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Assessing UST Corrective Action Technologies:

Diagnostic Evaluation of *In Situ* SVE-Based System Performance

by

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Notice

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a scientific knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The Laboratory research program focuses on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and groundwater; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies, develop scientific and engineering information needed by EPA to support regulatory and policy decisions, and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

Abstract

In situ corrective action technologies are being proposed and installed at an increasing number of underground storage tank (UST) sites contaminated with petroleum products in saturated and unsaturated zones. It is often difficult to accurately assess the performance of these systems for remediating soils and groundwater. Because of the complex subsurface characteristics encountered at leaking UST sites, a series of tests/tools are needed for evaluating the appropriate application and remediation performance of these corrective action technologies.

In response to this need, the U.S. Environmental Protection Agency (EPA) Office of Research and Development (ORD) National Risk Management Research Laboratory (NRMRL) has provided technical support to EPA Regions for evaluating in situ corrective action technologies. This report presents a series of test procedures that were developed for evaluating intrinsic biodegradation, bioventing, soil vapor extraction (SVE), and in situ air sparging (IAS), These procedures present diagnostic tools that are designed to assist in assessing remediation performance. Most of the discussions focus on evaluating systems designed for petroleum hydrocarbon contamination; however, these procedures can also be used to evaluate remediation performance of in situ technologies used to address a wide range of contaminants.

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Section 1

Introduction

Purpose

It is often difficult to accurately assess the performance of systems for remediating soils and groundwater. This is due in large part to the complexity and heterogeneous nature which exists in the subsurface at a given site. Because of the complex subsurface characteristics encountered at leaking underground storage tank (UST) sites, a series of tests/tools are needed for evaluating the appropriate application and remediation performance of selected corrective action technologies.

In response to this need, the U.S. Environmental Protection Agency (EPA) Office of Research and Development (ORD) National Risk Management Research Laboratory (NRMRL), UST Research Program has provided technical support to EPA Regions for evaluating selected corrective action technologies. Under this program, NRMRL developed a series of test procedures for evaluating intrinsic biodegradation, bioventing, soil vapor extraction (SVE), and in situ air sparging (IAS). The test procedures described here are diagnostic tools designed to aid in assessing remediation performance. While most of the discussions focus on the widespread problem of petroleum hydrocarbon contamination, these procedures can also be used to evaluate remediation performance of technologies used to address a wide range of contaminants.

Background

Releases of petroleum hydrocarbons fuels (e.g., gasoline, diesel, aviation fuel) frequently contaminate soil and shallow groundwater, and are widely recognized as an important environmental problem. Fuel spills are different than many other groundwater contamination problems, in that much of the fuel often exists in the subsurface as a nonaqueous-phase liquid (NAPL). NAPLs can be distributed in the subsurface as isolated "blobs" within pore spaces, or as larger continuous zones or "pools" near the water table or associated with heterogeneous zones in the medium. Vadose zone soils in the source area often contain "residual" hydrocarbons in isolated pore spaces. This residual may account for 10 to 60 liters of hydrocarbons per cubic meter of soil. Because petroleum NAPLs are less dense than water (LNAPLs), they often accumulate at the water table. They can occupy a significant fraction of the pore space in this region, and can often move up and down as the groundwater level changes. As the result of

fluctuating water tables, the NAPL can become entrapped below the water table in what has become known as a "smear zone."

At many sites, LNAPLs both above and below the water table represent long-term sources of contaminants. (Dense NAPLs also cause significant subsurface contamination and can be remediated by SVE and IAS; however, the focus of this discussion will be on LNAPLs.) As groundwater flows through NAPL zones, dissolution forms aqueous-phase plumes. These plumes move under the influence of groundwater flow and can migrate for significant distances. Because of limited solubilities of the fuels, the sources can be long-lived. As a consequence, treating the groundwater plume without removing the source can result in regrowth of the groundwater plume. This means that it is often necessary to treat both the plumes and the sources, although the approaches for each may be significantly different.

Remediation of NAPL-contaminated zones has generally been accomplished by flushing the appropriate fluid through the medium (i.e., air in the vadose zone, water in the groundwater zone). Under those "pump-and-treat" scenarios, mass is removed from the vadose zone by volatilization and from the groundwater zone by dissolution. Both of these technologies have demonstrated successes and failures. Failures can often be traced to heterogeneities in the medium and/or to the inability to effectively remove NAPL.

IAS is a relatively new remedial technology. During IAS, air is injected into the saturated zone to volatilize contaminants in much the same way that contaminants are volatilized in the unsaturated zone. In addition to volatilization/dissolution, remediation occurs by biodegradation. The operational conditions under which biodegradation is optimized are somewhat different than for volatilization/dissolution. For biodegradation, the primary criterion will be how well oxygen can be delivered to the contamination zone. In shallow, well-drained soils, molecular diffusion may be adequate to maintain aerobic conditions. In many cases, however, it will be necessary to actively flush air through the system to maximize biodegradation. Similarly, in some cases in the groundwater zone, there may be an adequate supply of compounds which are useful to degrade petroleum hydrocarbons (i.e., electron acceptors). In other cases it may be necessary to enhance the delivery of electron acceptors to achieve significant biodegradation in the groundwater zone.

There are a number of criteria which are important to the success of remediation by flushing. These include:

- Volatility/solubility of contaminant of interest
- Distribution of contaminants
- Current and potential biodegradation activity
- Soil permeability

- Heterogeneity of the medium
- Flow pathways of the flushing fluid

Of these six criteria, the physical properties of the contaminants and the bulk soil permeability are relatively easy to determine. For NAPL contamination sites, however, the heterogeneity of the medium (which is extremely important in controlling the distribution of contaminants) is very difficult to determine using conventional site characterization techniques, and significantly impacts how the flushing fluid flows through the medium, and therefore how well it contacts the NAPL. This difficulty is the reason the tracer test procedures presented here were developed.

Finally, the role of biodegradation, both in the vadose and groundwater zones, not only depends on the physical characteristics of the medium, but also on the chemical and biological characteristics of the system. These characteristics are often difficult to measure, and even if they are determined it is difficult to predict the role of biodegradation. Therefore, practical field procedures are presented here which directly measure biodegradation activity in the field. These measurements form the basis for determining the potential for successful bioremediation.

The five test procedures described here are diagnostic tools which can be used to evaluate remediation performance. Three of the procedures are tracer tests which can be used to evaluate air flow in the subsurface (SVE air flow, IAS air recovery, and IAS air distribution). The tracer tests are new procedures which have been tested at a small number of sites and can be expected to undergo significant changes in the future. The other two procedures are used to evaluate biodegradation in the subsurface (bioventing and natural attenuation). The biodegradation procedures have been demonstrated at a much larger number of sites and as a consequence are likely to undergo fewer changes. The five procedures have been designed as "stand-alone" sections. Section 2 provides procedures for SVE air flow tracer tests. Section 3 discusses IAS air recovery tests. Section 4 provides a procedure for determining air distribution in the saturated zone during air sparging. Section 5 presents procedures for evaluating bioventing. Section 6 summarizes test procedures for evaluating natural attenuation. Depending on the remedial objectives, these five procedures can be used either independently for a separate corrective action approach or, where appropriate, can be used together in an integrated approach to evaluate remediation.

Section 2

Procedures for Conducting Tracer Tests to Evaluate Air Flow During Soil Vapor Extraction

Introduction

Introduction to Soil Vapor Extraction (SVE)

SVE is a remediation technique in which air is drawn through the subsurface to remove volatile contaminants and to enhance aerobic biodegradation. It is generally designed to optimize mass removal through volatilization, although some biodegradation occurs in virtually all hydrocarbon remediation settings. In that context, conventional SVE and bioventing can perhaps be thought of as end members of a continuum of air flushing technologies. SVE is generally used to remediate "source zones" where contaminants may be present as nonaqueous-phase liquids (NAPLs). These NAPLs areas can be distributed within the unsaturated zone as a "residual" NAPL, perched above lower-permeability/higher-water-content zones, or in the vicinity of the water table (Figure 2-1). SVE is generally not applicable to the remediation of groundwater zone contamination. However, if water tables fluctuate significantly, seasonally the SVE system may be able to access portions of the subsurface zone which are sometimes saturated.

The success of SVE generally depends upon both the chemical/physical properties of the contaminants of concern and the physical properties of the soil to be remediated. For the purposes of this discussion it will be assumed that the contaminants of interest are petroleum hydrocarbons. To be effective, SVE must establish good contact between the flowing air and the contaminant (NAPL). Important factors include the permeability of the soil, the scale and severity of the heterogeneity, and soil water content. These factors will determine the distribution of the NAPL, the rate at which it will be possible to draw air through the system, and the pathways the air will follow.

To be effective, the contaminant of interest must also be sufficiently volatile to be effectively removed from the soil. Since the contaminants may be associated with the air, water, soil, or NAPL phases, all of these must be considered in the context of volatilization. Volatile gasoline-related compounds such as butane, pentane and hexane, for example, will be primarily associated with the air, water and NAPL phases. As a consequence, if air can be induced to move within a contaminated soil, they will be quickly removed. Less-volatile contaminants, such as those found in diesel or weathered

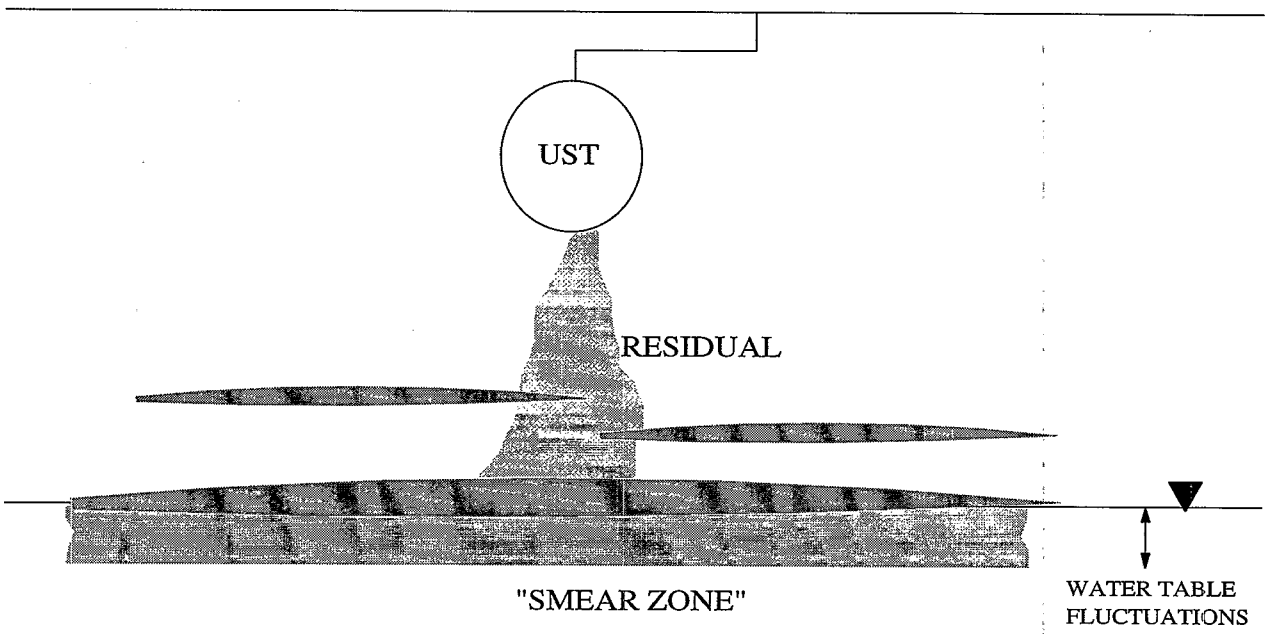


Figure 2-1. Schematic drawing of petroleum hydrocarbon distribution in the subsurface.

gasoline, do not readily volatilize and must therefore be treated over a longer timeframe via biodegradation or by some more-aggressive remediation technique (e.g., heating, chemical flooding). The relationship between vapor pressure and molecular weight is shown in Figure 2-2. The figure implies that the volume of air required to remove a given compound increases exponentially with increasing molecular size.

SVE System Design

The typical components of an SVE system are shown in Figure 2-3. One or more air extraction wells are generally placed in the zone of highest contamination. This is done in order to maximize the recovery of volatile contaminants. One or more injection wells (either actively or passively injected) may also be placed in the zone of remediation. The patterns of these wells may follow some simple geometry (e.g., concentric circles) or may be optimized for site stratigraphy. The construction of both the extraction and injection wells is often similar to conventional monitoring wells/points. Typically they will consist of 2-inch or 4-inch PVC well screen with a length of 5 to 20 feet connected to a PVC stand pipe. The wells are often installed using a hollow-stem drill rig; however, extraction points may also be implaced by direct pushing or other means. The extraction wells are often connected to a common manifold, which is in turn connected to the air handling and off-gas treatment system. These systems are made up of the following components:

1. A vacuum blower which is capable of 10 to 200 standard cubic feet per minute (scfm) at a 0.5- to 10-psi pressure drop. (The specific performance of the blower will depend upon site conditions, number of wells, off-gas treatment stream, etc.)

2. A "knockout drum" for removing liquids from the air stream will generally precede the vacuum blower. It must be designed to handle the range of sub-ambient pressures produced by the blower.

3. At most sites, some type of off-gas treatment of the blower exhaust will be required. This may include combustion, carbon filtration, biodegradation or other approaches.

SVE Operating Conditions

SVE has been applied over a wide range of field operating conditions. These are summarized briefly below:

Depth - SVE systems can be installed over a range of depths from 10 to 500+ feet. With shallow systems, one of the most difficult obstacles is minimizing surface leakage. With deeper systems, heterogeneity of the medium becomes a potentially important limitation.

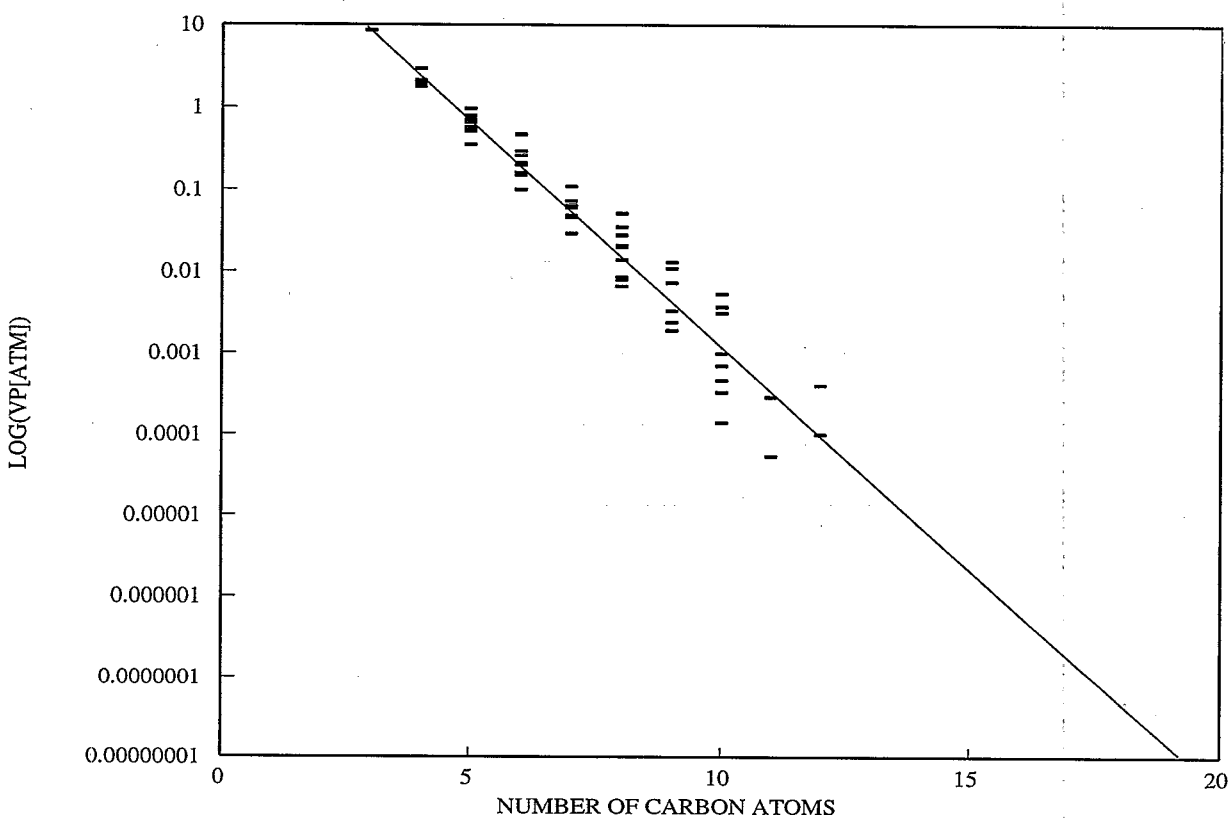


Figure 2-2. Relationship between compound vapor pressure and number of carbon atoms.

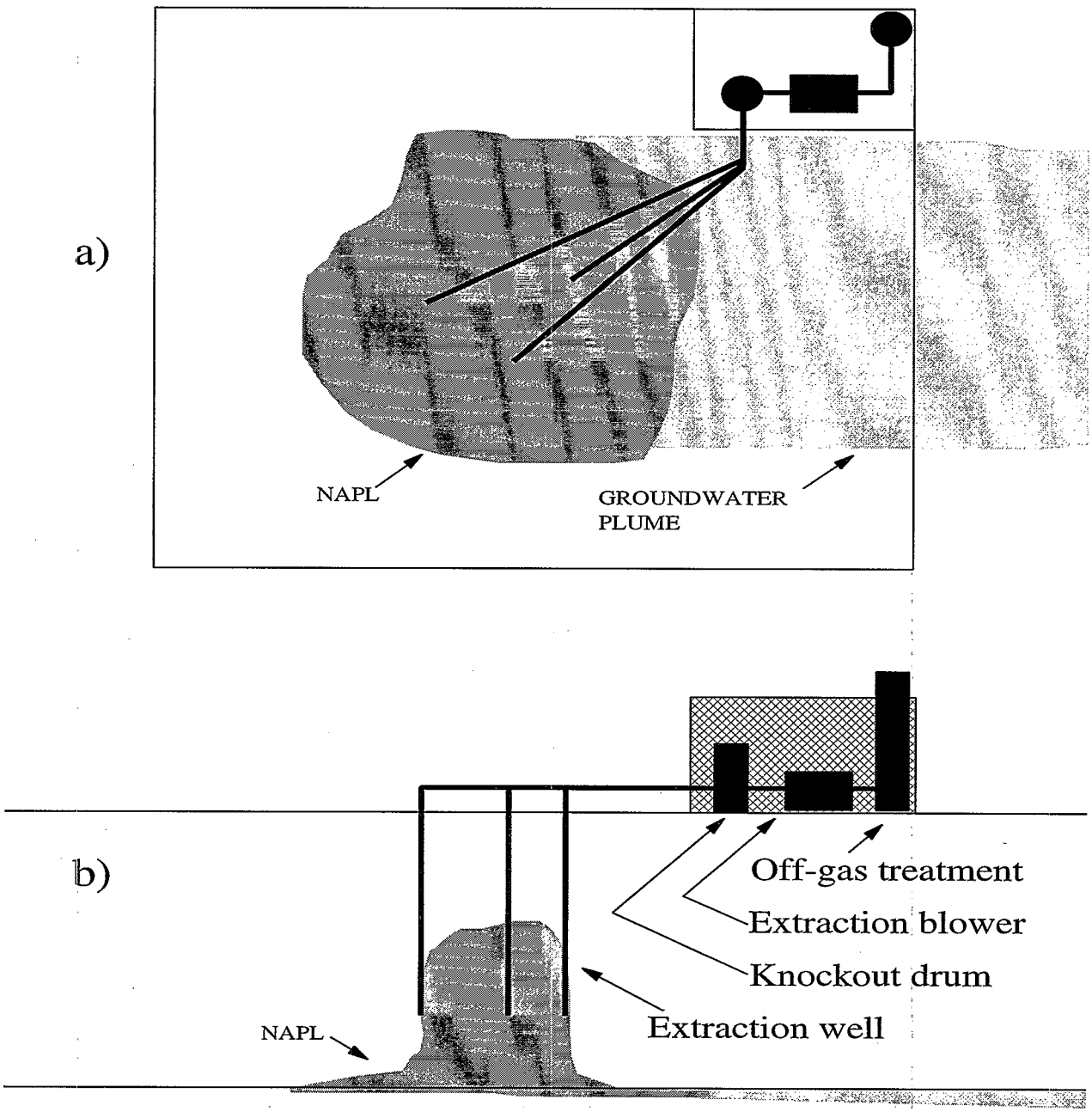


Figure 2-3. Schematic drawing of a typical SVE remediation system in plan view (a) and section view (b).

Flow rate - Flow rate is generally in the range of 10 to 100 scfm per well. This depends upon a number of factors, including the number of wells and the permeability, heterogeneity, and water content of the soil.

Soil permeability - SVE systems have been shown to be effective in soils ranging from gravel to clay. Once again, soil heterogeneity and water content are as important as bulk permeability.

Water content - Water content affects not only the air permeability of the soil, but also the pathways in which the air moves through the soil and the mass transfer of contaminants from the soil to the air. For example, in lower permeability soils, which often have higher water content, air may flow exclusively through channels separated by tens of centimeters. In these cases, mass transfer from the water-saturated zones between the channels may be quite slow.

Summary

SVE is a remediation technique which has been demonstrated to effectively remove volatile contaminants from a wide variety of soil types. In many cases, SVE has sufficiently remediated sites to allow their closure. In other cases, however, remediation has proved difficult. The reason for failure in these cases can often be traced to non-uniform air flow due to soil characteristics (heterogeneity, high water content, etc.). The procedures described in the following section provide a means of assessing air flow pathways and, as a consequence, evaluating the remediation performance using SVE.

Introduction to Air Tracer Tests

At most sites where SVE and/or bioventing using vapor extraction (BV) is used, it is difficult to relate measured soil vacuum data to the air flow field. Vacuum data are frequently used to define the radius of influence; however, the vacuum data do not provide much insight into the structure of the soil or the airflow pathways through the soil. Vacuum data tend to present a picture of the flow field which is much more uniform than is generally the case. Small strata of lower or higher permeability can have profound effects on flow patterns, and these effects may not be reflected in the vacuum data. At many sites, there is more flow from the surface than is commonly assumed, and at many sites there is less flow near the water table than is commonly assumed. As a consequence, at many sites the time required for soil cleanup using SVE/BV is much longer than predicted, based on simple calculations or analytical models.

Tracer tests to directly measure the air flow field are easy to perform, and have the potential to significantly improve the conceptual model of how air is actually flowing at a site. Both naturally occurring and introduced compounds can be used as tracers. Oxygen and carbon dioxide concentrations can be used to assess where air is flowing

in the subsurface. Inert gases such as helium or sulphur hexafluoride can be injected into the subsurface and tracked in situ and in SVE/BV off-gas.

Test Objectives

The primary objectives of SVE/BV tracer tests are to assess air velocities within the subsurface, and to assess the remediation performance of SVE/BV. The tests can be used to answer a number of critical questions, including:

- Do short-circuit pathways for the air exist?
- Are there significant stagnant zones?
- Is the zone of contamination being effectively flushed?
- Are current operating conditions optimizing vapor flow rates through the zone of contamination?
- Is SVE/BV delivering oxygen for biodegradation?

Theory

The procedures for conducting air flow tracer tests are straightforward. However, the interpretation of the observations may be more complicated, and numerical modeling may be required to fully understand air flow patterns. In addition, the number, types, and locations of the tracer injection points will have a significant impact on the extent to which the tests can be interpreted.

The basic procedure is to make an instantaneous injection of tracer at a point at some distance from an SVE/BV well and to watch the arrival of the tracer at the SVE/BV well or at intermediate points. The injection point can be a monitoring well, a soil gas probe, or virtually any other preexisting point in the unsaturated zone. However, locations with small diameters and short screened intervals will generally work best for these tests. In this context, driven soil gas probes are ideal as tracer sources. As soon as the tracer is released into the injection point, it will begin to move towards the SVE/BV well. Its transport velocity will depend upon the air permeability of the medium and the pressure gradient at that point.

If a single SVE/BV well is being used, the vacuum gradient and flow field strength will generally increase in a nonlinear manner as the tracer approaches the well. If high-permeability (i.e., high velocity) pathways exist, they may be at lower pressure than other portions of the system. As a consequence, the tracer will move towards a high-velocity zone. If the tracer is injected into a high-permeability zone, arrival at the SVE/BV well will be rapid. If it is injected into a lower-permeability zone or at a point which is separated from the extraction well by low-permeability media, travel time will be longer. In addition, if the tracer is injected into a lower-permeability zone, the resulting "pulse" of tracer arriving at the well may be spread out over a much longer time interval than the high-permeability case.

The tests should be conducted at a variety of distances from the SVE/BV well and at a variety of depths. The latter is particularly important because of the importance of the ground surface boundary and because unconsolidated soils often have a dominant horizontal structure. Again, it is very important to keep the vertical extent of the screened interval to a minimum. In this context, driven soil gas probes are ideal. It is also important to place injection points in close proximity to the zones of contamination. In this context, it is important to define the zone(s) where contamination is present. For petroleum hydrocarbons, for example, these zones will often be associated with lower-permeability materials in the unsaturated zone, or near the water table. As such, the effectiveness of mass removal will depend upon the soils in the immediate vicinity of the contamination. If the tracer tests are to be effective in evaluating air flow patterns, it is important to understand flow from these contaminated zones.

Steps in Conducting an Air Flow Tracer Test

There are eight major steps in the execution of an SF_6 tracer test (Figure 2-4):

1. Injection of the tracer - Under most circumstances an "instantaneous" injection of a known volume of SF_6 will be used.

2. Monitoring of the SVE/BV offgas - The SF_6 detector will be configured to collect a sample from the extraction manifold at regular time intervals (e.g., 2 to 20 minutes), depending upon the duration of the test.

3. Plotting of the SF_6 breakthrough - SF_6 concentrations in the offgas will be automatically determined using the SF_6 detector. These data can then be plotted as a function of time.

4. Calculation of the volume of SF_6 recovered - The concentration data can be multiplied by the SVE flow rate and the time between sample intervals to determine the volume of SF_6 recovered during each interval. These data can be summed to determine the total volume of SF_6 recovered.

5. Estimation of the fraction of SF_6 recovered - The total volume estimated in the previous step is compared to the injected volume of SF_6 to calculate the fraction of SF_6 recovered. Recovery should be between 50 and 150 percent.

6. Estimation of the breakthrough time - The volume data can be used to determine the breakthrough time of the tracer. The breakthrough time is the time at which 50 percent of the recovered volume is reached.

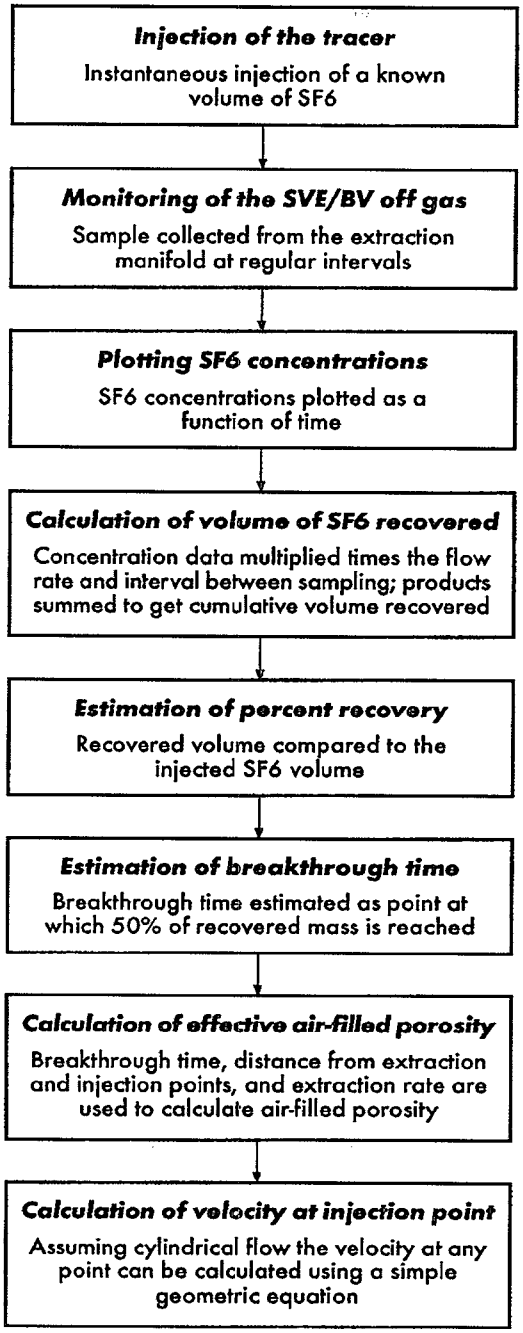


Figure 2-4. Flow diagram showing the major steps involved in in airflow tracer test.

7. Calculation of effective air-filled porosity using a simple geometry - If it is initially assumed that flow to the extraction well is radial, the velocity increases with decreasing distance to the well.
   - Calculate the volume of the cylinder containing the test ($\pi r^2 h$). Where r is the distance between the injection and extraction points and h is the thickness over which air is assumed to be flowing.
   - Calculate the extraction volume (flow rate x breakthrough time).
   - Calculate the effective porosity (n, breakthrough volume/cylinder volume).
   - In an ideal case, the value of n determined from each tracer test would be the same. In practice, n will vary depending upon the conditions encountered in the subsurface.
   - If the calculated value of effective porosity is not reasonable (e.g., greater than 1 or less than 0.1), any of a number of conditions shown in Figure 2-5 might exist (e.g., surface leaks, high-permeability zones, low-permeability zones).
   - If high-permeability zones exist, travel times may vary in a manner which does not relate well to distance. This is shown schematically in Figure 2-6.

8. Calculation of the velocity at the injection point - For the case of simple, homogeneous media with no surface leakage (i.e., cylindrical flow), velocity at any point can be described by the equation:

$$V = \frac{F}{2\pi R h n} \qquad (2\text{-}1)$$

where F = the extraction rate
R = the distance from the point of interest to the extraction well
h = the height of the cylinder
n = the effective air-filled porosity.

Interpretation of the Air Flow Tracer Tests

Once several tests have been conducted, it is possible to compare travel time and velocity data and develop a travel-time pattern for the site. For example, tracer injected at points near the water table at a certain distance from the extraction well may have much longer breakthrough times than points nearer the surface at the same distance. Those data can be used to identify additional locations within the remediation zone to conduct tracer tests.

If the site is a complicated one, or if there are several extraction wells, it may be necessary to evaluate the test data using an appropriate numerical model. The numerical model should be sophisticated enough to handle the complexities found at the site. In

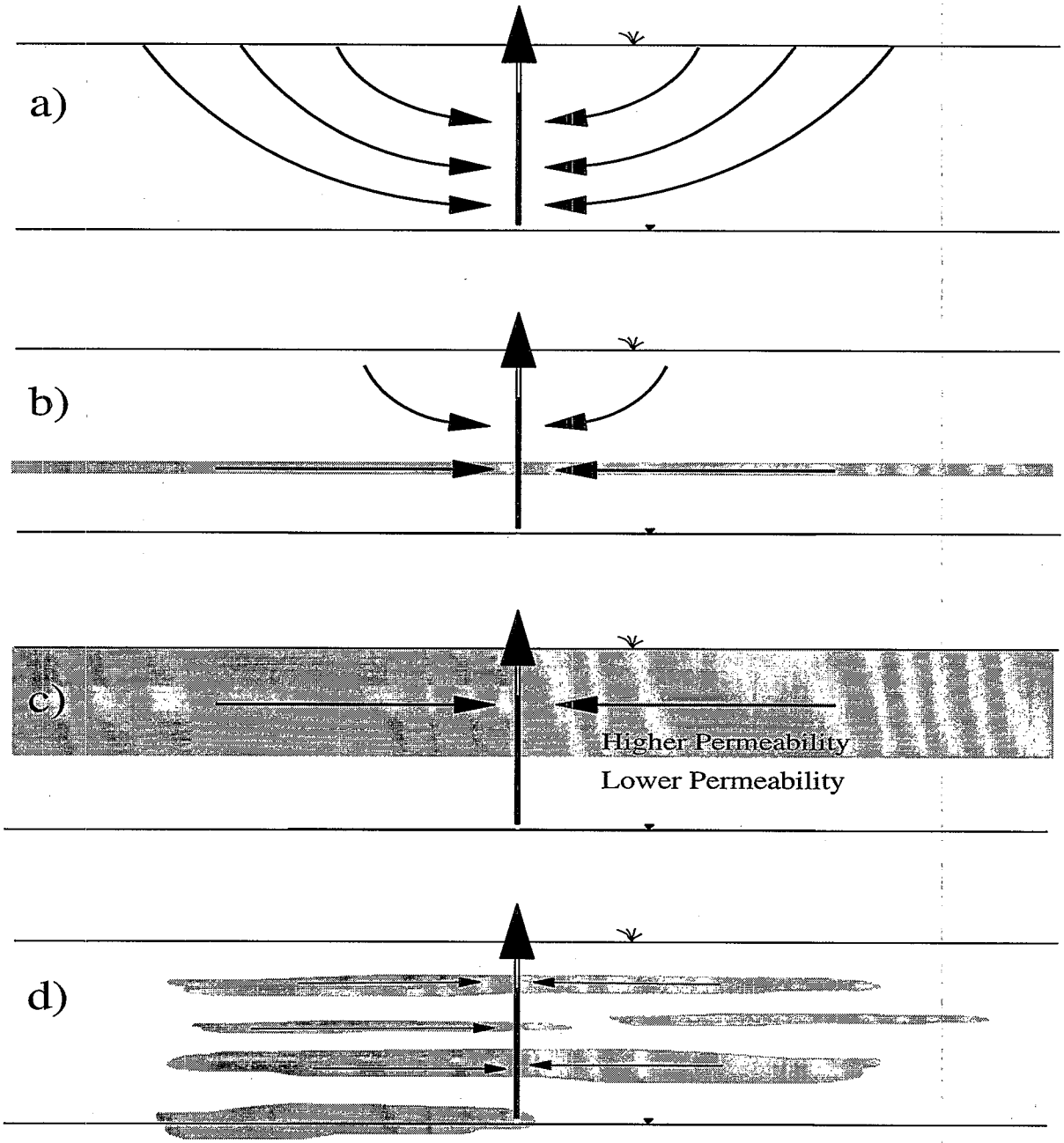


Figure 2-5. Schematic drawings of possible SVE flow configurations.

