reactions when the energy source (electron donor) is oxidized, transferring electrons to an acceptor and releasing energy conserved in the chemical bond. Once the electron donor has been completely oxidized, the compound is no longer a source of energy. The energy released from these compounds is used by the organism to maintain life-sustaining processes. An aerobic respiration pathway follows:

$$(BTEX) + 9O_2 \longrightarrow 7CO_2 + 4H_2O + energy \qquad (4 - 1)$$
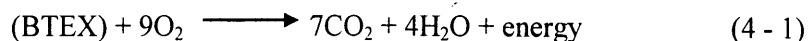
Table 4.1: Reduction Potential

Oxidized Species	Reduced Species	E (volts)
$O_2 + 4H + e^-$	$= 2H_2O$	+0.92

4.3.☐ Applicability

4.3.1. Contaminant

In order for air sparging to be effective, the VOCs must transfer from the ground water or from the saturated zone into the injected air, and oxygen present in the injected air must transfer into the ground water to stimulate biodegradation.

The criteria for defining strippability is based on Henry's Law constant being greater than 1 X 10^{-5} atm-m^3/mol. Compounds with a vapor pressure greater than 1.0 mmHg can be

volatilized easily, however, the degree of volatilization is limited by the flow rate of air. (Anderson, 1993)

Figure 4.2 describes the different mass removal phenomena in a simplified version under optimum field conditions. The amounts of mass removed by stripping and volatilization are grouped together, due to the difficulty in separating them in a meaningful manner. (Anderson, 1993)
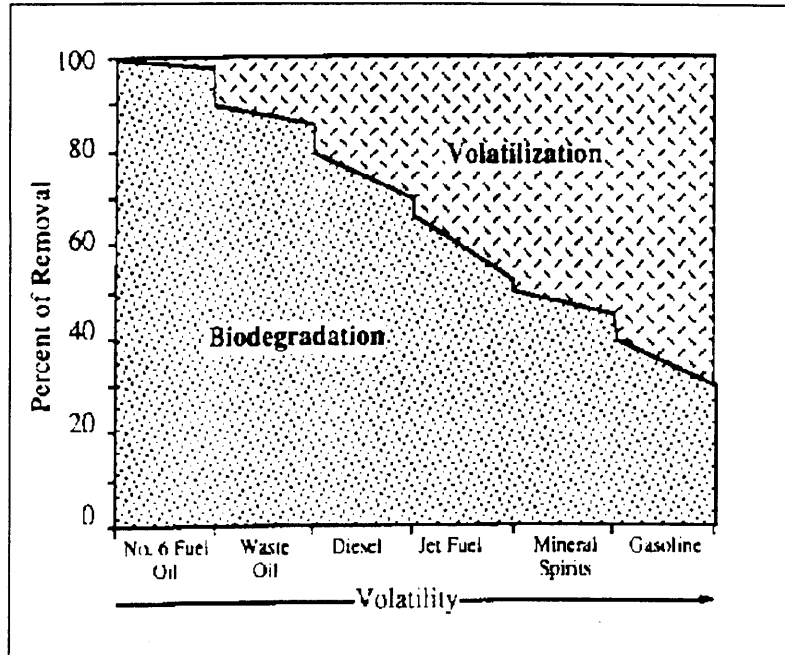
Figure 4.2: Volatility of different petroleum products

4.3.2. Geologic Considerations

Physical implementation of in situ air sparging is greatly influenced by the ability to achieve significant air distribution within the target zone. Good vertical pneumatic conductivity is essential to avoid bypassing or channeling of injected air horizontally, away from the sparge point (Ahlfeld,1994). Geologic characteristics of a site are very important when considering the applicability of in situ air sparging. The most important geologic characteristic is stratigraphic homogeneity. The presence of lower permeability layers under stratified geologic conditions will impede the vertical passage of injected air. In this condition, injected air may accumulate below the lower permeability layers and travel in a horizontal direction, thus potentially causing an enlargement of the plume. Any high permeability layers will also cause the air to preferentially travel laterally, again with the potential of enlarging a contaminant plume. Horizontal migration of injected air limits the volume of soils that can be treated by direct volatilization. Therefore, homogeneous geologic conditions are essential for the success and safety of in situ air sparging.

Table 4.2: Limits to the use of air sparging

Factor	Parameter	Limit / Desired Range
Contaminant	Volatility	> 2 mmHg
	Solubility	< 20,000 mg/l
	Biodegradability	BOD > 0.01 mg/l
Geology	Heterogeneity	No impervious layers above sparge point
		If layering present hydraulic conductivity increases above sparge point
	Hydraulic Conductivity	> 10^{-5} cm/s
Physical	Sparge Depth	> 4 feet, < 30 feet
	Depth to Water	> 4 feet

4.4. Description of AS Process

4.4.1. Air Injection

The ability to predict the performance of air sparging system is limited by the current understanding of air flow in the water saturated zone. There are two methods which describe this phenomena. The first, and widely accepted one, describes the injected air as traveling in the vertical direction in the form of discreet air channels. The second, describes the injected air as traveling in the form of air bubbles. Air flow mechanisms cannot be directly observed in the field.

Sandbox model studies tend to favor the "air channels" concept over the "air bubbles" concept. In laboratory studies simulating sandy aquifers (grain sizes of 0.75 mm or less) at low air injection rates, stable air channels were established in the medium, whereas under conditions simulating coarse gravel (grain sizes of 4 mm or larger) the injected air rose in the form of bubbles. At high air injection rates in sandy aquifers, the possibility for loss of soil cohesion around the sparge point exists, and thus the loss of control of the injected air may arise. (Wei et al., 1993)

4.4.2. Mounding of Water Table

As injected air enters the saturated zone, the water table elevation adjacent to the sparge point may rise due to the displacement of pore water by injected air. Displacement of ground water may initially form a mound around the injection well. Some concerns have been raised by regulatory agencies regarding the potential for enhanced transport of dissolved contaminants caused by movement of ground water away from the induced mound, however, the mound would not have the same kinetic energy as a pure water mound (Anderson, 1993).

4.4.3. Distribution of Air Flow Pathways

It is envisioned that air flow pathways developed during air sparging form an inverted cone with the point of injection being the apex, (see Figure 4.1). This would be true if soils were perfectly homogeneous or of larger sediments and injected air flow rate was low. Laboratory experiments simulating mesoscale heterogeneities in soil particle sizes resulted in distorted cone shapes caused by channels expanding, coalescing, and migrating upwards (Wei et al., 1993). It is reasonable to expect that distorted air channels will be dominant in natural conditions. During laboratory experiments using homogeneous media with uniform grain sizes, symmetric air flow patterns about the vertical axis were observed (Wei et al., 1993). Media with mixed grain sizes yielded nonsymmetric air flow patterns. The asymmetry results from minor variations in the permeability and capillary air entry resistance from pore scale heterogeneity (Ahlfeld, 1994).

4.5. System Design

With no reliable models for in situ air sparging processes, empirical approaches are used in the system design. The parameters of importance in designing an air sparging system are zone of influence, depth of air injection, air injection pressure and flow rate, and injection mode.

4.5.1. Zone of Influence

To design a full scale air sparging system consisting of multiple sparge points it is necessary to estimate the zone of influence of an air sparging point. This estimate is an important parameter for the design to determine the number of required sparge wells. The zone of influence should be limited to describing an approximate indication of the average of the furthest distance traveled by air channels from the sparge point in the radial direction under controlled conditions.

The zone of influence of an air sparging point is assumed to be a cone; however it should be noted that this assumption implies homogeneous soils of moderate to high permeability (Ahlfeld, 1993). During a numerical simulation study on air sparging (Lundegard and Andersen,

1993), three phases of behavior were predicted following initiation of air injection (Anderson, 1993). These are: (1) an expansion phase in which the vertical and lateral limits of air flow grow in a transient manner, (2) a second transient period of reduction in the lateral limits (collapse phase), and (3) a steady state phase, during which the system remains static as long as injection parameters do not change. The zone of influence has been found to be a roughly a conical shape during steady state phase.

Based on the inverted con air flow distribution model, air sparging system are designed based on the zone of influence measured by conducting field pilot tests. Many applications require multiple sparge points to cover the entire area such as hot spots or source areas, which make the layout of air sparging in a grid fashion, (see Figure 4.3). The grid is designed with overlapping zones of influence to provide complete coverage of the area under consideration for remediation.
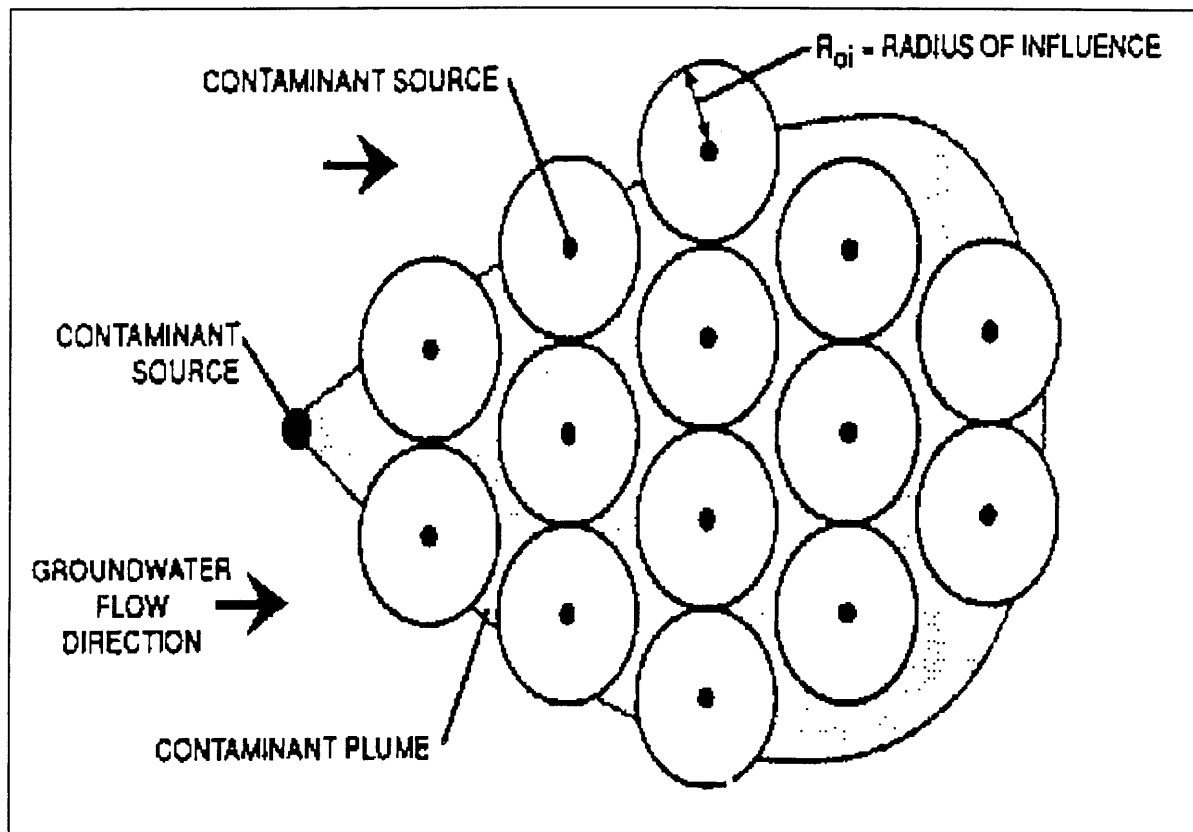
Figure 4.3: Air Sparging Grid

A properly designed test can provide valuable information, even with the limitations of time and money which often restrict field evaluations to short duration single well tests (Norris, 1994). Several potential measuring techniques of the zone of influence have been employed: (1)

measurement of lateral extent of ground water mounding, (2) increase in DO levels and redox potentials in comparison to pre-sparging conditions, (3) increase in head space pressure within sealed saturated zone monitoring probes which are perforated below the water table only, (4) the use and detection of insoluble tracer gases, (5) measurement of the electrical resistivity changes in the target zone of influence as a result of the changes in water saturation due to the injection of air, and (6) the actual reduction in contaminant levels due to sparging.

4.5.2. Depth of Air injection

Depth of injection is probably the easiest to determine since the choice is very much influenced by the depth distribution of the contaminant and stratigraphy. It is prudent to choose the depth of injection at least a foot or two deeper than the deepest known point of contamination (Anderson, 1993). The depth determination is very much influenced by soil structuring and extent of layering, since injection below any impermeable or very permeable zones should be avoided. The minimum depth of an air sparging system is 4 feet, the saturated thickness required to confine and force the air to cone out from the sparge point. The maximum depth is 30 feet, important from the standpoint of control and predictability. At depths greater than 30 feet it is difficult to predict where the sparge air will travel, making it difficult to design a control system for containing the sparged air with the area being treated. (Norris, 1994).

4.5.3. Air Injection Pressure

The injected air will penetrate the aquifer only when the air pressure exceeds the sum of the hydrostatic pressure of the water column and the threshold capillary pressure (air entry pressure). Capillary entry resistance is inversely proportional to the average diameter of the grains and porosity. The injection pressure necessary to initiate in situ air sparging must be able to overcome the hydrostatic pressure of the overlying water column at the sparge point and the capillary entry resistance to displace the pore water.

The capillary pressure can be described under idealized conditions by the following:

$$Pc = 2 s / r \qquad\qquad (4 - 2)$$

where

Pc = capillary pressure

s = surface tension between air and water

r = mean radius of curvature of the interface between fluids

The equation shows that as r decreases the capillary pressure increases. Generally, r will decrease as grain size decreases, the required pressure to overcome capillary resistance increases with decreasing sediment size.

The pressure of injection (Pi) in feet of water is defined as:

$$Pi = Hi + Pa + Pd \qquad (4 - 3)$$

where

Hi = saturated thickness above the sparge point

Pa = air entry pressure of the formation

Pd = air entry pressure for the well, diffuser

The air entry pressure is heavily dependent on the type of soil, it is higher for finer sediments (1 to 10 ft H_2O) than coarser sediments (1 to 10 in H_2O) (Anderson, 1993).