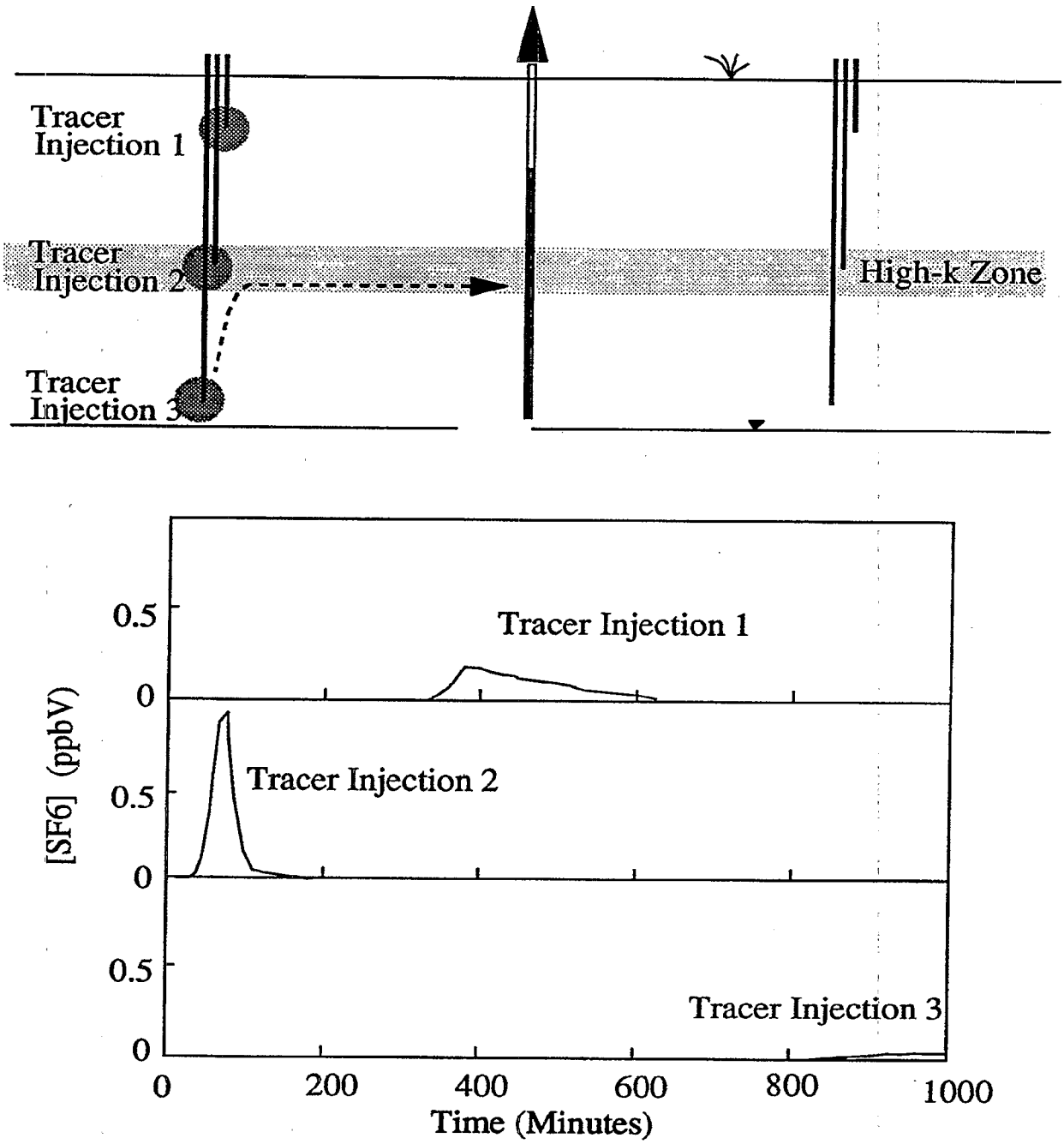


Figure 2-6. Schematic drawing of tracer "short-circuiting" through a higher-permeatibility zone.

general terms the model should include both flow and transport. It should be able to run either 3-D or 2-D axis-symmetric problems, and should be able to incorporate heterogeneities (e.g., layers) into the flow field.

Test Equipment

Overview of Experimental Setup

In order to simplify interpretation, the tests should be conducted using a single SVE/BV well. Tracer injection points should be placed in at least three depths and at a variety of locations of interest. If contamination is present near the water table, it is important to place tracer injection points there. Locations of the other points should be determined by stratigraphy and soil/vapor concentrations. They can be placed in both high- and low-permeability zones. In that context, soil boring logs may be useful in identifying site stratigraphy. Chemical analyses of cores or cuttings may be useful in identifying zones of contamination. Soil gas surveys may help identify those regions which are not being effectively remediated.

Design and Installation of Extraction Wells

In nearly all cases, the air flow tracer tests will be conducted in conjunction with vapor extraction or injection operations. In that context, the design and installation of the extraction/injection wells will be dictated by the remediation design. As a consequence, design and installation of the extraction/injection wells will not be discussed here. However, the design of the extraction/injection wells will have an impact on the design and installation of the tracer injection points.

Design and Installation of Tracer Injection Points

Wherever possible, tracer tests should be conducted using existing monitoring wells and vapor monitoring points. However, monitoring wells with screened lengths of greater than 5 feet should not be used. Frequently, test points will be part of other testing (e.g., in situ respirometry). In general, the locations are selected on the same basis as for in situ respirometry and soil gas measurements. The primary criterion for placement is that they be within contaminated zones so that air flow within those zones will be directly measured. Vapor monitoring points, especially driven vapor probes, are the best choice for tracer injection points. Again, they are best if the screened interval is small.

Most regulatory agencies do not regulate unsaturated-zone monitoring point construction. Nevertheless, prior to construction it is necessary to check with regulators to assure compliance with any regulations that may exist. Monitoring point construction will vary depending on the depth and the installation techniques. The following approaches are commonly used for installing points:

1. Hand-augured holes
2. Drill-rig augured holes
3. Pushed or driven probes

Tracer injections should be made at a minimum of three locations, and at each location to at least three depths. Whenever possible, the monitoring points should be located in contaminated soils. A sufficient number of points should be emplaced to characterize flow through the contaminated soil. If contamination has reached the water table, it is important to place points near the water table. Points should be located in both high and low permeability zones so that spatial variability in velocity can be examined. This typically involves a minimum of 3 or 4 locations and 3 to 4 depths each. Recommended spacings for tracer injection points are listed in Table 2-1. In general, the minimum number of points will increase if the site is heterogeneous.

Table 2-1. Recommended Spacings for Tracer Injection Points (adapted from Hinchee et al., 1992).[a,b]

Soil Type	Depth to Top of Vent Well Screen (feet)	Radial Distances for Placement of Monitoring Points (feet)
Coarse sand	1.5	1, 3, 6
	3	3, 6, 12
	>5	6, 9, 18
Medium sand	1.5	3, 6, 9
	3	4, 8, 12
	>5	6, 12, 18
Fine sand	1.5	3, 6, 12
	3	4, 9, 18
	>5	6, 12, 24
Silt	1.5	3, 6, 12
	3	4, 9, 18
	>5	6, 12, 24
Clay	1.5	3, 6, 9
	3	3, 6, 12
	>5	4, 9, 18

[a] Assuming 10 ft of vent well screen. If more screen is used, the >15-ft spacing will be used.

[b] Note that monitoring point intervals are based on a venting flow rate of 1 cfm/ft screened interval for clays to 3 cfm/ft screened interval for coarse sands.

In general each areal location should have a minimum of three tracer injection points at various depths. If contamination exists at the water table, one or more points should be located at that depth. The shallowest screen will normally be 1 to 2 m below ground surface. One or more points should be installed between these points. In general, one point can be located near the depth of the top of the extraction well screen. If the soil in the contaminated zone is heterogeneous, additional points should be installed at appropriate depths. In this context it is important to have enough site characterization data to allow good placement of the points.

The ideal design of a tracer injection point, in most cases, will consist of a short (10 to 30 cm) well screen connected to ground surface via a small-diameter tube. Depending upon the emplacement technique, the screen may be positioned within a sand pack or in direct contact with the soil. In general, single completion wells are preferred over multiple completion wells. This is because of possible problems in isolating the various layers from one another. If points are installed with a drill rig, it may be necessary to use multiple completions to minimize cost.

In general, materials used for monitoring well construction will be appropriate for tracer points. The specific materials chosen will depend upon the types of samples to be collected from the point. (For SF_6, Teflon tubing should be avoided. The preferred choices are high-density polyethylene or stainless steel.)

Each point should be clearly labeled with a unique identification code, which includes, at a minimum, designators for the areal location of the point and for the vertical position of the point. In most cases, the vertical position should be identified using the depth of the well screen below ground surface.

Calibration of Analytical Equipment

SF_6 Detector

There are several types of detectors for SF_6 analysis. A gas chromatograph with an electron capture detector is the basic instrument for detecting SF_6 at low concentrations in vapor samples. There are a wide variety of commercially available gas chromatographs ranging from sophisticated research instruments to more "user friendly" instruments. An SF_6-specific gas chromatograph is available from Lagus Applied Technologies (LAT) in San Diego, CA. It is automated and has a detection limit of ~10 parts per trillion by volume. In the following discussion, it will be assumed that a LAT Autotrac is being used.

One of the features of the LAT Autotrac is that it comes with an internal cylinder of calibration gas. As a consequence, single-point calibrations in the field can be easily accomplished. However, it is desirable to conduct multipoint calibrations to verify linear instrument response. Standards can be obtained commercially, prepared by dilution, or by using a dynamic calibration instrument.

Air Flow Meters

Flow rates for the SVE system will generally be in the 10- to 200-scfm range. Vacuum levels will be at 10 to 200 inches of water below ambient pressure. The flow meter calibration system is shown in Figure 2-7. At the high flow rates, a large dry gas meter will be required. An alternate approach will be to use another calibrated flow meter to

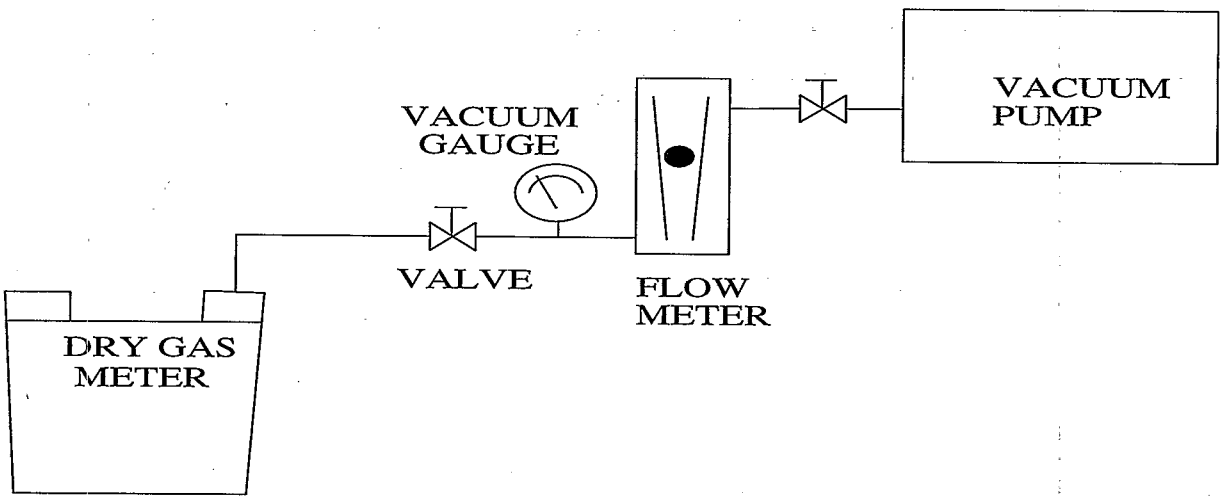


Figure 2-7. Schematic drawing of the flow meter calibration system.

calibrate the one to be used at the site. Actual versus observed flow rates should be determined over the range of the flow meter at several vacuums between 0 and 0.9 atmosphere. Those data should be plotted as a family of curves with each line corresponding to a different vacuum value.

Flow rates for the IAS system will generally be less than those used for the extraction system. However, pressures will be above atmospheric, rather than below. The apparatus used to calibrate flow meters at above atmospheric pressure is shown in Figure 2-8.

The tracer gas can be used not only for the tracer tests, but also to determine the extraction air flow rate. To measure extraction air flow rate, a continuous injection of tracer into the extraction manifold can be made, and the observed dilution of the tracer can be used to determine the extraction air flow rate. In general, flow rates for continuous tracer injection will be in the range of 0.1 to 1 L/min. The apparatus for calibrating the flow meter for continuous tracer injection is the same as for air injection (Figure 2-8).

Evaluation of the Sampling Pump

Under most operating conditions, the SVE/BV manifold will be under sufficient vacuum that most automated analytical equipment will not be able to draw a sample from the manifold. In these cases, it will be necessary to use a good quality vacuum pump to draw samples from the manifold and deliver them to the automated analytical equipment. In the context of tracer tests, two potential problems arise with respect to the pump. First, the pump must be able to move sufficient volumes of air to meet the needs of the analytical equipment, and second the pump should not leak air, which can provide additional dilution of the sample stream. The procedures below describe how a pump performance can be measured.

Prior to obtaining a sampling pump, check the specifications of any automated sampling equipment to be used to determine the volumes of air required by each. (The Autotrac detector requires ~100 mL/min.) Next, connect the sampling pump to be tested to the apparatus shown in Figure 2-9. If two dry test meters are not available, two calibrated flow meters of the appropriate ranges can be used. Turn on the pump and open the valve so that no vacuum is observed on the gauge. Determine the flow into and out of the pump by recording the volume of flow that occurs in one minute on each of the dry test meters. Partially close the valve to produce a vacuum of 5 inches of mercury, and determine the flow rates into and out of the pump.

Repeat the previous procedure with vacuums of 5, 10, 15, 20, and 25 inches of mercury. Prepare a plot of flow rate in and out versus vacuum. Determine if the pump flow rate is adequate for the analytical equipment and vacuum to be used. Determine if the

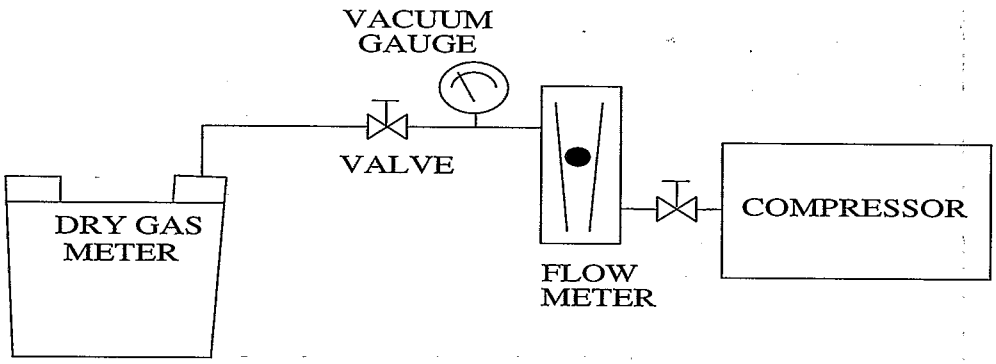


Figure 2-8. Schematic drawing for flow meter calibration under positive pressure.

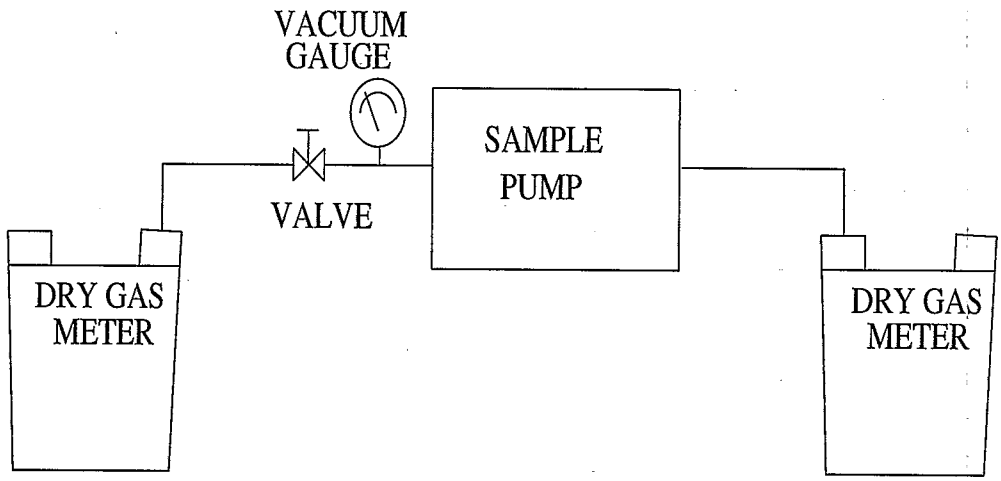


Figure 2-9. Schematic drawing showing setup for measurement of sample pump flow rate vs.vacuum and leakage vs. vacuum.

leakage of the sampling pump is acceptable (e.g., inflow rate is within a factor of two of outflow rate).

Test Procedures

Overview of Procedures

Test activities can be divided into the following seven components. Each of them are described briefly in the following sections.

1. Installation of SVE/BV extraction wells
   - Usually part of some remediation strategy.
2. Installation/identification of tracer injection locations.
3. Calibration of analytical instrument.
4. Calibration of the air flow system/determination of SVE/BV flow rate.
5. Make preliminary measurements.
6. "Instantaneous" injection of SF_6 into soil gas point.
7. Collect samples from SVE/BV off-gas.
8. Determine effluent concentrations.

Measurement of SVE/BV Flow

It is necessary to determine the actual flow of the SVE/BV system if mass removal rates are to be calculated. Measurement of SVE/BV air flow can be made either by using a direct-reading flow meter or a tracer. Both procedures are described below.

Flow Measurement Using a Flow Meter

If a flow meter is used to measure SVE/BV flow, it is essential that the flow meter be calibrated by the procedure described above. This needs to be done at the appropriate pressure/vacuum. The apparatus is shown in Figure 2-10. Prior to measuring flow, the extraction flowrate should be adjusted to the desired flow/vacuum using the ball valve between the flow meter and the pump. If more than one extraction well is being used, it is desirable, although not necessary, to measure the flow at each well. This involves placing a ball valve, vacuum gauge, and a flow meter in line with each well. Read the vacuum and flow rate from the gauge and meter and use the calibration table for that flow meter to determine actual flow.

Flow Measurement Using the Tracer Gas to Determine SVE/BV Flow

If an independent calibration of the flow meter is not available, the tracer gas can be used to calibrate the SVE/BV flow system. In some cases (especially when the extraction vacuum is large), water in the system makes it difficult to get good flow meter readings, and the tracer procedure is preferred.

The apparatus for tracer calibration is shown in Figure 2-11. Prior to beginning the procedure, it is necessary to estimate the SVE/BV flow. The specifications for the extraction blower are adequate for this. Next, calculate SF_6 inflow rate to produce a

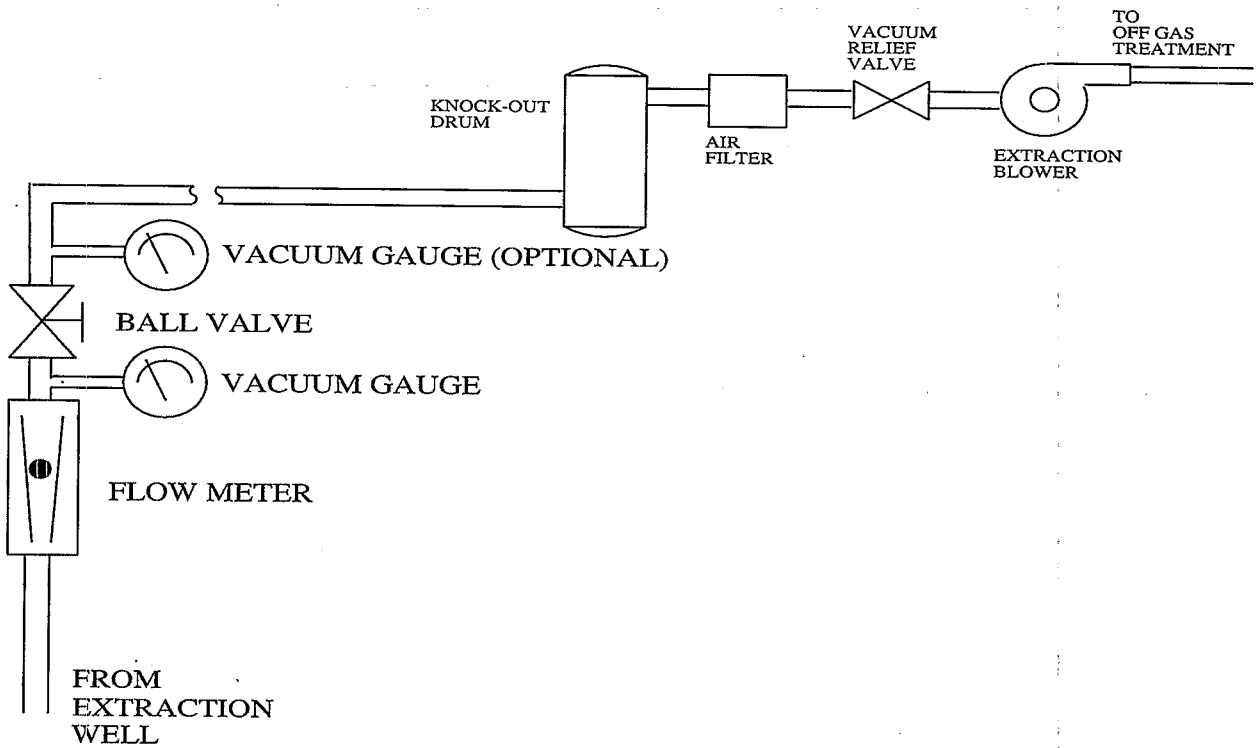


Figure 2-10. Schematic drawing of the flow measurement system for the SVE/BV system

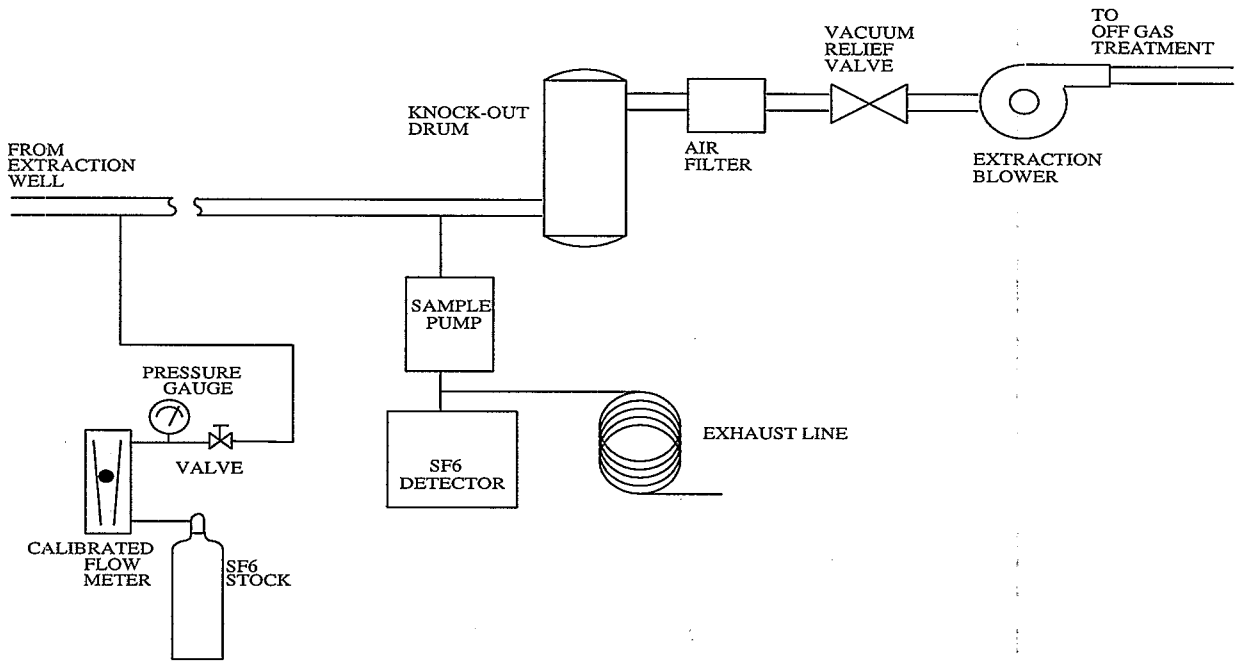


Figure 2-11. Schematic drawing showing the system for measuring SVE/BV flow using a tracer gas.

concentration of 1 ppbV. An air flow rate in the 0.1- to 1-L/min range is desired. (Use an SF_6/air mixture with a concentration of ~1000 ppmV for this.) Example Calculation 2-1 shows how these calculations are to be done. Next, install a good vacuum pump (metal bellows or diaphragm) to the manifold--this will be the same setup as for the tracer tests themselves. Make sure the pump does not leak at the system pressure. Connect the SF_6 detector to the sampling pump.

Determination of tracer injection rate

Approximate SVE Flow rate = 35 scfm = 1000 L/min
tracer mix concentration = 100 ppmV = 10^5 ppbV
Desired final concentration = 10 ppbV
need a dilution of 10^4
tracer flow rate = 1000 L/min / 10^4 = 0.1 L/min

Calculation of actual SVE/BV flow

Using a flow rate of 0.1 L/min and an input concentration of 10^5 ppbV the actual SVE/BV flow rate is determined by dividing the input concentration by the effluent concentration and multiplying by the tracer injection flow rate.

If the observed effluent concentration were 20 ppbV, the actual flow would be:

10^5 / 20 * 0.1 L/min = 500 L/min ~ 17.7 scfm

Example Calculation 2-1. Calculation of actual SVE/BV flow using a tracer.

To begin the flow measurement, connect the SF_6 source to the manifold near the extraction point and add SF_6 at the prescribed rate. Monitor tracer concentration in the extraction system until it stabilizes. (This should take only a few minutes.) Calculate the observed dilution factor (influent tracer concentration/effluent tracer concentration). The SVE flow rate is calculated by the dilution factor times the SF_6 inflow rate.

Vacuum Survey

The procedure described below assumes that the remediation system is already in operation. It is important to collect subsurface vacuum data prior to initiation of the tracer tests. These data provide insight into the general nature of the flow system. For example, if little or no vacuum is recorded at a monitoring point, it can be expected that there is little flow at that point. Large vacuums may indicate areas of active flow; however, these values can also occur within low-flow regions adjacent to higher flow regions. Nevertheless, these data can frequently be helpful in understanding the general nature of air flow at the site.

The general approach will be to measure soil vacuum with differential pressure gauges (e.g., Magnehelic™ gauges). However, the same measurements could also be made with a manometer or other calibrated gauge. For most sites, it will be necessary to have Magnehelics in the following ranges (in inches of water): 0 to 1 inches, 0 to 10 inches, and 0 to 100 inches. Vacuums of less than 1 inch of water are subject to error from a variety of sources including barometric pressure effects and should be interpreted with caution. After the remediation system has been operating several hours, determine the soil vacuum at each point in the system by connecting the appropriate gauge to the point. After connection to the monitoring point, sufficient time should be allowed for the vacuum to stabilize (commonly 1 minute).

Soil Gas Permeability Test Procedures - Steady-State Method

Prior to beginning the soil gas permeability test, examine the site for any structures that could serve as vertical conduits for gas flow. These must be sealed to prevent short-circuiting and to ensure the validity of the soil gas permeability test. Next, values of the permeability and the radius of influence can be estimated using the equations described in the following example calculations. For the purposes of the tracer tests, estimation of permeability using the steady-state method is acceptable.

Estimation of the "Radius of Influence"

The term radius of influence should be used with caution. The procedure described below is often used to estimate the region over which the SVE system is effective. As described in this procedure, air flow can be spatially quite variable and as a consequence a pressure-based radius of influence is subject to considerable uncertainty.

The example in Figure 2-12 is taken from Hinchee et al., 1992, p.77. The first step is to conduct a soil vacuum survey such as the one described in the previous section. Next, plot the final pressures of each point versus the log of its radial distance from the vent well. Then, extrapolate the best-fit straight line through the data to zero vacuum. That distance is the estimated radius of influence. The radius of influence in Figure 2-12 is ~30 m.

Estimation of Permeability

The example is once again taken from Hinchee et al., 1992, p. 77. The equation for permeability to vapor flow from steady-state pressure data is:

$$k = \frac{Q\mu \ln(R_w/R_l)}{H\pi P_w[1-(P_{atm}/P_w)^2]} \qquad (2\text{-}2)$$

where
- k = permeability
- Q = flow rate (cm^3/s)
- u = viscosity of air (1.8×10^{-4} g/cm-s)
- R_w = radius of well (cm)

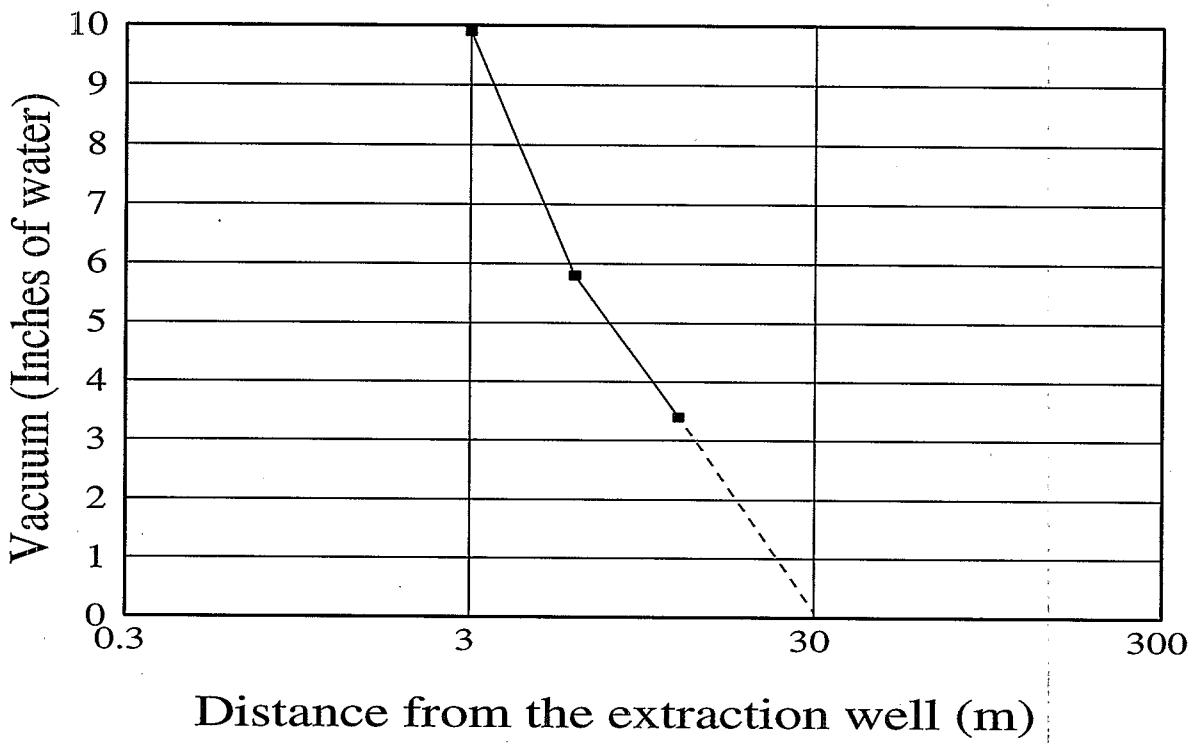


Figure 2-12. Example showing estimation of radius of influence of the SVE/BV system from steady-state pressure data.

R_I = radius of influence (cm)
H = depth of well screen (cm)
P_w = absolute pressure at well (g/cm-s^2)
P_{atm} = air pressure (1.013×10^5 g/cm-s^2)

The calculation of permeability for this example is shown in Example Calculation 2-2.

In this example the following values are used:

Q = 1.4×10^4 cm^3/s
H = 2.7 ft. = 81 cm
P_w = -80 in.H2O = 0.816×10^6 g/cm-s^2
R_w = 2.54 cm
R_I = 457 cm

The value of the air permeability calculated from those data is 1.2×10^{-7} cm^2.

Example Calculation 2-2. Estimation of soil permeability from steady-state pressure measurements.

Measurement of Background SF_6 Concentrations

In most cases, background concentrations of SF_6 will be essentially zero. However, it is important to make that determination prior to starting any test. These measurements can be made while the extraction system is in continuous operation. If previous tracer tests have been conducted at the site, initial concentrations will probably be non-zero. If concentrations are decreasing with time (i.e., on the tail of the previous test), then if possible, conditions should be allowed to stabilize prior to initiation of the next test. If it is not practical to wait additional time prior to initiating the test, the volume of injected tracer can be increased. However, this may necessitate diluting samples prior to analysis.

Measurement of Oxygen and Carbon Dioxide Concentrations

Measurements of oxygen and carbon dioxide are very important in that they provide insight to areas where air is or is not flowing. Since SVE/BV tracer tests will often be conducted in conjunction with in situ respirometry tests, information on oxygen demand and carbon dioxide production may also be available. The combination of concentration and respirometry measurements provides a good measure of the extent to which flushing is occurring. If biodegradation is the primary remediation pathway, these tests may be sufficient and the tracer tests described here may not be necessary. If additional information on flushing is desired, tracer tests in conjunction with the oxygen and carbon dioxide data can provide a good picture of air flow.

Preparation of SF_6 for Injection

The first step in the preparation of SF_6 for injection is the estimation of the volume of pure SF_6 to be injected. The Autotrac detector has a working range of 0.01 ppbV to 50 ppbV. A good target concentration is 1 ppbV. It is desirable to predict the extent to which dilution will occur so that the correct volume of SF_6 will be injected. This will be most easily accomplished once several tracer tests have been conducted at the site. Initially a simple air flow geometry can be used. An example of this is shown in Example Calculation 2-3 and the geometry is shown in Figure 2-13.

Distance between injection and extraction points	5 m
Thickness of the unsaturated zone	5 m
Estimated air-filled porosity	0.20
SVE flow rate	2.8 ^{me}/min (~100 scfm)
Target SF_6 concentration in offgas	10 ppbV (10^{-8} vol/vol)
Air volume in cylinder of soil surrounding the extraction well. The radius of the cylinder is equal to the distance between the injection point and the extraction well ($\pi * 5 * 5 * 5 * 0.25$)	~100 ^{me}
Desired volume of pure SF_6 ($100^{me} * 10^{-8}$)	10^{-6} ^{me} = 1 mL

Example Calculation 2-3. Calculation of the volume of SF_6 to be injected.

The second step is to determine the total volume of gas (air+SF_6) to be injected. This is necessary because when tracer tests are conducted it is important to introduce all of the SF_6 into the medium quickly. To do this, the volume of gas injected must be sufficiently large to flush the bulk of the SF_6 out of the well into the formation. At the same time it is desirable to keep the injection volume as small as possible in order to estimate the air flow rate in the stratum of interest. In general, the volume of SF_6 necessary for the test will be very small. In this case, the SF_6 must be diluted with air to produce the final injection volume.

The injection volume should be ~3 times the volume of the well. This insures that a significant fraction of the SF_6 gets out of the well point into which it is injected and directly to the subsurface. Injection volumes for conventional wells can become substantial. Therefore, it is desirable to use smaller volume wells (e.g., vapor monitoring points). An alternate approach for conventional wells is to pack off the well just above the well screen and inject below the packing. In this case, the injection volume is calculated based on the length of the well screen. Injection of the tracer should be followed

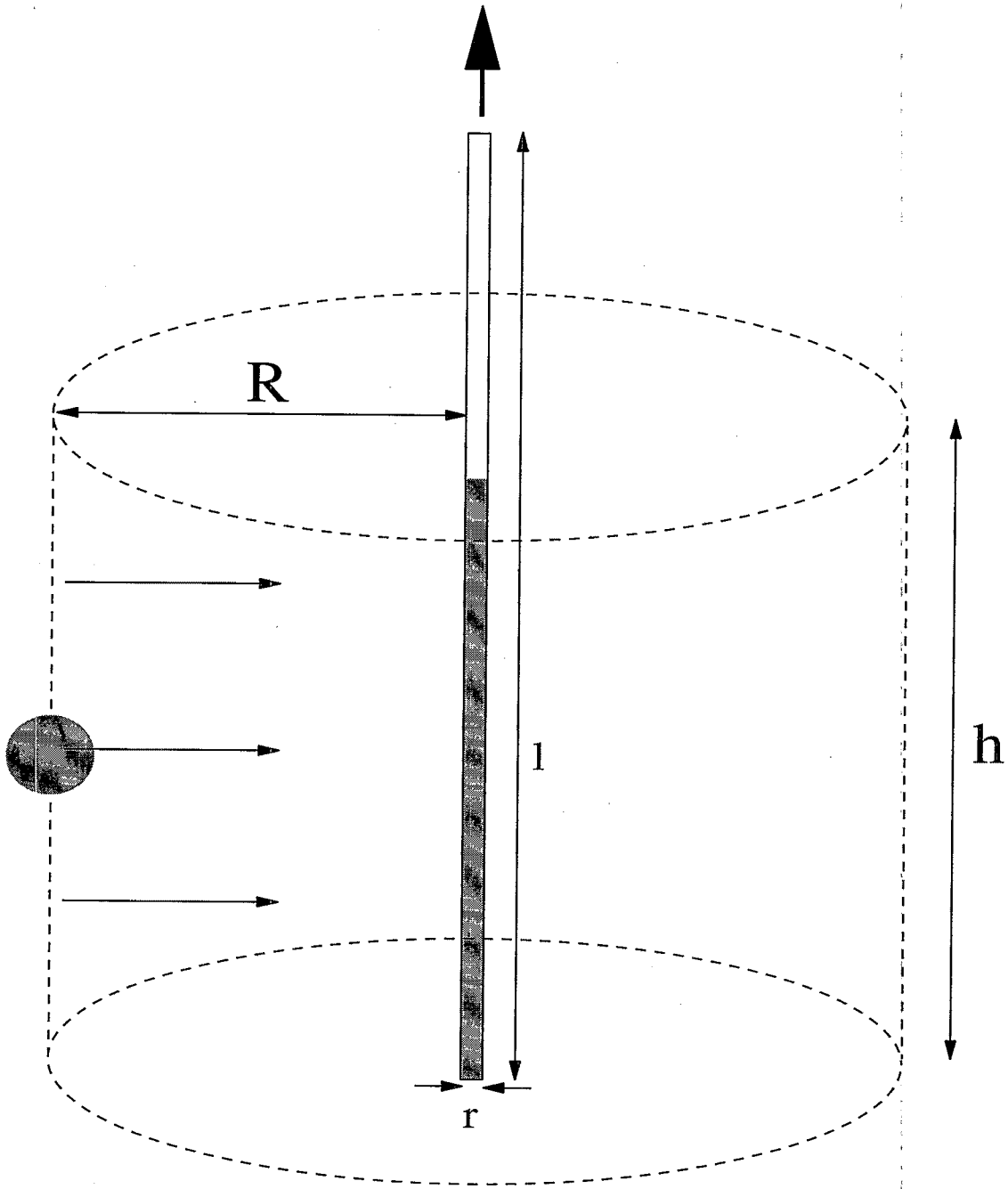


Figure 2-13. Geometry for calculation of tracer dilution.

immediately by the injection of flushing air to move the remainder of the tracer out of the well.

As discussed above, it is desirable to move all of the SF_6 out of the injection point and into the formation. To accomplish this, a volume of air should be injected into the injection point following the introduction of the tracer. In general terms, this flushing volume should be ~3 times the volume of the well. Example Calculation 2-4 shows the volume of air+tracer to be injected.

Total length of the well (l)	= 6 m
Inside radius of the well (r)	= 0.019 m (0.75 inch pipe)
Volume of the well ($\pi r^2 l$)	= 0.014 ^{me}
	= 1.4 L

Injection volume (3X well volume) ~ 4.2 L

Example Calculation 2-4. Calculation of the volume of air+tracer to be injected.

In most cases, the injection volume will be on the order of 1 to 10 liters. In general, the best way to introduce the tracer into the subsurface will be delivery from a pressurized canister. Dilutions can be prepared on a volume or pressure basis. For example, SF_6 stock can be introduced into an evacuated canister to bring the pressure up to a predetermined value which represents the volume of SF_6 to be injected. The canister can then be pressurized up to some final positive pressure which reflects the total injection volume. It is important to remember that the injection volume will be determined by the gauge pressure, but that some of the SF_6 will remain in the canister at the conclusion of the injection. Therefore, the actual volume of SF_6 injected must be adjusted accordingly. An example of this is shown in Example Calculation 2-5. Once the injection volume has been prepared, prepare a second pressurized canister filled with air at approximately the same final pressure as the tracer injection sample for use in flushing the SF_6 out of the well.

Volume of SF_6 placed in the canister	1.25 mL
Total injection volume	4 L
Volume of canister	1 L
Gauge pressure to produce the injection volume	4 atm
Total air volume in the canister	5 L [1 L * (4+1) atm]
Volume of SF_6 injected into the subsurface	1 mL [1.25 mL * 4 L / 5 L]

Example Calculation 2-5. Calculation of actual SF_6 injection volume.

Introduction of SF_6 Into the Subsurface

Once the preliminary data has been collected and the analytical instrument is calibrated, the tracer test can be initiated. The analytical instrument should be set on automatic operation, and the initial SF_6 concentration in the subsurface should be determined. Next, the pressurized canister should be attached to the injection point (The manner in which this connection is made will depend upon the construction of the injection point.) The valve on the injection volume canister should be opened and the time noted. The pressure at the injection point should be monitored to insure that the canister has dropped to atmospheric pressure or below so that no tracer is lost to the atmosphere when the canister is removed. Immediately following tracer injection, the flushing volume should be injected.

Sample Collection (Figure 2-14)

Samples should be collected prior to the extraction pump to avoid dilution and other errors which may occur in the extraction pump. (Samples can be collected after the extraction pump if the system is correctly calibrated; however, that procedure will not be discussed here.) The pressure at this point will be below atmospheric, so care must be taken to insure that a good sample is collected. In general, samples can be taken using a good quality diaphragm pump or metal bellows pump, or manually by syringe. (Care should be taken to insure that the pump does not leak and introduce dilution air.) Pressures below 0.5 atm require extreme care to insure that a good sample is collected.

In high-vacuum situations, the capacity of the pump in the SF_6 detector may exceed the capacity of the sample pump. This problem can be addressed either by getting a larger sample pump or by adding an exhaust line (e.g., a 30 m length of 0.06 m tubing onto the flow system; see Figure 2-14). Because the SF_6 detector samples intermittently, the exhaust line will be continuously flushed with extraction air, and therefore a good sample can be drawn from the line when needed by the detector. If necessary, samples can be injected manually into the Autotrac via a syringe port on the front of the instrument. A 10-mL gas sample is required. Manual sampling is useful if analyzing samples from vapor monitoring points, but is not recommended for monitoring breakthrough unless sample dilution is required.

Sample Dilution

As described above, the LAT SF_6 detector has a useful range of 0.01 to 50 ppbV. If breakthrough occurs more rapidly than expected, SF_6 concentrations may exceed 50 ppbV. In that case it will be necessary to dilute the sample into the useful range of the instrument. A number of procedures are available for this, and depend upon the extent of the dilution. However, it is important to realize that any dilution process increases the chances for errors in the measurements. Therefore, whenever possible the tests should be conducted such that dilutions are not necessary.

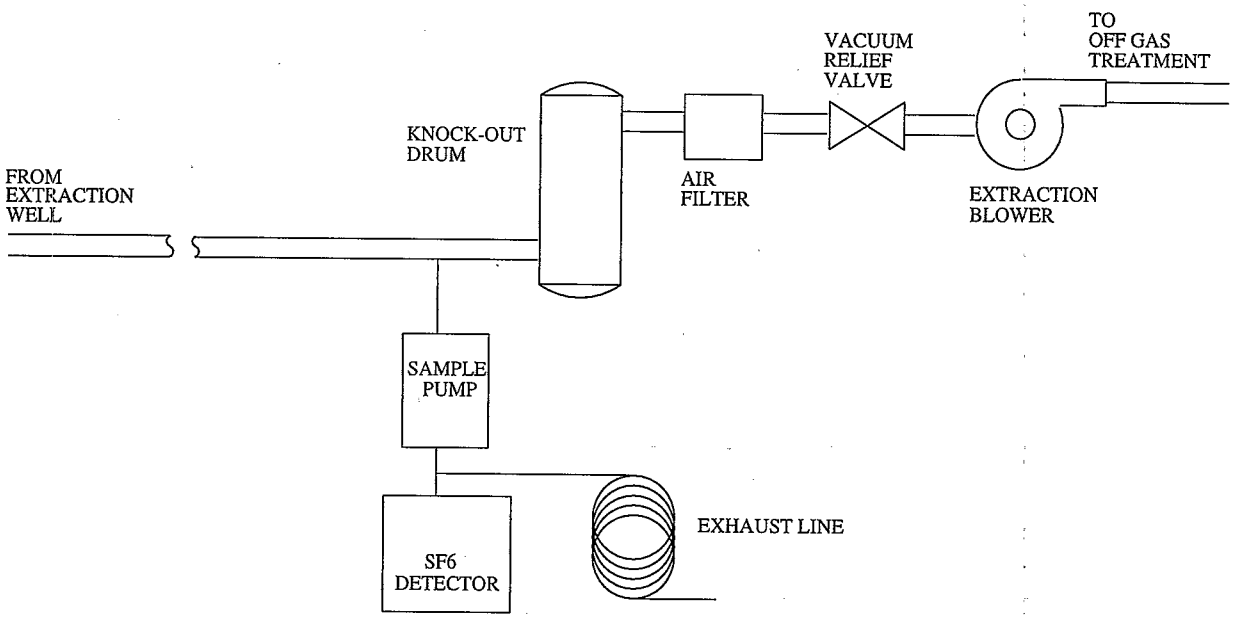


Figure 2-14. Schematic drawing of the sample collection apparatus.

The procedures for sample dilution depend upon the magnitude of the dilution. Dilutions of 2x to 10x can often be accomplished within the syringe in which the sample is collected. For example, a 5x dilution can be prepared by drawing 2 mL of sample into a 10-mL syringe, and the remainder of the syringe filled with SF_6-free air. For dilutions greater than 10x, it is generally necessary to inject a known volume of sample into a larger vessel filled with SF_6-free air. The vessels can be canisters, Tedlar bags, or other containers. Once the dilution is complete, a 10-mL sample can be analyzed by injection into the septum port on the SF_6 detector.

Determination of Concentration

The Autotrac automatically reports concentrations in ppbV (or pptV, parts per trillion by volume). The concentration data can be written to a DOS-compatible disk for direct transfer to a spreadsheet or other data management system.

Data Analysis

Calculation of Recovery Efficiency

The SF_6 volume removal rate can be calculated from the concentration data by multiplying the concentration by the air flow rate for the SVE/BV system and by the sampling interval. The individual measurements can be plotted as a function of time to obtain the breakthrough curve, and the measurements can be integrated to determine the cumulative recovery of SF_6 (Figure 2-15). If sampling times are regular, integration of the breakthrough curve can be made by simply summing the volumes collected during each sampling interval.

The SF_6 recovery efficiency can be calculated by dividing the total SF_6 recovery by the volume of SF_6 injected (Example Calculation 2-6).

Injection:	2 L of 1000 ppmV SF_6
Equivalent volume of SF_6:	2×10^{-3} L
Extraction rate:	2830 L/min
Sample interval:	10 min

To calculate the volume of SF_6 removed at each interval multiply:

$$[\text{ppbV}] \times 10^{-9} \times 2830 \times 10 = [\text{ppbV}] \times 2.83 \times 10^{-5}$$

To calculate the total volume of SF_6 removed, sum the volumes for each interval.

The fraction recovered is the sum divided by 2×10^{-3} L

For the example in Figure 2-11, the total volume was 1.7×10^{-3} L, and the fraction recovered was 0.85.

Example Calculation 2-6. Calculation of fraction of injected mass recovered.

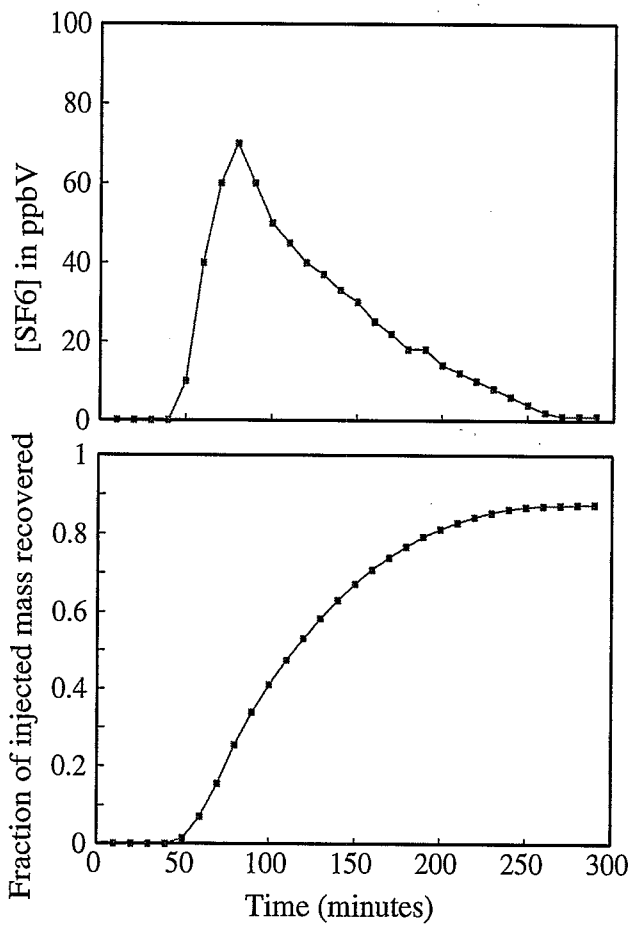


Figure 2-15. a) Tracer breakthrough curve; b) Fraction of volume recovered during the tracer test.

Calculation of Breakthrough Time

Breakthrough curves may be highly nonsymmetrical. Significant tailing may result due to mass transfer limitations during the movement of the tracer towards the extraction well. An example of this was shown in Figure 2-6. Tracer injection 1 shows considerable tailing due to mass transfer limitations out of the lower permeability zone into which it was injected. For this reason, the breakthrough time should be chosen as the time at which 50 percent of the recovered mass has been removed from the subsurface.

Calculation of Effective Porosity

Effective porosity can be estimated from the tracer test using a simple geometry. As discussed in Section 3, this estimate provides a useful evaluation of air flow. The steps in calculating effective porosity are shown in Example Calculation 2-7. For most soils, the air-filled porosity will be between 0.05 and 0.25. If the calculated value is outside of that range, it is likely that significant heterogeneity exists in the soil or that leakage from the ground surface is significant.

Estimation of Velocity Near the Injection Point

As described in Example Calculation 2-8, if the flow field is assumed to be radial, velocity will increase moving towards the extraction well. The flow rate, the distance between the injection and extraction wells, and the effective porosity can be used to approximate the velocity near the injection point (see Theory):

$$V = \frac{F}{2\pi R h n} \qquad (2\text{-}3)$$

Comparison of Velocity Distributions of Several Tests

Comparison of velocity profiles of several tracer tests can provide insight into spatial variations in air velocity in the subsurface. In most cases this analysis will be qualitative, in part because the number and locations of the tests will be limited. However, it is certainly possible to use the tracer data, combined with other site information, to evaluate air flows using numerical models.

Field Examples

Tracer Tests in the OGI Large Layered Experimental Aquifer

Air flow tracer tests were conducted in a large (9 m x 9 m x 3 m deep) physical model at the Oregon Graduate Institute. The model consists of layers of sand, gravel, and clay as shown in Figure 2-16. Air was extracted only from the sand at the bottom of the model. Travel times in minutes are listed in Figure 2-16b. As can be seen from the data, the highest velocities were in the gravel layer above the screened sand interval. The data in Figure 2-16b also indicate that there is significant leakage through ground surface. This occurred despite the presence of a PVC barrier. Numerical modeling indicated that approximately half of the total flow through the model was leaking through ground surface.

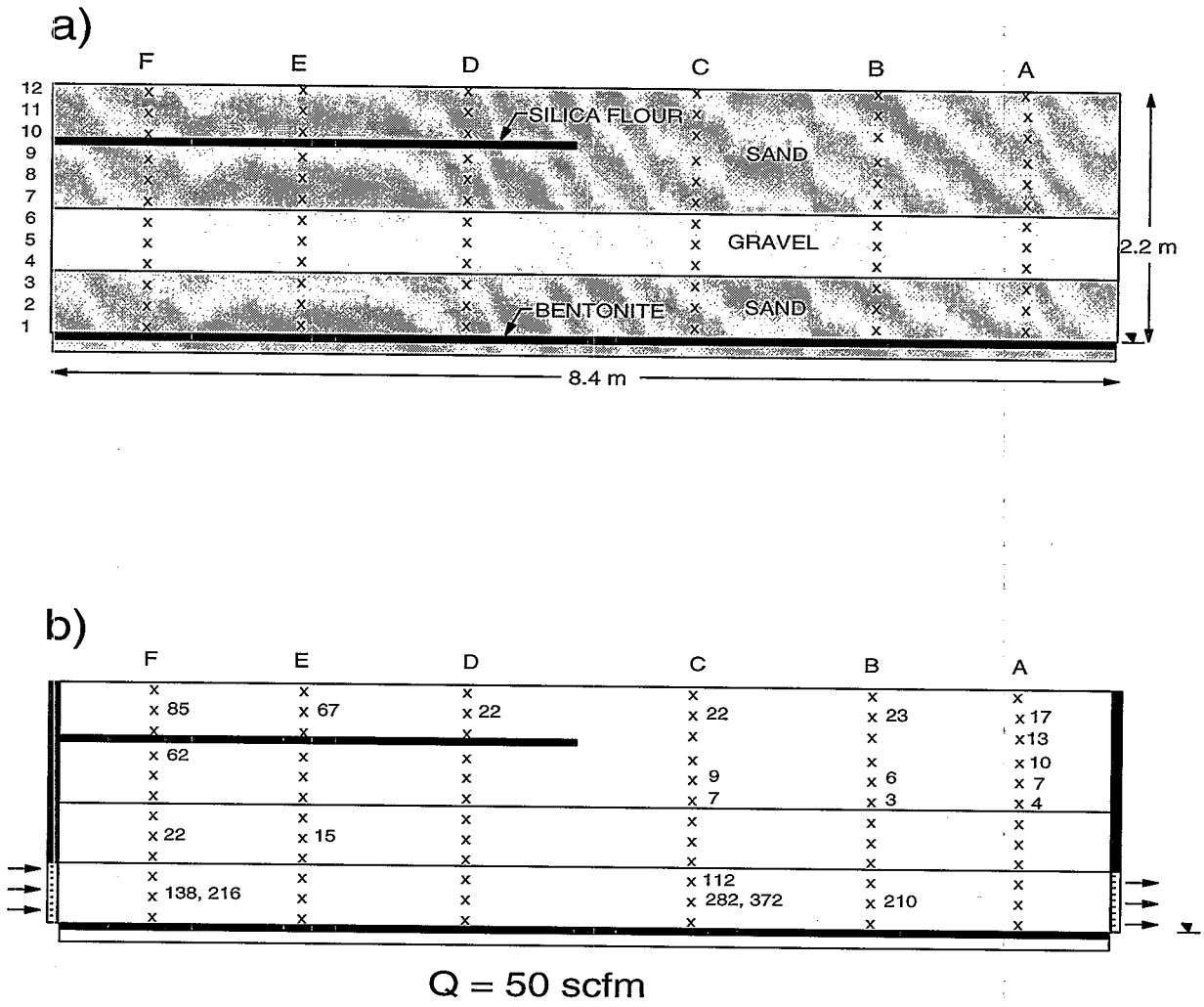


Figure 2-16. Travel times from various locations within the OGI large physical model.

Assume, as in Figure 2-11, that the breakthrough time was 105 min and that the following conditions were present at the site:

Distance from injection to extraction point:	5 m
Thickness of unsaturated zone:	5 m
Depth of injection point:	4 m

If a cylindrical geometry is assumed, the breakthrough time should be the time required to sweep the air from a 5 m radius around the extraction well.

Volume of a cylinder with a 5-m radius:

$5*5*5*\pi* \sim 400$ ^{me}

The volume of air extracted in 105 minutes was:

105 min * 2830 L/min / 1000 L/^{me} ~ 300 ^{me}

The effective porosity is then estimated to be 300/400 or 0.75. This value is unrealistically high. The most likely explanation for the high effective porosity is that the injection point lies within a region where air flow is low. Since the injection point is near the bottom of the unsaturated zone, it is possible that air is leaking from the surface and short-circuiting to the extraction well.

Example Calculation 2-7. Calculation of effective porosity using a simple geometry.

Flow rate (^{me}/min)	= 2.8
Radius of cylinder (R) (m)	= 5
Height of cylinder (h) (m)	= 5
Air-filled porosity	= 0.25

$V = 2.8/[2*\pi*5*5*0.25]$
$= 0.071$ m/min

Example Calculation 2-8. Estimation of velocity at the tracer injection point.

References for Section 2

Hinchee, R. E., S. K. Ong, R. N. Miller, D. C. Downey, and R. Frandt. 1992. Test Plan and Technical Protocol for a Field Treatability Test for Bioventing. Prepared for the U.S. Air Force Center for Environmental Excellence. Revision 2, May 1992.

Section 3

Procedures for Conducting Tracer Tests to Evaluate Recovery of Injected Air During In Situ Air Sparging

Introduction

Introduction to In Situ Air Sparging (IAS)

IAS is a groundwater remediation technique in which air is injected directly into a water-saturated medium to remove contaminants by volatilization and to enhance aerobic degradation. IAS is used both to remediate aqueous groundwater plumes and to treat sources which contain nonaqueous-phase liquids (NAPLs).

The setup of an IAS remediation system is shown schematically in Figure 3-1. It generally consists of one or more air injection wells and one or more SVE wells. As mentioned above, the primary purposes of the injection well(s) are to volatilize contaminants and to increase aerobic biodegradation by introducing additional oxygen into the groundwater. These wells are usually designed in a manner similar to groundwater monitoring wells, except that they generally have short screens (i.e., 1 to 2 ft) and are screened entirely below the water table.

The principal purpose of the extraction wells is to prevent the off-site migration of vapors volatilized by the IAS system. Generally, the setup of the extraction wells is similar to conventional soil vapor extraction (SVE) systems. This often will include an air blower, a "knockout" drum for removing liquids, and an off-gas treatment system (Figure 3-1).

The equipment required for the IAS portion of the system is minimal. In addition to the injection well, all that is generally required is a compressor capable of delivering air at the desired flow rate at a pressure governed by the depth of injection. It is also desirable to be able to measure and control air flow and pressure at the injection well.

Introduction to Air Recovery Tests

Air recovery tests are an important means of evaluating the performance of SVE systems for capturing air injected below the water table as part of an IAS remediation system. The recovery tests are important because they provide direct evidence of the extent to which injected air may be moving off site. Off-site migration is potentially

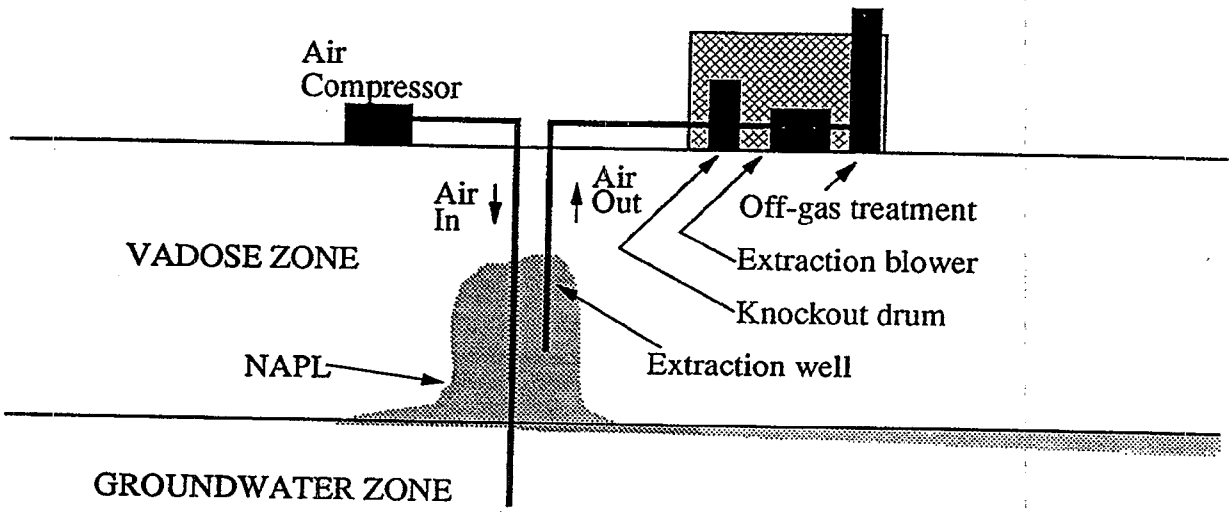


Figure 3-1. Schematic configuration of an IAS/SVE remediation system.

important because it is a means by which potentially hazardous concentrations of contaminants can be carried to adjacent properties.

Test Objectives

General Comments

In order to prevent off-site migration of vapors during IAS, combined IAS/SVE systems are often designed in such a way that extracted air flow exceeds air injection by some multiplicative factor (e.g., 5X). In addition, to demonstrate that the design is working, soil gas vacuum surveys in the vicinity of the IAS/SVE system are usually conducted. It is generally concluded that if no pressures greater than ambient are observed, all of the IAS air is being captured by the SVE system. However, it is generally difficult to relate vacuum data to recovery of IAS air. This is the case because numerous potential air flow patterns in the groundwater zone can exist. For example, if IAS air is injected into sand below a continuous clay layer, the air may move laterally beyond the radius of influence of the SVE well before it has the opportunity to reach the water table. In this case, the sparge air might not be captured by the SVE system.

The previous example implies that under some circumstances pressure measurements alone will not conclusively demonstrate that IAS air is being captured. As a consequence, it is important to conduct tests which can unambiguously determine if all of the IAS air is being captured by the SVE system.

Primary Objective

The primary objective of helium recovery tracer tests described here is to unambiguously determine the recovery efficiency of air injected during IAS.

Theory

Underlying Principal

The principal underlying the helium recovery tests is simple. Helium is injected into the subsurface at a known rate and the rate of helium recovery at the SVE is calculated from the observed helium concentration in the SVE effluent and the SVE flow rate.

Practical Considerations

In order to successfully conduct a helium tracer test, it is necessary to accurately measure flow rates and helium concentrations. As a result, calibration of the analytical equipment (both flow meters and the helium detector) is extremely important. It is also very important to have a system which is free of leaks. This means not only the injection and extraction systems, but also the sampling and analysis systems.

Steps in Conducting a Helium Recovery Test

There are four steps in conducting the helium recovery test (Figure 3-2). They are:

1. Determination of the "100 percent recovery" concentration

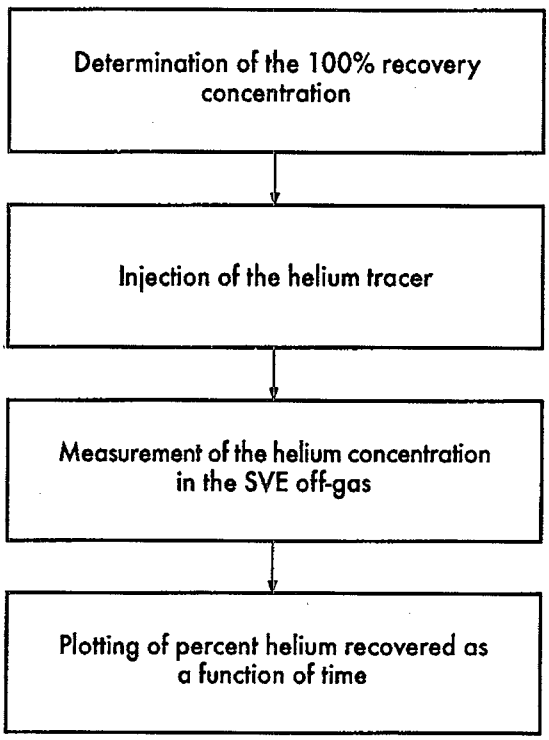


Figure 3-2. Steps in conducting helium recovery tracer test.

Helium is injected at a known rate (the same rate used in the tracer test) directly into the extraction manifold prior to the helium detector. The concentration measured at the helium detector is the 100 percent recovery concentration.

2. Injection of the helium tracer

   Once the 100 percent recovery concentration is determined, helium injection into the sparge air can be initiated. This injection rate must be the same as the rate used to determine the 100 percent recovery concentration.

3. Measurement of the helium concentration in the SVE off-gas.

   Once helium injection in the sparge air has been initiated, air samples are collected from the extraction manifold at regular intervals until the helium concentration in the effluent stabilizes.

4. Plotting of percent helium recovered as a function of time.

   Observed helium concentrations divided by the 100 percent recovery concentration times 100 are plotted as a function of time since the initiation of helium injection. The final values represent the fraction of the injected helium which is recovered by the SVE system.

Test equipment

Overview of Experimental Setup

In order to simplify interpretation, the tests should be conducted by injection of helium into a single IAS well and recovery from a single SVE well. In nearly all cases, tracer tests will be conducted in conjunction with vapor extraction and injection operations. In that context, the design and installation of the extraction/injection wells will be dictated by the remediation design. As a consequence, design and installation of the extraction/injection wells are not discussed here.

Calibration of Analytical Equipment

Calibration of the Helium Detector

Helium in the extracted air will be measured with a Mark Products helium detector Model 9822 or equivalent with a minimum sensitivity of 100 ppm (0.01 percent). Calibration of the helium detector is made using the experimental setup shown in Figure 3-3.

The helium detector should be turned on and equilibrated for at least 10 minutes prior to conducting a calibration or obtaining measurements. As part of the calibration process, the internal sampling pump of the helium detector should be checked prior to operation to ensure that it is functioning.

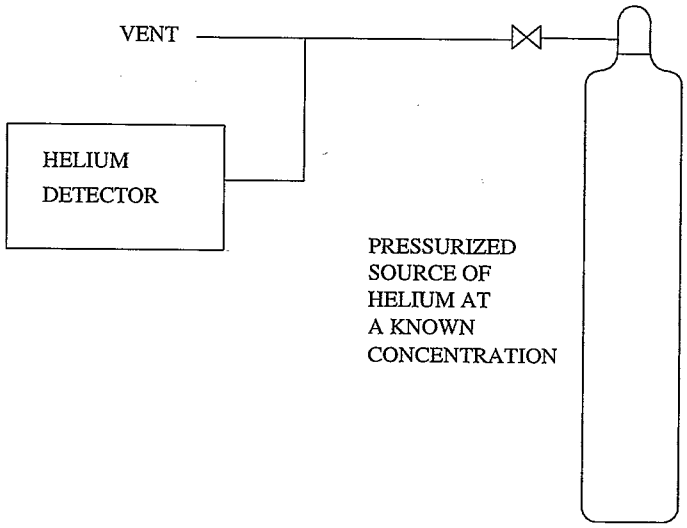


Figure 3-3. Schematic drawing of the equipment used to calibrate the helium detector.

The helium detector should be calibrated each day using helium calibration standards in air. These standards should be pressurized cylinders of 10, 1, 0.1, and 0.01 percent helium in air. The instrument is calibrated by connecting it to one of the pressurized standards and adjusting the flow from the cylinder such that some flow comes out of the vent line. Flow should continue until a stable reading is achieved on the meter (~30 seconds).

Once measurements have been made for each concentration, a calibration curve can be constructed. If any measured value differs from the reported standard value by greater than 20 percent, that standard should be reanalyzed. If the value fails to agree upon reanalysis, the source of the problem should be identified.

Helium standards can be purchased from a specialty gas supplier or they can be prepared on a pressure or volume basis. The pressure-based approach will be discussed here. In general, standards should be prepared in canisters which can withstand 10 atmospheres of pressure and which do not affect the quality of the standard. The final pressure of the standards described here will be 9 atm gauge pressure, which corresponds to a 10-fold dilution of the concentration of helium added to the canister. Preparation of standards can begin with canisters filled with helium-free air at a pressure equal to atmospheric. Standards should be prepared using good-quality pressure gauges which are calibrated against a reference. Water or mercury manometers are excellent references. The canister should be connected to a helium source--either 100 percent helium or a certified mixture (e.g., 1 percent He in air) and a Magnehelic™ gauge as shown in Figure 3-4. Helium is allowed to flow into the canister until the pressure rises to a predetermined gauge pressure. Typical values are listed in Table 3-1. The canister can then be brought to a final pressure of 9 atmospheres.

Table 3-1. Typical Pressure Values Used in Preparing Helium Standards.