The minimum injection pressure is that which is required to overcome the water column (1 psi for every 2.3 feet of hydraulic head). As pressure is increased above this minimum, air is injected laterally into the aquifer. As seen in Figure 4.4, there is an initial linear relationship between the sparge pressure and direction of air travel.
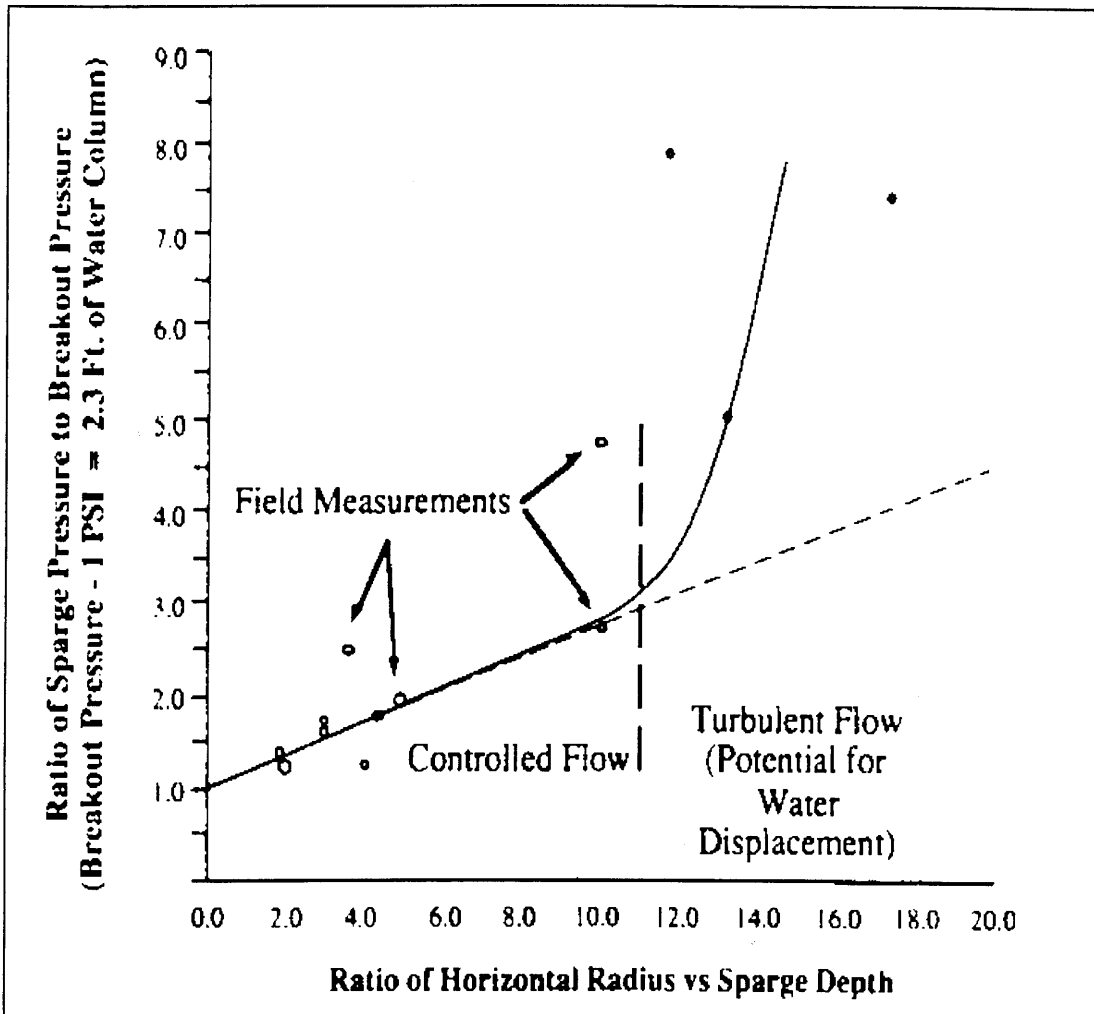
Figure 4.4: Effect of injection pressure on air flow

At low sparge pressure the air travels 1-2 feet horizontally for every foot of vertical travel. As the sparge pressure increases, the degree of horizontal travel increases. Enhanced horizontal travel allows a single well to treat a greater area of contamination. However, increasing the pressure does not always provide a benefit. Increased pressure may cause air flow to become turbulent, and the added pump energy is wasted. The danger under turbulent conditions is that a dissolved plume of contaminants could be pushed away from the sparge point. Figure 4.4 shows a point of inflection, where the increase in injection pressure does not give a corresponding increase in air flow radius. (Norris, 1994)

4.5.4. Flow Rate

Typical values of injected air flow rates reported in literature ranges from 1 cfm to 10 cfm (Anderson, 1993). Injection air flow determinations are influenced by the ability to

recover the stripped contaminant vapors through SVE by containing the injected air within a controlled air distribution zone.

4.5.5. Contaminant Type and Distribution

Volatile and strippable compounds are most favorable to air sparging. Nonvolatile but biodegradable compounds can also be remediated by air sparging. This means that most petroleum hydrocarbons and chlorinated solvents can be treated with air sparging.

The mass distribution of the contamination should be known in order to effectively utilize air sparging. The vertical extent of adsorbed phase contaminants below the water table must be determined in order to obtain the depth of sparging wells. The lateral extent of adsorbed phase contamination below the water table must be known to ensure complete coverage of the remedial area. In addition, the downgradient dissolved ground water concentrations should be delineated in order to allow monitoring of the plume during sparging operation. (Norris, 1994)

4.6. Limitations of Air Sparging

In situ air sparging appears to be a simple process: injection of air into a contaminated aquifer below the water table with the intent of volatilizing VOCs and providing oxygen to enhance biodegradation. It is also important to know when to apply air sparging, and its limitations which follow:

- Tight geologic conditions with hydraulic conductivities less than 10 cm/sec. The vertical passage of the air may be hampered and the potential for the lateral movement will be increased, as will be the potential for inefficient removal of contaminants (Anderson, 1993).

- Heterogeneous geologic conditions, with the presence of low permeability layers overlying zones of higher permeabilities. The potential for the enlargement of the plume exists due to the inability of the injected air to reach the vadose zone efficiently.

- Contaminants present are nonstrippable, nonvolatile, and non-biodegradable.

- Mobile free product has not been removed or completely controlled. Air injection may enhance the uncontrolled movement of this liquid away from the air injection area.

A fundamental issue in any remedial process is having control over the process. With processes that are based on extraction such as SVE or ground water recovery, the process begins with the system under control because contaminants are being drawn to a point of collection. By contrast, injection systems such as air sparging start with no control because flow is away from the

injection point. Since injection of air can displace both vapors and water, unless control is established and maintained, this displacement can accelerate and aggravate the spread of contamination. (Norris, 1994)

4.7. Air Sparging Implemented Design

The air sparging design was solely based on a pilot study to determine radius of influence through several methods. Table summarizes the results which varied from 87 ft to 144 ft for the radius of influence.

Table 4.3: Summary of Pilot Study Results

Parameter	Radius of Influence (feet)
Water Level	144
Tracer Gas	87
Oxygen Levels in Vadose Zone	87
Carbon Dioxide Levels in Vadose Zone	87
Air Pressure	87
Dissolved Oxygen	87

The pilot system was able to effect change in the water table as far as 144 ft from the sparging well. The distance of 75 feet was chosen for the effective radius of influence to be used for the air sparging design. The is would provide a reasonable factor of safety and some overlap between adjacent wells. A similar geometric approach to the SVE design was used for the well layout, which was determined to be a 150 ft by 150 ft grid, Figure 4.5. The operating parameters for the AS wells are a flow rate of 100 cfm, pressure of 30-35 psi, and sparge depth of 60 feet below water table (Davis, 1997).
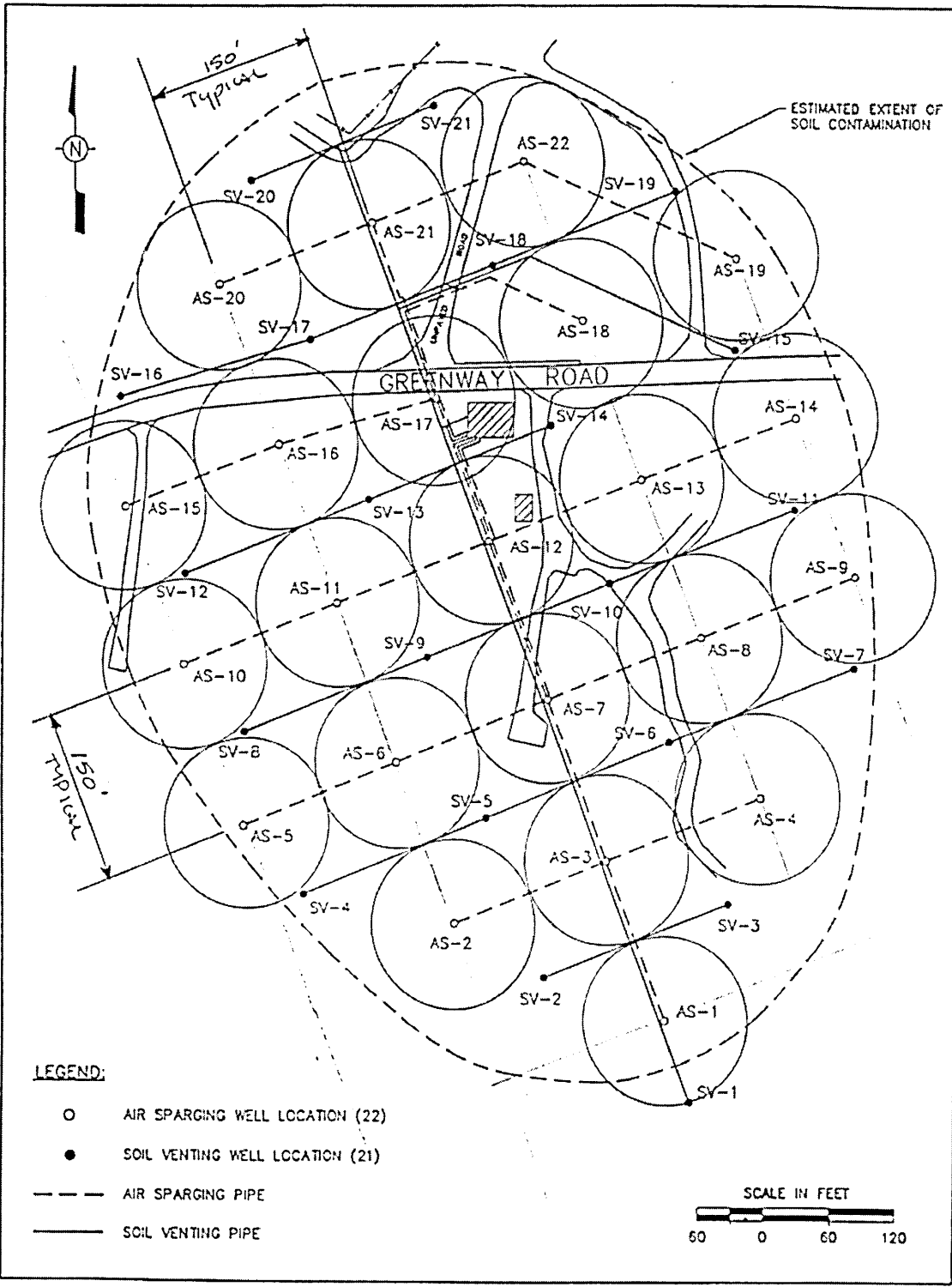
Figure 4.5: AS Well Layout

5.   Self-Potential Method

5.1. Introduction

The major environmental and engineering applications of the self-potential (SP) method have been the investigation of subsurface water movement. The method has also been used to a lesser extent for subsurface thermal investigation. Self-potential anomalies are generated by flows of fluid, heat, or ions in the earth; hence SP investigations have been used to help locate and characterize sources associated with these flows. The method was first introduced for mineral exploration and today is used in that field. In recent years SP has found increasing use for geothermal engineering and environmental applications. The method offers relatively rapid field data acquisition and the ability to respond directly to changes in flow. It often is cost effective for reconnaissance and initial field investigation of an area prior to more intensive studies using geotechnical or other geophysical techniques (Corwin, 1990).

Interpretation of self-potential data is often qualitative, using visual correlation between observed profile or contour patterns and known or suspected flow paths or contaminant sources. The use of available geometric source models can provide useful first estimates of source depth and configuration. Computer programs based on analytical modeling techniques or inversion packages can be used to calculate self-potentials generated by subsurface gradients of pressure, temperature, or chemical concentration.

5.2. SP Generation

The mechanisms of SP generation must be capable of producing stable electric currents over large volumes for long periods of time. This implies that a great source of energy is involved since current flowing in a resistive material dissipates energy. Some form of an electrochemical system can explain SP anomalies.

5.2.1. Electrochemical Cell

There are many chemical reactions that are accompanied by release of electrical energy, producing a current. An example is the electric cell or battery. A simple cell can be formed by immersing a zinc rod and a copper rod in a dilute acid. At the negative electrode, Figure 4.1, zinc atoms give up electrons to form zinc ions, which go into solution.

$$Zn \longrightarrow Zn^{++} + 2e^{-} \qquad (5-1)$$
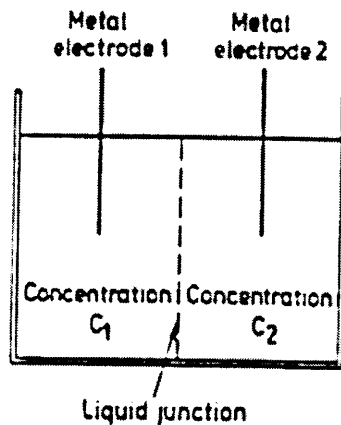
Figure 5.1: Typical Electrolytic Cell

This is called a half reaction, and since it involves zinc giving up electrons and going into solution, it is an oxidation and anodic reaction. The released electrons would like to move through the external circuit to the positive electrode, but they cannot move until the switch completes the circuit. At the positive electrode (cathode) the electrons are picked up by the hydrogen ions in the acid to form hydrogen atoms and, in turn, hydrogen molecules. In this example cell the cathode eventually becomes coated with hydrogen gas and the reaction stops.

$$2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2 \text{ (gas)} \qquad (5-2)$$
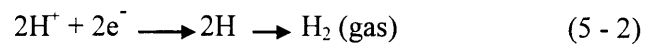
This is another half reaction, but this time it is a reduction and cathodic reaction.

In the electrolyte the current is carried between the electrodes by the ions in solution, where by convention the current flow is in the same direction as the positive ion flow, but in the opposite direction to electron flow or negative ion flow.

In this cell the two chemicals zinc and hydrogen constitute an electrochemical couple. The reaction occurring between the electrochemical couple in the cell is called an oxidation-reduction reaction and can be simply written as

$$Zn + 2H^+ = Zn^{++} + H_2 \qquad (5-3)$$
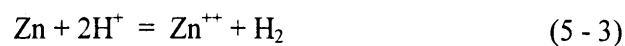
The electron releasing or attracting power of ions in solution is called the electromotive force or standard electrode potential. The term "oxidation potential" (Eh) is essentially the same

thing, but the potential is of the opposite sign. It is not possible to measure the voltage of a half reaction alone; there must be two half reactions. For the purpose of the electromotive force, the voltage of the hydrogen half reaction is set to zero and the voltages of other elements in ionic solutions are referred to this. (Beck, 1981)

In general, the electrochemical reaction in aqueous media can be given in the form,

$$aA + wH_2O = bB + mH^+ + ne^{-1} \qquad (5 - 4)$$
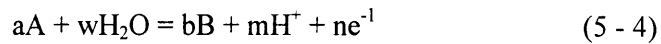
where a, w and b are the mole numbers of the participating substances, m is the hydrogen ion concentration (pH) which is a measure of the influence of hydrogen ions, and n is the oxidation potential (Eh) which is a measure of the influence of the electrons (Beck, 1981).