Final Concentration (%)	Stock Concentration (%)	Final Pressure of Stock in Standard Canister (atm)
90	100	9
10	100	1
0.9	1	9
0.1	1	1
0.01	1	0.1

Calibration of the Air Flow Meters

Flow rates for the SVE system will generally be in the 10- to 200-scfm range. Vacuum levels will be at 10 to 200 inches of water below ambient pressure. The flow meter calibration system is shown in Figure 3-5. At these high flow rates, a large dry gas meter will be required. If a large dry gas meter is not available, an alternate approach is to

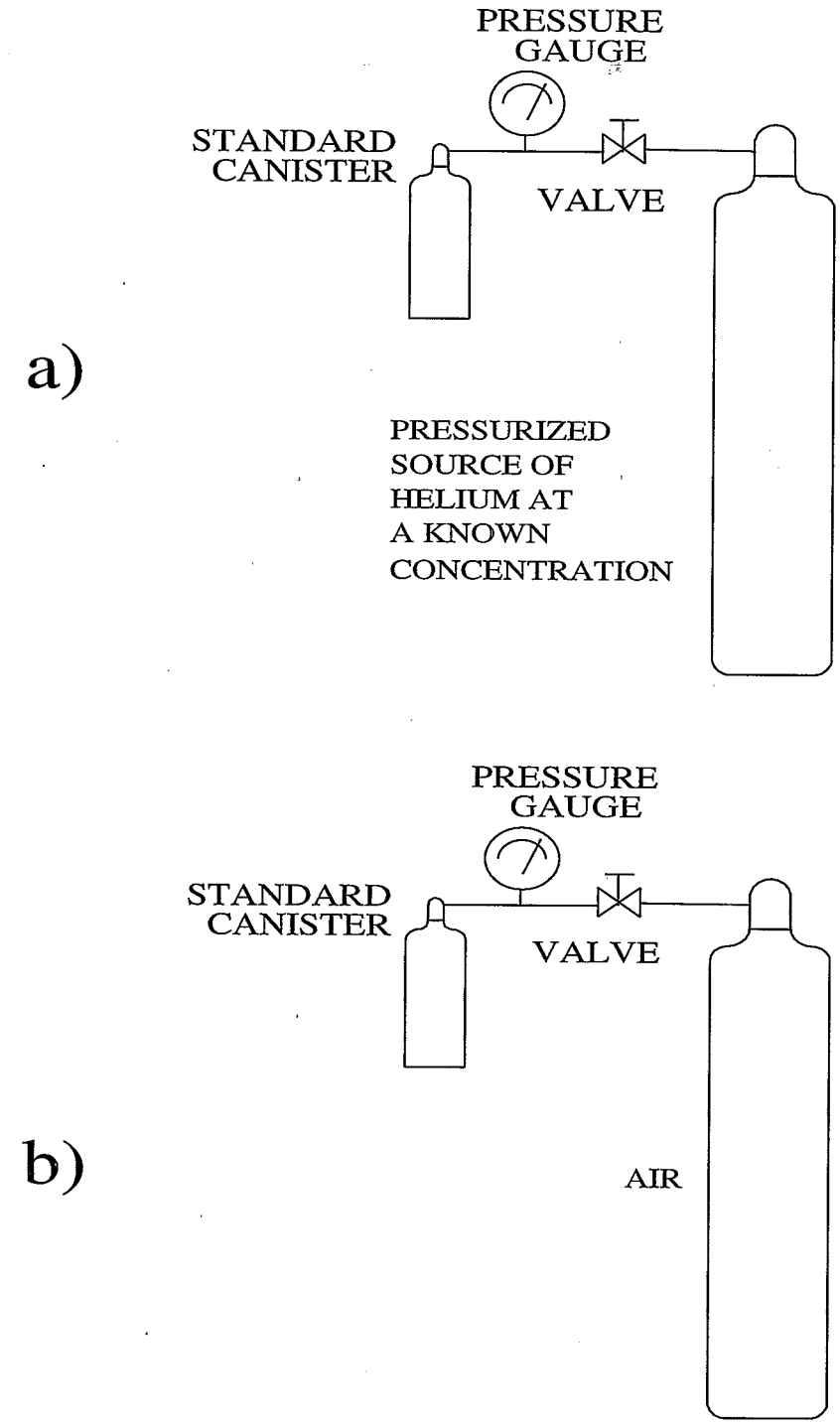


Figure 3-4. Schematic drawing of the equipment used to prepare helium standards.

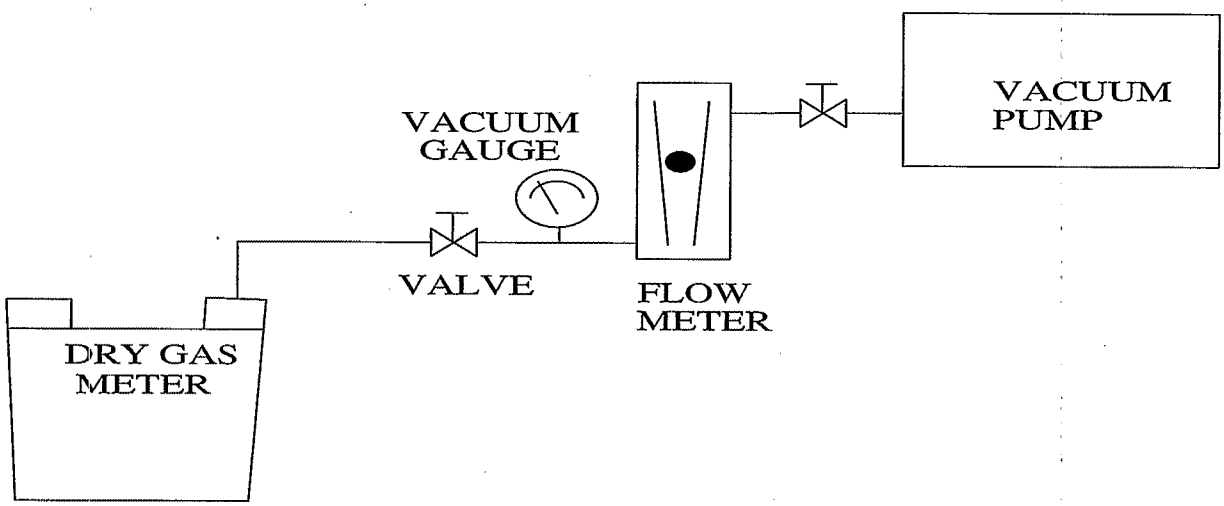


Figure 3-5. Schematic drawing of the flow meter calibration system.

use another calibrated flow meter to calibrate the one to be used at the site. Actual versus observed flow rates should be determined over the range of the flow meter at several vacuums between 0 and 0.9 atmosphere. Those data should be plotted as a family of curves with each line corresponding to a different vacuum value.

Flow rates for the IAS system will generally be less than those used for the extraction system. However, pressures will be above atmospheric, rather than below. The experimental apparatus used to calibrate flow meters at above atmospheric pressure is shown in Figure 3-6.

Flow rates for tracer injection will be in the range of 0.1 to 1 L/min. The experimental apparatus for calibrating the flow meter for tracer injection is the same as for air injection (Figure 3-6).

Calibration of the Sampling Pump

Under many operating conditions the SVE manifold will be under sufficient vacuum that automated analytical equipment will not be able to draw an adequate sample from the manifold. In these cases it will be necessary to use a good quality vacuum pump to draw samples from the manifold and deliver them to the automated analytical equipment. In the context of tracer tests, two potential problems arise with respect to the vacuum pump. First, the pump must be able to move sufficient volumes of air to meet the needs of the analytical equipment, and second the pump should not leak air which can provide additional dilution of the sample stream. The procedures below describe how pump performance can be measured.

Prior to selecting a sampling pump, check the specifications of any automated sampling equipment to be used to determine the volumes of air required by each. (The Mark Products helium detector requires ~100 mL/min.) The first step is to connect the pump to be tested to the apparatus shown in Figure 3-7. If two dry test meters are not available, two calibrated flow meters of the appropriate ranges can be used. Then turn on the pump and open the valve so that no vacuum is observed on the gauge. Determine the flow into and out of the pump by recording the volume of flow that occurs in 1 minute on each of the dry test meters or the flow rates on the flow meters. Partially close the valve to produce a vacuum of 5 inches of mercury, and determine the flow rates into and out of the pump.

Repeat the previous procedure with vacuums of 10, 15, 20 and 25 inches of mercury. Prepare a plot of flow rate in and out vs. vacuum. Based on those data, determine the maximum vacuum that provides sufficient flow for the helium detector. Next, determine the sampling pump leak ratio as a function of vacuum. Determine if the leakage of the sampling pump is acceptable (e.g., inflow rate is within a factor of two of outflow rate).

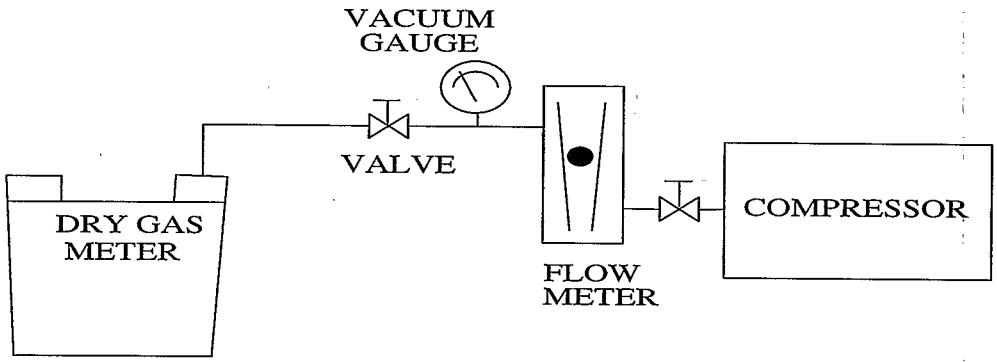


Figure 3-6. Schematic drawing for flow meter calibration under positive pressure.

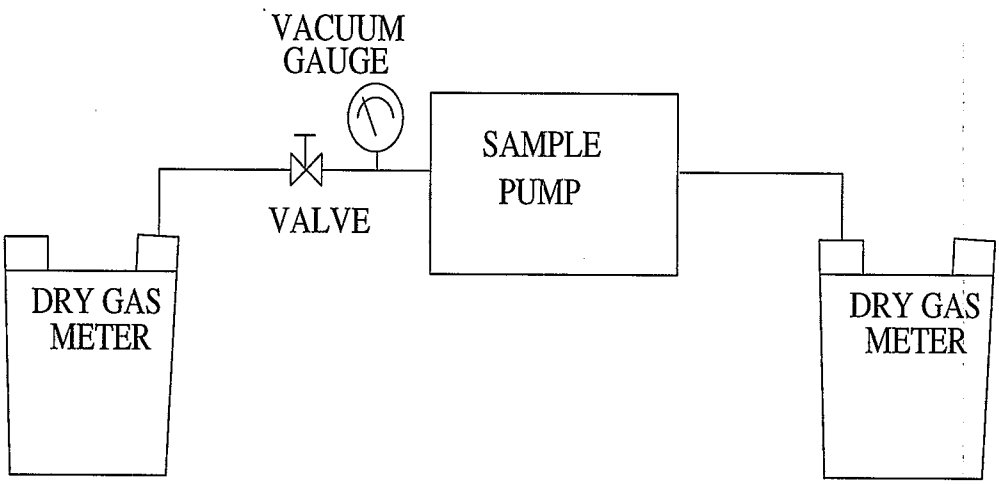


Figure 3-7. Schematic drawing showing setup for measurement of sample pump flow rate vs.vacuum and leakage vs. vacuum.

Test Procedures

Overview of Experimental Procedures

Experimental activities can be divided into the following components. Each is described briefly in the following sections.

1. Determination of the "100 percent recovery" concentration
2. Injection of helium into an IAS point
3. Collection of samples from SVE off-gas
4. Determination of recovery rate (percent) of helium

Determination of "100 Percent Recovery" Concentration

It is necessary to determine the concentration of helium in the off-gas which represents the concentration at "100 percent recovery" of helium. To do this, helium is injected into the extraction manifold prior to the sample pump at a rate which is the same as will be used for the recovery test. The apparatus for this is shown in Figure 3-8. The steps involved in determining the "100 percent recovery" concentration are:

1. Estimate the SVE flow for preliminary calculations (e.g., use the flow meter reading).

2. Calculate the inflow rate of 100 percent helium to produce 1 percent concentration in the effluent (See Example Calculation 3-1).

3. Install a good vacuum pump (metal bellows or diaphragm) to the manifold. (This will be the same setup as for the tracer tests.) Make sure the pump has adequate flow and does not leak at the system pressure.

4. Connect the helium source to the manifold near the extraction point and add helium at the prescribed rate using a calibrated flow meter.

5. Monitor tracer concentration in the extraction system until it stabilizes. (This should take only a few minutes.) This value represents the 100 percent recovery" concentration.

Vacuum Survey

It is important to collect subsurface vacuum data prior to initiation of the tracer tests. These data provide insight into the general nature of the flow system. For example, if little or no vacuum is recorded at a monitoring point, it can be expected that there is little flow at that point. Large vacuums may indicate areas of active flow; however, these values can also occur within low-flow regions adjacent to higher flow regions. Nevertheless, these data can frequently be helpful in understanding the general nature of air flow at the site.

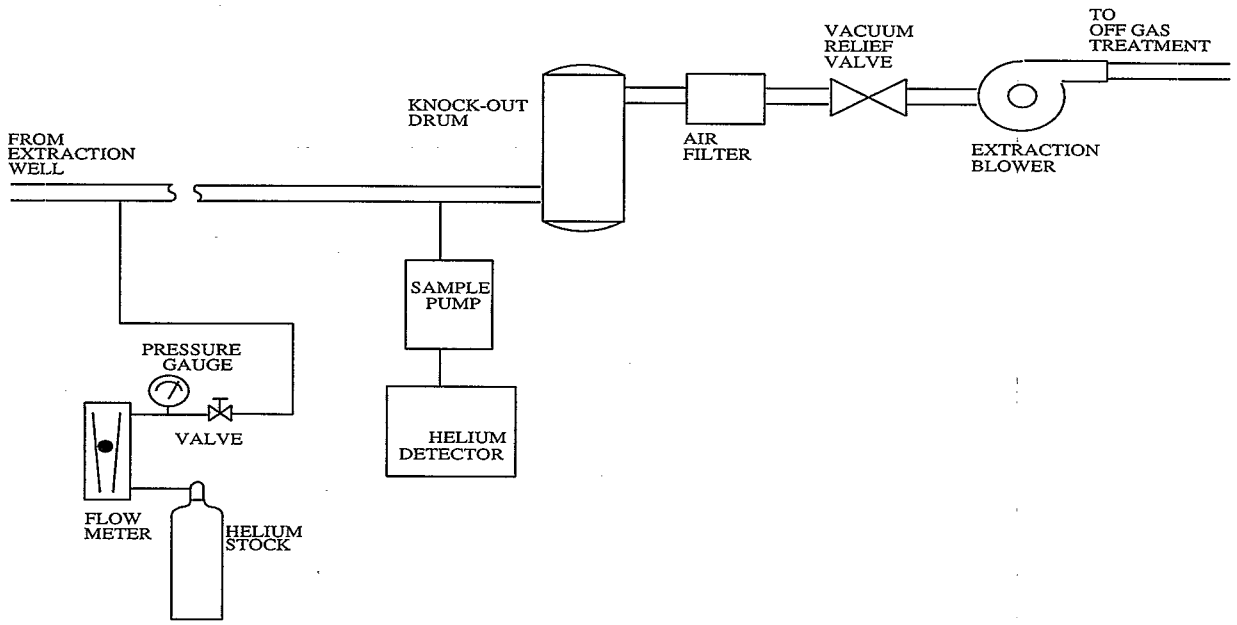


Figure 3-8. Schematic drawing showing the system for measuring SVE flow using a tracer gas.

Determination of tracer injection rate

Approximate SVE Flow rate	= 35 scfm = 1000 L/min
Tracer concentration	= 100%
Desired final concentration	= 1.0%
need a dilution of 10^2	
tracer flow rate = 1000 L/min / 10^2	= 10 L/min

Calculation of "100 percent recovery" concentration

To determine the concentration which corresponds to 100 percent recovery, pure helium is injected into the extraction manifold at the same rate (e.g., 10 L/min) that will be used during the tracer test. The helium concentration observed under these conditions is considered to be the value which corresponds to 100 percent recovery.

Example Calculation 3-1. Calculation of actual SVE flow using a tracer.

The general approach will be to measure soil vacuum with Magnehelic™ gauges. The same measurements can be made with a manometer or other calibrated vacuum gauge. For most sites it will be necessary to have gauges in the following ranges (in inches of water): 0 to 1 inch, 0 to 10 inches, and 0 to 100 inches.

When the remediation system has been operating for more than one day, determine the soil vacuum at each point in the system by connecting the appropriate gauge to the point. After connection to the monitoring point, sufficient time should be allowed for the vacuum to stabilize (commonly 1 minute).

Measurement of Background Helium Concentrations

In most cases, background concentrations of helium will be essentially zero. However, it is important to make that determination prior to starting any test. These measurements can be made while the extraction system is in continuous operation. If previous tracer tests have been conducted at the site, initial concentrations may be non-zero. If concentrations are decreasing with time (i.e., on the tail of the previous test), then if possible, conditions should be allowed to stabilize prior to initiation of the next test. If it is not practical to wait for stabilization prior to initiating the test, the volume of injected tracer can be increased. However, helium concentrations in the influent air should be kept below 5 percent.

Estimation of the Rate of Pure Helium to be Injected

A volume fraction of helium in the effluent stream in the range of 0.002 to 0.01 (0.2 to 1 percent) is desired. To estimate the rate of helium injection necessary to produce this concentration, some initial estimate of SVE air flow must be made. The input rate for helium is simply the approximate SVE air flow rate times the target volume fraction. If the IAS rate is low (e.g., <20 percent of the SVE rate), the target effluent volume

fraction should be kept at the bottom end of the range to avoid buoyancy effects in the injection air (i.e., helium concentrations in the influent air should be kept below ~5 percent).

Introduction of Helium into the Subsurface

Once the preliminary data have been collected and the analytical instrument is calibrated, the tracer test can be initiated. The IAS/SVE system should have been in operation for a period of several days prior to initiation of the tracer test. The first step is to start the analytical instrument and determine the initial helium concentration in the subsurface. If these concentrations are adequately low, the helium source can be connected to the IAS well and the test initiated.

Sample Collection

Samples should be collected prior to the extraction pump to avoid dilution and other errors which may occur in the extraction pump (Figure 3-9). (Samples can be collected after the extraction pump if the system is correctly calibrated; however, that procedure will not be discussed here.) The pressure at this point will be below atmospheric, so care must be taken to insure that a good sample is collected. In general, samples can be taken from the extraction manifold using a good quality diaphragm pump or metal bellows pump, or manually by syringe. (Once again, care should be taken to insure that the pump does not leak and introduce dilution air.) Pressures below 0.5 atm require extreme care to insure that a good sample is collected. In high-vacuum situations, the capacity of the pump on the helium detector may exceed the capacity of the sample pump. This problem must be addressed by using a sampling pump with adequate capacity.

Data Analysis

Calculation of Recovery Efficiency at a Particular Point in Time

Recovery efficiency is simply calculated as the ratio of the observed concentrations to the "100 percent recovery" concentration determined at the beginning of the test (Example Calculation 3-2)

SVE flow rate	= 1000 L/min (~35 scfm)
Injection rate of pure helium	= 10 L/min
Expected concentration	= 1% by volume
Observed concentration	= 0.65%
Recovery efficiency	= .65/1*100 = 65%

Example Calculation 3-2. Calculation of expected concentration and recovery efficiency.

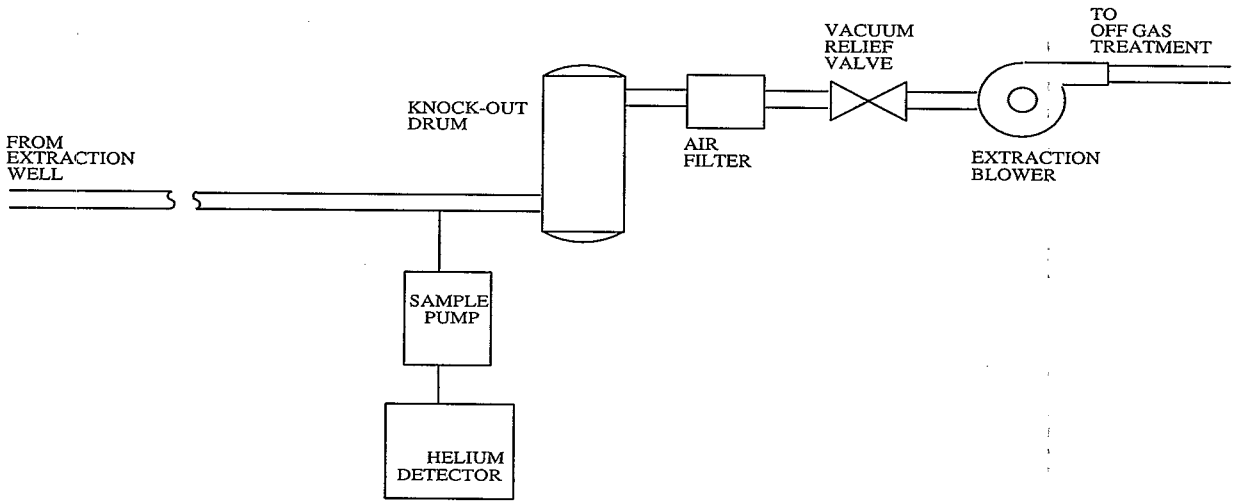


Figure 3-9. Schematic drawing showing the setup for sample collection during the tracer recovery test.

Time-Series Analysis of Recovery Data

In most cases helium will begin to be recovered within an hour of the initiation of tracer injection. Helium concentrations can be expected to rise rapidly initially and then to asymptotically approach some final value. It may be necessary to continue the test for a period of 24 hours or more to establish the final value of recovery efficiency.

Interpretation of the Recovery Efficiency Data

Recovery efficiencies of less than 100 percent imply that some of the IAS air is escaping the SVE system. The significance of the lost air will depend upon the potential risks posed by off-site migration of the sparge air. There is, of course, some uncertainty in the measurement of recovery efficiency. That uncertainty stems from uncertainty in flow measurements (injected helium, extracted air) and measured helium concentrations. In this context, recoveries of greater than 80 percent probably indicate adequate recovery, and efficiencies of less than 50 percent generally indicate incomplete recovery.

Field Examples

IAS In an OGI LEAP Tank

An air recovery test was conducted at one of the OGI large experimental aquifers. During the test the air injection rate was 3.5 scfm and the SVE extraction rate was 30 scfm. The depth to water was ~1 m and the surface was covered with a PVC barrier. Helium was injected into the sparge air at ~1.5 L/min. The data in Figure 3-10 indicate that the helium recovery rate climbed to 100 percent of the injection rate in a period of ~2 hours.

References for Section 3

Hinchee, R. E., S. K. Ong, R. N. Miller, D. C. Downey, and R. Frandt. 1992. Test Plan and Technical Protocol for a Field Treatability Test for Bioventing. Prepared for the U.S. Air Force Center for Environmental Excellence. Revision 2, May 1992.

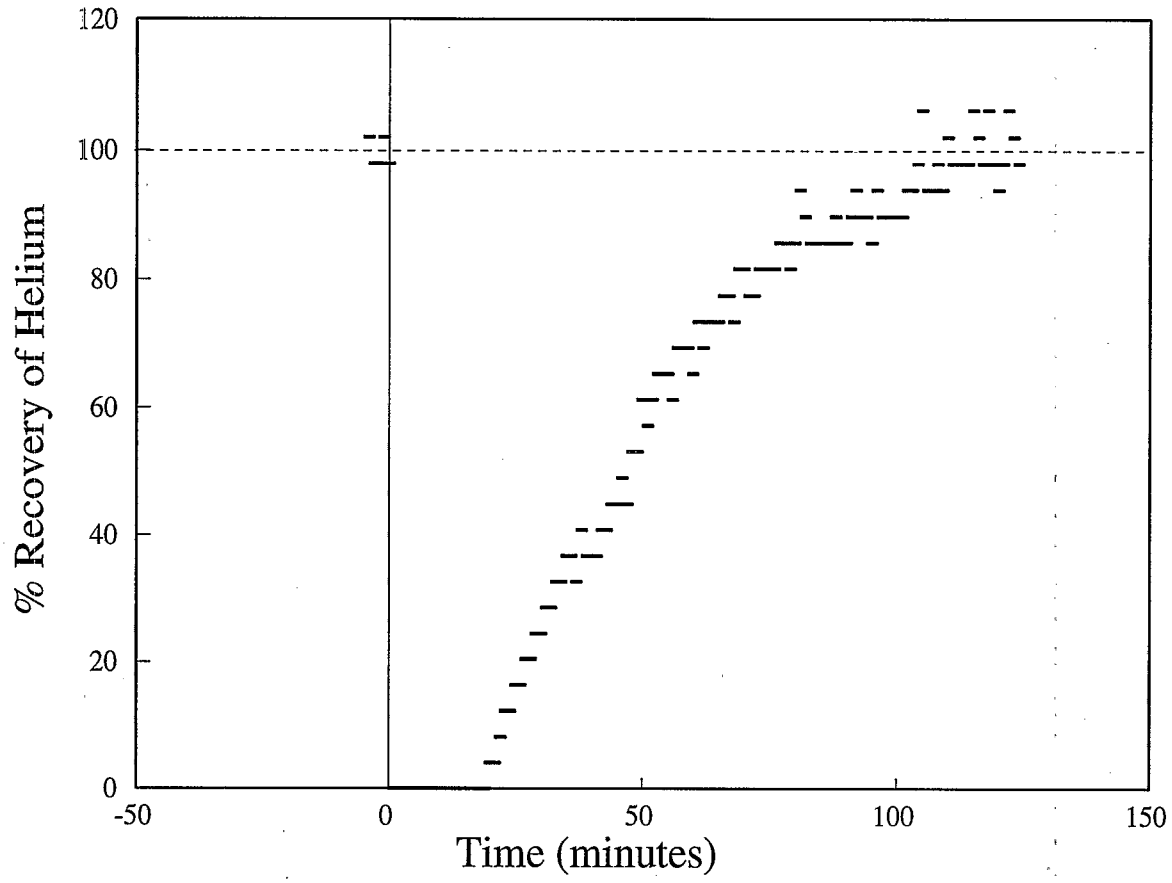


Figure 3-10. Recovery of helium during an air recovery test in an OGI large experimental aquifer.

Section 4

Procedures for Conducting Tracer Tests to Evaluate the Distribution of Injected Air During In Situ Air Sparging

Introduction

Introduction to In Situ Air Sparging (IAS)

IAS is a groundwater remediation technique in which air is injected directly into a water-saturated medium to remove contaminants by volatilization and to enhance aerobic degradation. IAS is used both to remediate aqueous groundwater plumes and to treat sources that contain NAPLs.

The setup of an IAS remediation system is shown schematically in Figure 4-1. It generally consists of one or more air injection wells and one or more soil vapor extraction wells. As mentioned above, the primary purposes of the injection well(s) are to volatilize contaminants and to increase aerobic biodegradation by introducing additional oxygen into the groundwater. IAS wells are usually designed in a manner similar to groundwater monitoring wells, except that they generally have short screens (i.e., 1 to 2 ft) and are screened entirely below the water table.

The principal purpose of the extraction wells is to prevent the off-site migration of vapors volatilized by the IAS system. Generally, the setup of the extraction wells is similar to conventional SVE systems. This often will include an air blower, a "knockout" drum for removing liquids, and an off-gas treatment system (Figure 4-1).

The equipment required for the IAS portion of the system is minimal. In addition to the injection well, all that is generally required is a compressor capable of delivering oil-free air at the desired flow rate at a pressure governed by the depth of injection. It is also desirable to be able to measure and control air flow and pressure at the injection well.

Introduction to IAS Air Flow Tracer Tests

IAS air flow tests are conducted by injecting a gas-phase tracer, such as SF_6, along with the IAS air and determining the distribution of tracer in the subsurface by collecting water samples from discrete locations and depths and determining the concentration of the tracer in the water. In the approach described below, tracer can be injected for a period of 1 week, followed by groundwater sampling in the vicinity of the IAS well.

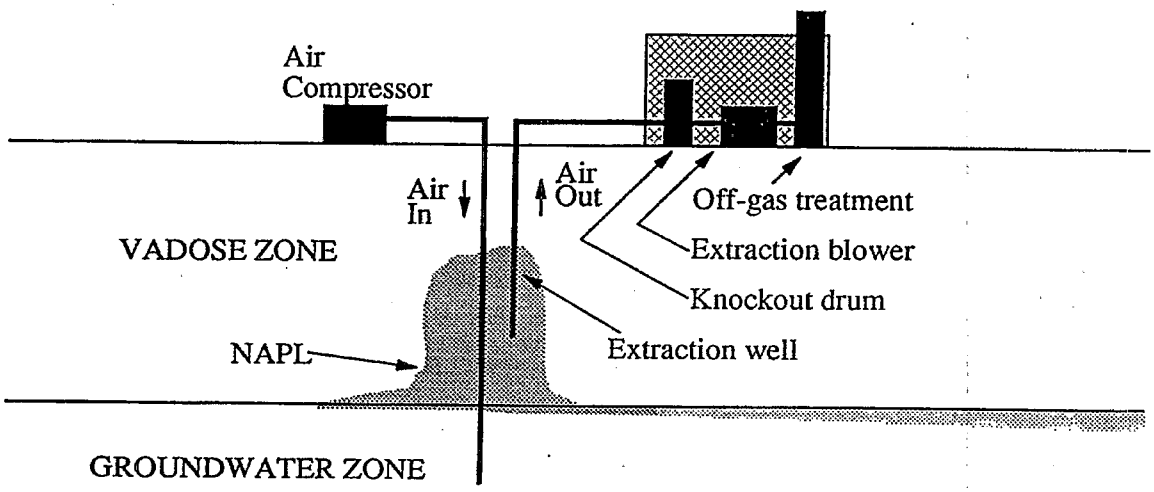


Figure 4-1. Schematic configuration of an IAS/SVE remediation system.

Introduction to Vertical Groundwater Profiling

Vertical groundwater profiling (VGP) is a technique that allows water samples to be collected at a number of discrete depths in the subsurface. It is generally accomplished by driving a small (e.g., 1-inch) -diameter pipe into the ground. The leading edge of the pipe usually consists of a drive point followed by a screened interval through which water can be drawn. The pipe assembly can be advanced by hammering, vibrating, or pushing.

Water samples can be drawn to the surface using a variety of devices. If the water table is within the suction limit, water can be drawn to the surface through a tube connected to a peristaltic pump. If the water table is deeper, a small-diameter bailer or bladder pump may be used. Vertical profiles are generally made at a number of locations and distances around the IAS well to create a three-dimensional picture of the air distribution.

Test Objectives

General Comments

Air pathways produced by IAS are highly erratic. As a consequence, it is difficult to define the "radius of influence" using conventionally measured parameters (e.g., dissolved oxygen in wells, water level changes). Tracer tests and vertical profiling during IAS provide a means of not only characterizing the radius over which the air is moving, but also the vertical distribution of the air. The latter is important because for the IAS process to be effective at remediating zones of residual NAPL contamination, there must be good contact between the contaminated zones and the sparge air.

The IAS air distribution test described below should be applicable to porous media sites where the permeability is greater than 0.001 cm/s (e.g., fine sand or coarser). At permeabilities below this range it will be difficult to withdraw water from the subsurface using the small-diameter driven sampler. In this case, core samples may be appropriate for characterizing the air distribution.

Primary Objective

The primary objective of tracer tests described here is to characterize the distribution of air pathways below the water table at IAS sites.

Theory

Underlying Principal

The principal underlying the IAS air distribution tests is that as the air moves through the groundwater zone, some of the tracer introduced with the sparge air will partition from the air to the groundwater during the sparging process. For the water in immediate contact with the sparge air, tracer concentrations will rise to or near saturation values with respect to the tracer input concentration. An injection period of 1 week is adequate to give a representative picture of air flow patterns, but short enough to

minimize advective transport of the tracer in the groundwater. In areas not in direct contact with the sparge air, tracers can arrive by diffusion or groundwater advection and concentrations will generally be significantly lower.

Practical Considerations

In order to successfully conduct an IAS air distribution test it is necessary to be able to collect groundwater samples at discrete depths below the water table. The groundwater samples must be collected without headspace or volatilization losses during sampling. This can generally be accomplished by vertical profiling and careful groundwater extraction.

A variety of tracers can be used to conduct this test. SF_6 is the tracer used in the procedure described below. SF_6 is a gas at room temperature and pressure; it has a modest solubility (40 mg/L) and a high dimensionless Henry's gas constant (~150). Its primary advantage is that it can be detected at very low concentrations in air and water. These properties are similar to those of oxygen. Consequently, the distribution of SF_6 tracer can be seen as an analog for oxygen distribution.

Steps in Conducting an IAS air distribution test

The five steps in conducting the IAS air distribution test (Figure 4-2) are as follows:

1. Injection of the tracer
2. Determination of the tracer injection concentration
3. Groundwater sample collection
4. Analysis of SF_6 in groundwater samples
5. Mapping of the percent saturation of SF_6 in plan and profile views

Test Equipment

Overview of Experimental Setup

In order to simplify interpretation, the tests should be conducted by injection of SF_6 into a single IAS well and recovery from a single SVE well. In nearly all cases, tracer tests will be conducted in conjunction with vapor extraction and injection operations. The design and installation of the extraction/injection wells will be dictated by the remediation design. Therefore, design and installation of the extraction/injection wells will not be discussed here.

The tracer is added to the IAS air from a pressurized cylinder attached to the injection manifold. The rates of air and SF_6 injection determine the concentration in the IAS air and the concentrations which will be observed at 100 percent saturation in the groundwater.