5.2.2. Field Conditions

The potential difference which produces the currents and hence the potentials is due to the difference in the oxidation potentials of the solutions immediately in contact with the source (contaminant or mineral body) at its upper and lower end. Near the upper end the substances and solution are in relatively reduced states. The half cell reaction at the upper end is where the oxidation-reduction reactions take place between the relatively oxidized state of the country media reducing material at the surface of the source. At the lower end the relatively reduced states of the surrounding soil react to oxidize material at the surface of the lower end of the source. The oxidation process at the lower end of the source releases electrons which then travel through the source to the upper surface (Figure 5.2). The electrons then being donated to the material at the upper end of the source as it is being reduced by the oxidized states of the country media. The current flow through the source is therefore from top to bottom, the return current in the surrounding medium being by motion of ions through the pore fluids; the positive ions traveling from the lower end to the upper end and the negative ions from the upper end to the lower end.
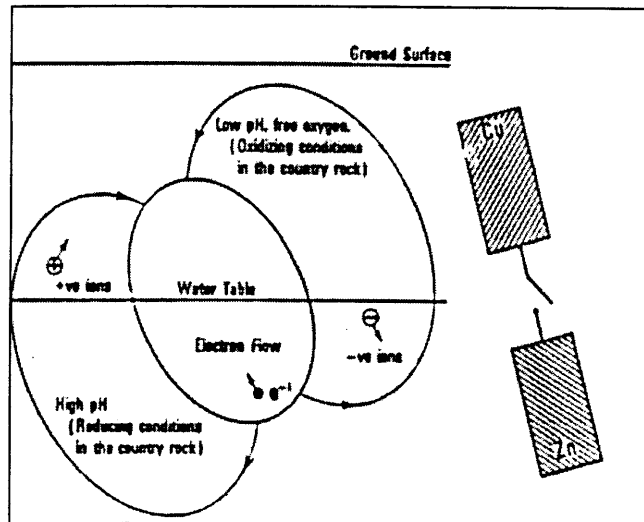
Figure 5.2: Typical Subsurface Condition and Current Flow System

Essentially there are two half cell reactions, one anodic and one cathodic, which could be chemically unrelated to one another but may go on regardless of whether or not a source is present. However, when they are coupled through a medium of electric conduction, such as a source, spontaneous polarization may take place generating self potential anomalies. Independently, the two half reactions may produce electrons at different rates, but once they are coupled they become self balancing, since the reaction with the lowest rate limits the other. The source does not need to be partially immersed at the water table, although such a condition increases the probability of the appropriate electrochemical couple being produced.

The specific reactions which occur in any given field condition are not very well understood. However, the primary source of energy that maintains reactions over long periods of time is essentially oxygen. If free oxygen is readily available, it can combine with hydrogen or hydroxyl ions to form hydrogen peroxide, which in turn can decompose to form hydroxyl ions and free energy (Parasnis, 1986).

5.2.3. Concentration Differences (Diffusion)

Concentration differences of electrolytes in the subsurface can cause SP anomalies of the order of fractions of a millivolt to several hundred millivolts (Parasnis, 1986). An electrolytic cell such as the one shown in Figure 4.3, has two metal electrodes in two electrolytic solutions of concentrations C_1, C_2 in contact with each other. When the cell is in action, a net transfer of charge from one electrode to the other within the cell takes place through the positive ions. The

overall electromotive force (the difference potential of electrode 2 minus the potential of electrode 1) of such a cell is

$$U = [\, 2v \, / \, (u + v) \,] \, [\, RT \, / \, nF] \, [\, Ln \, (\, C_1 \, / \, C_2 \,) \,]$$ (5 - 5)

where u, v are the velocities (m / s) of the positive and negative ions, R = the universal gas constant (8.314 J / K mol), T = absolute temperature (K), F = Faraday's constant (96487 C/ mol) and n = valence of the ions (Parasnis, 1986).
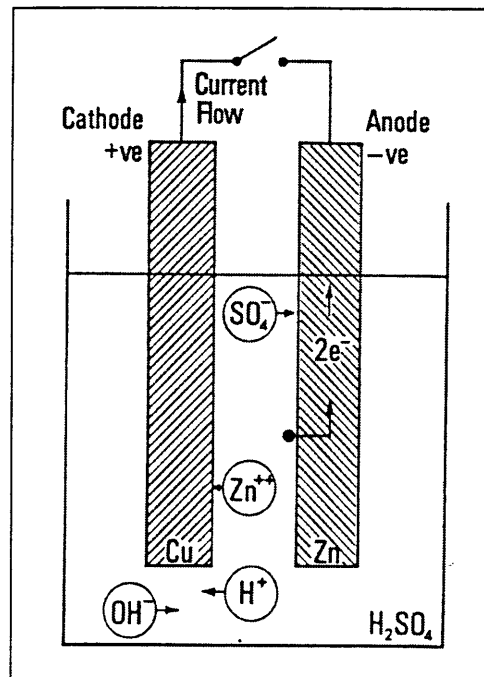
Figure 5.3: Electrolytic Concentration Cell

If an electrolyte is chosen such that u = v, then the electromotive force of the cell becomes

$$U_0 = [\, RT \, / \, nF] \, [\, Ln \, (\, C_1 \, / \, C_2 \,) \,]$$ (5 - 6)

U_0 is simply $U_{M2}(C_2) - U_{M1}(C_1)$ if $U_M(C)$ is the potential of the metal electrode in contact with an electrolyte of concentration C. Hence the difference $(U - U_0) = U_j$ is attributed to the fact that u does not equal v. U_j is called the "liquid-junction potential" although its cause is not the junction but rather the unequal velocities of the positive and negative ions when the cell is in action.

$$U_j = [\, (u - v) \, / \, (u + v) \,] \, [RT \, / \, nF \,] \, [\, Ln \, (\, C_2 \, / \, C_1 \,) \,]$$ (5 - 7)

Equation (5 - 7) is written with the convention that U_j represents the difference potential of solution on the right minus potential of solution on the left.

5.3. Equipment

The equipment required for data acquisition is extremely simple, consisting of electrodes connected by wire to a voltmeter. There are, however, some very important restrictions on the electrodes and the voltmeter that are discussed below. Unlike most other geophysical equipment, complete SP equipment sets are not readily available commercially and must be assembled by the user (Corwin, 1990).

5.3.1. Electrode

Electrode performance depends on the polarization and drift characteristics of the electrode pair. Polarization is defined as the potential measured at a given time between electrodes in the absence of external electric fields, and drift refers to time variation of the polarization value. Although electrodes of stainless steel and copper-clad steel have been used for SP field measurements, non-polarizing electrodes have been found to give much more reliable data (Corwin and Butler, 1989). Such electrodes consist of a metal element immersed in a solution of the metal salt, with a porous junction forming the boundary between the solution and the soil. Electrode polarization and drift response to variations in environmental parameters such as temperature and soil moisture are of greatest interest for SP measurements. Laboratory and field measurements of such responses have been performed for a variety of non-polarizing electrode types, including copper-copper sulfate, silver-silver chloride, lead-lead chloride, and zinc-zinc sulfate.

For most applications, commercially available copper-copper sulfate and silver-silver chloride electrodes have been found to give SP field data of acceptable quality if drift and polarization effects are monitored and corrected (Corwin, 1990). The response of these electrodes to environmental variations is well documented and indicates that under most conditions they do not affect significantly the error and noise level of SP measurements (Beck, 1981). The response to changes in soil moisture content is of the order of +0.3 to +1.0 mV per percent moisture content increase, and a maximum response of +70mV has been shown for an electrode pair connected between saturated and very dry desert clay. Soil moisture variations can represent a significant noise source when signal levels are a few tens of mV. The temperature response is on the order of +0.5 to +1.0 mV per degree C. This refers to the temperature difference between the electrolytes of the electrodes rather than that between the soils at the measuring stations, so the effect of a change in soil temperature will not be seen until the electrolyte temperature begins to change (Corwin, 1990). Maximum temperature polarization values are on the level of 10 to 20 mV.

5.3.2. Voltmeter

Important considerations for the voltmeter used for SP field measurements include: resolution, range, input impedance, AC interference rejection, and suitability for field use. Resolution of 1 mV and a range of +/- 10 V dc is sufficient for SP measurements. Noise in the 10 to 100 Hz range is common in developed areas, hence inclusion of low-pass filtering in the voltmeter is necessary (Corwin, 1990). Electrode contact resistance ranges from a few hundred ohms in very conductive soil to several mega-ohms in snow, frozen soil, very dry soil, and rocky soil. A voltmeter input impedance of ten mega-ohms is generally sufficient.

It is important to measure and record electrode contact resistance at each station. This measurement ensures that there are no breaks in the connecting wire, that contact resistance is low enough to avoid loading the measuring circuit, and that ground contact conditions are relatively uniform from station to station (Corwin, 1990). Most of the requirements for the meter are met by inexpensive, commercially available digital multimeters (DMM).

5.3.3. Wire

Most of the resistance in the measuring circuit is in the electrode-to-soil contact, therefore the resistance and gauge of the connecting wire usually is not important. A wire of small diameter, or high strength, high resistance conductor such as cadmium bronze should be used to minimize weight and bulk (Corwin, 1990). Insulation integrity is critical, as any exposed wire in contact with wet soil will produce error potentials of hundreds of millivolts.

5.4. Field Configuration

A variety of survey configurations are used to obtain SP field data. For all configurations, SP polarity convention requires the negative terminal of the measuring voltmeter to be connected or referred to the electrode at the survey base station, and the positive terminal to be connected or referred to the electrode at the measurement survey.

5.4.1. Leapfrog

The leapfrog, (also called gradient, dipole, or fixed-electrode) configuration utilizes two electrodes and a connecting wire of fixed length equal to the separation between measurement stations. The voltmeter is connected between one electrode and one end of the connecting wire. After the potential difference is measured between the two electrodes, the array is moved forward

along the survey line, with the trailing electrode occupying the station of the previous leading electrode.

The SP value at a given station is obtained by successive addition of individual dipole readings. Polarity is carefully observed so that the total SP field obtained by summing the gradient readings is properly calculated. If the dipole length is small relative to an anomaly wavelength, a plot of dipole readings essentially represents the component of the gradient or derivative of the total SP field in the direction of the survey line (Parasnis, 1986).

5.4.2. Fixed-Base

The fixed-base or total field configuration uses a stationary base electrode, a reel carrying the connecting wire, and a moving measuring electrode. The outer end of the connecting wire is attached to the base electrode and the reel is carried by foot or vehicle from station to station. The positive lead of the meter is connected to the measuring electrode and the negative lead is connected through a takeout at the inner end of the wire on the reel to the base electrode (Telford, 1990). Station locations are determined by pre-surveying lines, flagging the wire, or using a portable distance measuring device.

The wire is not dragged over the ground surface during deployment or retrieval; therefore, the usable wire length is not limited by friction or obstructions as for a stationary reel arrangement (Corwin, 1990). This allows the maximum number of readings to be made from a single base electrode and thus minimizes accumulation of errors.

5.4.3. Multi-electrode

A multi-electrode configuration is similar to a long-term SP monitoring network in that an electrode is installed at each measuring station and all electrodes are connected to a base station terminal through a multiconductor cable. Measurements are made by sequentially connecting each electrode through the meter to the base station electrode, or by using a multichannel data acquisition system.

An advantage of this configuration is that it facilitates repeat measurements and the application of data processing techniques. As for the fixed-base array, cumulative error is minimized by the use of a single base station.

5.4.4. Survey Line

Once the configuration for a given survey is chosen, it is necessary to select survey line orientation and spacing and to determine the spacing of measurement stations along the survey

line. Survey line orientation should be perpendicular to an anticipated anomaly that is elongated. For low signal-to-noise ratios, closely spaced measurements along widely spaced survey lines are preferable, but the reverse is true for high ratios. Measurement station spacing depends on the anticipated anomaly wavelength, which is a function of size, orientation, and depth to the source.

5.4.5. Reference Potential

There is no universal zero potential reference level for SP measurements; hence selection of the zero potential point for a given data set is arbitrary. A station remote from expected or observed anomalous activity is assumed to be at zero potential. Locating the survey base station in such a "quiet" area and assuming the base station potential to be zero facilitates computation and may improve data reproducibility (Corry, 1985). On the other hand, locating the base station centrally within the survey area reduces the required wire lengths, and running survey lines outward from anomalous areas makes it easier to determine when anomalous activity has ended and sufficient background has been measured. However, a centrally located base station may result in higher noise levels.

5.5. Field Measurement Errors

Selection and implementation of appropriate survey field procedures are critical for maintenance of SP data quality. Appropriate field procedures are those that eliminate or minimize errors related to data acquisition and provide methods for the recognition and removal; of errors from the data. Geologic noise includes measurement errors caused by electrode polarization and drift, changing soil contact conditions, and time varying potentials.

5.5.1. Electrode Polarization and Drift

Electrode polarization and drift are a major component of SP measurement error. For a survey conducted from a single base station, the first field reading will be in error because of the initial polarization potential between the base and measurement electrodes, and the last field reading will be in error because of the final polarization value (Corwin, 1990). Measurement of these polarization values immediately before installation and after removal of the base electrode will allow subtraction of these polarization errors from the measured values, with corrections for intermediate measurements obtained by interpolarization (Corwin and Butler, 1989).

Electrode performance also depends on the condition of the electrodes. The electrolyte solution should be kept saturated with crystals in the solution, to avoid polarization potentials related to concentration changes. Polarization of electrode pairs in equilibrium should be checked

frequently in a bath of electrolyte solution. Values exceeding several millivolts are not acceptable.

5.5.2. Electrode to Soil Contact

When an electrode is removed from and put back into the same location, the SP reading will almost always change. For moist, conductive, compact soils this change may be only a few millivolts, and generally is less than 5 or 10 mV for most soils. For dry, resistive, loose soil the change may be several tens of millivolts or higher. This uncertainty represents an important component of irreproducible error (Corwin, 1990). For very dry soil conditions, or where soil moisture conditions change considerably, watering of the electrode holes may help improve contact consistency

To obtain the most consistent readings, the electrode holes must be dug deep enough to penetrate dry surface soil so as to encounter vadose soil moisture and to minimize surface temperature variations. In compact soils this depth may only be a few centimeters, but dry, loose, rocky soil may require 50 cm or more (Corwin, 1990).

5.5.3. Time Varying

Time variations of SP readings may be caused by changing site conditions such as soil properties or subsurface resistivity variations due to changing saturation levels; or by electric fields generated by natural or artificial sources (Corwin, 1990). It is important that these variations be recognized and removed from the data to avoid measurement errors or misinterpretation of time variations as anomalies.

Site conditions are constantly changing, and can generate SP variations over periods ranging from minutes to months or longer. Some of these variations are significant for a survey with a duration of hours or days. Variations are generated by changes in soil properties due to temperature variation, rainfall, or construction activity; changes in topographic effects due to rainfall, varying water table depth, and changes in corrosion fields.

Significant time variations of SP readings may also be caused by vertical movement of near surface vadose water. Such movement may be related to evapotranspiration by vegetation, or solar heating of near surface soil. In some instances these variations may reach several tens or hundreds of millivolts and may be a significant source of noise and error.

5.5.4. Telluric Currents

The other category of time varying noise is generated by telluric currents caused by time variations of the earth's magnetic field or by artificial sources. Telluric current variations have periods ranging from milliseconds to hours. For SP surveys, the most significant periods are those in the 20 to 30 s range and those of about 0.1 s, which sometimes appear as high frequency noise on DMM voltage readings (Corwin, 1990). Amplitudes of telluric currents are generally on the order of several millivolts per kilometer, so they usually do not exceed a few millivolts for most surveys. For variations of this magnitude, a reasonable approximation of the steady state value can be obtained and averaged over several cycles. Telluric variations may be on the order of tens or hundreds of millivolts per kilometer in areas of high resistivity, in conductive zones, or during magnetic storms.

Time varying artificial currents are generated by grounded electrical machinery and are very common in developed areas in which environmental and engineering SP surveys are conducted. Stray currents from corrosion processes may also change with time, but these changes are much longer in time compared to grounded machinery (Corwin, 1990). High frequency noise may be generated by overhead or buried power lines, but such noise is usually suppressed by filters in most DMMs.

The routine use of a telluric monitor to record time varying potentials in the survey area is good practice. Without such a record it is difficult to detect long period variations. Potentials generated by such variations can be mistaken for spatial anomalies (Corwin, 1990).

5.6. Data Interpretation

SP anomalies may be generated by gradients of pressure, temperature, or chemical concentration in the earth. The anomaly amplitude depends on the products of the gradients and the cross coupling coefficients that relate the flow of fluid, heat, or matter to the generated potential, and on the electrical resistivity structure of the earth (Corwin, 1990). Voltages generated by fluid flow are called electrokinetic or streaming potentials, and those related to heat or ionic flow are called thermoelectric and electrochemical potentials.

5.6.1. Qualitative

Qualitative interpretation involves preparation of data profiles and contours and visual inspection of these to look for patterns known or thought to be characteristic of desired sources. This approach has been proven to be useful in many cases where SP data was used primarily to indicate locations for more detailed geotechnical or geophysical investigations.

5.6.2. Geometric Models

The geometric interpretation involves the use of calculated curves and contours generated by relatively simple SP source models to match the observed field data. Available models include polarized points, lines, cylinders, spheres, sheets and other geometric forms. Matching of field data to the curves generated by these sources provides useful information about the form, depth, and orientation of inferred anomaly sources (Corwin, 1990).

5.6.3. Computer Models

Analytical SP modeling techniques are based on concepts of irreversible thermodynamics and coupled flows of fluids, heat, electrical current, and chemical diffusion. The computer programs which run these models require parameters describing the different potential source generators such as cross-coupling coefficients, electrical resistivity, and earth material conductivity (hydraulic, thermal, or electrochemical).

5.7. SP Application at FS-12

5.7.1. Self Potential Source

There are five possible voltage potential sources at the FS-12 source area. One is due to geochemical variations (gradients in contaminant concentration). Another mechanism for the SP anomaly is an electrochemical cell with the smear zone of the benzene acting as the source through biodegradation (oxidation/reduction reactions). A third source could be potentials generated by the air & water movement due to the air sparging and soil vapor extraction. Another possibility is that an electric ground is acting as a source. It could also be from the combination of some or all of the above sources. Currently there is not a definitive conclusion as to the mechanism(s) of how self potentials are generated, particularly in relation to subsurface contamination and remediation technologies.

5.7.2. Equipment Specification

The electrodes are copper, immersed in a supersaturated solution of NaCl in the pot. The electrode is housed in plexiglas with a rubber stopper on one end to provide insulation for the connection of the copper to an insulated electric wire. The electrode is placed in a porous pot that is sealed along its height only allowing contact with the soil through the bottom.

The voltmeter is a commercially available DMM, a Micronta. It has an input impedance of 10 m-ohm, resolution of 0.1 mV, and a range of +/- 400Vdc.

5.7.3. Data Acquisition

The survey lines were aligned with the sparging or extraction wells of the AS-SVE system since this provided the most effective and least difficult means bv which to cover the source area. In the process of installing the wells pathways were created through the forested area which served as the survey lines, see Figure 5.4. Data was acquired at least every two weeks starting with the March 28 data set, and on two successive occasions (April 15 & 22) the AS-SVE system was shut down. Throughout the period starting in February polarization of each pair of electrodes was monitored on a weekly basis, thereby decreasing the amount of potential errors in the field measurements.
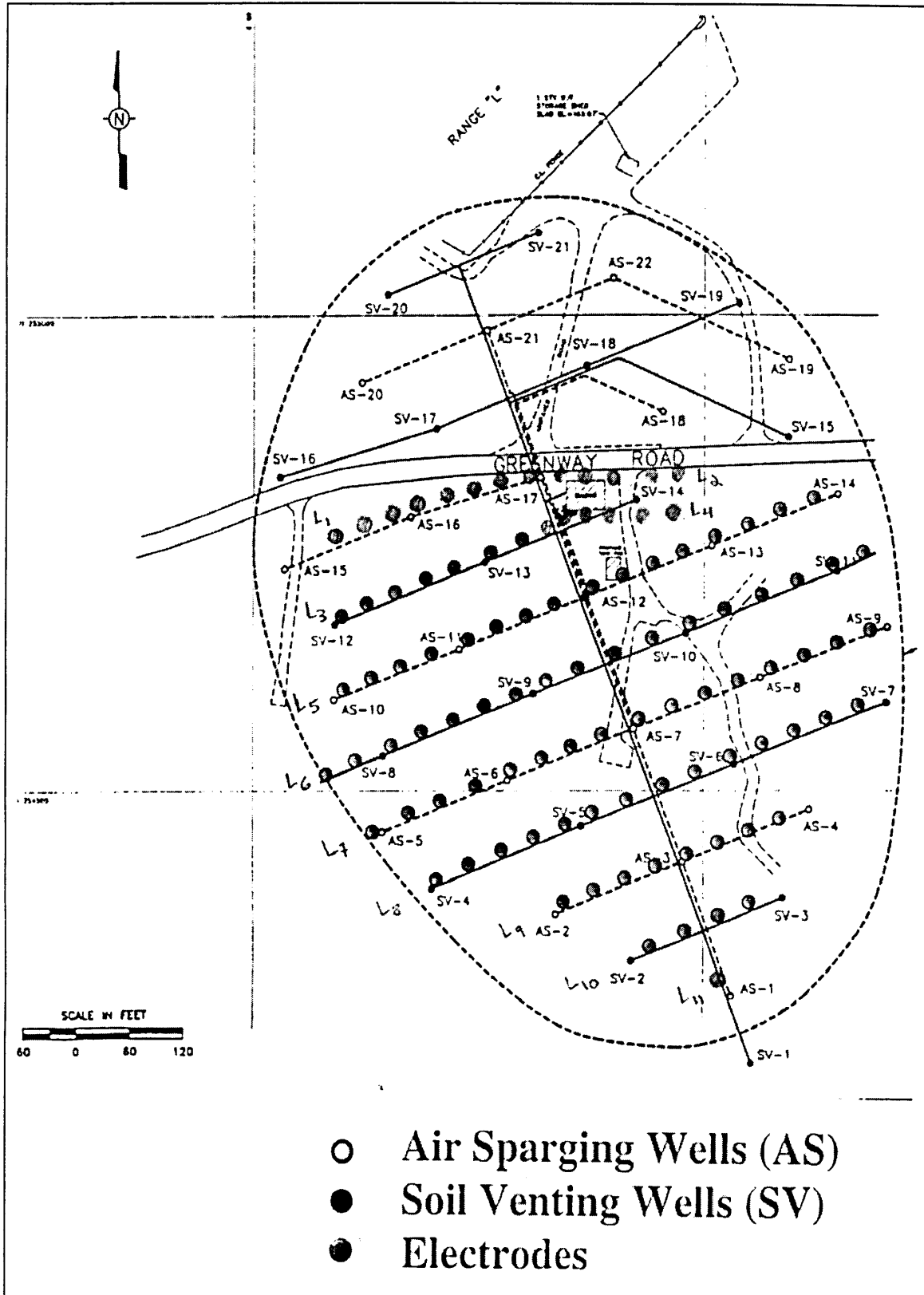
Figure 5.4: Electrode Array at FS-12 Source Area

5.8. Data Interpretation

5.8.1. Qualitative

Contour plots were generated using the Matlab computer program. The raw data (Appendix A) was referenced to a single point, the zero reference. After the data calibration, interpolation and smoothing was used where needed to generate the contour plots. The plots delineate the areas of greatest absolute potentials in mV. The extent and degree of an anomaly is easily observed from the contour plots.

6.   Analysis

6.1. Self Potential

6.1.1. Data Zero Reference

Each data set collected is referenced to a single point to obtain absolute values of potential. The zero reference point is chosen at a location of known minimal concentrations of contamination, at the FS-12 site the reference chosen was next to GMW-41.

6.1.2. Contour Plots

Contour plot are generated by using the MatLab program. The referenced data values are plotted with smoothing and interpolation where needed. The plots provide a means of quickly delineating an anomaly, its size, relative strength, and migration of the anomaly.

6.2. Soil Vapor Extraction

6.2.1. Estimate Number of Wells

6.2.1.1.Removal Rate

The number of wells can be estimated by dividing acceptable removal rate, R_{accept}, by the estimated removal rate, R_{est}.

$$R_{est} = C_{est}\, Q \qquad\qquad (6 - 1)$$

where

R_{est} = estimated removal rate

C_{est} = concentration in vapor phase = 0.1477 Kg/m^3

Q = flow rate = 4062 m^3/day

The maximum estimated removal rate is 600 Kg/day.

$$R_{accept} = M_{est}\, /\, t_{cleanup} \qquad\qquad (6 - 2)$$

where

R_{accept} = acceptable removal rate

M_{est} = estimated mass of contamination

$t_{cleanup}$ = maximum acceptable cleanup time

The acceptable removal rate is 255 Kg/day.

The minimum estimated number of wells by removal rates is three wells.

6.2.1.2.Screening Level

The number of wells needed for a SVE system using the screening level equation (3 – 7) yields a total minimal number of 12 wells using an average concentration equal to the maximum concentration of benzene (0.068 ppm). Therefore, the 12 wells would correspond to the worst condition that can be found at FS-12. The minimum volume of vapor required to achieve cleanup per unit mass of contaminant, α, was calculated is calculated in section 6.2.2. The target time of two years was used which is equal to the target time of the IRP.

$$N = (52759.75*0.068*6.25*2100) / (5844.0*730) = 11.04$$

6.2.2. Maximum Removal

Maximum number of Kg of contaminant mass that can be removed by 1 m^3 of air is given by:

$$n = (P\ M_w) / (R\ T) \qquad (6 - 3)$$

where

n = maximum number of Kg removed by 1 m^3

P = vapor pressure = 0.04077 atm

M_w = molecular weight = 91 g/mol

R = gas constant = 0.082 L atm/mol K

T = temperature = 283 K

For BTEX, the maximum number of Kg removed by 1 m^3 of air is 0.16 which yields a minimal volume for removal of 1,163,875 m^3. The number of wells on a volume basis is 48 derived by dividing the minimal volume by the extraction volume of each well.

6.2.3. Contaminant Removal Time

Assume BTEX held in soil moisture and equilibrium conditions (Henry's Law). Best possible performance of SVE when all soil moisture accessible to air. The mass removal rate under these conditions follows:

$$(dM / dt) = (C_{vapor}\ Q) - (K_H\ C_{solution}\ Q) \qquad (6 - 4)$$

where

dM / dt = mass removal rate

C_{vapor} = vapor concentration

Q = flow rate

K_H = Henry's Law constant

$C_{solution}$ = concentration in solution

Time to total mass removal is 646.25 days and is given by:

$$t_{100} = (w \ V_T) / (K_H \ Q) \qquad (6 - 5)$$

where

t_{100} = time for total removal

w = porosity = 35%

V_T = 866,253.33 m³

K = Henry's Law constant

Q = flow rate = 85,300 m³/day

The time for total removal of benzene is 646.25 days and time to MCL is 598.73 days.

6.3. Air Sparging

6.3.1. Injection Pressure

The needed injection pressure, Pi = 60 + 0.8333 = 60.833 feet from equation (4 - 2). The AS system is using 30 to 35 psi, which corresponds to 69 to 80.5 feet of water. The ration of system pressure to minimal required pressure is approximately equal to 1.23 and the ratio of horizontal radius to sparge depth is 1.25. From Figure 4.4 it can be seen that the system is operating within a region of controlled flow where water displacement is not a factor.