The SF_6 concentrations in the groundwater are determined by gas chromatography using an electron capture detector. A wide variety of gas chromatographs, ranging from

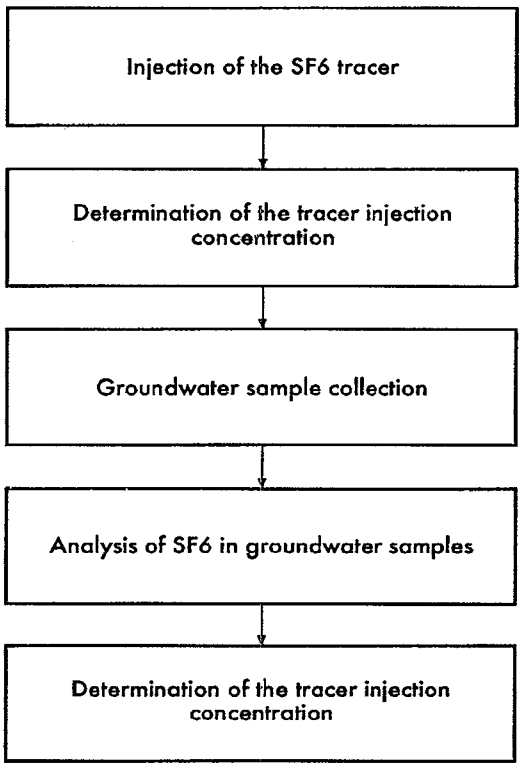


Figure 4-2. Steps involved in am IAS air flow tracer test.

sophisticated research instruments to more "user friendly" instruments, are commercially available. For this application an instrument that is robust enough and portable enough for field use is desirable. In addition, it should have a very low detection limit and an automatic data acquisition system. An SF_6-specific gas chromatograph, available from Lagus Applied Technologies (LAT) in San Diego, California, is one instrument that satisfies all of the above criteria. It is automated and has a detection limit of ~10 parts per trillion (0.01 ppbV) by volume. In the following discussion it will be assumed that a LAT Autotrac is being used.

Calibration of Analytical Equipment

SF_6 detector

Because the LAT Autotrac is equipped with an internal cylinder of calibration gas, single-point calibrations can be easily accomplished in the field. However, it is desirable to conduct multipoint calibrations to verify linear instrument response. Standards can be obtained commercially, prepared by dilution, or prepared using a dynamic calibration instrument. For field applications such as the one described here, pressurized canisters over a range of concentrations provide a convenient means of multipoint calibration.

Air flow meters

All flow meters to be used in the tests should be calibrated with the appropriate gases over the appropriate pressure ranges. For the IAS system, pressures will be above atmospheric. The flow meter calibration system for systems above atmospheric pressure is shown in Figure 4-3. Actual versus observed flow rates should be determined over the range of the flow meter at several pressures between 1 and 5 atmospheres. Those data should be plotted as a family of curves with each line corresponding to a different pressure value.

Test Procedures

Overview of Experimental Procedures

Experimental activities can be divided into the following components:

1. Injection of the tracer
2. Determination of the tracer injection concentration
3. Groundwater sample collection
4. Analysis of SF_6 in groundwater samples

Each is described briefly in the following subsections.

Injection of the Tracer

The setup for injection of the tracer is shown schematically in Figure 4-4. The tracer is added to the sparge air between the compressor and the point at which the air enters the subsurface. Because the air injection line is at a positive pressure relative to the

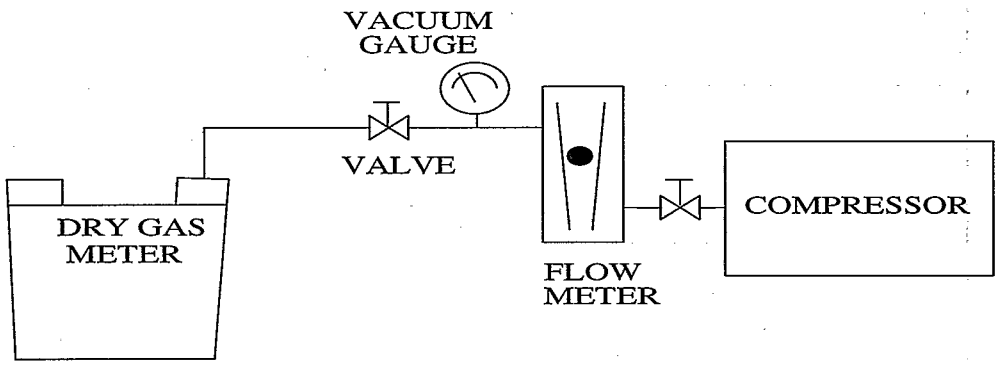


Figure 4-3. Schematic drawing for flow meter calibration under positive pressure.

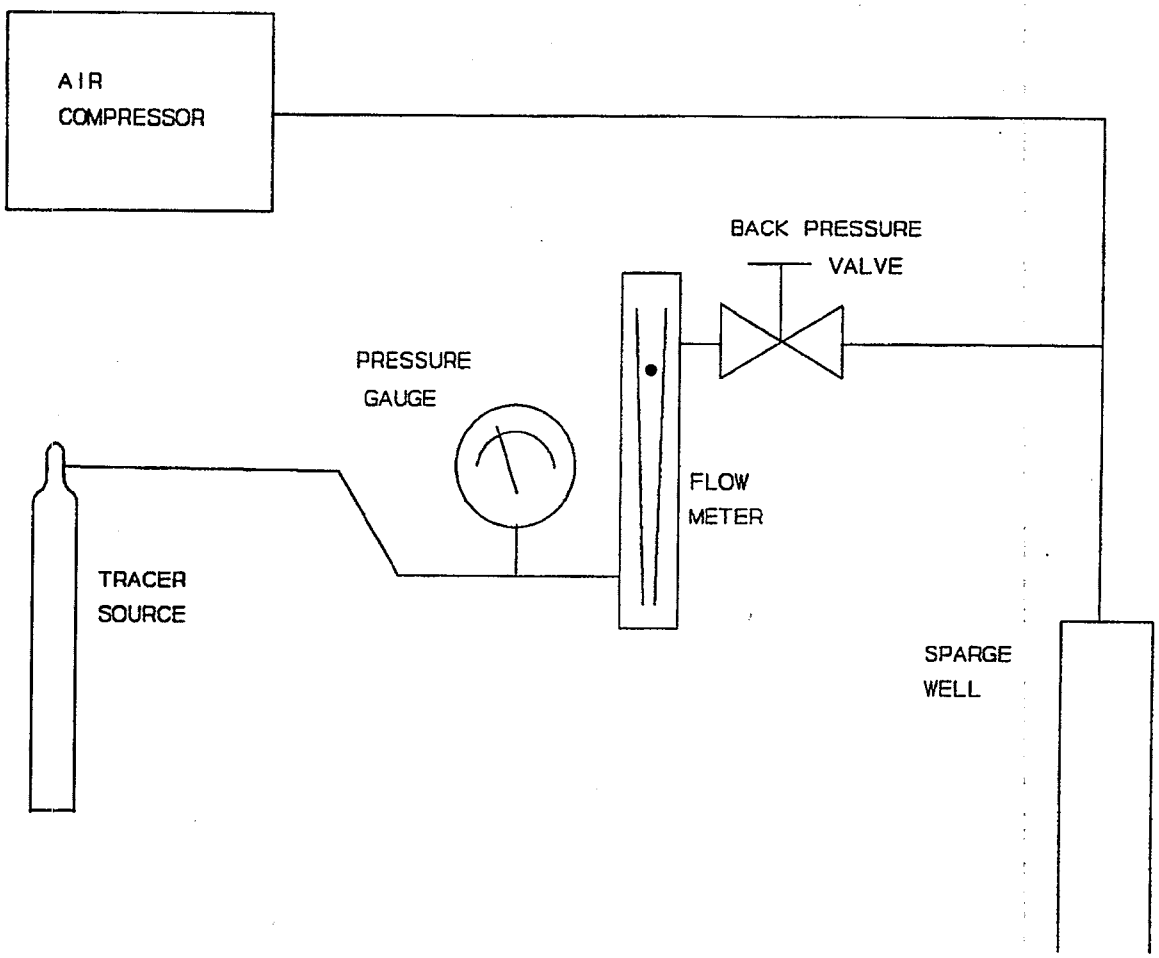


Figure 4-4. Schematic drawing of the tracer gas injection system.

atmosphere, the tracer must be injected at a greater pressure. To ensure a stable flow of tracer, it is recommended that the cylinder valve and backpressure valve be adjusted such that the desired flow is achieved at a pressure of ~50 psi. In general, this will be sufficiently above the air injection pressure that the tracer flow will remain constant, despite changes in air flow conditions.

To produce the desired SF_6 concentration in the sparge air, the following calculation can be used: if the IAS air flow is 150 L/min (~5 scfm), an SF_6 flow rate of 45 mL/min will produce an input concentration of 3×10^5 ppbV.

Determination of the Tracer Injection Concentration

As described in the previous subsection, SF_6 is injected at a known rate directly into the IAS manifold. To determine the SF_6 input concentration, an air sample is collected from the manifold after the SF_6 injection point and the tracer concentration in the air sample is determined. For the example described here, an injection concentration of ~3×10^5 ppbV was used. Therefore, the samples must be diluted approximately 10,000-fold to get them in the range of the LAT detector. This can be easily accomplished, for example, by filling a Tedlar bag with 10 liters of SF_6-free air and injecting 1 mL of the IAS air into the bag (~2 minutes should be allowed for the air to mix in the bag).

Groundwater Sample Collection

The collection of good-quality groundwater samples is key to the success of this tracer test. The sample collection technique must be capable of collecting samples from discrete depths and delivering those samples to a storage vessel (e.g., a 40-mL vial) without volatilization loss. As described previously in this section ("Introduction to IAS Air Flow Tracer Tests"), a variety of methods can be used to accomplish this. Most involve advancing a pipe with a screened tip using a percussion hammer or vibration.

If the water table is less than ~25 feet, it is generally possible to use suction to draw water through the pipe to the surface using a peristaltic pump. If a steady stream of water can be produced (e.g., no air bubbles in the sampling line), the water flowing from the pump can be delivered to a sample bottle for storage. To ensure that a good sample is collected, the tube from the peristaltic pump should be placed in the bottom of the sample bottle and the water delivered to the vial in a "gentle" manner (i.e., no splashing, etc.). If samples are collected in 40-mL vials, a rate that fills the bottle in ~10 seconds is appropriate. If 40-mL vials are used, they should be overfilled with ~100 mL of water, and then the tube should be slowly removed from the vial. The cap should be placed on the vial such that no headspace remains in the vial. The samples should then be stored inverted in the dark until the time of analysis, which should be within 2 weeks.

If a steady supply of water cannot be drawn to the surface with vacuum,a variety of alternative approaches are available to accomplish this. Small-diameter bailers are the simplest means of accomplishing this, but small-diameter bladder pumps are the best

means of delivering a high-quality water sample. Another approach is to use evacuated vials that can be lowered down the pipe and opened at depth (e.g., BAT™ samplers, Hogentogler and Co., Inc, Columbia, Maryland).

Analysis of SF_6 in Groundwater Samples

In order for profiling to provide an accurate picture of air distribution in the groundwater zone, an accurate measure of concentration is required. This can be accomplished using a variety of analytical approaches on a gas chromatograph with an electron capture detector (e.g., headspace, direct aqueous injection). An LAT detector will be used for discussion purposes in the following example. Although it has excellent sensitivity for SF_6, the LAT detector requires a 10-mL air injection, which somewhat complicates sample preparation.

Because SF_6 is analogous to oxygen, it is useful to report concentrations as a percent of saturation. In that context it is useful to report values that range from 100 percent of saturation with respect to the input concentration down to ~1 percent. The first step in calculating the percent saturation is to measure the aqueous concentration of the tracer in the water sample, and then convert that value to a percent of saturation based on the input air concentration.

The easiest way to measure aqueous concentrations of SF_6 using the LAT detector is by headspace analysis. This requires that conditions be adjusted to provide a headspace concentration within the range of the LAT. The following example outlines this method.

If an SF_6 input concentration of 3×10^5 ppbV is used, based on a solubility of 40 mg/L (a dimensionless Henry's constant of 150), concentrations in the groundwater could reach ~1.2×10^{-5} g/L. If a headspace of equal volume to the water is created by removing half of the water, essentially all of the SF_6 (>99 percent) will partition to the headspace. As shown in Example Calculation 4-1, this will produce a headspace concentration of ~2000 ppbV, which is greater than the maximum concentration for the LAT detector. A maximum headspace concentration on the order of 20 ppbV is desired. To accomplish this, a headspace to water ratio of ~100 should be used. This is achieved by injecting 0.4 mL of water sample into a 40-mL vial that had been previously flushed with SF_6-free air. The water and air should be allowed to equilibrate for 1 to 2 minutes before an air sample is withdrawn.

As mentioned above, the LAT detector requires that ~10 mL of air be injected into the sample loop. This is accomplished by withdrawing the air through the septum cap using a 10-mL syringe. However, using a syringe to withdraw that volume from a 40-mL vial will cause a significant reduction in the internal pressure of the vial. When the syringe is exposed to the atmosphere, ambient air will be drawn into the syringe. If the ambient air contains SF_6, this will lead to errors in the analysis. To prevent this, 10 mL

of clean air should be injected into the vial as the sample is withdrawn. If this is done carefully (e.g., one needle tip at the top of the vial, one at the bottom), dilution of the sample by the injected air can be avoided.

SF_6 input concentration	$= 3 \times 10^{5}$ ppbV $= 3 \times 10^{-4}$ mole fraction
SF_6 concentration in water at equilibrium with tracer	$= 0.04$ g/L $* 3 \times 10^{-4}$ $= 1.2 \times 10^{-5}$ g/L
Concentration in air at equilibrium with an equal volume of water saturated with respect to the injection air	$= 1.2 \times 10^{-5}$ g/L / 6 g/L $= 2 \times 10^{-6}$ mole fraction = 2000 ppbV
Concentration in air at equilibrium with water saturated with respect to the injection air at an air:water ratio of 100:1	$= 1.5 \times 10^{-5}$ g/L / 6 g/L / 100 $= 2 \times 10^{-8}$ mole fraction = 20 ppbV

Example Calculation 4-1. Calculation of headspace concentration.

Once the concentration of SF_6 in the headspace is determined, the concentration in the aqueous phase can be determined by calculating the total mass in the headspace and dividing that number by the volume of water in the vial. The aqueous concentration can then be expressed as a percent of the saturation value (Example Calculation 4-2).

Measured headspace concentration	= 5 ppbV $= 6$ g/L $* 5 \times 10^{-9}$ $= 3 \times 10^{-8}$ g/L
Volume of air in the vial	= 40 mL
Total mass in headspace	= 0.04 L $* 3 \times 10^{-8}$ g/L $= 1.2 \times 10^{-9}$ g
Volume of water in the vial	= 0.0004 L
Aqueous concentration	$= 3 \times 10^{-6}$ g/L
Saturation concentration (fraction SF_6 in IAS air * solubility)	$= 3 \times 10^{-4} * 0.04$ g/L $= 1.2 \times 10^{-5}$ g/L
Percent saturation	$= 3 \times 10^{-6}$ g/L / 1.2×10^{-5} g/L * 100 = 25%

Example Calculation 4-2. Calculation of percent saturation.

Data Analysis

Once percent saturation in groundwater numbers have been calculated, it is useful to construct plots of concentration versus distance below the water table for the profile locations. If, for example, several profiles were made in a vertical plane through the sparge well, these data could be plotted together to show the distribution of air as a function of distance from the sparge point.

Alternatively, profile data from the site can be plotted in plan view with individual plots located approximately where the profiles were taken. [An example of this is shown later in this section (Field Example).] If data on hydrocarbon concentrations as a function of depth are available, it is useful to plot the SF_6 and hydrocarbon data together to assess the extent of contact between the two.

The data collected and presented as described above can be used to examine the areal and vertical distribution of the air from an IAS well. The test can also be used to assess the contact between the IAS air and the zone of contamination. It is assumed in this discussion that the zone of contamination includes residual NAPL at or below the water table. In this case, good contact between the air and the NAPL is important for cleanup to be accomplished within a reasonable timeframe. If the vertical distribution of contaminants is known, the test described here can provide a good measure of the contact between the NAPL and the air. If vertical profiles have been made at a number of locations at the site, the test can also provide a good indication of the area over which the IAS well is effective. If the vertical distribution of the contaminants is not known, the test can still provide useful information about the vertical and areal distribution of the sparge air; however, it may be difficult to assess the effectiveness of the IAS well for remediating the site.

One of the most commonly measured parameters with regard to an IAS well is the "radius of influence" (ROI) of that well. Most measures of ROI (e.g., groundwater mounding, vadose zone pressure) produce a picture that is areally much more uniform than field data (e.g., Field Example) suggest is the case at many sites. The test described here provides a much more accurate picture of the zone over which IAS is active, in both the vertical and areal directions.

The example described above uses a single IAS well. The test can also be applied at sites where multiple sparge wells are in operation. In the latter case, the same profiling and analysis procedures can be used. However, it may be desirable to increase the number of profile locations in order to adequately describe the distribution of air at the site.

Field Example

Figure 4-5 shows a plan view of the sparging test site at which an IAS air flow tracer test was conducted. The subsurface at the site consisted of fine to coarse sands over

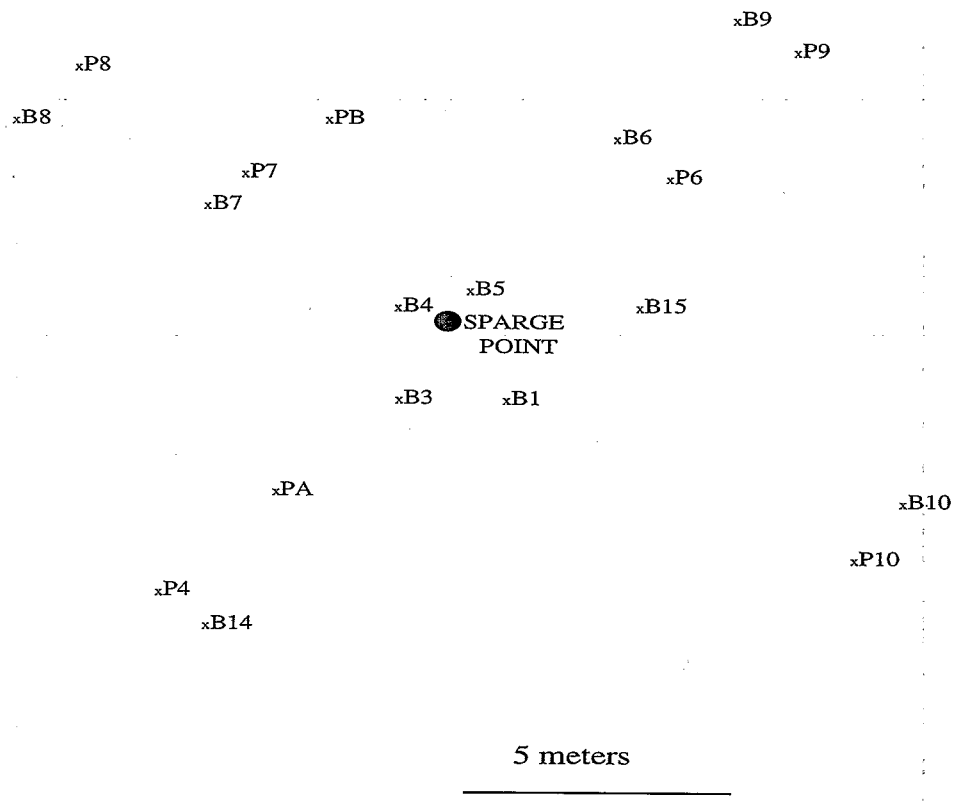


Figure 4-5. Plan view of sparging test site showing the locations of the monitoring wells (B-series) and the vertical profile locations (P-series).

the entire treatment zone. The water table was at a depth of ~6 meters and the sparge air was injected at a depth of ~9.5 m.

In Figure 4-6, the SF_6 data are superimposed on a plan view map of the site. As the figure shows, the distribution of SF_6 around the sparge well is not uniform, either areally or vertically. These data, combined with observations during sampling, have significant implications for IAS at the site.

During sampling it was observed that in the vicinity of Wells B-6, B-9, and B-10, there appeared to be a lower permeability zone from the water table to a depth of approximately 7 m. The samples immediately below that depth produced a significant amount of air with the water. These samples also showed significant SF_6 concentrations. This suggests that an areally extensive air pocket had formed beneath the lower-permeability layer and that upward air flow was low.

In Figure 4-7, SF_6 data from B-6 are plotted along with previous soil sample data. The data indicate that air flow occurs below the depth of highest soil contamination. Based on the field observations, it would appear that the high soil concentrations correspond with a lower-permeability zone above 7 m and that the high air flow region corresponds to a higher-permeability zone below that depth. This suggests that air may be bypassing the most contaminated zones at the site.

In the vicinity of Wells B-7 and B-8, little SF_6 was observed in the water samples and IAS appears to be ineffective. It has been speculated that this is caused by anisotropic medium. Our observations suggest that the lower-permeability zone above 7 m was not as pronounced in this area; as a consequence, lateral air movement under the layer was less significant. SF_6 and soils data obtained near Well B-7 (Figure 4-8) show a pattern similar to those obtained near Well B-6. In the case of Well B-7, the SF_6 concentration is quite low, indicating that air flow is limited. However, the data do suggest that air flow once again appears to bypass the zone of highest contamination.

Throughout the site there appeared to be limited air distribution below a depth of 8 m. Once again, our interpretation of these data is that the distribution of air was controlled primarily by lower-permeability zones above ~7 to 8 meters which covered portions of the site.

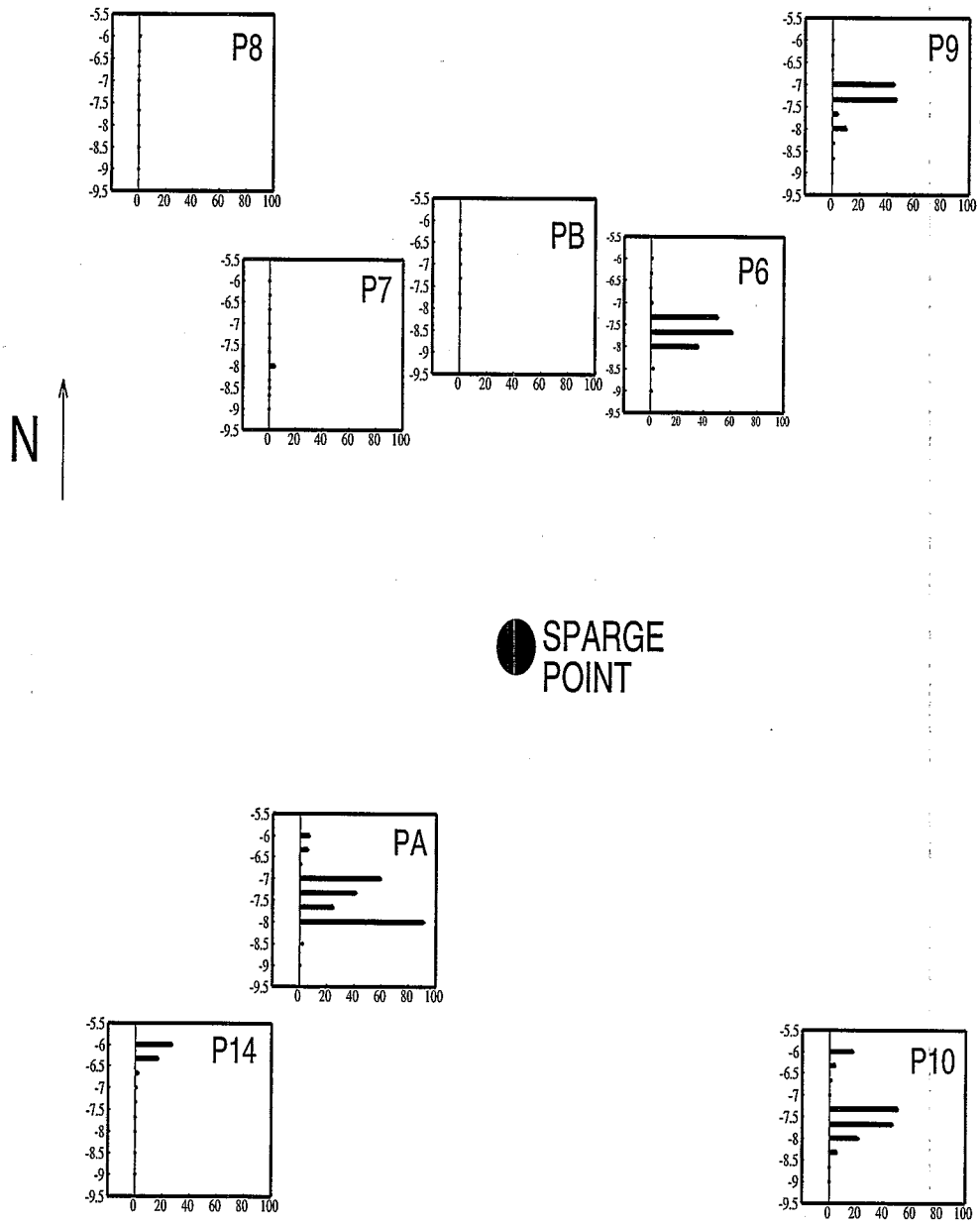


Figure 4-6. Site plan view showing SF_6 vertical profiles.

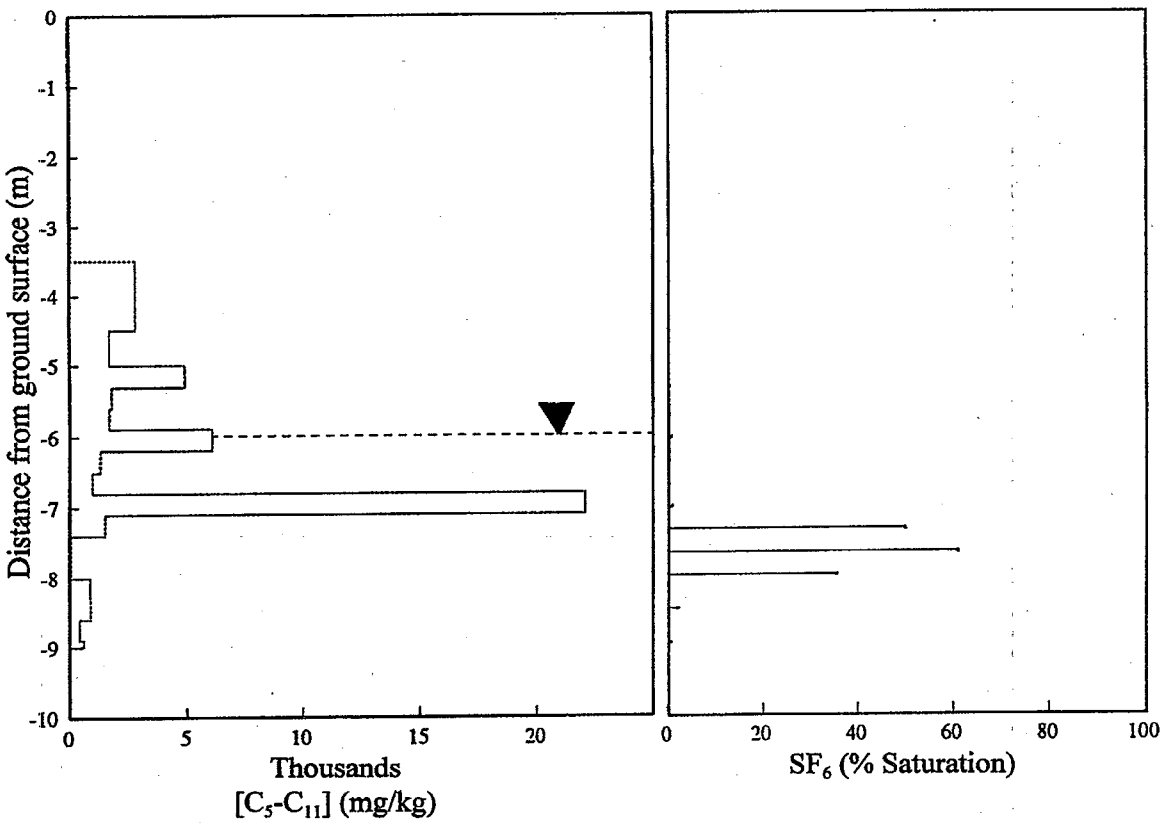


Figure 4-7. SF_6 and vertical distribution of contaminants near monitoring well B6.

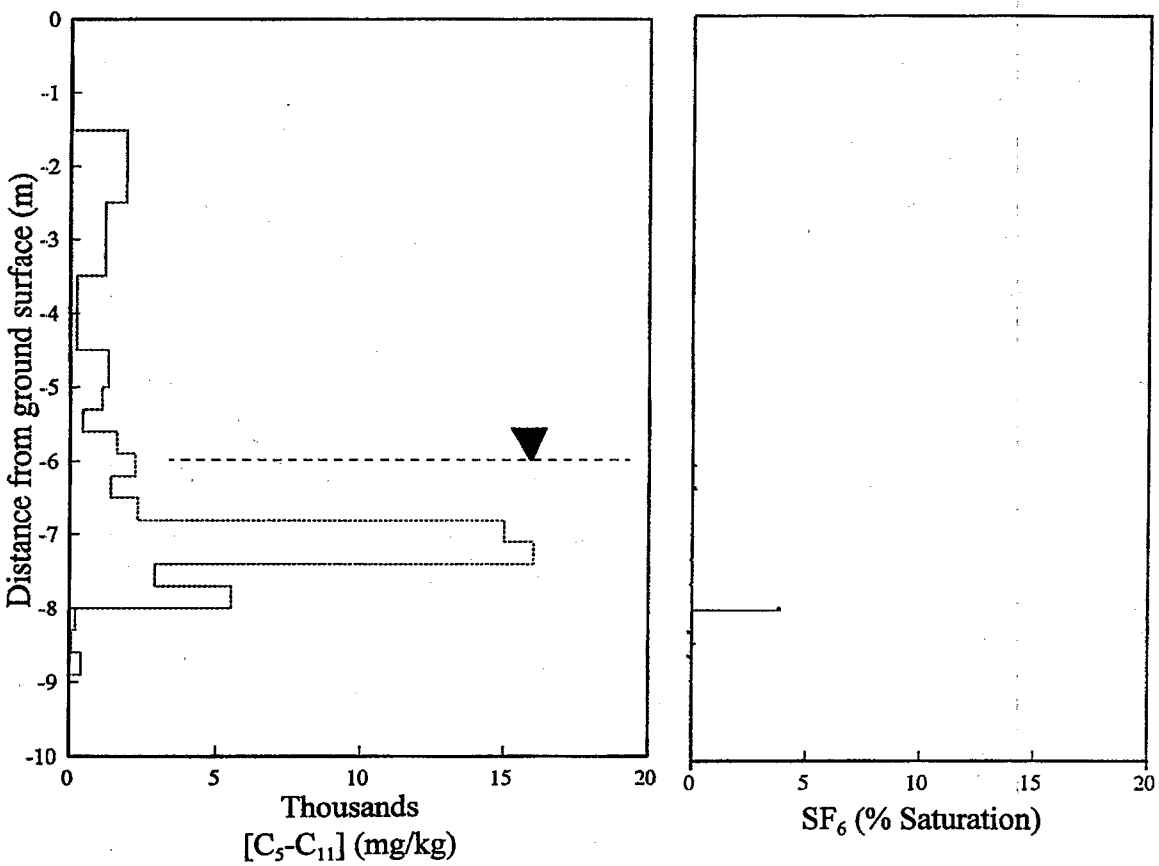


Figure 4-8. SF_6 and vertical distribution of contaminants near monitoring well B7.

Section 5

Procedures for Bioventing Field System Design and Evaluation Air Flow, Tracer, and In Situ Respiration Tests

Introduction/Purpose

Conventional soil vapor extraction (SVE) systems are designed to optimize system performance by maximizing air flow rates and air/contaminant contact to yield a maximum recovery rate of volatiles from contaminated soil. Performance may deteriorate over time, however, due to occluded residual saturation and enrichment of residual contamination in the less volatile waste components.

Bioventing is a modification of the conventional, gas based soil remediation technology which has been successfully applied and documented for the remediation of hydrocarbon contaminated soils either used alone or for the "polishing" of residual, semi-volatile contaminants remaining in soil following high rate SVE. Bioventing entails the use of SVE systems for the transport of oxygen to the subsurface, where indigenous organisms are stimulated to aerobically metabolize contaminants located there. Bioventing systems are designed and configured to optimize oxygen transfer and oxygen utilization efficiency, and are operated at much lower flow rates and with significantly different configurations from than those of conventional SVE systems.

This procedure has been developed to provide an integrated approach for the evaluation of air flow/air permeability (characteristics of gas phase remediation systems common to both SVE and bioventing systems), along with biodegradation rates (characteristic of the biologically based bioventing technology) quantified from respiration measurements collected under field conditions for use in the design and evaluation of field-scale in situ bioventing systems. Both air flow data, relating to oxygen supply, and biodegradation rate data, relating to oxygen utilization, are required for the rational design of bioventing systems, and both types of data can be collected in the field procedure described below.

Background/Theory

Biological Remediation of Contaminated Soils

The biodegradation of organic compounds in soil environments has been extensively described in the technical literature, and details of metabolic pathways and microbial

populations responsible for compound biotransformation have been summarized in a large number of textbooks and reviews on soil microbial ecology (Alexander, 1977; Atlas, 1981; Dragun, 1988). For direct biodegradation of hazardous organics to be successful, four conditions must be satisfied. First, the contaminants of interest must serve as a carbon and energy source for the indigenous microbial population, i.e., they must be able to serve as an electron donor. Secondly, an appropriate electron acceptor must be available so that energy can be extracted from the electron donors at environmentally significant rates. Thirdly, macro- and micronutrients essential for the production of cellular material must be available in the appropriate ratio for microbial growth to proceed unhindered (C:N:P mass ratios typically recommended for soil bioremediation applications are 100:10:1). Finally, environmental conditions within the contaminated soil environment must not be inhibitory to the indigenous microflora soil environmental conditions to ensure effective bioremediation include: soil water at 50 to 80 percent of soil field capacity ≈ 1/3 bar; soil pH from 5.5 to 8.5; soil temperature in the mesophilic range from 15 to 45°C; and an absence of organic or inorganic toxicants that can inhibit microbial activity.

The most critical limitation to successful bioremediation is generally the lack of appropriate electron acceptors. A variety of electron acceptors can be used by soil microorganisms to carry out the oxidation of organic contaminants. These include oxygen, nitrate, sulfate, iron, manganese, carbon dioxide and organic carbon. Of these, oxygen provides the organism with the highest energy yield, providing nearly twice that of nitrate, and an order of magnitude higher energy release to the microorganism when it is utilized as an electron acceptor as compared to sulfate, carbon dioxide and organic carbon. Oxygen metabolism is therefore energetically selected for, and subsequently, oxygen utilizing microorganisms are ubiquitous in soil environments. Oxygen is also the preferred electron acceptor from an engineering standpoint, as accelerated degradation rates generally occur under aerobic (oxygen rich) conditions as compared to anoxic or anaerobic (oxygen deficient) conditions.