6.3.2. Remediation Time

6.3.2.1. Air Bubbles

The air sparging cleanup rate used for the design of the system was developed by Sellers & Schreiber at Camp Dresser and McKee. The cleanup rate equation derived from their model follows:

$$C_t = C_o \ e^{-Bt} \qquad (6 - 6)$$

where

C_t = concentration at time, t

C_o = initial groundwater concentration

B = decay coefficient

t = time

The equation yields a total cleanup time of 10.2 years for Benzene with C_o = 0.068 ppm and B = 0.00086 days^{-1}. The time to reach MCL (0.005 ppm) is 8.3 years.
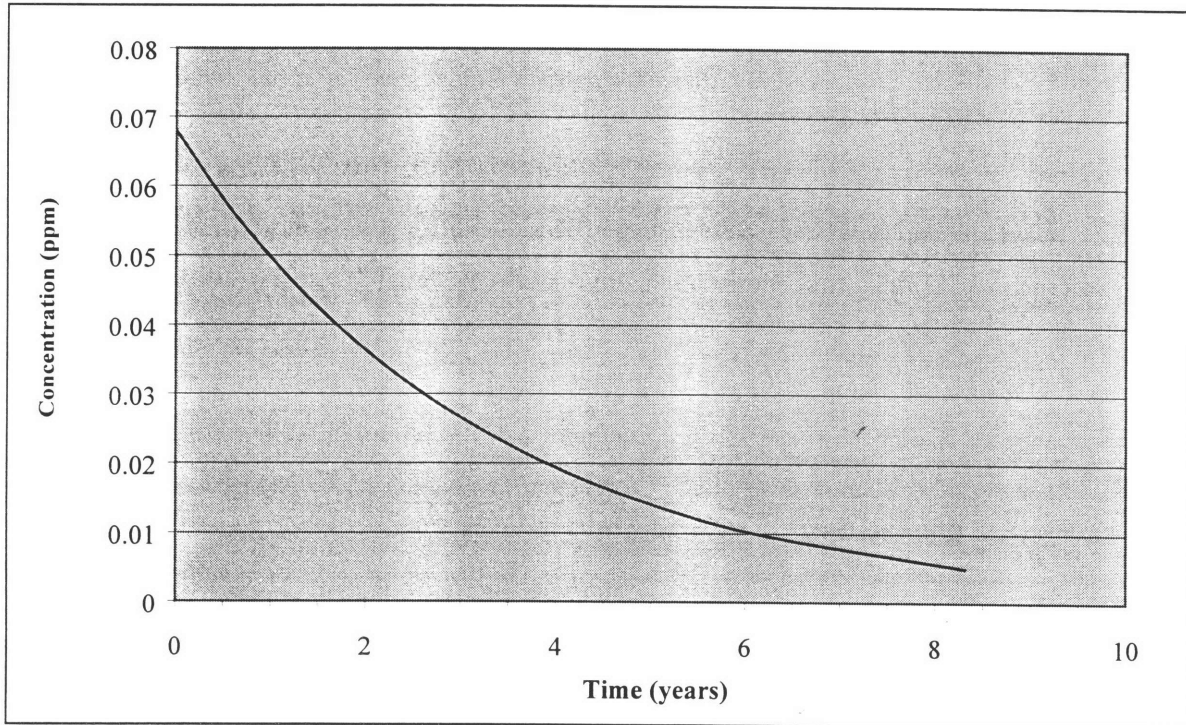
Figure 6.1: AS Remediation Curve (Bubble Flow)

6.3.2.2. Channel Flow

The CDM model was modified to account for channel flow hence the cleanup rate equation is the same form as for bubble flow with the difference being in the decay coefficient, B = 0.0000096 days^{-1} (Lockwood, 1997). Time to reach MCL is 744.88 years.
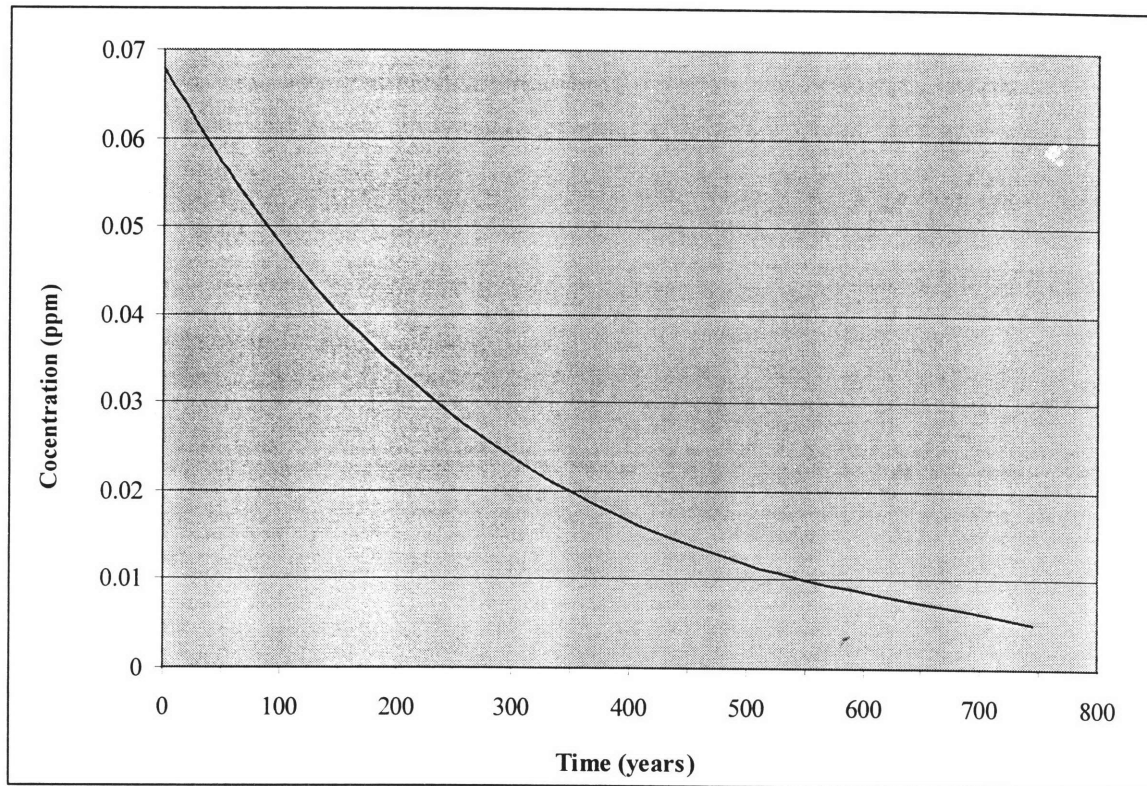
Figure 6.2: AS Remediation Curve (Channel Flow)

6.4.□ Biodegradation Remediation Time

An aerobic biodegradation process is used considering the site conditions. A first order model for approximation of cleanup time gives the following solution:

$$C_t = C_0 \, e^{-Kt} \qquad\qquad (6 - 7)$$

where

C_t = concentration at time, t

C_o = initial concentration

K = rate constant

t = time

The reaction is defined by the contaminants half-life, from which the rate constant is derived.

$$K = [\, Ln \, (1/2) \,] \, / \, t_{1/2} \qquad\qquad (6 - 8)$$

The half-life of benzene is 10 days which gives a rate constant equal to 0.06932 days^{-1} and the time to reach MCL is 37.65 days and time for total cleanup is 260.17 days.
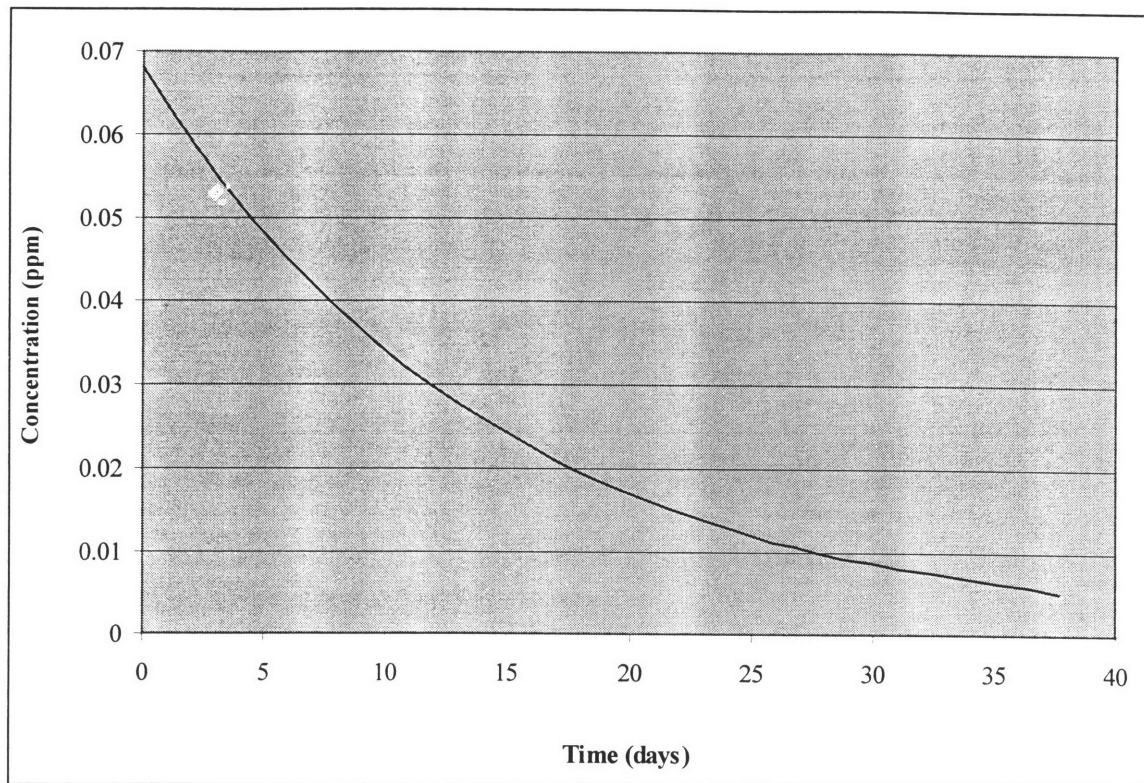
Figure 6.3: Biodegradation Remediation Curve

6.5. Estimated Total Time to Reach MCL

As an estimate of total remediation time the percent removal ratio of biodegradation to volatilization for jet fuel was used from Figure 4.4, 60% biodegradation to 40% volatilization.

$$t_{Total} = (0.6\ t_{bio}) + (0.4\ t_{vol}) \qquad\qquad (6 - 9)$$

$$t_{Total} = (0.6*0.1032) + (0.4*8.3) =\ 3.382\ \text{years}$$

7.   *Results*

7.1. Air Sparging & Soil Vapor Extraction

7.1.1. Applicability

The contaminants of concern at FS-12 the BTEX, and in particular benzene, have the proper compound and soil properties for the remediation technologies to be effective, as summarized in Table 3.1. The BTEX compounds have high vapor pressures above 5 mmHg and very high for benzene at 76 mmHg which makes them very amenable to partition into the gaseous phase and thereby be removed by the SVE system. They have moderate solubilities with benzene being the most soluble, which enhances biodegradation by making more of the compounds available for microbial uptake by being dissolved in the pore water. However, these moderate solubilities can also pose a potential threat by spreading the plume downgradient. SVE efficiency and VOC removal by air stripping are both Henry's Law dependent, therefore the high constants of the BTEX compounds makes them optimal for these two remediation technologies. The half lives of these compounds are also high thereby increasing the effects of removal through biodegradation. Turning to the soil properties, the porosity of the sand is 35% which will increase the SVE efficiency by increasing soil permeability and the diffusive transport from the soil surface to the soil gas. Clay soil composition is a major factor as it can reduce efficiencies by increasing the presence of water reducing space for vapor transport and the small micropores of clay minerals increase transport path lengths. The total soil organic content strongly correlates with the binding capacity of the soil for organic chemicals, the soils at FS-12 have a low organic content thereby being favorable to remediation. The site is a homogeneous medium sand improving the possibility of air flow reaching all areas requiring remediation. There are not any known layers of finer grain material above the sparge depths eliminating the possibility of extensive spreading, but one must still consider this factor as any heterogeneity will lead to spreading of some extent. However, the sparge point depths are twice that normally used in sparging systems therefore there is a real concern in regard to control of the process considering the depth of 60 feet below the water table. Overall the site is very well suited for vapor extraction and sparging mainly due to the contaminant properties which make them highly strippable and volatile and also the homogeneous nature of the aquifer.
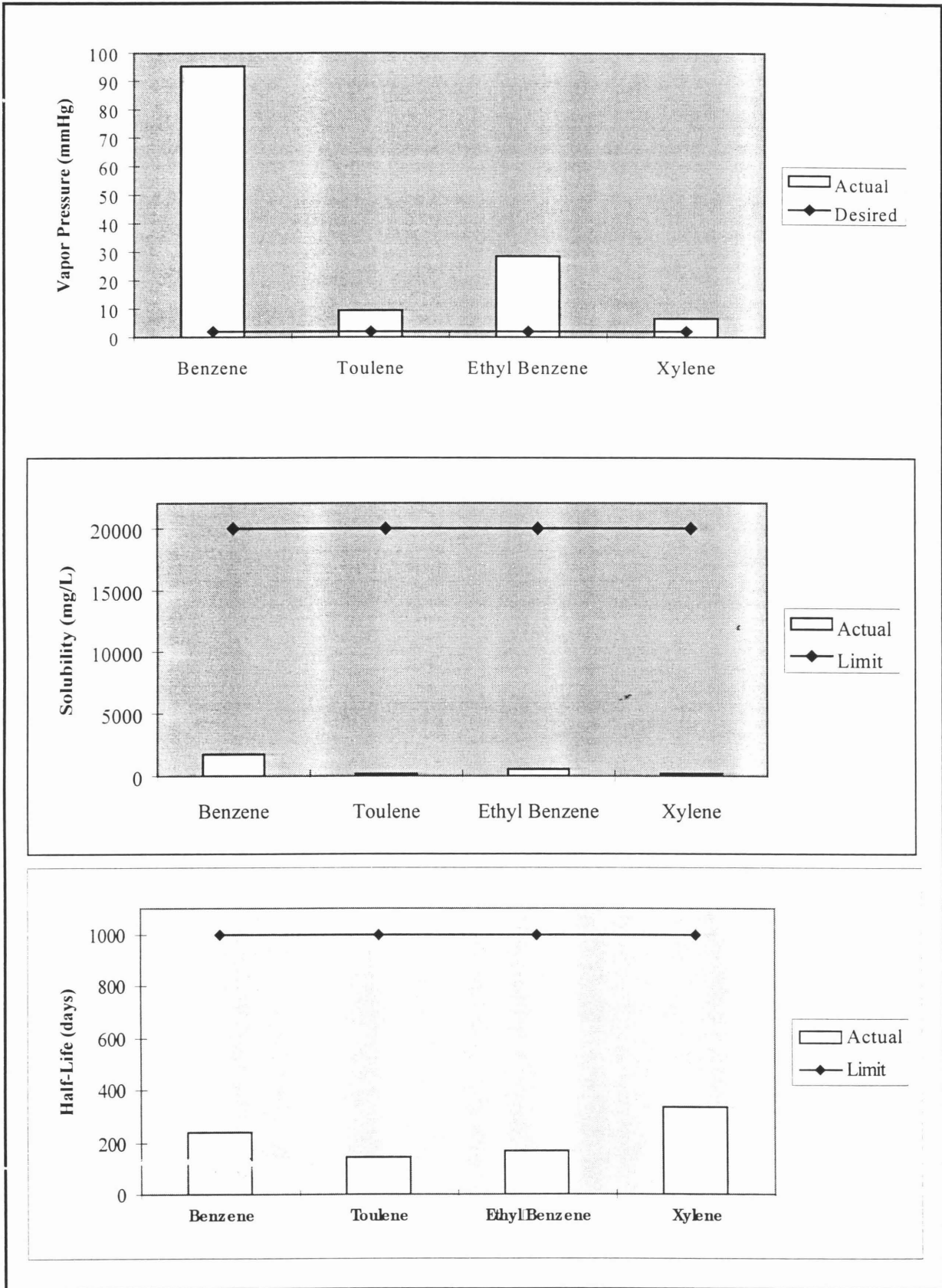
Figure 7.1: Summary of Applicability

7.1.2. Remediation Time

There is a large variation in remediation time to MCL depending on the technology employed. Table 7.2 summarizes time to reach MCL for each technology.

Table 7.1: Summary Remediation Time

	Bubble Flow	**Channel Flow**	**Biodegradation**	**SVE**	**Estimated Total**
Time to reach MCL (years)	8.3	744.88	0.1032	1.64	3.382

The biodegradation has the minimal time of 37.65 days and the estimated total time matches well with what has been observed at FS-12. The SVE time most closely resembles what has been taken place in the source area, where the sparging estimates are much higher with the more realistic channel flow approach has the greatest time of 744.88 years.
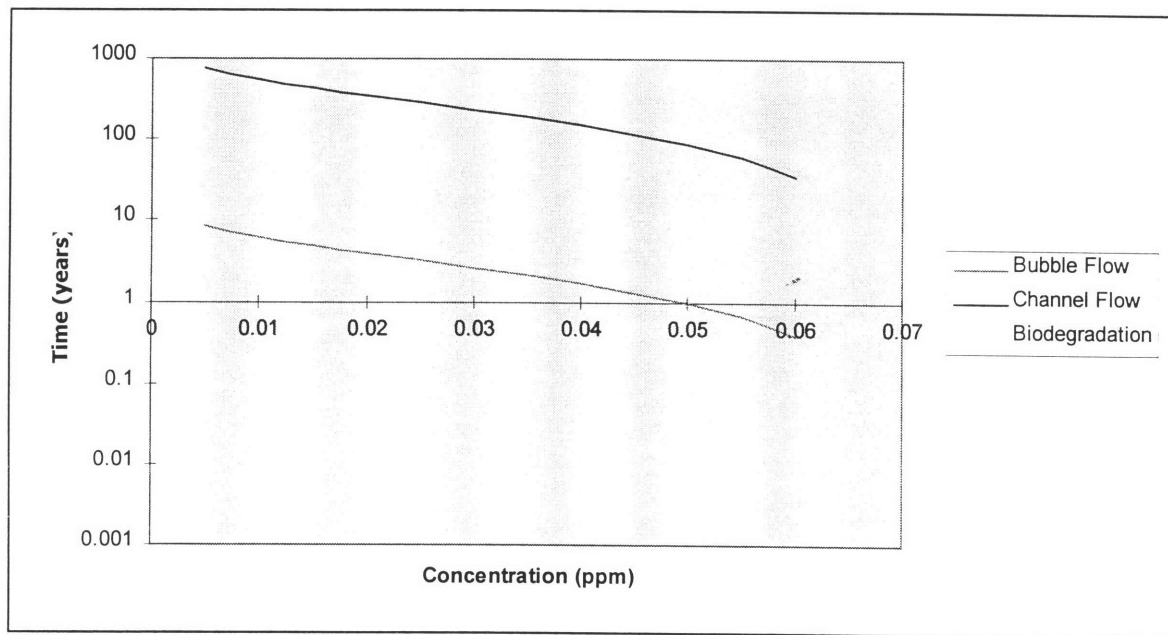
Figure 7.2: Remediation Time Comparison

7.1.3. Biodegradation

An analysis performed by Microbial Insights, Inc. in 1993 determined that in areas of no contamination there was no biomass, in the immediate spill area the environment was too toxic, but in the remaining areas there was a healthy microbial community. Their conclusion was that an increase in oxygen would greatly increase their growth rate. During the AS pilot study the dissolved oxygen and vadose zone oxygen levels were observed to be at saturation levels, which greatly increase the opportunity for biodegradation of the contamination.

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7.2. ☐ Self Potential Method

7.2.1. Concentration Contours

The contour plots show a well defined area of a large negative anomaly with a length of 300 feet directly downgradient from Greenway Road with the center axis located at 280 feet.
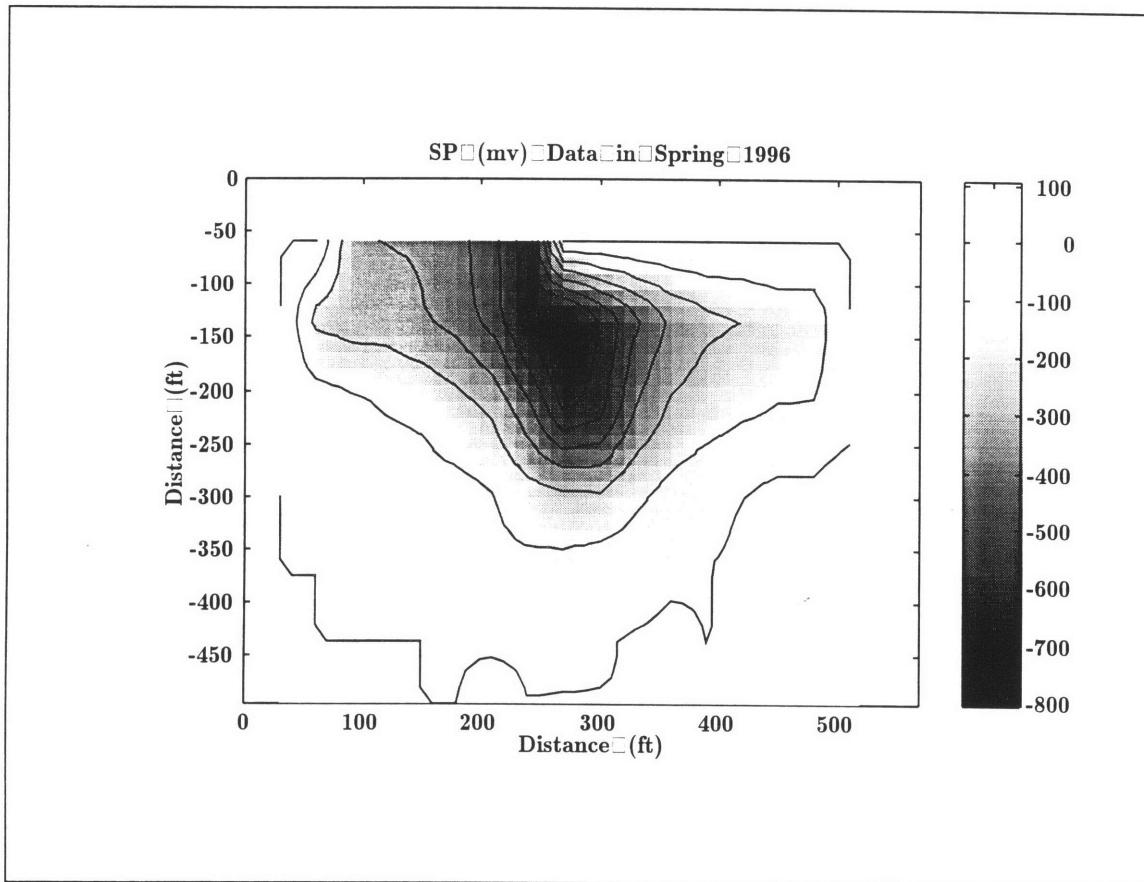
Figure 7.3: Contour Plot, Spring 1996 (ERL)
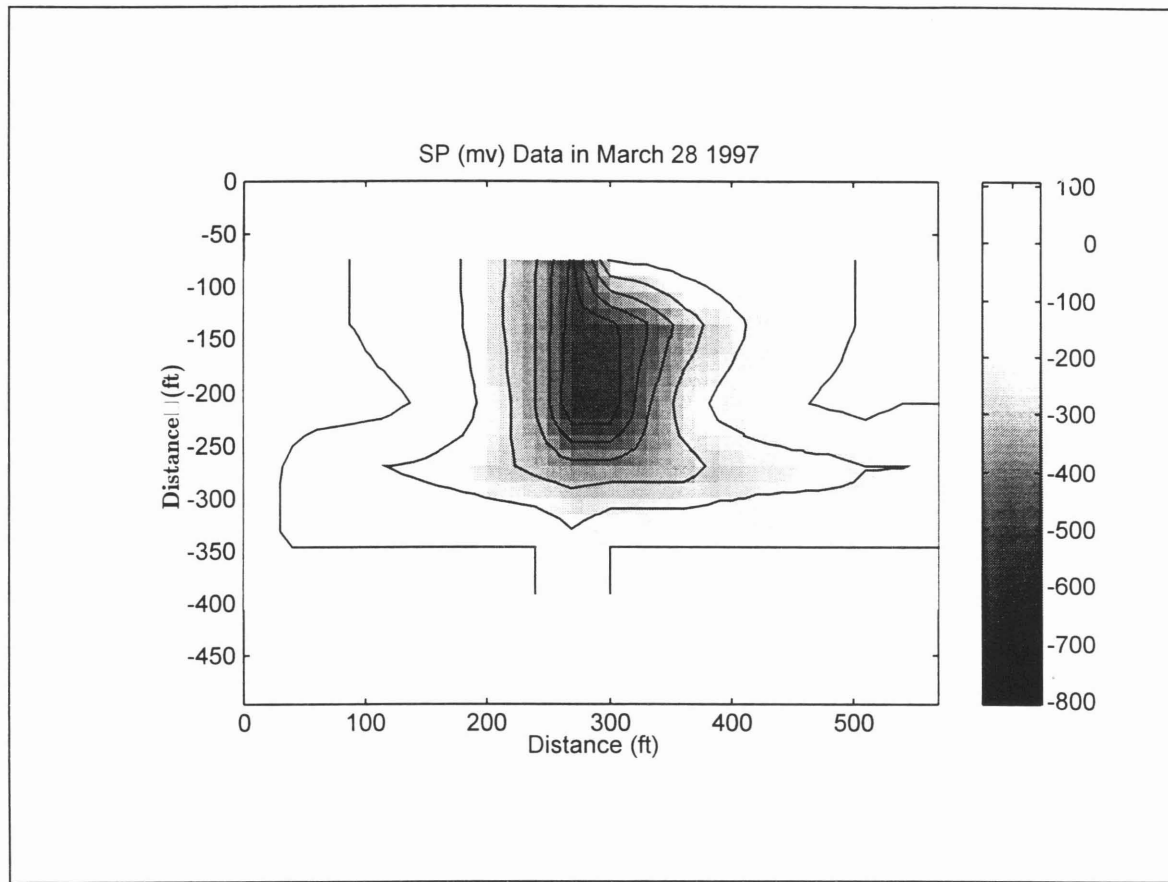
Figure 7.4: Contour Plot 3/28/97
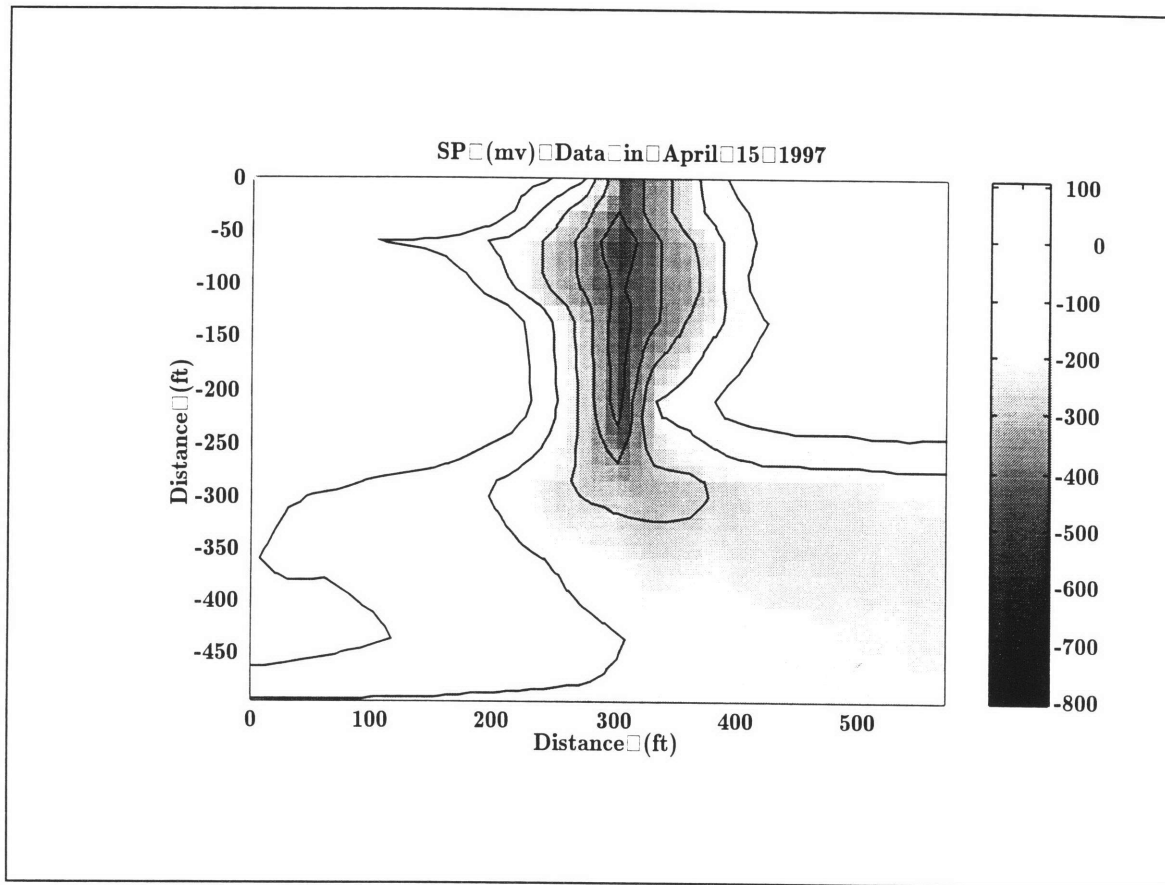
Figure 7.5: Contour Plot 4/15/97