These principles of biodegradation have historically been applied to the in situ aerobic bioremediation of contaminated soils and ground water using water to carry oxygen to subsurface contamination. Efforts have been made to increase the level of oxygen in this water by saturating the water with pure oxygen or through the addition of hydrogen peroxide. These efforts have generally met with limited success, however, because of the inability to transfer adequate oxygen to areas of subsurface contamination. This oxygen transfer is caused by the physical limitations to the transfer of this oxygen saturated liquid through contaminated soils (Downey et al., 1988; Hinchee and Downey, 1988; Hinchee et al., 1989; Lee et al., 1988; Wetzel et al., 1987).

The inherent disadvantage of utilizing water as the carrier medium for the transfer of oxygen to the subsurface can be graphically illustrated by determining the mass of water required to transport a unit mass of oxygen when the carrier medium is saturated

with oxygen. These values are summarized in Table 5-1 and show that due to the low solubility of oxygen in water, prohibitively large amounts of oxygen-saturated water are required, even when using pure oxygen or hydrogen peroxide saturated solutions. This oxygen supply limitation is exacerbated by the high oxygen demand of hydrocarbon contaminants, as indicated by the simple stoichiometric reactions for hexane oxidation shown below, assuming no substrate incorporation into cell material:

$$C_6H_{14} + 9.5\ O_2 \rightarrow 6\ CO_2 + 7\ H_2O \qquad (5\text{-}1)$$
$$3.5\ g\ O_2/g\ C_6H_{14}$$

Table 5-1. Carrier Fluid Oxygen Supply Requirements.

	lb carrier/lb oxygen
Water	
Air Saturated	125,000
Pure Oxygen Saturated	25,000
Hydrogen Peroxide Saturated (500 mg/L)	10,000
Air (20.9% Oxygen)	4.8

Assuming an oxygen requirement of only 3 g O_2/g hydrocarbon for hydrocarbon mineralization, a 3,785 L (1,000 gal) fuel spill weighing approximately 3,175 kg (7,000 lb) would require 9,525 kg (21,000 lb) of oxygen. This equates to an air-saturated water volume of approximately 1,191,000,000 L (315,000,000 gal), a pure O_2 saturated volume of 238,000,000 L (63,000,000 gal), or a saturated peroxide solution volume of 95,300,000 L (25,200,000 gal) to provide the required oxygen for fuel bioremediation. It becomes apparent from these calculations that hydraulic limitations would be severe for the remediation of a spill even as small as 3,785 L (1,000 gal) due to massive water volumes required when using liquid carrier bioremediation approaches in either the saturated or the unsaturated zone.

Bioventing Technology Description

Bioventing describes the process in which the air medium is utilized to deliver oxygen to the subsurface to stimulate the in situ biodegradation of organic contaminants. As indicated in Table 5-1, air is an extremely efficient oxygen transfer medium due to its high oxygen content (20.9 vol. percent, i.e., 209,000 ppmV) and low viscosity as compared to that of saturated water. Bioventing represents a hybrid physical/biological process utilizing SVE systems for oxygen transfer, while focusing not on contaminant stripping, but rather on in situ aerobic contaminant biodegradation for the remediation of a contaminated site.

Consideration of SVE for oxygen transfer to the subsurface was proposed in 1988 by Wilson and Ward (1988), who noted that systems designed for the removal of volatiles from soil could also be used to transport oxygen. A number of other authors have discussed the potential improvement of in situ, aerobic, subsurface bioremediation using SVE for oxygen transfer (Bennedsen, 1987; Riser, 1988; Ely, and Heffner, 1988; Ostendorf and Kampbell, 1989; Stapps, 1989), and there has been ample recent evidence demonstrating field-scale bioventing system effectiveness for fuel contaminated site remediation (Dupont et al., 1991; Miller et al., 1991; Hinchee et al., 1991; Ong et al., 1994; van Eyk, 1994).

Bioventing systems are composed of hardware identical to that of conventional SVE systems, with vertical wells and/or lateral trenches, piping networks, and a blower or vacuum pump for gas extraction. They differ significantly from conventional systems, however, in their configuration and philosophy of design and operation. As indicated above, the primary purpose of a bioventing system is to use moving soil gas to transfer oxygen to the subsurface where indigenous organisms can utilize it as an electron acceptor to carry out aerobic metabolism of soil contaminants. As such, bioventing system extraction wells are not placed in the center of the contamination as in conventional SVE systems (Figure 5-1), but on the periphery of the site (Figure 5-2), where low flow rates [4.6 to 23 actual L/s (10 to 50 acfm) versus 46 to 700+ actual L/s (100 to 1,500+ acfm)] for conventional SVE systems) maximize the residence time of vent gas in the soil to enhance in situ biodegradation and minimize contaminant volatilization.

Because it is a biological treatment approach, however, bioventing does require the management of environmental conditions to ensure maintenance of bioactivity at the site. Management of soil moisture and soil nutrient levels to avoid inhibition of microbial respiration within the vadose zone can be accomplished fairly easily, and have been used to optimize contaminant biodegradation at field sites when other variables, e.g., toxicity, do not limit microbial activity (Dupont et al., 1991; Miller et al., 1991).

Oxygen transfer to the subsurface via SVE systems is generally more rapid than oxygen uptake rates observed under field conditions (Dupont et al., 1991; Hinchee et al., 1991). This results in the oxygenation of soil gas to near ambient levels if vent system blowers are operated on a continuous basis. To minimize system operating costs, and more importantly to reduce or even perhaps eliminate off-gas treatment requirements entirely, cyclic or "surge" pumping of vent systems in bioventing operations is recommended. Surge pumping in a bioventing mode entails operating the blower system until soil gas oxygen levels reach near ambient conditions throughout the site being remediated. The system is then shut off for some period of time, during which soil gas

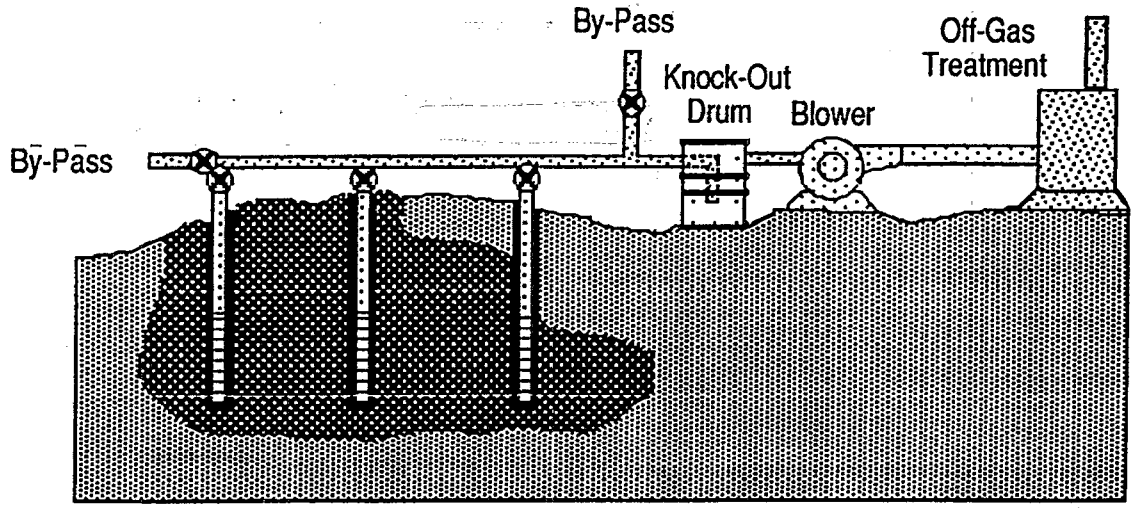


Figure 5-1. Typical SVE system with labeled system components.

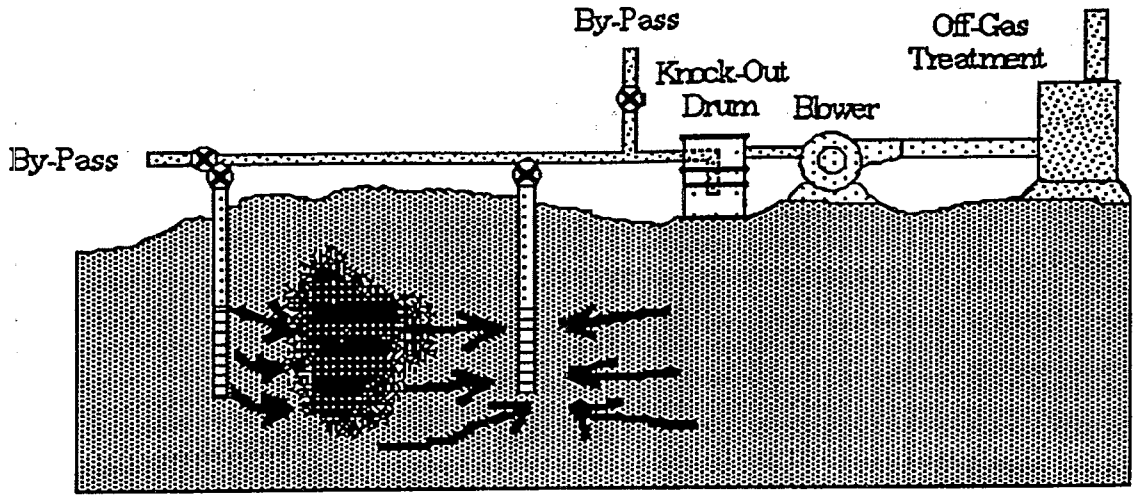


Figure 5-2. Typical bioventing system schematic. Note extraction and injection from the periphery of contamination.

oxygen concentrations would be routinely monitored until they reach a level which inhibits aerobic microbial activity. Once this limiting soil gas concentration is reached, the vent system would be restarted, and the on-off cycle would continue once again. Based on a Henry's Law constant for oxygen, a limitation would be expected to occur at a soil gas concentration of approximately 2.0 vol. percent, corresponding to soil water oxygen concentrations of approximately 1 mg/L. An inhibition of soil respiration has been reported at the 2.0 vol. percent soil oxygen level in venting systems treating JP-4 contaminated soils (Dupont et al., 1991) and in vented soil piles contaminated with PCP waste (McGinnis et al., 1994), suggesting that this value represents a good operating number for field scale applications.

Based on observed field respiration data from various JP-4 jet fuel contaminated sites (Dupont et al., 1991; Hinchee and Ong, 1992; Ong et al., 1994) and bioventing of PCP contaminated soil piles (McGinnis et al., 1994), field oxygen uptake rates of 0.03 to 1.4 vol. percent /hour (0.8 to 39.7 g O_2/m^3 soil-d @ air filled porosity = 40 vol. percent) can be expected. These rates can be nearly an order of magnitude lower as remediation progresses to near de minimis soil hydrocarbon levels (Dupont et al., 1991), allowing typical bioventing systems to be operated on schedules of 8 hours on, 16 hours off at the initiation of remediation, to 8 hours on, 7 days off near the end of the field effort, while still maintaining aerobic conditions within the contaminated soil during non-venting periods. Table 5-2 presents a summary of general design, operational and application considerations appropriate for conventional SVE systems versus those utilized in a bioventing operating mode.

Bioventing System Design

Despite the large number of bioventing systems being implemented in both the public and private sectors for hydrocarbon contaminated soil remediation, there is currently a lack of quantitative design recommendations for their application and performance evaluation. The U.S. Air Force has been a leader in the development and implementation of bioventing systems for remediation of many of their fuel release sites, and they have developed, through the Air Force Center for Environmental Excellence (AFCEE), a field treatability procedure for bioventing system design (Hinchee et al., 1992). In addition, an addendum to this procedure document detailing the integration of soil gas survey results into bioventing system evaluation was published by AFCEE in 1994 (Downey and Hall, 1994). These AFCEE field bioventing procedure documents were written as a guide for the field scale evaluation of the potential application of bioventing for remediation of Air Force sites, and focus heavily on field methods for in situ respiration/degradation rate determinations using procedures adapted from Hinchee and Ong (1992). While the importance of air flow and permeability evaluation is clearly stated, little detail is provided regarding field-scale permeability determinations nor is information provided on the use of tracer tests for improved site assessment and system design.

Table 5-2. General Design and Application Considerations Appropriate for Conventional Versus Biovention SVE Systems.

Parameter	Conventional SVE	Bioventing
Compound type	Volatile at room temperature	Biodegradable
Vapor pressure	>100 mmHg	NA[a]
HC (dimensionless)	>0.01	NA
Aqueous solubility	<100 mg/L	NA
Soil concentration	>1 mg/kg	<1%
Depth to groundwater	>20 ft	NA
Air-phase permeability	>1 x 10^{-4} cm/s	
Subsurface conditions	Little or no stratification	
NAPL phase	Little or none	Biodegradable
General vent well placement	Within contamination	Outside contamination
General injection well placement	Outside contamination	Within contamination
Operating mode	Maximum soil gas exchange rate	Maximum retention time and aerobic conditions
Flow rate	46 to 700+ actual L/s (100 to 1500+ acfm)	4.6 to 23 actual L/s (10 to 50 acfm)
Pore volumes/d	1 to 15	0.1 to 0.5
Optimal soil moisture	≈25% field capacity	≈75% field capacity
Nutrient requirement	NA	C:N:P ≈ 100:10:1[b]
Soil gas O_2 levels	NA	>2 vol.%
Toxicants	NA	Little or none

[a] NA = Not available.

[b] Caution should be used in considering a nutrient requirement as field-scale; bioventing research has shown mixed results in performance with nutrient addition. This ratio represents a maximum theoretical requirement that may or may not be needed at a given site.

The procedure described in this document relies heavily on the methodology as described in the AFCEE procedure, but attempts to improve on it by more completely integrating field bioventing system evaluation and design from the initial site characterization activities through the system design, process monitoring and performance evaluation steps. Schematically this improved bioventing system test procedure is summarized in Figure 5-3, describing the objectives, activities and outcome/interpretation of each of its five phases.

Bioventing System Test Procedure for Treatability Assessment, Design, Process Monitoring and Performance Evaluation

Phase I - Assessment of the Potential for Contaminant Biodegradation Under Field Conditions

This phase is the first step in the evaluation of the potential application of bioventing, or more generally, any biologically based remediation system at a given field site under existing site conditions. To determine the potential for in situ biodegradation of vadose zone contaminants via bioventing, existing soil microbial activity should be quantified during site assessment investigations. This can be readily accomplished through the analysis of soil gas O_2 and CO_2 composition, in addition to the more routinely measured total hydrocarbon concentrations, prior to venting activity at the site. Total petroleum hydrocarbon as well as O_2 and CO_2 concentrations can be measured during standard soil gas surveys using a variety of measurement techniques. While both respiration gases can be easily measured, oxygen concentrations are considered a better indicator of microbial activity in soil systems because there are rarely abiotic sinks for oxygen in these environments. CO_2 is produced through anaerobic as well as aerobic microbial activity and can also be affected by assimilation or dissolution of carbonate rock.

The key to the evaluation of soil bioactivity using these methods is the determination of the extent of O_2 depletion and CO_2 enrichment in soil gas at a site with respect to background, uncontaminated soil levels. It cannot be overemphasized that these determinations must be based on a comparison to uncontaminated soil conditions, as only levels of O_2 depletion and CO_2 enrichment in excess of background are indicative of increased microbial activity compared to normal, basal respiration levels seen in uncontaminated soils at the site. It is also important to note that despite the collection of hydrocarbon concentration data during initial site investigations conducted using soil gas surveys, respiration gas (O_2/CO_2) measurements are rarely made, even though they can be made using the same soil gas probes, and virtually at the same time as hydrocarbon measurements are taken. These respiration gas readings are unequivocal indicators of microbial activity at the site under actual field conditions, and as indicated in Figure 5-3, are critical in evaluating the next step in bioventing feasibility assessment at a given site.

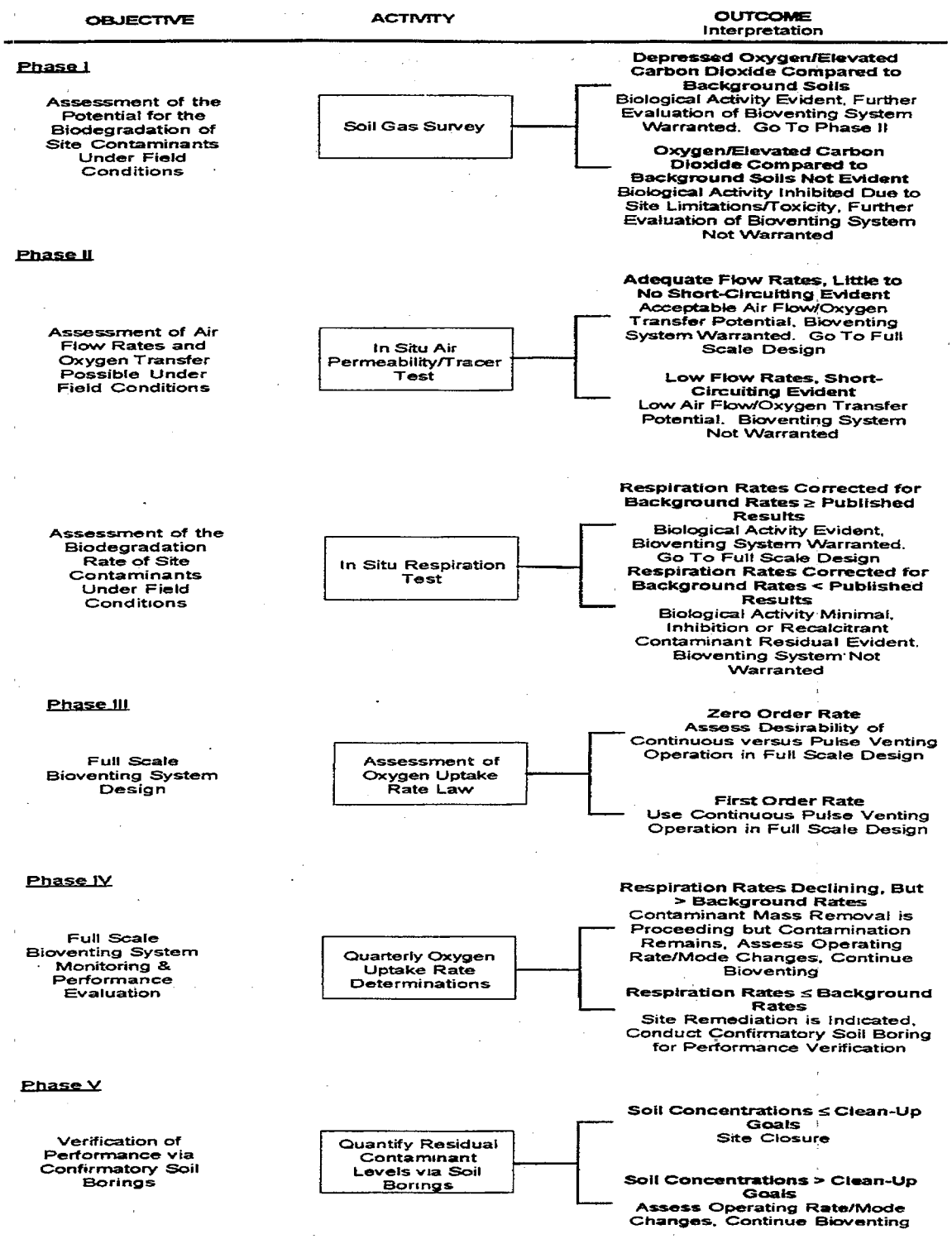


Figure 5-3. Field bioventing system treatability assessment, design, and performance evaluation procedure.

If soil gas organic vapor and soil core data show contamination, but microbial respiration has not yielded O_2 uptake and CO_2 production concentrations above background levels, conditions within the contaminated soil have resulted in soil microbial toxicity and/or severe inhibition, or significant nutrient or moisture limitations exist at the site. Unless soil moisture is the cause of this limitation, bioremediation has limited application, and alternative remediation schemes should be considered.

If soil contamination exists and microbial activity above background levels is evident from soil gas measurements, quantification of maximum respiration rates under field conditions can be carried out utilizing in situ respiration measurement techniques described below. The reader should refer to the addendum to the AFCEE bioventing test procedure by Downey and Hall (1994) for additional examples of soil gas data interpretation related to the feasibility of the application of bioventing for site remediation.

Phase II - Assessment of Air Flow and In Situ Respiration Rates Under Field Conditions

Once biological activity has been verified at the site, quantitation of the rate of air/O_2 supply, as well as the rate of in situ O_2 utilization must be determined. As described above, the remediation of most contaminated sites is limited by the supply of electron acceptor, namely O_2, and rational engineering design of bioventing systems requires a focus on supplying the oxygen needed to meet the in situ O_2 demand.

Air Flow and Tracer Tests

Air flow and tracer tests are first conducted as described in the procedure section entitled "Tracer Tests to Evaluate Air Flow During Soil Vapor Extraction and Bioventing" to provide data regarding the existence of short-circuit pathways, stagnant zones, and general conditions of vapor flow and oxygen transport in the subsurface throughout the site. These data are essential as efficient oxygen supply to the subsurface is key to optimal bioventing system design. Once subsurface air velocities are estimated from these air flow/tracer tests, O_2 transfer rates and transfer efficiencies can be estimated for various points throughout the area of contamination.

As stressed in the air flow/tracer test procedure, data from multiple lateral and vertical points throughout the contaminated soil should be collected to provide information regarding the spatial distribution and heterogeneity of air flow and oxygen transfer throughout a site. A minimum of three radial distances and three vertical locations (a minimum of nine total sampling points) should be used to provide the air flow and permeability data necessary to assess gas transport conditions at a typical site. Potential O_2 transfer rates can be estimated knowing that 1 standard cubic foot/minute (scfm) of air equals 0.21 scfm of O_2 which, from the ideal gas law is equivalent to 7,700 mg O_2/min at 1 atm and 25°C. Table 5-3 provides an estimate of O_2 transfer rates for various soil types under a uniform SVE system operating condition of 30 in H_2O for a 4-in.-diameter extraction well, a radius of influence of 30 ft, and a well slotting of 10 ft,

assuming simple one dimensional, radial flow into the well. Table 5-3 indicates that even in clayey soils where operating flow rates are low, significant O_2 transfer rates (275 mg O_2/min = 396,000 mg O_2/day) are possible in bioventing systems.

Table 5-3. Potential Oxygen Transfer Rates in Various Soils.

Soil Type	Air Flow Rate (scfm)	Oxygen Transfer Rate (mg O_2/min)
Medium sand	35.6	275,000
Fine sand	3.56	27,500
Silty sand	0.36	2,750
Clayey sand	0.04	275

These potential O_2 transfer rates as calculated from the air flow/tracer data and subsequent air velocity/flow rate determinations, are representative of actual field conditions, and are directly indicative of system performance that can be expected under full-scale conditions. The final data necessary in this phase of the bioventing treatability assessment is for the in situ oxygen demand, or in situ oxygen respiration rate produced by the site microbial population in the degradation of contaminants found there.

In Situ Respiration Tests

In situ respiration tests are conducted following the air flow/tracer tests to quantify the rate of oxygen demand expressed under actual field limiting conditions. In order to expedite and minimize efforts and cost of bioventing treatability assessment and design, the in situ respiration tests are recommended to be coupled to the air/flow tracer test efforts. Using this approach, in situ respiration tests would be initiated following completion of the air permeability/tracer tests when the entire area of influence of the permeability/tracer test extraction well is oxygenated. In this way, all tracer injection and soil gas monitoring points installed as part of the air permeability/tracer test can be utilized for soil respiration rate determinations. Use of these identical monitoring points provides air flow and respiration data that correspond directly to one another and laterally and vertically distributed data necessary to ascertain the spatial variability and distribution of microbial activity throughout the site. Finally, the background, uncontaminated site location used as a baseline for the soil gas survey should also be incorporated into the in situ respiration test effort. This allows for a quantitative determination of the significance of measured respiration rates within the contaminated area with respect to background oxygen uptake rates in uncontaminated soil. It also requires that the background point be oxygenated separately via air injection for a 16- to 24-hour period if it does not fall within the area of influence of the air permeability/tracer test extraction well.

With the entire flow field oxygenated, the in situ respiration test is initiated by first stopping air flow to the contaminated soil (as would be done at the completion of the air

flow/tracer test), followed by the measurement of O_2 uptake and CO_2 production at the soil gas probes over time. Typical soil gas respiration data are shown in Figure 5-4. Selection of an appropriate sampling interval should be flexible based on actual site conditions, and should be adjusted based on initial readings collected at 3- to 4-hour intervals following blower shutdown, to an interval of 6 to 48 hours from Day 2 to the end of the test. With this as a guide, a typical respiration gas sample collection schedule would be as follows: Day 1 - 0, 3, 6, 12, 18, and 24 hours; Day 2 - 30 and 42 hours; Day 3 - 56 and 68 hours; Day 4 - 80 hours; Day 5 - 104 hours; Day 6 - 128 hours; Day 8 - 176 hours; and Day 10 - 224 hours.

Respiration Data Reduction. Respiration data reduction is carried out using either a zero or first order reaction rate model to generate either zero or first order respiration rate values (vol. percent/hour or 1/hour, respectively) from the slope of these linear regression relationships. A zero order reaction is described as one in which the change in the dependent variable (in our case respiration gases) over time is independent of the variable's concentration. This independence of the removal rate is mathematically described as follows:

$$dC/dt = -k_o \qquad (5\text{-}2)$$

yielding the integrated form:

$$C - C_o = -k_{ot} \qquad (5\text{-}3)$$

where C = concentration of the dependent variable a time t, mg/L or vol. percent
C_o = initial concentration of the dependent variable a time t = 0, mg/L or vol. percent
k_o = zero order reaction rate constant, mg/L or vol. percent/time

This relationship is linear when plotted as measured respiration gas concentration versus time as indicated in Figure 5-5, the slope of which is k_o.

A first-order reaction is described as one in which the change in the dependent variable (in our case respiration gases) over time is directly related to the variable's concentration. This dependence of the removal rate is mathematically described as follows:

$$dC/dt = -k_1C \qquad (5\text{-}4)$$

yielding the integrated form:

$$\ln(C) - \ln(C_o) = -k_1t \qquad (5\text{-}5)$$

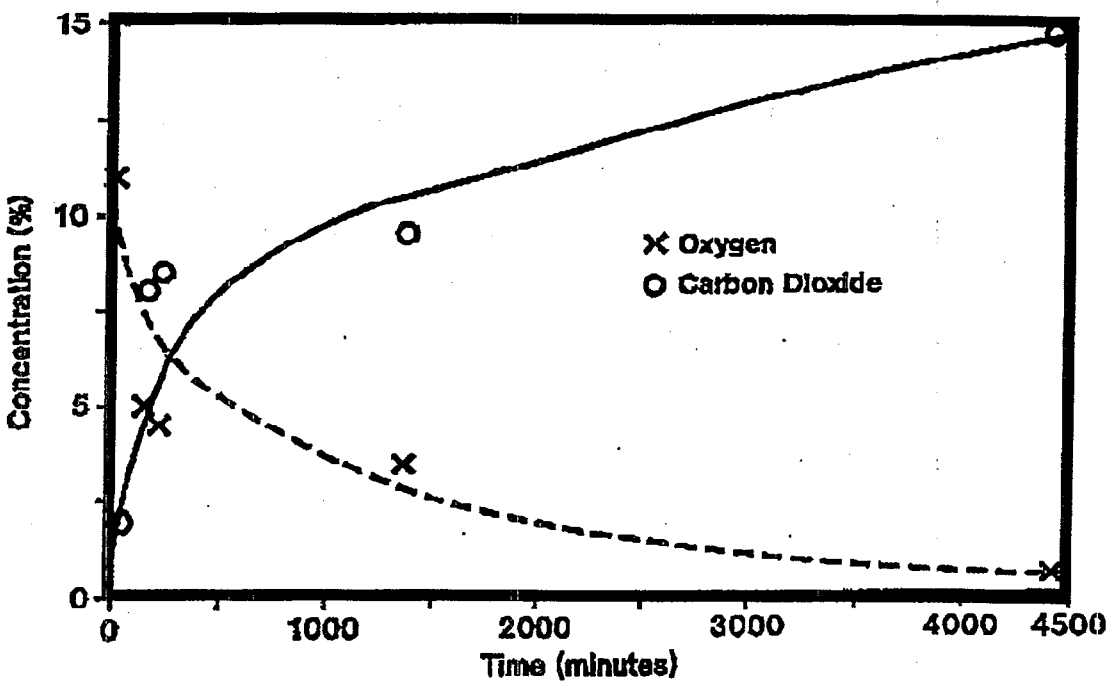


Figure 5-4. Typical soil respiration gas data collected during field in situ respiration test.

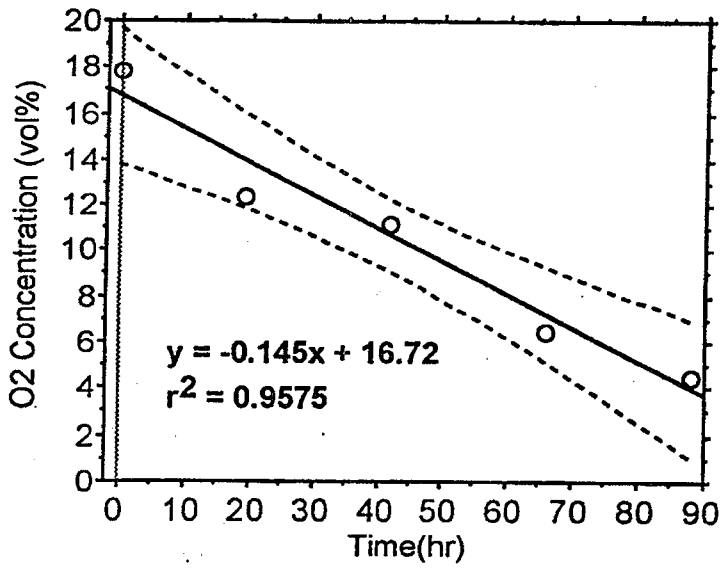


Figure 5-5. Typical zero order soil respiration gas data collected during field in situ respiration test. Zero order respiration rate = -0.145 vol%/hour.

where k_1 = the first order reaction rate constant, 1/time. This relationship is non-linear when the measured respiration gas concentration is plotted versus time as indicated in Figure 5-4, but can be linearized by plotting the natural log transformed gas concentration versus time as indicated in Figure 5-6.

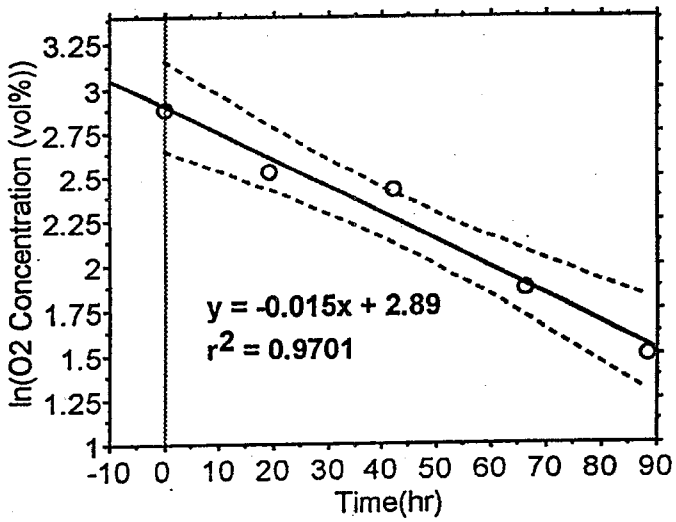


Figure 5-6. Typical first order soil respiration gas data collected during field in situ respiration test. First order respiration rate = -0.015/hour.

These regression relationships are generated from linear least-squares analysis of the field respiration data. The least-squares regression calculations can be carried out using standard statistical packages available on microcomputers and many hand held calculators. The regression analyses and plots presented in Figures 5-5 and 5-6 were generated using StatViewII on a Macintosh computer. These figures show the measured data, the regression line of best fit, the 95 percent confidence bands (dotted curves) of the slope of the best fit regression line for the data, the resultant linear regression equation, and the r_2 value for the relationship. Quantification of the observed respiration reactions using this statistical approach provides a quantitative description of microbial activity observed at each monitoring point, and allows the quantitative comparison of respiration rates spatially at a given point in time, and temporally at a given location in the contaminated site. These comparisons can be made using data shown in Figure 5-7, generated from regression analyses, that include: the F-test and t-test statistics, the p value or probability of a significant regression, and the confidence interval of the slope of the regression relationship.

The first question that must be answered regarding the regression data should be whether the relationship is significant, i.e., whether the measured oxygen uptake rate is significantly greater than zero using a zero or first order regression model. If the slope

Simple Regression X_1 : Time(hr) Y_1: O2 Concentration (vol%)

Count:	R:	R-squared:	Adj. R-squared:	RMS Residual:
5	.9785	.9575	.9434	1.2443

Analysis of Variance Table

Source	DF:	Sum Squares:	Mean Square:	F-test:
REGRESSION	1	104.7431	104.7431	67.6497
RESIDUAL	3	4.6449	1.5483	p = .0038
TOTAL	4	109.388		

No Residual Statistics Computed

Simple Regression X_1 : Time(hr) Y_1: O2 Concentration (vol%)

Beta Coefficient Table

Variable:	Coefficient:	Std. Err.:	Std. Coeff.:	t-Value:	Probability:
INTERCEPT	16.7158				
SLOPE	-.145	.0176	-.9785	8.2249	.0038

Confidence Intervals Table

Variable:	95% Lower:	95% Upper:	90% Lower:	90% Upper:
MEAN (X,Y)	8.7091	12.2509	9.1704	11.7896
SLOPE	-.2011	-.0889	-.1865	-.1035

Figure 5-7. Typical regression results for linear regression analysis of field respiration data for bioventing system.

of the regression line is statistically greater than zero, the p value of the regression will be less than 0.05, and the 95 percent confidence intervals will not include 0. As shown in Figure 5-7, with a p value of 0.0038, the slope of this regression is significantly different from zero, and is represented by a mean zero order oxygen uptake rate of -0.145 vol. percent/hour with a 95 percent confidence interval of the slope (the range of the zero order oxygen uptake rate described by the data accurate within 5 percent of the true value) of -0.089 to -0.201 vol. percent/hour.