SP (mv) Data in April 22 1997
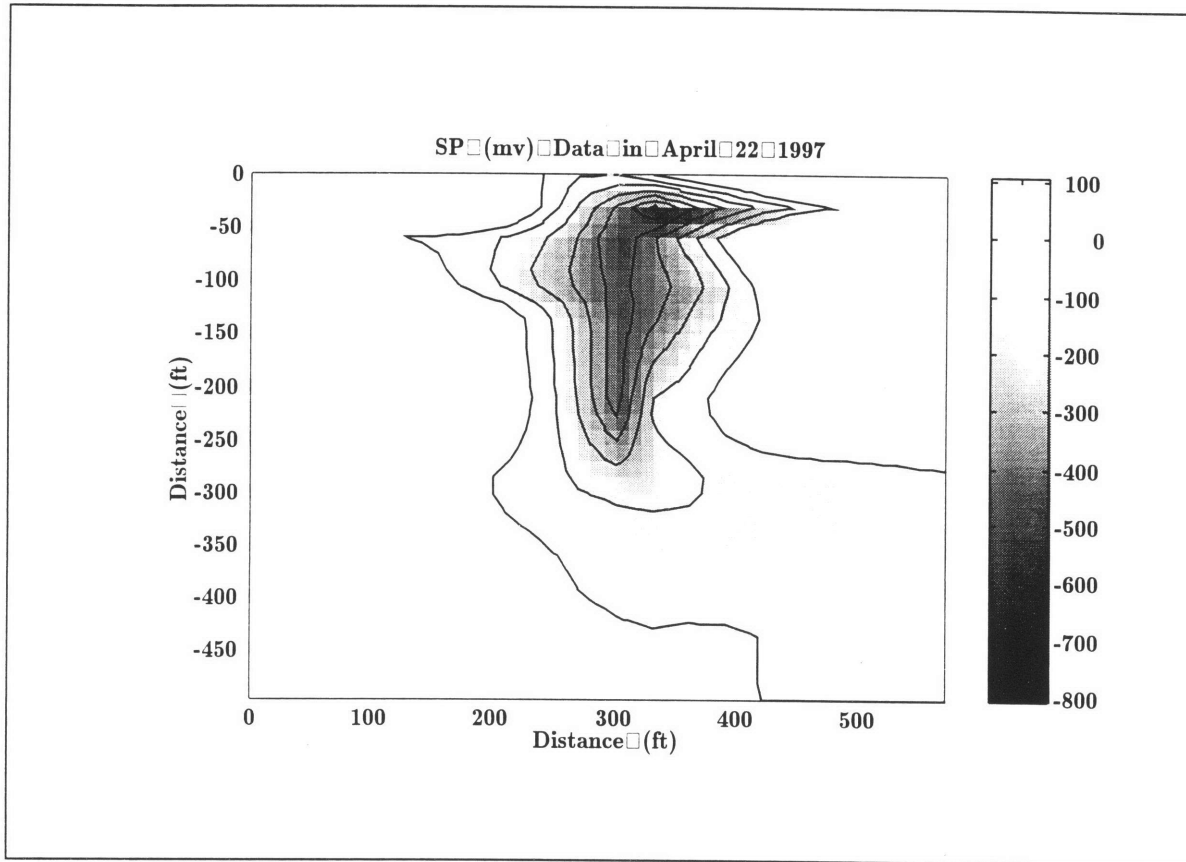
Figure 7.6: Contour Plot 4/22/97
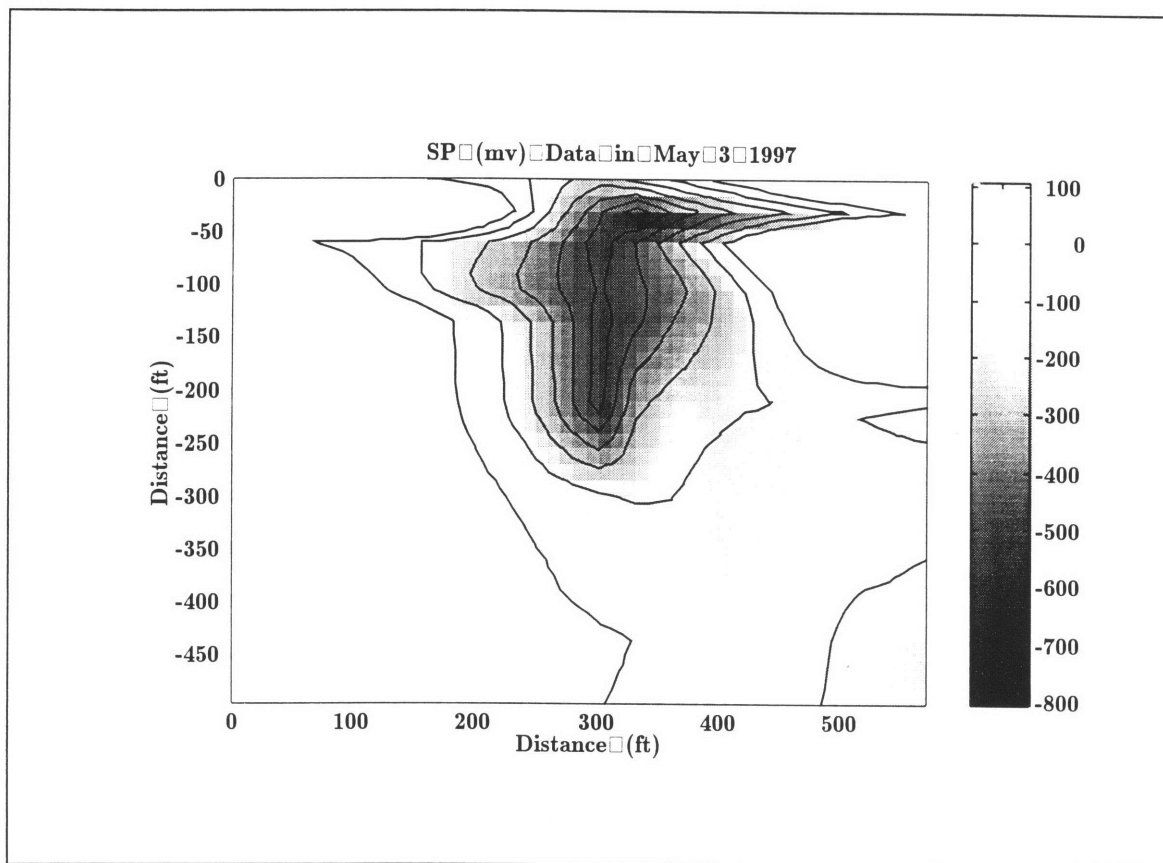
Figure 7.7: Contour Plot 5/3/97

Table 7.2: Anomaly Dimensions

Parameter	Spring 1996 (ERL)	March 28, 1997	April 15, 1997	April 22, 1997	May 3, 1997
Length (ft)	315	300	365	285	285
Width at 100'	380	170	150	150	210
Width at 250'	200	160	60	70	100
Max SP (mV)	-750	-625	-450	-475	-575

The data from April 15, 22 and 1996 were taken when the AS-SVE system was shut down and on all other dates the system was in operation. The strong anomaly in the center remains stationary throughout the period and the data is reproducable. The greatest width of the anomaly is constantly at the length of 100 feet which is the only area where it bulges out and the

remainder of the anomaly is shaped similar to a pencil. In all the plots, except from 1996, the strongest anomalous area is symmetric about the longitudinal axis. Several of the plots, especially from April 15, show an area with potentials of -100 mV to -175 mV to the southeast corner of the source area. The leading tip of the anomaly also shows a feature to the southeast direction. The regional ground water flow in the area is also in a south-southeasterly direction which indicates that the anomaly is at least partly generated by the aqueous phase. However, the hydraulic velocity is 0.274 ft/day which makes the observed changes from April 15 to 22 and April 22 to May 3 impossible.

7.2.2. One Year SP Difference

The comparison of the data from 1996 to 1997 will provide a means by which to verify the remediation effects of the AS-SVE system.

Table 7.3: One Year Comparison

Year	Length (ft)	Width at 100 ft	Width at 250 ft	Max SP Potential (mV)
Spring 1996	315	380	200	-750
Spring 1997	305	170	100	-510
Difference	10	210	100	240
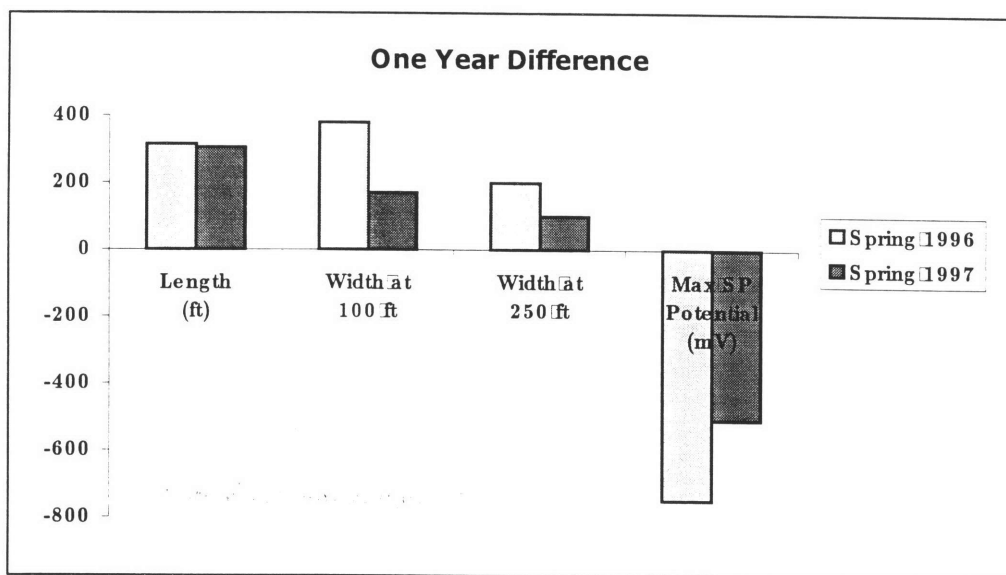
Figure 7.8: One Year Comparison

As seen in Table 4.2, in one year the anomaly has significantly shrunk in width and the maximum SP potential has dropped by 240 mV, while the length has remained constant. The data shows that the remediation system is working, however at this time there is not a quantitative measure to correlate the potential values to concentration. There is also not a means to determine which mechanism is dominant in the remediation process of the site.

A second analysis approach of the one year comparison is obtained by subtracting a 1997 plot from the 1996 plot, see Figure 7.9, which clearly shows the area where contamination has been removed as negative and the areas where contamination has migrated to a positive values. There is a significant region near the current remediation system's trailers which has been remediated, particularly the area of the greatest SP levels from 1996.
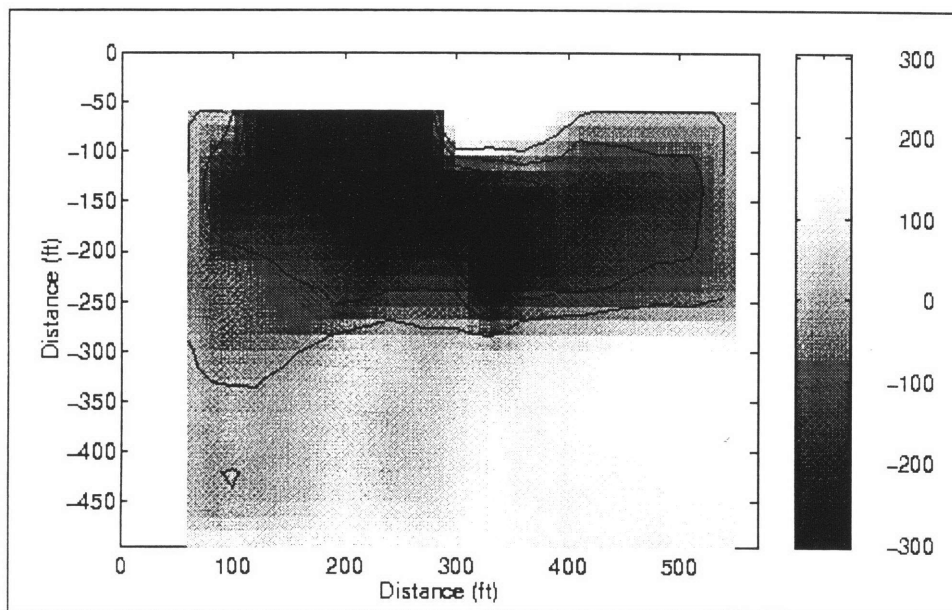
Figure 7.9: One Year Subtraction

7.2.3. Air Sparging - Soil Vapor Extraction

A comparison of the plots with the systems on and off does not yield a significant result, however the subtraction of the plots with the systems on and off clearly delineates the area the AS and SVE are effecting. A comparison of this effective remediation area with the negative areas of Figure 7.9 which show where the greatest remediation has taken place over the last year, yields an excellent result as the two areas are very similar in size and cover the same positions. Hence, SP has great potential to be used in monitoring remediation systems and in providing a measure of their effective.
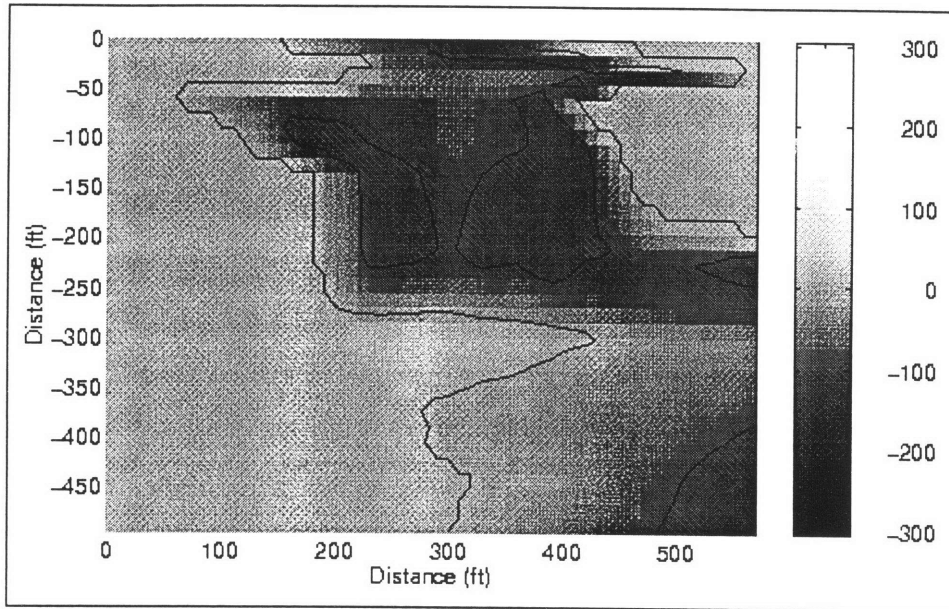
Figure 7.10: Subtraction With AS & SVE Operating and When Off