Once the respiration rates are evaluated for statistical significance, background soil respiration rate values should be used to correct contaminated soil values for basal soil respiration taking place at the site. An inert gas tracer may be injected during soil aeration so that respiration rate measurements can also be corrected for diffusion of O_2 away from and CO_2 diffusion to the sampling probe during respiration rate determinations (Hinchee and Ong, 1992). However, the determination of background respiration rates in uncontaminated soils accounts for both physical diffusion, as well as biological reaction mechanisms, and tracer use during respiration rate determinations at any time other than immediately following air flow/tracer tests is not necessary. If background respiration rates are significantly greater than zero, they should be subtracted from respiration rates determined at locations throughout the contaminated to yield background-corrected respiration rates. If background rates are not significantly different from zero, no correction to rates measured in the contaminated soil is necessary.

Finally, background-corrected respiration rates can be compared to rates published in the literature for field scale bioventing systems to assess the relative biological activity measured at the field site. Table 5-4 summarizes reported treatability test and field demonstration respiration rate data from various sources that can be used for this comparison. If background-corrected field respiration rates compare favorably with these reported data, significant biological activity is evident, and full-scale bioventing system design and implementation is warranted. If background-corrected field respiration rates are significantly lower (based on 95 percent confidence interval values) than these reported data, less than optimal conditions are evident due to moisture or nutrient limitations, and/or the presence of inhibitory materials, and the application of a bioventing system may not be practical at this field site.

Consideration should then be given for the use of a laboratory treatability study to attempt to identify the cause of this limited microbial activity, or an alternative, nonbiological remediation scheme should be evaluated for use at the site.

Determination of the Governing Rate Law. Determination of the governing rate law can be made by investigating the nature of the regression residuals generated during the regression analysis. A residual is defined as the difference between the actual data point and the value of the dependent variable on the regression line, and can have

Table 5-4. Example Treatability Study and Full-Scale Bioventing System Respiration Rates Reported From Various Sources.

Site Location	Oxygen Utilization Rate (vol. %/day)	Temperature (°C)	Source of Data[a]	Reference
Alaska	13.2	4 to 5	Treat.	Ong et al. (1994)
	6.9 ± 0.0	16	Treat.	Ong et al. (1994)
	4.2± 2.6	8	Treat.	Ong et al. (1994)
	7.7	4 to 5	Field	Ong et al. (1994)
Florida	10 ± 0.5	25	Treat.	Hinchee et al. (1992)
Maryland	3.0 ± 0.2	21	Treat.	Hinchee et al. (1992)
Nevada	6.0 ± 0.2	21	Treat.	Hinchee et al. (1992)
Oklahoma	4.0 ± 0.5	17	Treat.	Hinchee et al. (1992)
Utah[b]	0.19 to 7.7	15	Field	Dupont et al. (1991)
	0.10 to 3.6	15	Field (+H_2O)	Dupont et al. (1991)
	0.06 to 1.3	15	Field (+Nutr.)	Dupont et al. (1991)
	0.0 to 0.02	15	Field (Back.)	Dupont et al. (1991)

[a] Treat. = field in situ respiration treatability test results; Field = field bioventing system performance data; +H_2O = with moisture addition; +Nutr.) = with inorganic nutrient addition, and Back. = background soil respiration rates.

[b] These data were described by first-order relationships, with values in the table representing maximum rate values calculated from K_1 x 21 vol. percent.

either a positive or negative value. A standardized residual is the residual divided by the value of the dependent variable at the point where the residual is calculated. If a given rate expression describes a data set, not only should the p value be less than 0.05, and the 95 percent confidence of the regression slope not include 0, but the standardized residuals should also be randomly distributed over the range of the independent variable used in the regression. If a pattern is observed in the standardized residuals plot, the assumption that a particular linear model fits the data is not valid, and an alternative model should be selected for use to describe the data. If the residuals' plots for a number of models are similar, showing no particular pattern, as a matter of practice, the simpler model form is selected.

Figure 5-8 shows the zero order linear regression for a set of hypothetical in situ respiration rate data, indicating that the regression coefficient is high (0.8964), and the p value is well below the 0.05 criteria point. The residual plot for this data set, shown in Figure 5-9, clearly indicates that the linear model is not an adequate descriptor of these data, due to the obvious pattern of the residual values. The first order model, shown in Figure 5-10, is much improved, particularly when one inspects the residuals plot for this set of data as shown in Figure 5-11. Based on these results, a first order oxygen uptake rate of -0.01/hour would be reported for these data.

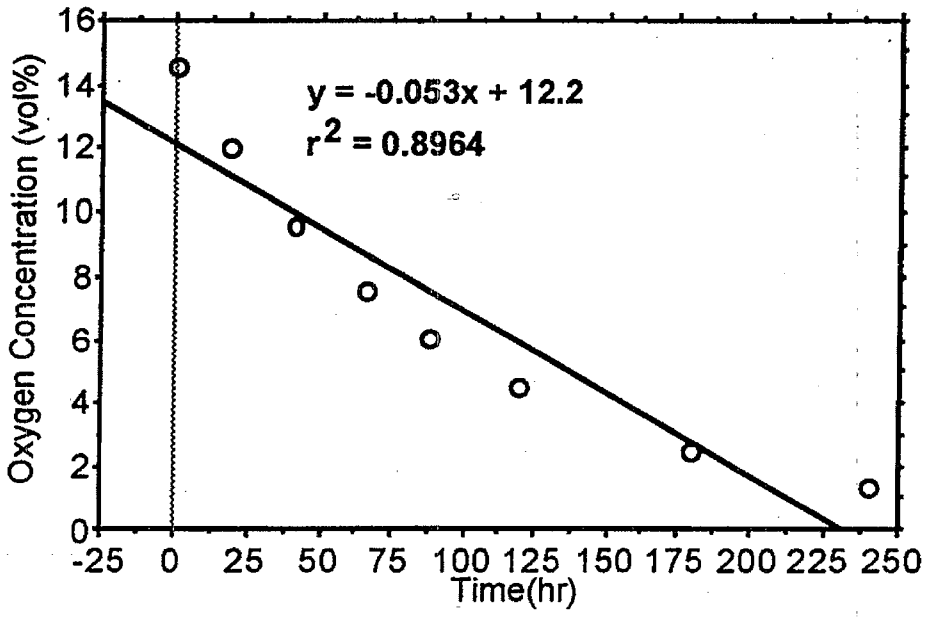
Hydrocarbon Rate Determinations. Hydrocarbon rate determinations can be made using field determined in situ respiration data assuming the 3.5:1 O_2:hydrocarbon mass stoichiometry presented in Equation 5-1, and from known or estimated properties of the site soil using the following expression:

$$\text{Hydrocarbon degradation rate } (mg/kg\ soil\text{-}d) = \frac{10\ k_o}{3.5}\ \frac{\Theta_A}{BD}\ \frac{P\ (32)}{(0.08205)\ (273 + T)} \qquad (5\text{-}6)$$

where qa = air filled porosity, unit less
BD = soil bulk density, kg/L soil
P = pressure, atm
T = temperature, °C

Assuming average values for these parameters of: qa = 0.3, BD = 1.4 kg/L soil, P = 1 atm, and for a temperature = 25°C, the following relationship between measured zero order degradation rates and equivalent hydrocarbon removal rates can be developed:

$$\text{Hydrocarbon degradation rate } (mg/kg\ soil\text{-}d) = \frac{10\ k_o}{3.5}\ \frac{(0.3)}{(1.4)}\ \frac{1\ (32)}{(0.08205)\ (298)} = 0.8k_o \qquad (5\text{-}7)$$



Simple Regression X_1: Time(hr) Y_1: Oxygen Concentration (vol%)

Count:	R:	R-squared:	Adj. R-squared:	RMS Residual:
8	.9468	.8964	.8792	1.6019

Analysis of Variance Table

Source	DF:	Sum Squares:	Mean Square:	F-test:
REGRESSION	1	133.2526	133.2526	51.931
RESIDUAL	6	15.3957	2.566	p = .0004
TOTAL	7	148.6484		

No Residual Statistics Computed

Figure 5-8. Zero order linear regression results for a set of hypothetical in situ respiration rate data.

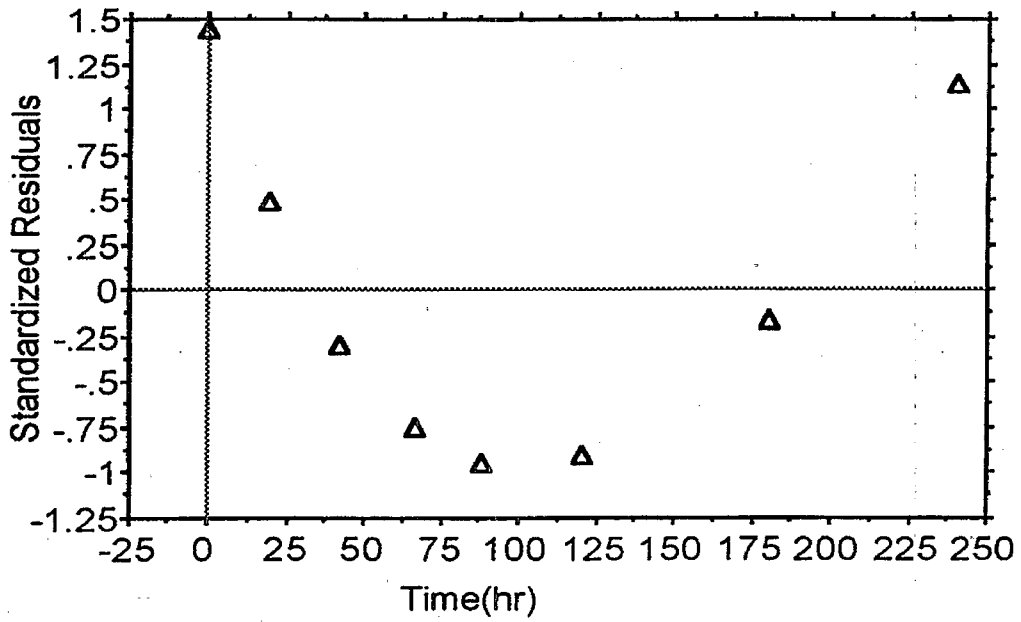


Figure 5-9. Residuals plot for zero order linear regression results for the set of hypothetical in situ respiration rate data.

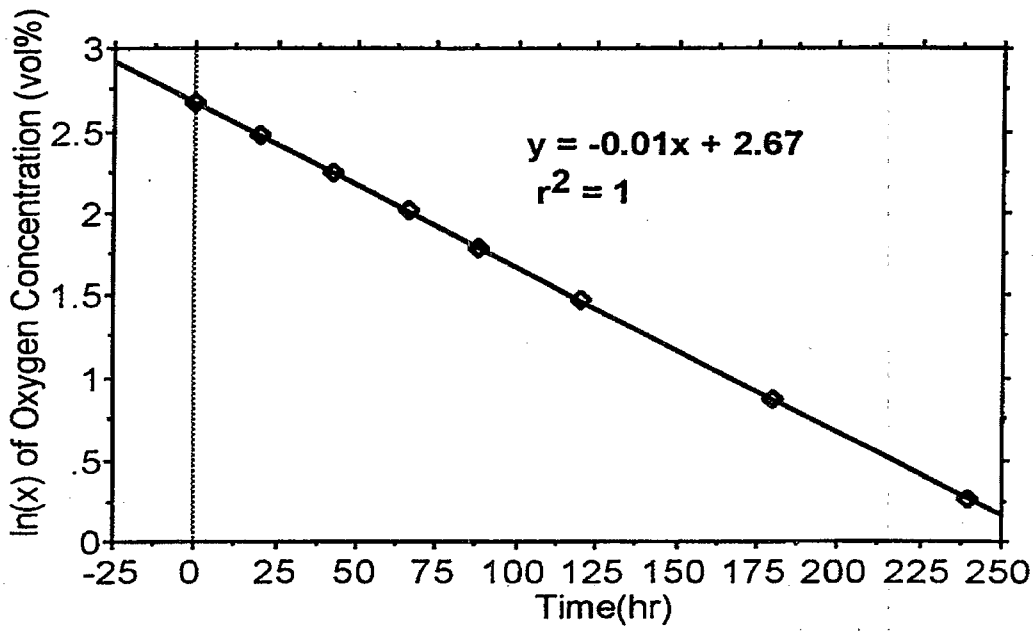


Figure 5-10. First order linear regression results for a set of hypothetical in situ respiration rate data.

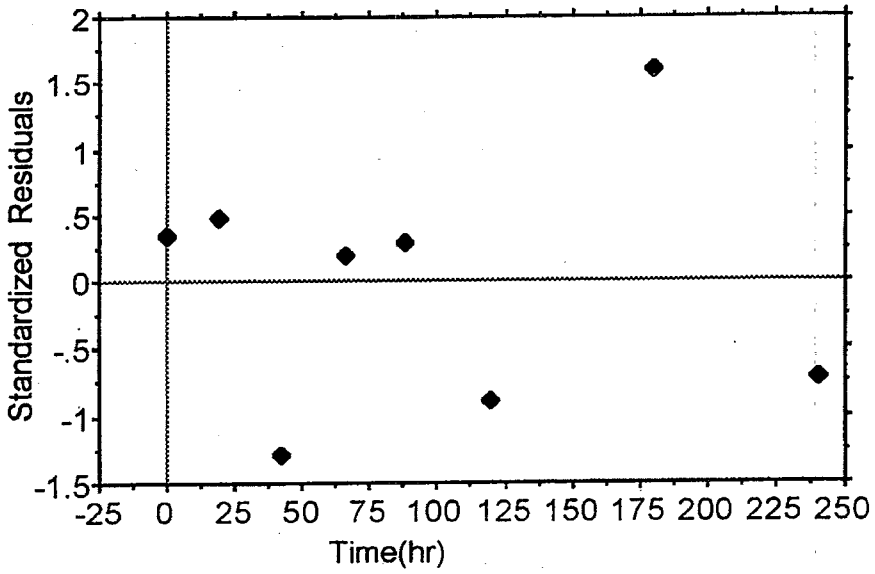


Figure 5-11. Residuals plot for first order linear regression results for the set of hypothetical in situ respiration rate data.

As indicated earlier in Table 5-4, these calculations can be made for sites where first order oxygen utilization rates are observed by multiplying the first order rate (1/time) by the concentration of oxygen occurring within the soil at the site (typically 21 vol. percent) to yield an equivalent oxygen utilization rate with units identical to that of k_o. The oxygen utilization rate, however, changes directly with oxygen concentration if removal follows a first order relationship, so predicted hydrocarbon degradation rates will be dependent on oxygen concentrations maintained within the contaminated site under these conditions.

Remediation Time. Remediation time can be estimated from these hydrocarbon degradation rates knowing the initial concentration of contaminant existing at the site. Respiration rates decrease linearly with decreasing contaminant concentrations below approximately 3,000 mg/kg total petroleum hydrocarbons (TPH) (Ravipaty, 1994), so the time for site remediation provided by Equation 5-8 is the minimum time to site clean-up. The actual time to reach soil closure levels will likely be two to three times longer. Equation 5-8 provides an initial estimate of "best-case" time for preliminary evaluation of the feasibility of a bioventing system applied at a given site.

$$\textit{Minimal Time to Remediation} = \frac{(\textit{Soil Contamination, mg/kg TPH})}{(\textit{Hydrocarbon Degradation Rate, mg/kg soil-d})} \qquad (5\text{-}8)$$

$$\text{Expected Time to Remediation} \approx 2 \text{ to } 3 \times (\text{Minimal Time to Remediation}) \qquad (5\text{-}9)$$

Phase III - Bioventing System Design - Interpretation of Utilization Rate

Once in situ oxygen respiration rate values have been estimated, corrected for background respiration at the site, and determined to reflect biological activity that warrants application of a bioventing system at the site, full-scale system design should be carried out. Review of detailed bioventing system design procedures is outside the scope of this document; however, the application of system design to air flow/tracer test and in situ respiration test results presented above will be highlighted.

Air Flow Considerations

Air flow considerations are critical to optimal bioventing system design, as it is imperative that the full-scale system effectively deliver the required oxygen to the locations and at a rate needed to maintain optimal aerobic activity, while minimizing air flow to reduce or even eliminate volatile emissions from the site. The air flow rates that must be maintained can be determined directly from oxygen uptake rate measurements described in "In Situ Respiration Tests." This requires careful consideration of tracer test/air permeability test results, so that design components can be incorporated into the full-scale system and overcome air flow limitations due to dead zones, low permeability lenses, short-circuit pathways, etc., which limit vapor flow rates through the zone of contamination. These design components may include: passive/ active injection wells strategically placed to minimize dead zones, multiple air injection/ extraction wells used to treat distinct soil layers existing at the site, etc. The reader is referred to the section of this document entitled "Procedures for Conducting Tracer Tests to Evaluate Air Flow During Soil Vapor Extraction and Bioventing" for further details regarding the conduct of tracer tests and test data interpretation.

System Operating Conditions for Full-Scale Design

System operating conditions for full-scale design are determined in large part by the governing rate law for oxygen utilization observed throughout the field site. As indicated above, if the oxygen uptake data are governed by a zero order rate law, oxygen utilization, and concomitant contaminant degradation rates are independent of soil gas oxygen concentrations until oxygen limitations ($\approx$ 2 vol. percent oxygen) occur. From a practical standpoint this means that a constant inflow of oxygen to the subsurface is not required to maintain optimal oxygen uptake rates. Under these conditions, a pulse pumping system is possible where a blower would be operated for short periods of time for soil oxygenation, followed by longer periods with no air flow during which time soil "incubation" and contaminant removal takes place without air movement and possible air emissions. This pulsed system could take advantage of existing schedules of facility operations and maintenance personnel or existing blower equipment, or might provide a cost effective approach for satisfying stringent requirements on mass emission rates, limitations on operating hours due to noise considerations, etc. Regardless, zero order uptake rates allow a much wider range of operating modes than does a system exhibiting first order in situ oxygen uptake rates.

Field systems governed by first order oxygen uptake relationships offer no flexibility in their operating mode. Performance of these systems is enhanced with increased soil oxygen concentrations, and they must be operated in a continuous mode to maximize removal of contaminants. One option that is currently being assessed by the U.S. Air Force to maximize contaminant removal, while still minimizing vapor emissions in first order rate dominated sites, is the use of pure oxygen in place of atmospheric air as the gaseous oxygen source. While this option has increased costs associated with pure oxygen generation, a reduction in air flows by a factor of approximately five significantly reduces air emissions, and reduces many overall system costs associated with these reduced flow rates. The overall cost effectiveness of these pure oxygen systems has yet to be proven, but may be the only way to significantly enhance bioventing systems whose performance is found to be sensitive to soil gas oxygen levels.

Phase IV - System Monitoring and Performance Evaluation

Routine system monitoring is essential to the optimal operation and control of a field-scale bioventing system. The SVE well and vapor monitoring probes installed for conducting the initial air flow/permeability and in situ respiration testing should be incorporated into the full-scale field system as much as is practical. Additional wells should be placed as described above to overcome air flow limitations evident from tracer test results. In addition, multi-level vapor probes should be added as necessary to provide a representative, three dimensional picture of contamination existing at the site prior to initiation of the full-scale system. The logical places for these monitoring points are at the locations from which soil core samples are collected for initial contaminant quantitation. Multi-level, nested probes, such as those described in the AFCEE procedure by Hinchee et al. (1992), minimize the effort and expense of probe placement, as well as field sample collection and analyses, by utilizing common bore holes for multiple vapor probe depths, and should be considered strongly for use at new bioventing field sites. As a rule of thumb, a minimum of nine vapor monitoring points (three spatial, radial locations at three depths each) should be installed per SVE well to provide the data necessary to adequately monitor vapor flow, respiration and contaminant removal within a field site. The reader is referred to the "Procedure for Conducting Tracer Tests to Evaluate Air Flow During Soil Vapor Extraction and Bioventing" for additional discussion related to vapor probe design and placement.

Following complete bioventing field system installation, the soil vapor probes should be monitored daily to verify that the specified system design and operating mode is providing air flow to the site that was anticipated. System operating flow configuration and/or flow rate changes may be necessary to adapt the bioventing system to actual full-scale conditions encountered at the field site. This "shake-down" period is expected to last one to two weeks, with operation after that time being fairly stable, requiring only minimal adjustment and maintenance. It is recommended that routine system monitoring be conducted monthly for the first six months of operation, and then quarterly

thereafter, to verify proper system operation and allow system "fine-tuning" as remediation takes place throughout the site.

Routine system monitoring should include, at a minimum, the following parameters: system flow rate (preferably flow rate to each injection/extraction well in the system); extraction system gas characteristics (O_2/CO_2, TPH, temperature, relative humidity, vacuum) if an air extraction system is utilized; soil gas monitoring point characteristics (O_2/CO_2, TPH, temperature, relative humidity, vacuum/pressure); and blower vacuum/pressure.

In addition to the collection of routine system monitoring data to ensure system operating effectiveness, quarterly to semi-annual system shut-down tests should be conducted to assess the progress of remediation taking place throughout the site. These shutdown tests are conducted in a manner identical to those described in "In Situ Respiration Tests" in which the air injection/extraction system is shut off and oxygen uptake is allowed to proceed without oxygen replacement. As was done with the Phase II in situ respiration data, data collected from these routine shut-down tests are statistically evaluated for their significance. Comparisons of overlapping confidence intervals of the slope of the oxygen uptake relationships, measured at given sampling locations but at previous time periods, are made to evaluate whether a significant reduction in respiration rates is occurring (inference that a significant reduction in contaminant levels is occurring as well). In addition, contaminated site respiration rate confidence intervals are compared to background respiration rates to determine if microbial activity at the site is reaching background activity, suggesting that clean-up levels are being reached at the site.

Respiration rates can decrease due to limited nutrient availability, and/or low soil water contents (< 25 percent field capacity) in addition to reduced soil hydrocarbon levels. With on-going soil vapor relative humidity measurement, soil drying should be evident over time. Drying is minimized in bioventing systems due to low air flow movement through the soil, but if it becomes an obvious limitation to system performance, controlled surface irrigation in coarse grained soils, or injection of water saturated vapor into fine grained soils, can aid in modifying soil water content to acceptable levels for improved microbial activity. Nutrient limitation is a more difficult matter, as nutrient supply and profusion into soils is limited by the high sorptive capacity of soils for typical inorganic nutrients used in remediation systems. Evidence from field scale bioventing systems treating fuel contaminated soils is available which indicates that nutrient addition in the field does little to nothing to improve the performance of these systems (Dupont et al., 1991; Miller 1991), and nutrient limitation should not be considered a major cause of significant respiration rate reductions observed at a field site.

The primary cause of significant decreases found in in situ respiration rates, if soil water is not limiting, is a significant reduction in degradable contaminant concentrations in the

soil. This respiration rate/contaminant concentration relationship has been suggested from field data, and is well documented in the wastewater literature, but has only been verified recently in laboratory-scale microcosm studies conducted at Utah State University (Ravipaty, 1994). Some of the results of this work for JP-4 contaminated soil from Hill AFB, Utah is presented in Figure 5-12 for 10 JP-4 concentrations levels from 0 to 10,000 ppm, and at two soil water contents of 50 and 75 percent field capacity.

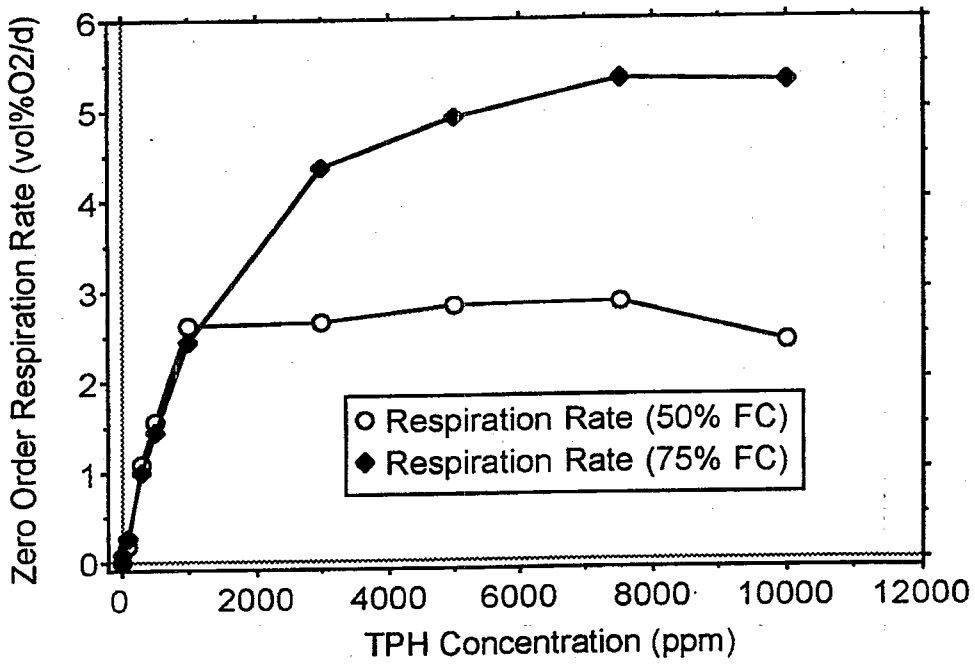


Figure 5-12. Respiration rate/contaminant concentration relationships generated in laboratory-scale microcosm studies conducted with JP-4 contaminated soil from Hill AFB, Utah (from Ravipaty, 1994).

As indicated in Figure 5-12, respiration rate appears to vary linearly with contaminant concentration to a soil level of approximately 1,000 ppm TPH, beyond which respiration rate reaches a pseudo steady-state value. The actual steady-state value reached varies with soil moisture content. This variance with soil water content is postulated to be related to an increased mass of contaminant available to the soil organisms due to an increase in the volume of the soil water compartment as soil water content increases. However, more critical to the use of field determined respiration rates for the evaluation of the progress of remediation is the fact that respiration rate approaches zero as a function of soil contaminant level independent of soil water conditions at which this respiration is taking place. This makes the use of declining respiration rates,

particularly as they approach zero, or background respiration rate levels, a powerful indicator of the extent to which contaminant mass removal is taking place at the site.

With this being the case, the possible outcomes of this phase of the bioventing procedure are as follows: 1) respiration rates are shown to remain statistically greater than background respiration rate levels and within the range reported in the literature (Table 5-4), contaminant concentrations remain high (> 2,000 ppm TPH) and bioventing should continue; 2) respiration rates are shown to be greater than background levels but are decreasing over time, contaminant mass removal is continuing, contaminant concentrations in the soil are approaching ≈ 1,000 ppm TPH, and bioventing should continue; and 3) respiration rates are shown to be equal to background levels, contaminant removal and site remediation are indicated, and confirmatory soil borings (Phase V) should be collected to verify that remedial soil concentration goals have been met.

Phase V - Verification of System Performance

The final step in the bioventing test procedure, that of verification of bioventing system performance using confirmatory soil core results, is reached through a positive outcome from Phase IV described above. Again, if respiration throughout the site approaches or is statistically equivalent to background levels, low residual contaminant levels are indicated and verification of this result should be provided from soil concentration values. Soil core samples should be collected in a manner identical to that used in preliminary site assessment activities to allow direct comparison of results between sampling time intervals. In addition, due to the large variability inherent in soil sampling and contaminant distribution, confirmatory samples should be collected as close as possible to the locations of the original soil cores, if valid comparisons of contaminant levels are to be made over time.

If contaminant mass removal has occurred, and low respiration rate results are indicative of low residual contaminant concentrations, these confirmatory soil core results should show low levels of both volatile and semivolatile constituents remaining at the site. If measured soil concentrations are below regulated site soil clean-up levels, the site would be considered for a closure action, and the bioventing system would no longer have to operate at this site. If soil concentrations remain above regulatory action levels, the rate and mode of operation of the bioventing system should be evaluated, and system modifications should be made to enhance the removal of remaining contaminant so that closure can be accomplished in the future. In the latter case a modified bioventing system would go back into operation, and respiration rates during shutdown periods would continue to be monitored on a quarterly basis until once again background oxygen uptake rates are observed, initiating the collection of a new round of confirmatory soil core samples.

Summary and Conclusions

The bioventing test procedure presented in this document details an approach to the site specific determination of the feasibility of bioventing technology that is integrated with system monitoring and performance evaluation from initial site assessment activities through final confirmatory soil core analyses. The procedure is composed of five phases of activity which include the following:

Assessment of the Potential for Contaminant Biodegradation Under Actual Field Conditions

In this first phase of the procedure respiration gas (O_2/CO_2) characterization is incorporated into conventional soil gas survey activities to detect the magnitude and extent of biological activity, and consequently, oxygen depletion/carbon dioxide enrichment of the soil gas at the site. If bioactivity is evident from soil gas survey results, the next phase of the procedure is carried out.

Assessment of Air Flow and In Situ Respiration Rates Under Actual Field Conditions

With biodegradation evident at the field site, air flow/air permeability distribution and actual oxygen uptake rates must then be determined. The test procedure describes a combined air flow/tracer-in situ respiration test procedure that takes advantage of monitoring probes and subsurface oxygenation provided during the air flow test for collecting site wide respiration data. Procedures are described to reduce the respiration data to generate respiration rates and to assess their statistical significance relative to site background respiration rate levels. Finally, procedures for converting respiration rates into equivalent hydrocarbon degradation rates are provided, along with estimation procedures for the time to site remediation.

Bioventing System Design

Based on air flow and in situ respiration rate results from Phase II, the potential oxygen supply rate (air flow) is matched with the oxygen demand rate (in situ respiration rates) in rational bioventing system design. The nature of the respiration rate law observed from Phase II results are used to recommend either a pulse operating mode system (zero order reactions) or continuous mode system (first order reactions) to optimize overall system performance.

Full-scale System Monitoring and Performance Evaluation

The procedure describes the use of routine shutdown tests to monitor the changes taking place in respiration rates over time as contaminants are removed from the site. These respiration rates are statistically compared to background respiration levels so that when only background activity is detected throughout the site, soil core samples may be taken to confirm system performance.

System Performance Verification

The final phase of the procedure describes the use of soil core samples, collected from locations near those used for initial site characterization based on quarterly in situ respiration results, as the ultimate proof that soil remediation has proceeded to the point where site closure is possible.

With the use of this integrated approach to site assessment, bioventing system design, and system performance monitoring and evaluation, an optimal design for site remediation using this innovative bioremediation technology can be possible. The key to this optimal design, however, is the collection and interpretation of system performance and bioactivity data from the initial site assessment stages to the completion of a project so that the flexibility and economy of this air based bioremediation system can be taken advantage of on an on-going basis as the "bioreactor," represented as the contaminated site soil, evolves and system operating demands change during the course of site remediation.

Calibration of Field Instrumentation for Hydrocarbon and Oxygen/Carbon Dioxide Determinations - Electronic Detection Instruments

Field Preparation Activities

1. Visually inspect meters for damage before field sampling event. Check air or liquid filters (clean or replace if necessary) as appropriate and check battery condition.

2. Calibrate meters in laboratory before field sampling event using procedures below. Replace O_2 sensor or return instruments to manufacturer for repair if instruments will not calibrate. Collect equipment and recording sheets as required.

Hydrocarbon Meter

(While the specific meter utilized at a given site will vary, the procedures outlined below are representative of those necessary to ensure that accurate, representative and reproducible data are collected from a field effort. Refer to the Owner's Manual for details of operation and calibration specific for the instrument being used.)

1. Turn the meter on and allow to warm up for 5 minutes.

2. Adjust the meter to read 0 while sampling atmospheric air using the external zero knob.

3. Calibrate the meter using hexane calibration gas (a concentration above the maximum expected field concentration should be used).

a. Fill a Tedlar bag with calibration gas. Purge and refill.
b. Attach the Tedlar bag to the meter and adjust the meter to read the calibration gas concentration using the internal span adjustment.

4. Check the zero while sampling atmospheric air. Adjust if necessary.

5. Check the calibration following Step 3 above. Adjust if necessary.

6. A calibration check should be done a minimum of three times daily.

7. Record initial and continuing calibration readings on a calibration data sheet (see Figure 5-13 for sample format).

O_2/CO_2 Meter

(While the specific meter utilized at a given site will vary, the procedures outlined below are representative of those necessary to ensure accurate, representative and reproducible data are collected from a field effort. Refer to the Owner's Manual for details of operation and calibration specific for the instrument being used.)

CO_2 Calibration

1. Turn the meter on and allow to warm up for 5 minutes.

2. Adjust the meter to read 0.05 percent while sampling atmospheric air. Use the CO_2 zero knob to adjust.

3. Calibrate the meter using calibration gas (15.0 percent CO_2 typically used).

   a. Fill a Tedlar bag with calibration gas. Purge and refill.
   b. Attach the Tedlar bag to the meter and adjust the meter to read the calibration gas concentration using the appropriate span adjustment.

4. Check the atmospheric air reading. Adjust if necessary.

5. Recheck the calibration following Step 3 above. Adjust if necessary.

6. Check the calibration using a calibration check gas of a different concentration (5.00 percent CO_2 typically used). Recalibrate using the calibration gas if the calibration check is off by more than ±15 percent of the known concentration.

Initial Calibration Date: _____

Time	Vapor/Gas	Calibration Concentration	Measured Concentration	Instrument Number

Calibration Check

Time	Vapor/Gas	Calibration Concentration	Measured Concentration	Instrument Number

Figure 5-13. Sample initial and continuing calibration data record sheets for hydrocarbon and respiration gas measurement instruments.

7. A calibration check should be done a minimum of three times daily.

8. Record initial and continuing calibration readings on a calibration data sheet (see Figure 5-13 for sample format).

O_2 Calibration

1. Turn the meter on and allow to warm up for 5 minutes.

2. Adjust the meter to read 21 percent while sampling atmospheric air. Use the appropriate oxygen calibration knob to adjust the meter to the proper setting.

3. Zero the meter using calibration gas (5.00 percent CO_2 in N_2 typically used).

   a. Fill a Tedlar bag with calibration gas. Purge and refill.
   b. Attach the Tedlar bag to the meter and adjust the meter to read zero using the appropriate oxygen zero potentiometer.

4. Check the atmospheric air reading. Adjust if necessary.

5. Recheck the calibration following Step 3 above. Adjust if necessary.

6. Check the calibration using a calibration check gas of a different concentration (7.0 percent O_2 typically used). Recalibrate atmospheric and zero readings if calibration check is off by more than ± 15 percent of the known concentration.

7. A calibration check should be done a minimum of three times daily.

8. Record initial and continuing calibration readings on a calibration data sheet (see Figure 5-13 for sample format).

Field Sampling and Analysis for Hydrocarbon and O_2/CO_2 Determinations - Electronic Detection Instruments

Routine Soil Gas Monitoring

1. Calibrate instruments following the directions specified in "Calibration of Field Instruments for Hydrocarbon and Oxygen/Carbon Dioxide Determinations - Electronic Detection Instruments."