7.2.4. Test of SP Method at FS-13

Along the same fuel pipeline as FS-12 they have been several much smaller leaks of similar contaminants, one of which is FS-13. The site has not been characterized but the estimate is that an area 10 to 15 feet wide and 100 to 120 feet long is contaminated. This site was chosen to verify that the method is measuring potentials that correspond to contaminants and not other sources. Due to the size of the contaminated area a single survey line was chosen down the axis of the area. The results show a clear anomaly which matches well with the estimated location and length of the spill, the suspected location of the leak is somewhere within the range of 80 to 110 meters.
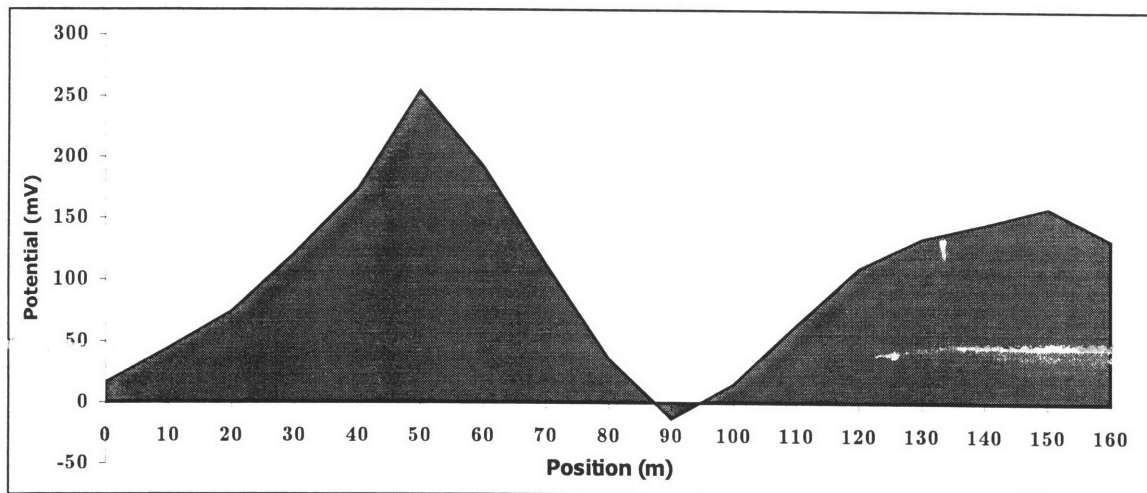
Figure 7.11: FS-13 Test Result

7.2.5. SP Potential Source at FS-12

The result of this study clearly shows a SP anomaly at the FS-12 source area but the source of current is not completely understood. An electric ground is not an option since the anomaly remained even when the system was shut down with no equipment running. The possibility of water/air movements due to the AS and SVE is also dismissed because the anomaly is not observed over the entire remediation area which includes 21 SVE and 22 AS wells, (see Figure 3.5 & Figure 4.5). Diffusion due to concentration variations is a possible source from the FS-13 test and the nature of the anomaly. When the system is in operation the anomaly is slightly wider which may be caused by the mixing of areas with lower and higher concentrations or as a result of increased concentrations in the vadose zone. The other likely source of potential generation is biodegradation. The contaminants in the source area have a hydraulic velocity of 0.2 ft/day which is very low and the greatest water table elevation variation during one year is 10 ft, these conditions create an abundant supply of substrate for biodegradation. Analysis performed in 1993 shows that there is a healthy microbial community which with an increase in oxygen will have tremendous growth rates which is the case since AS raises oxygen levels to saturation. The conditions at FS-12 are very favorable to biodegradation. Jet fuel is 60% biodegradable and 40% volatilized which points to this mechanism as the primary remediation process. Diffusion and biodegradation are also linked in that biodegradation will only occur in areas which contain the proper concentration levels of contamination. Currently, there is not a means by which to separate these potentials therefore the only conclusion that can be made is that one or both of these processes are generating the observed anomaly.

8.   Conclusions

Self potential geophysics has many possible applications in the area of environmental engineering. The potential of SP in monitoring water movement has been developing and research is being conducted on its capabilities. SP and other geophysical methods can revolutionize the entire remedial investigation arena by providing reliable, quick, and cost effective means to delineate contaminated areas. Currently an operator of a remediation system such as SVE or AS has no real time answers as to what is happening in the subsurface and questions related to the success of the technology and the cleanup rate (concentration levels at any time). With a well developed strategy and careful implementation it is possible to obtain greater detail from SP than what has been presented within the scope of this thesis, with the use of 2D contour plots.

The determination of extent of contamination is vital at any contaminated site, the method of choice today is to drill a few wells from which the concentration profile of an entire site is interpolated. In this process the choice of location of wells is critical, it is possible that one can conduct a field investigation in a contaminated zone but conclude that the area is clean simply because no wells are located in the contaminated zone(s). But with the use of self potential the entire area can be surveyed and the possibility of missing contaminated areas is diminished, however the contaminant(s) needs to be generating a potential. The cost of drilling a single well can run from $10,000.00 to $20,000.00 whereas the equipment cost for conducting a self potential survey is under $100.00. With a well you obtain good data but with a certainty equal to just greater than the radius of the well, with SP you have freedom to investigate all areas of interest and to whatever degree is necessary. Self potential data acquisition, analysis, and results are obtained in a rapid manner with good quality if the proper measures are taken. The results of this thesis verify the use of SP in delineating areas of contamination. Further study is needed to establish a range of contaminants which can be delineated by using SP and their relative maximum potentials. At the very least conducting a SP survey before further investigation through geotechnical or geophysical methods commence would provide guidance as to which areas need to be investigated or monitored. Again, keeping in mind the relative rapidness of the method and its low cost, it truly would be a bargain to have some picture of the subsurface even if it is not completely clear.

Another use of self potential is in monitoring remediation and/or contamination levels. The case with most remediation technologies is that there are not direct ways to verify their proper operation and remediation effectiveness. Self potential can provide a breakthrough in this

area by having the capability to measure the coupled flow of air and water that is observed in today's technologies such as air sparging and soil vapor extraction. The remediation times and mass removal rates of these systems can only be estimated by using modeling methods. Once a system begins operation greater confidence can be attained from the collected data for determination of system efficiency. Depending on the site and the available resources, ground water and soil samples may only be taken on a yearly basis which are the only means by which to obtain a true assessment of the subsurface if performed and designed properly. Self potential geophysics can augment these sampling events by collecting data on a shorter time period, where when anomalies are observed proper measures can be taken to further investigate these "hot spots" or the spreading of contamination. SP can be a valuable tool for a system operator in having a quick and cost effective check of what his system data is showing and in cases where there is no data it may be used to verify if remediation is taking place. This study has shown that this is possible in a qualitative way through the results shown in the plot subtractions, however they do not provide quantitative answers. But that is possible by generating 3D images of the SP data and monitoring the volume of the anomaly which would be correlated with the amount of contamination removal.

For SP to truly have a real impact some correlation needs to be developed between measured potentials and concentration levels. When enough SP data has been compiled and analyzed this may be established. A credible and reproducible method of converting from potentials to concentration would be a tremendous leap forward for the method in environmental applications. But first the method needs to be accepted by the engineering and scientific community as a credible method of delineation and not be hyped as to give it capabilities which are not feasible. Another similar possibility is in estimating decay rates by collecting data at the same location over some time frame. The decay or removal may be correlated to maximum potential values or the surface area/volume of the observed anomaly.

Considering the high costs and mobilization requirements of drilling operations for delineation and monitoring, SP can be a very attractive alternative, or be used as a preliminary study in the investigation of any contaminated site. SP has the ability to delineate areas of BTEX contamination but further study with other contaminants is needed and the mechanism(s) of SP generation need to be well understood.

8.1. Recommendations for Future Study

This study has clearly shown that SP has great potential for use in environmental engineering but for its effective application several factors need to be better understood and

developed. Laboratory work would involve sandbox models and field work would be used to verify results and to attempt the use of SP in other applications.

The laboratory work would study the mechanisms of diffusion and flow potential generation. Diffusion models would comprise of creating two cells separated by a diffusive/porous material where drops of a non-hazardous contaminant could be placed on one side and potentials measured over time as the contaminant diffuses to the other side. In the case of flow there are several flows to be considered: fluid (water), air, contaminant, sparge simulation, and a combination of the above.

The field work would entail studying a site with no remediation systems to again verify the methods ability to observe contaminants. An SVE or AS well should be localized, the study would only try to capture the air /water movements caused by these systems, by placing electrodes out from a well to a distance just greater than their radius of influence. Sites with non-hydrocarbon contaminants should be studied to determine if SP can detect them as well and to determine if biodegradation or diffusion is the source of a SP anomaly.

9.   References

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APPENDICES

Appendix - A

Stratigraphic Cross-Sections at FS-12

LEGEND

SAND, POORLY GRADED, WITH MINOR GRAVEL		CLAY, SILTY		† INTERPRETATION IS BASED ON SPLIT-SPOON SAMPLES
SAND, SILTY		SILT, CLAYEY		
SAND, CLAYEY		WATER TABLE 3/93		

HAZWRAP

SCALE:	AS NOTED
DATE:	08-30-94
FILENAME:	M48H257.DGN

B — FEET — B'

0   500   1000   1500   2000   2500

GMW-38   GMW-31   GMW-34   GMW-36   GMW-52

FEET ABOVE MSL

150
100
50
0
-50
-100

50   25   0   50
SCALE IN FEET
VERTICAL

500   250   0   500
SCALE IN FEET
HORIZONTAL

LEGEND

SAND, POORLY GRADED, WITH MINOR GRAVEL

SAND, CLAYEY

WATER TABLE 3/93

HAZWRAP

HAZARDOUS WASTE REMEDIAL ACTIONS PROGRAM
DEPARTMENT OF ENERGY / MARTIN MARIETTA ENERGY SYSTEMS, INC.

SCALE: AS NOTED
DATE: 08-30-94
FILENAME: MMRH258.DGN

Appendix - B

Raw Data

	28-Mar	15-Apr	22-Apr	3-May
Line 1				
1		-1.8	-1.1	7.6
2		-3.2	2.6	3.5
3		63.2	61.6	62
4		36.3	31	37.2
5		28.8	32.4	28.1
6		33.6	42.5	40.9
7		91.5	92.1	82.5
8		84	87.1	95.6
Line 2				
1			201	183.5
2		-141	-189	-182
3		-128.5	-140	-115.2
4		-82.7	-115.3	-94.1
5		-85.2	-90.5	-62
6		-0.7	-17.6	-8.6
Line 3				
1		23.2	23.2	32.5
2		24.5	22.5	35.9
3		43.6	43.2	50.6
4		47.2	47.9	55.7
5		79.2	81.6	81.3
6		114.6	122.1	116.1
7		159.1	182.1	163.6
8		238	248	230

All data in mV

Electrode spacing = 28 ft

Line 4				
1		-105	-95.1	-83.5
2		-64.5	-72.9	-62.6
3		-160	-155.8	-133.6
4		-120	-98.6	-85.3
Line 5				
1		26.2	24.7	28.9
2		33.2	31.1	40.9
3		43.4	45.6	48.3
4	-23.4	61.5	62.7	65.7
5	-34.5	53.9	62.2	60.7
6	-80.1	111.8	124.2	121.5
7	-114.7	168.4	173.2	160.3
8	-246	217	221	200
9	-120.5	-122.1	-125.1	-107.1
10	-149.2	-135.1	-142.1	-126.2
11	-102	-96.7	-103.5	-97.1
12	-83.3	-86.2	-91.5	-83.4
13	-61.2	-47.4	-53.1	-120.1
14	0.9	-19.2	-22.2	-115.4
15	-29.9	-11.3	-13.5	-114.7
16	-6.6	-3.1	-1.2	-106.1
17	2.5	-10.6	-3.9	-67.3

Line 6				
1	-22.1	12.2	17.7	22.4
2	-2.5	33.3	27.7	36.1
3	-10.9	37.2	47.4	45.7
4	-17.5	44.4	49.2	54.5
5	-35.8	61.4	66.2	62.3
6	-48.4	104.5	113	110.9
7	-91.3	179.1	184	171.3
8	-150.5	239	239	213
9	-280.2	-360	-369	-332
10	-266	-47.9	-48.4	-63.2
11	-166.1	-73.4	-90.5	-28.6
12	-78.9	-31	-37.3	-20.1
13	-40.3	-24.5	-27.2	-0.8
14	-26.2	4.1	-5	-13.7
15	-18.7	-20.7	-19.3	12.3
16	-15.1	0.2	3.9	-0.6
17	-7.9	-6.7	-5.7	

Line 7				
1		18.5	16.6	26.1
2	-6.5	11.4	10.8	15.1
3	-6.2	11.9	9.3	15.2
4	-9.8	19.8	31.8	27.9
5	-11.2	15.3	12.3	29.6
6	-24.9	34.3	42.4	38.5
7	-36.9	41.1	45.7	46.1
8	-35.6	46.7	28	35.8
9	-24.9	39	56.5	54.6
10	-0.2	22.8	19.4	22.3
11	1.6	5.2	11.7	15.6
12	-58.3	-7.31	-14.9	-6.8
13	-26.9	-48.3	-41.2	-37.3
14	-12.5	-23.4	-25.5	-24.4
15	-9.5	6	0.8	14.1
16	-26.5	-6.1	-7.2	3.3
17	-2.3	0.4	-0.1	7.5
18	-13	-15	-11.7	-5.7
19	-1.2	5.6	2.9	-4.8
20		8.6		12.8

Line 8				
1		23	16.6	14.1
2		-8.9	-3.1	12.3
3		14.4	6.6	12.2
4		15.5	1.2	13.5
5		17.7	9.4	25.8
6		11.3	12.9	19.4
7		21.8	18.8	22.2
8		17	19.1	25.1
9		25.4	31.4	38.9
10		16.6	13.4	16.7
11		5	5.6	12
12		-2	3	3.6
13		-4.4	-6.1	1.1
14		10.4	-5.2	16
15		-7	0.5	-3.5
16		10.8	8.5	17.1
17		3.2	-5.4	11.8
18		1.4	-5.8	2.7
19		5.3	-0.3	13.9
20		-5.1	1.4	-0.8

Line 9				
1		24.7	3.2	21.3
2		11.8	11.1	24.4
3		11.2	12.8	20.2
4		7.1	7.5	18.7
5		13.8	10.9	15.6
6		10.8	5.1	9.8
7		12.8	-3.3	8.4
8		-8.1	2.2	-2.3
9		7.7	5.3	27.5
10		-3.3	-1.1	21.4
Line 10				
1				21.1
2				22.4
3				6.4
4				18.3
5				27.6
Line 11				
1				4.6

Center Line				
1		321	323	303
2		78.8	79.4	80.5
3		-60.9	-60.4	-57.6
4		25.6	27.3	38.1
5		-7.7	-5.7	6.7
6		-143.4	-327.5	-447
7		-115.8	-115.4	-88.5
8		-36.7	-40.1	-21.5
9				8.9
10				4.6