2. Fill a Tedlar bag with the gas sample using the vacuum pump. Purge and refill. The total sampling time should not exceed 1 minute. Record the vacuum gauge reading while sampling on a soil gas monitoring data record sheet (see Figure 5-14 for sample format). If vacuum reading is less than 6 in Hg, check pump for broken connections.

Monitoring Point	O_2 (vol. %)	CO_2 (vol. %)	TPH (ppm)	Vacuum (in.H_2O)	Comments

Figure 5-14. Sample format for soil gas monitoring data record sheet.

3. Analyze the gas samples by connecting the hydrocarbon and O_2/CO_2 meter to the Tedlar bags. The meter can be connected in series when TPH readings are expected to be below 200 ppm. Record the O_2, CO_2, and TPH readings on a soil gas monitoring data record sheet (see Figure 5-14 for sample format).

   a. If the soil gas O_2 concentration is less than 12 percent, a dilution fitting may be necessary as per manufacturer's requirements for the specific instrument being used, and should be noted on data sheet. Hydrocarbon readings are recorded directly and should be multiplied by a factor of 2 prior to final data analysis when a dilution fitting is used. (Some manufacturers recommend the use of dilution fitting when less than 10 vol. percent O_2 occurs in the sample, and require its use when the O_2 content is less than 8 vol. percent O_2.)

   b. Recheck atmospheric readings for O_2, CO_2 and TPH periodically and recalibrate meters as necessary.

   c. Analyze samples indoors during cold weather (below 20°F).

4. Measure the soil gas temperature following procedures specified by the manufacturer. Record the temperature on a soil gas monitoring data record sheet (see Figure 5-14 for sample format).

Respiration Shutdown Test Monitoring

1. Shut blowers off to begin respiration test.

2. Analyze up to four soil gas samples from each probe per day, following the procedures specified in the "Soil Gas Monitoring" section above at various time intervals. Record data, including the date and time, on an in situ respiration test data record sheet (see Figure 5-15 for sample format).

Date	Time	O_2 (vol. %)	CO_2 (vol. %)	TPB (ppm)	Pump Vacuum (in.H_2O)	Soil Temp. (°F)	Comments

Figure 5-15. Sample format for in situ respiration test data record sheet.

3. Continue for up to a 10-day period, or until the soil gas O_2 level reaches 2 vol. percent.

4. Turn blowers on at the end of the respiration test.

5. Analyze respiration data according to methods presented in "Respiration Data Reduction."

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Section 6

Procedures for Evaluating Natural Attenuation in Groundwater

Introduction

Natural attenuation is a risk management strategy that invokes intrinsic bioremediation, dilution, dispersion, sorption, and other physical loss mechanisms to control exposure to contaminants and restore the environment. Several criteria should be considered before choosing natural attenuation as the principle remedial strategy (Wiedemeier, 1994, Wisconsin Department of Natural Resources, 1993; Underground Tank Technology Update, 1993). These include:

- Risk of further environmental damage.
- Risk of human endangerment [Defining the risk associated with a hazardous waste site is beyond the scope of this chapter; however, the natural attenuation rate can greatly influence the calculated risk associated with a contaminated site. The Emergency Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites (ASTM ES 38-94) provides a practical approach for conducting risk assessments].
- Detrimental consequences to local flora and fauna.
- Technical feasibility, practicality, and effectiveness of other technologies.
- Site-specific evidence for successful application of intrinsic bioremediation.
- The cost of natural attenuation compared to other options

When these issues can be addressed in favor of natural attenuation, the technology is a cost effective and practical remedial alternative for soil and groundwater.

Intrinsic bioremediation is the preferred term to describe the natural biological processes that lead to contaminant biodegradation (Wiedemeier et al., 1994). Intrinsic bioremediation can occur in any environment that supports microbiological activity; however, the rate of biodegradation may be slow due to the lack of a suitable respiratory

substrate (such as oxygen) or inorganic nutrients (such as fixed nitrogen), an extreme pH, low soil moisture, or limited contaminant bioavailability. Elimination of the contaminant source is essential for the successful application of intrinsic remediation. Accurate delineation of contamination, understanding subsurface conditions and characteristics, and contaminant migration rates and direction are critical for evaluating the success of natural attenuation and for establishing regulatory support for its use at a site (Davis, Klier, and Carpenter, 1994; Davis et al., 1994; Wiedemeier et al., 1994, Wilson, 1993, Wisconsin Department of Natural Resources, 1993).

Major obstacles that complicate the application of natural attenuation at appropriate sites include defining the potential for natural attenuation and developing a practical, cost effective monitoring plan that provides conclusive evidence of contaminant mass reduction. Identification and selection of useful monitoring parameters require a thorough knowledge of site characteristics. The site characterization methods and monitoring parameters used to evaluate natural attenuation are presented here. Table 6-1 lists some of the commonly used analytical methods for these parameters. The mention of a site characterization or monitoring parameter does not, however, mean that the parameter must be analyzed at each site undergoing natural attenuation. Inclusion here is to point out potential parameters, each of which may be useful at a particular site. Characterization and monitoring parameters are discussed separately, with monitoring parameters segregated based on the contaminant loss mechanism they are intended to illuminate.

Site characterization data should include:

- Site topography and geology
- Hydraulic conductivity of the aquifer
- Depth to groundwater, groundwater gradient, direction of flow, flow rate, and recharge rate
- Contaminant composition, location of non-aqueous phase liquids (NAPL), location of dissolved-phase contaminants, and the mass of contaminant present
- Physical and chemical properties of the contaminant
- Groundwater quality parameters
  - Temperature
  - pH
  - Dissolved oxygen

Table 6-1. Analytical Methods for Natural Attenuation.

Parameter	Method
	Lab Measurements
VOCs	SW-846, Method 8260
TPH	SW-846, Method 8015
BTEX	SW-846, Method 8202
MTBE	SW-846, Method 8020
Nitrate	SW-846, Method 9056, SW-846, Method 300
Nitrite	SW-846, Method 8260, SW-846, Method 300
Sulfate	SW-846, Method 8260, SW-846, Method 300
Methane	Headspace analysis by IT Biotechnology Laboratory
Ammonium	Standard Methods for Analysis of Water and Wastewater, 4500-NH3, SW-846 Method 350.2
Total Kjeldahl N	Standard Methods for Analysis of Water and Wastewater, 4500-Norg, SW-846 Method 351.2
Phosphate	Standard Methods for Analysis of Water and Wastewater, 4500-P, SW-846 Method 365.3
Alkalinity	Standard Methods for Analysis of Water and Wastewater, 2320 B, SW-846 Method 310.1
pH	Standard Methods for Analysis of Water and Wastewater, 4500-H+ or SW-846 Method 150.1
Chloride	Standard Methods for Analysis of Water and Wastewater, 4500-Cl, SW-846 Method 300
	Field Measurements
Iron (II)	Standard Methods for Analysis of Water and Wastewater, 3500-Fe D
Temperature	Standard Methods for Analysis of Water and Wastewater, 2550 B
Conductivity	Standard Methods for Analysis of Water and Wastewater, 2510 B
Redox	Standard Methods for Analysis of Water and Wastewater, 2580 B
pH	Standard Methods for Analysis of Water and Wastewater, 4500-H+ or SW-846 Method 150.1
Dissolved oxygen	Standard Methods for Analysis of Water and Wastewater, 4500-O G

- Methane
- Total Organic Carbon
- Alkalinity
- Oxidation/reduction potential (Redox)
- Nitrate
- Iron(II)
- Sulfate
- Sulfide
- Ammonium
- Phosphate
- Total Kjeldahl Nitrogen
- Chloride
- Conductivity

A major division of monitoring parameters is biological and physical/chemical. Potentially useful biological monitoring parameters include the following:

- Microbial respiration
- Conversion/consumption of respiratory substrates
- Biologically induced changes in geochemistry
- Biodegradation rates

Potentially useful physical/chemical monitoring parameters include:

- Dilution and dispersion
- Volatilization
- Sorption
- Contaminant mass loss
- Contaminant concentration reduction
- Appearance of degradation products

The conventional monitoring parameter under current regulatory legislation is reduction in contaminant concentration, and this may be limited to groundwater only or include both soil and groundwater.

The final section of this chapter presents a stepwise approach for developing a natural attenuation site management plan. The approach provides a skeleton from which natural attenuation can be defined and a responsible site management plan implemented. Explicit details are intentionally omitted to avoid casting an approach that may not make sense in total or in part for a given site. Site specific characteristics, the current level of site knowledge, previous remedial activities, and public, regulatory, and environmental sensitivities must be merged to yield an acceptable natural attenuation model and verification or monitoring plan.

Site Characterization and Selection of Natural Attenuation for Site Remediation
Defining site conditions is the first action required to develop a site management plan employing natural attenuation. Because each aspect of the site characterization requires technical proficiency in specialized areas, discussion will be limited to highlighting particularly usefully or common techniques and approaches. These will be generally appropriate for most sites; however, site specific conditions will often mandate modifications to assure collection of valid data.

Site Topography, Geology, and Hydrology
The surface and subsurface characteristics impact the application of natural attenuation. Surface contours can influence water infiltration, plume migration, the ability to install monitoring wells or treatment systems. The soil type and nature of the aquifer material influences the practicality of treatment alternatives, since contaminant distribution is directly related to the subsurface geology. For example, fractured rock formations provide significant flow pathways for NAPL and dissolved contaminants. Sandy soil provides for a higher level of rainwater infiltration which may leach contaminant to the groundwater. Because of differences in pore space geometry, less residual contamination is held in sandy soil compared to silty or clay soils (Charbeneau et al., 1992). Therefore, local geology and topography can provide important insights into contaminant and groundwater behavior.

Local aquifer use, the location of drinking water, industrial, or agricultural wells, and potential exposure routes and receptors should be identified as part of the overall site characterization. These parameters are instrumental for defining the relative health and environmental risk associated with the contaminated groundwater.

Aquifer Characteristics
Thorough characterization of the aquifer is essential for predicting the long-term impact of the free NAPL, residual NAPL, and dissolved contaminant. Several parameters should be determined using standard techniques. Wells will be required for some tests, whereas simple monitoring points will be adequate for others.

Groundwater Movement
The movement of groundwater directly affects the progress of natural attenuation; therefore, defining local aquifer characteristics contributes to an accurate prediction of the performance of the natural attenuation process. Hydraulic conductivity of the aquifer is determined using falling or rising head slug tests or actual pump tests. Pump tests usually give more accurate results, but they also generate relatively large quantities of water that must be contained and disposed.

The depth to groundwater and the groundwater gradient are also determined in the contaminated area. If a significant change in gradient or depth is expected based on local topography and geology, these parameters should be determined in the

downgradient direction. The groundwater flow rate and direction can be calculated based on hydraulic conductivity and groundwater gradient data (Example Calculation 6-1). The risk associated with the contaminated groundwater is evaluated using these and other parameters.

Site-Specific Data:

Hydraulic gradient--a unitless measure of change in depth per change in length. For example, an aquifer whose groundwater level changes from 750 feet above sea level to 740 feet above sea level over the distance of 100 feet has a hydraulic gradient of:

$$\frac{dH}{dL} = \frac{(750-740)\ feet}{100\ feet} = 0.1$$

Hydraulic conductivity--a measure of an aquifer's ability to transmit water. Hydraulic conductivity is determined from pumping or slug test data. Hydraulic conductivity is expressed as length per time, typically as cm/sec.

Effective porosity--the percentage of a volume of undisturbed aquifer solids that is occupied by water which is available to flow along the hydraulic gradient. Total porosity is the total void volume in a volume of aquifer solids. Depending on the type of solids, the effective porosity may be significantly less than the total porosity.

Calculation of Groundwater Flow Rate

$$\overline{v} = \frac{-K\ dH}{n_e\ dL}$$

Where:

$\overline{v}$ = average groundwater velocity, units are length per time
K = hydraulic conductivity
n_e = effective porosity
dH/dL = hydraulic gradient

Example Calculation 6-1. Groundwater flow rate.

Recharge and Discharge

The rate of aquifer recharge and the areas where recharge from the surface and discharge to the surface is likely to occur is determined. These characteristics facilitate a more accurate determination of plume dilution. Discharge points are considered during risk evaluations since they represent areas for potential contact with contaminated water.

Contaminant Composition, Concentration, Mass, and Properties

Contaminant composition, location of non-aqueous phase liquids (NAPL), location of dissolved-phase contaminants, and the mass of contaminant present are critical aspects for understanding the natural attenuation process. Isopach maps showing the location and thickness of NAPL and isopleth maps showing the location and concentration of dissolved contaminants are useful visual approximations of subsurface contamination derived from contaminant concentration data.

The physical and chemical properties of the contaminant also affect the behavior of the contaminant in the subsurface. Once the composition of the contaminant is known, properties of individual components are usually available in the published resources. Particularly useful properties include aqueous solubility, the octanol-water partition coefficient, the soil adsorption coefficient, and the Henry's Law Constant. The application of these characteristic properties is shown in various example calculations which follow.

Contaminant Composition

The chemical composition of the contaminant can be determined using several standard analytical methods. Knowing the chemical composition of the contaminant permits changes in composition to be evaluated against time and distance migrated. This information is then used to make predictions regarding the attenuation rate, the biodegradation rate, and the change in concentration due to physical mechanisms.

During site characterization, contaminant chemical composition should be evaluated with two objectives. First, the concentration change in chemicals that are likely to biodegrade anaerobically should be determined. Second, the change in chemicals that are not likely to biodegrade anaerobically should be determined. Concentration changes in the latter can be used to correct for physical losses in the biodegradable compounds. Key target compounds for petroleum fuels that are very slow to biodegrade anaerobically include 2,3-dimethyl pentane, trimethyl benzenes, and tetramethylbenzenes (Cozzarelli et al., 1990, Cozzarelli et al., 1994, Wilson et al., 1993, Wilson et al. 1994, Wiedemeier). These compounds have solubility and sorption characteristics similar to benzene, toluene, ethyl benzene, and xylenes (BTEX) and, thus, they can serve as practical markers of contaminant movement and BTEX biodegradation. This approach is the simplest method for calculating dilution, dispersion, and sorption effects on contaminant concentration (Example Calculation 6-2). When site analytical data do not contain a suitable conserved marker compound, benzene can be used to normalize

Site-Specific Data:

One or more site-specific conserved chemicals must be identified. Key characteristics include the consistent presence of the conserved chemical(s) in all or most groundwater monitoring wells. The conserved chemical(s) must be much less likely to biodegrade anaerobically than other target chemicals. The conserved chemical(s) must have chemical properties similar to target compounds.

Contaminant concentration data from monitoring wells located along downgradient vectors.

The concentration of a target contaminant is normalized or corrected for abiotic losses based on the change in concentration of the conserved compound(s):

$$\frac{M_t}{M_o} = R$$

Where:
M_o = conserved chemical concentration in the upgradient monitoring well
M_t = conserved chemical concentration in the downgradient monitoring well
R = ratio of change in conserved chemical between the upgradient and the downgradient wells. This value is taken to represent the relative amount of abiotic loss expected in all chemicals with similar properties.

(If data for more than one conserved chemical are present, an average abiotic loss ratio "R" can be calculated.)

The abiotic loss factor "R" is used to normalize or correct biodegradable target compound concentrations for the amount of compound removed abiotically. If the ratio for the target compound in the downgradient well is greater than or equal to "R", no biodegration is occurring in the aquifer. If the target compound ratio is less than "R", the difference represents the contribution of biodegradation to the overall reduction in contaminant concentration. Normalization for abiotic loss can be conducted using either the upgradient or downgradient contaminant data; however, using the downgradient data results in a slightly simpler equation:

Example Calculation 6-2. Application of a conserved chemical's concentration to calculate the rate and magnitude of abiotic changes in concentration.

Example Calculation 6-2 (continued)

$$\frac{C_t}{R} = C_{tnorm}$$

Where:

C_t = measured contaminant concentration in the downgradient monitoring well
C_{tnorm} = normalized contaminant concentration in the downgradient monitoring well. This value represents the concentration that would be expected in the well if no abiotic loss occurred. (The validity of this approach can be seen by dividing M_t, the conserved chemical concentration, by "R".)

The biodegradation rate is calculated using the first-order decay equation:

$$C_{tnorm} = C_o e^{kt}$$

NOTE: The problem of limited site data often makes the initial evaluation of natural attenuation challenging, because insufficient data are available to adequately define intrinsic processes. When BTEX data are available, examination of site maps and the benzene-to-toluene (B/T) ratio in each monitoring well often indicates a significant shift in the B/T ratio as distance from NAPL or the source area increases. This is because fresh fuel oils usually have more toluene than benzene, but since toluene is more susceptible to anaerobic biodegradation than benzene, the ratio shifts to more benzene than toluene when anaerobic biodegradation is occurring. This shift is a qualitative indicator of intrinsic biodegradation.

In some cases benzene can be used as a conserved compound to calculate the abiotic loss of toluene and xylene within the impacted aquifer. Although this approach is not as rigorous as that described above, it can be used to make a first approximation of natural attenuation until better data are collected.

anaerobic toluene biodegradation and attenuation in BTEX contaminated aquifers. However, this approach tends to under estimate biodegradation.

Contaminant Concentration

The standard procedure for quantitating a remedial process is reduction in contaminant concentration measured with U.S. EPA approved methods. The accuracy of this approach for describing the effectiveness of an in situ remedial activity is questionable. Contaminant concentration is sensitive to dilution, sorption, and chemical transformations of the primary contaminant to other compounds that usually are not detected using standard methods.

Contaminant Mass

The mass of contaminant in soil and dissolved in groundwater is an important parameter for quantitating natural attenuation. Unfortunately, accurate measurement of contaminant mass is difficult and is usually not done with acceptable accuracy. Methods to determine contaminant mass involve estimation methods to extrapolate the amount of contaminant between monitoring points. Defining the mass of contaminant in a soil sample can be accomplished using several analytical methods. Defining the actual dimensions and concentrations of contaminant in three dimensions is challenging and expensive.

Soil Core Analysis. One approach is to collect intact soil cores and analyze sections of the core to determine the depth distribution of contaminant and the mass of contaminant in each section (Figure 6-1) (Wilson, 1993). Lateral contaminant distribution is estimated based on soil sampling at multiple locations.

Contaminant Mass and Center of Mass Estimation. Estimation of the amount of contaminant present at a site can be estimated using a relatively simple technique known as the Thiessen Method (Dupont, 1995). Its original use was to calculate the amount of rain that fell over an area using data collected from rain gauges. The approach is outlined in Figure 6-2. Using monitoring well data, the method will yield an arbitrary and unbiased estimate of contaminant mass as well as the center of mass. As indicated in Figure 6-2, results collected over time can provide useful insights into the natural attenuation process and the effect of a contaminant source such as NAPL on contaminant migration and dissolved concentration.

The accuracy of the Thiessen Method contaminant mass estimate is questionable, but the results are generally precise and can be compared at multiple time intervals. By combining the contaminant concentration and location data generated from soil core analysis with the Thiessen Method, the accuracy of the contaminant mass estimate can be improved.

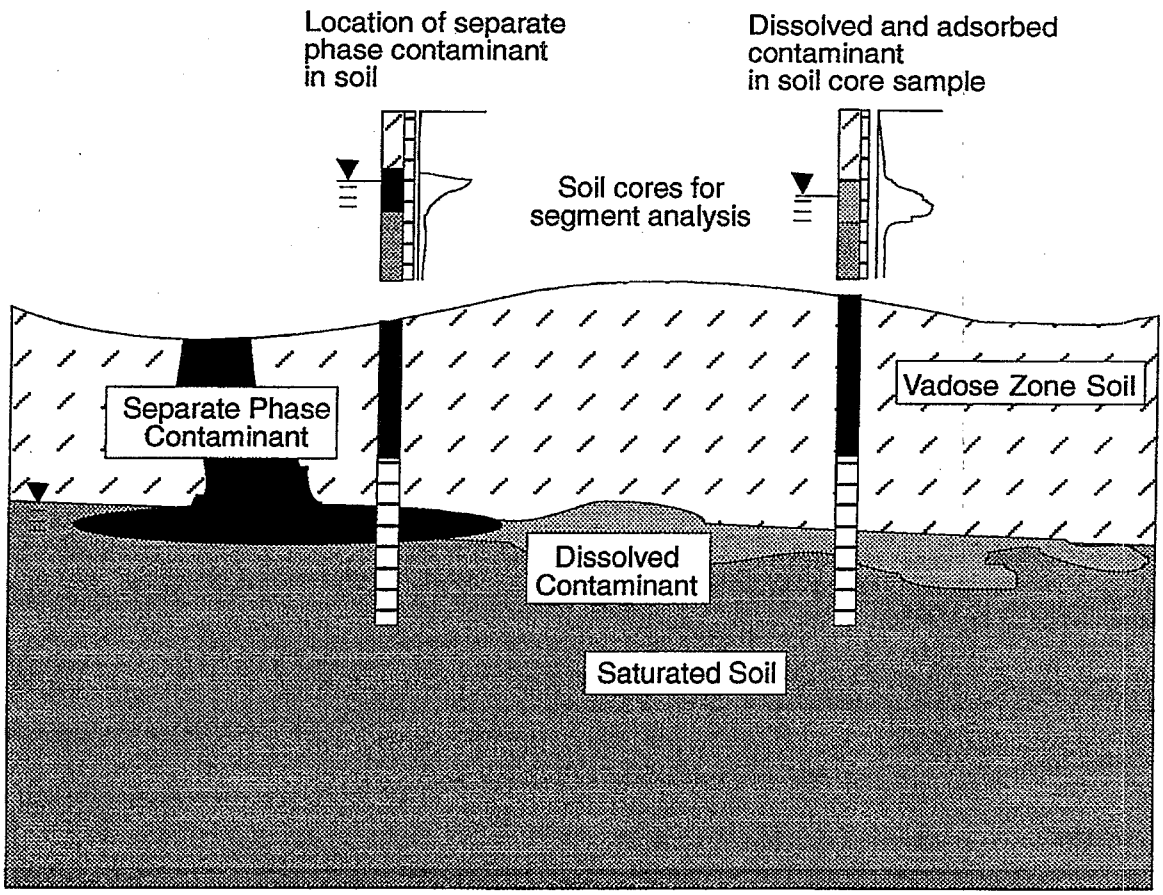

Figure 6-1. Analysis of soil core segments accurately defines location of separate phase and dissolved phase contaminants.

The Thiessen Method involves the identification of specific sampling locations within a sampling network, and the determination of associated areas based on the construction of polygons surrounding the sampling points (monitoring wells in this example).

Polygons are constructed in the following manner:

Step 1. Define the outer boundary of the contaminant plume.

Step 2. Connect all monitoring wells to all adjacent wells to create a group of triangles.

Step 3. Place a perpendicular line at the bisection point of each line used to connect monitoring wells. Extend the perpendicular lines to intersect one another.

Step 4. Connect the intersection lines to form polygons.

The area within each polygon is calculated and used to calculate the volume of soil or groundwater within the area assigned to each monitoring well. For quality assurance, the total area of the plume and the summed areas of the polygons should agree within 5 percent.

The contaminant concentration in each well is used to determine the total mass of contaminant present within the polygons associated with the monitoring wells. The center of mass (centroid) can also be determined using this approach. Trends observed in the results collected with time can reveal the occurrance of natural attenuation.

Summary of concentration mass and center of mass trends as indicators of natural attenuation (Dupont, 1995).

Contaminant Mass	Center of Mass	Interpretation
Increasing	Moving downgradient	Continuous source, unstable plume, contaminant migration
Constant	Moving downgradient	Finite source, plume migrating, minimal natural attenuation
Constant	Stable	Continuous source, stable plume, contaminant attenuation
Decreasing	Moving downgradient	Finite source, plume migrating, contaminant attenuation
Decreasing	Moving upgradient	Finite source, plume attenuation, rapid contaminant attenuation

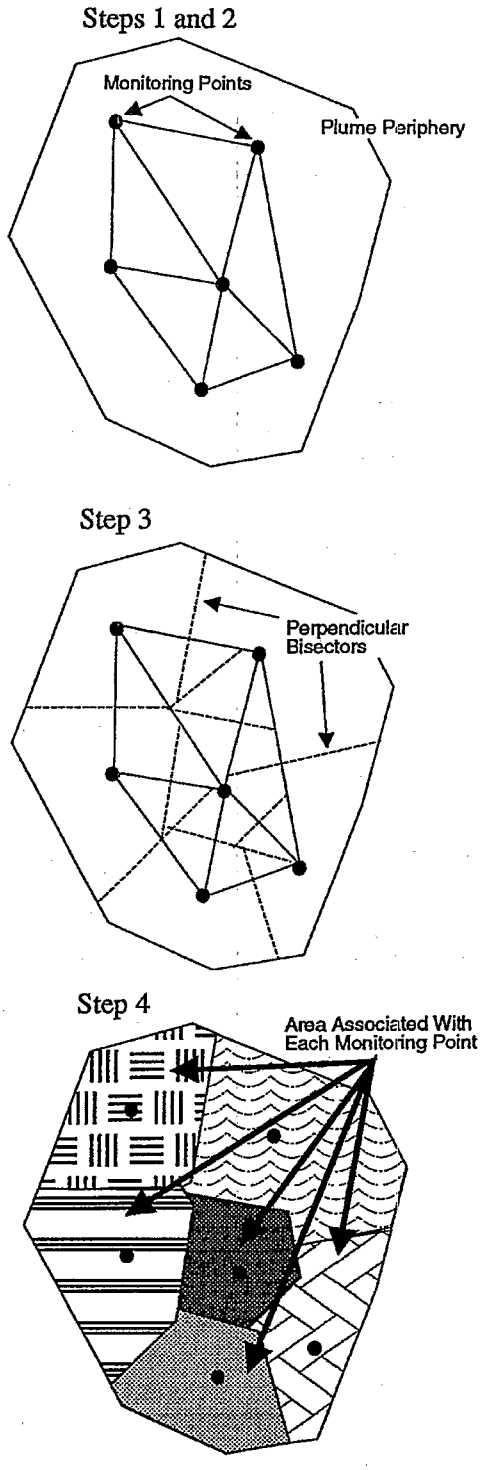

Figure 6-2. Contaminant mass estimation using the Thiessen Method for area assignments.

Contaminant Physical and Chemical Properties

Physical and chemical properties of contaminants affect their distribution and movement in groundwater and soil gas. The octanol-water partition coefficient, Henry's Law Constant, and aqueous solubility of contaminants can be used to estimate the interaction of the contaminant with air, water, and soil. The accuracy of these estimates is usually questionable; however, general ranges can be useful for predicting the behavior of the contaminant (Example Calculations 6-3 and 6-4). Retardation coefficients that reflect the relative mobility a contaminant in an aquifer are useful for comparing the expected plume migration rate with observed plume movement (Example Calculation 6-5).

Biological Monitoring Parameters

Biological monitoring parameters are indicators of microbiological activity in the subsurface. In all cases, microbial activity is the most likely if not the only explanation for the observed changes. Therefore, changes or activity observed in a contaminated area that do not occur or do not occur to the same magnitude in uncontaminated soil can often be attributed to biodegradation.

Microbial Respiration

Microbial respiration is the biochemical process that leads to the oxidation of reduced organic carbon. Examples of reduced organic carbon include every organic compound that contains carbon and hydrogen in its chemical composition. Demonstrating aerobic respiration is relatively simple in the vadose zone. However, it is not very practical in the saturated zone. Therefore, laboratory evaluations may be used as a surrogate to in situ demonstrations.

The principle benefit of demonstrating microbial respiration in laboratory studies is that they indicate that microbial respiration can occur in the contaminated area. Although the observed respiration rate from laboratory microcosms is frequently higher than that observed in situ, the laboratory microcosm can set an upper limit for in situ respiration. Table 6-2 outlines a simple microcosm study that evaluates aerobic and anaerobic respiration and abiotic contaminant loss.

Conversion/Consumption of Respiratory Substrates

In situ observation of the results of microbial respiration is often obvious when the concentration of respiratory substrates (electron acceptors) are compared within and outside of a contaminated area. The biodegradation potential of an aquifer [also known as the "expressed biodegradative capacity" (Wiedemeier, 1994)] can be estimated using the concentration of respiratory substrates and products (Example Calculation 6-6).

In addition to estimating the biodegradation potential of the aquifer, respiratory substrate and product concentrations are critical data used to support the occurrence of intrinsic bioremediation. The observations described below are indicative of intrinsic

Site-Specific Data:

Type of contaminant

Mass of NAPL present

Mass fraction of target contaminants in the NAPL

The maximum amount of contaminant that will dissolve from the NAPL into groundwater is calculated using the fuel-water partition coefficient and the concentration of individual chemicals in the NAPL. The fuel-water partition coefficient is given by:

$$\log K_{fw} = 6.099 - 1.15 \log S_t$$

$$K_{fw} = 10^{6.099} - 1.15 \log S_t$$

Where:

K_{fw} = fuel-water coefficient, the ratio of the concentration of a chemical in the NAPL to the concentration dissolved in water.

The concentration of a chemical in NAPL is calculated by multiplying the mass fraction of the chemical by the density of the NAPL.

$$C_t = F_t \, p_f$$

Where:

C_t = volumetric concentration of chemical in the NAPL
F_t = mass fraction of the chemical on the NAPL
P_f = density of the NAPL

The amount of chemical that can dissolve into the groundwater is:

Example Calculation 6-3. Contaminant dissolution from nonaqueous-phase liquids (NAPL).

Example Calculation 6-3 (continued)

$$C_w = \frac{C_t}{K_{fw}}$$

Where:

C_w = concentration of the target chemical in the groundwater.

From Bruce et al., 1991.

The diffusive movement of contaminant in NAPL into the groundwater constrains the time required for natural attenuation to restore an aquifer. So long as NAPL is present and contributing dissolved contaminants to the groundwater, the aquifer will continue to be contaminated. The rate of dissolution is limited by the diffusion of contaminant into the water. Ideally, all NAPL would be physically extracted from the soil; however, in practice only 40 to 60 percent is typically removed. This leaves a large amount of NAPL in the ground which will continue to contaminate groundwater. The diffusion of target contaminants in the residual NAPL becomes an important parameter for estimating the time required to remediate the aquifer because the water will be constantly recontaminated until the NAPL is depleted.

The diffusivity of the target contaminant into water can be calculated using several methods (Handbook of Chemical Property Estimation Methods, Chapter 17). The Hayduk and Laudie method is presented because of its simplicity and small absolute average error (5.8 percent).

$$D_{BW} = \frac{13.26 \times 10^{-5}}{n_w^{1.14} V_B^{0.589}}$$

Where:

D_{BW} = diffusivity of compound "B" into water "W"
n_w = viscosity of water
V_B = molar volume calculated using the method of LeBas (see Table 17.5, Handbook of Chemical Property Estimation Methods, for details).

Using the diffusivity value generated above, the mass flux of contaminant B into groundwater can be calculated based on Fick's Second Law of Diffusion.

$$N_B = \frac{pD_{BW}(C_{B1} - C_{B2})}{f_t(z_2 - z_1)}$$

Where:

N_B = mass flux of compound B into water
D_{BW} = diffusivity of B into water
$(C_{B1} - C_{B2})$ = concentration gradient of compound B

Example Calculation 6-4. Mass flux of contaminant in NAPL to water.

Example Calculation 6-4 (continued)

$(z_2 - z_1)$ = distance
f_t = tortuosity, a soil property typically ranging from 2 to 100 as applied above (Handbook of Chemical Estimation Methods and Jury et al., 1991)

The results of the mass flux calculation are in units of mass/(area * time); therefore, the time required for the available contaminant to diffuse into the groundwater can be estimated.

$$T = \frac{M_B}{AN_B}$$

Where:

T = time to complete diffusion of compound B into water
M_B = total mass of compound B available to diffuse into water
A = area covered by NAPL or separate-phase compound B

The retardation coefficient for a chemical species describes the movement of a dissolved chemical relative to the advection movement of groundwater. Groundwater contaminants frequently migrate at a slower rate than the groundwater itself. Retardation results in exposure of dissolved contaminants to more electron acceptors than would otherwise occur if contaminant and groundwater moved in unison. The retardation coefficient also can affect the calculation of anaerobic biodegradation rates when data from monitoring wells lying along a flow vector are used. If contaminant takes twice as long as the groundwater to travel from one monitoring well to the next, the biodegradation rate will be inaccurately estimated using groundwater velocity to calculate contaminant travel time between the wells. The retardation coefficient for a dissolved chemical may be estimated as shown:

$$R = 1 + \frac{(p_b K_d)}{n_e}$$

Where:

R = retardation coefficient
P_b = bulk density of the aquifer (mass per volume)
K_d = distribution coefficient
n_e = effective porosity

The distribution coefficient describes the distribution of dissolved and sorbed contaminant. In simple terms, the distribution coefficient indicates the amount of contaminant that is dissolved and the amount that is stuck to the soil in the aquifer. The distribution coefficient is the product of the mass fraction of total organic carbon in the aquifer and the soil adsorption coefficient.

$$K_d = K_{oc} f_{oc}$$

Where:

K_{oc} = soil adsorption coefficient (usually determined using published values, Jeng et al., 1992)
f_{oc} = mass fraction of organic carbon in the soil expressed as mass of organic carbon per mass of soil

Example Calculation 6-5. Retardation coefficient.

Table 6-2. Simple Microcosm Study to Define Aerobic and Anaerobic Biodegradation.

Treatment	Replicates (minimum)	Description
Aerobic	3	Microcosm vessel containing contaminated groundwater. Use a manometer or respirometer to measure oxygen consumption. Analyze for contaminant concentration and carbon dioxide produced over time.
Anaerobic	3	Establish microcosm vessels in an anaerobic chamber, fill the vessel to eliminate headspace, sparge water with inert, oxygen-free gas, or add an oxygen scavenger to generate and maintain anaerobic conditions. Depending on the setup, multiple vessels may be required for intermediate contaminant and electron acceptor analysis. Additional vessels are required if denitrification, sulfate reduction, or methanogenesis are evaluated.
Abiotic loss	3	The loss of contaminant due to laboratory manipulations is quantitated using an abiotic control treatment. Microcosms are established as described for either of the other treatments. The control is incubated at 4°C and sampled like the other instruments. In some cases, before and after treatment sampling is adequate to define abiotic losses. Inhibitors such as azide or mercury may be used to inhibit biological activity.

Site-Specific Data:

Maximum and average contaminant concentration within the plume.

Electron acceptors and respiratory product concentrations in the plume and at background locations. Electron acceptors include dissolved oxygen, nitrate, and sulfate. Respiratory products include ferrous iron (Fe II) and methane.

The following calculations are based on benzene. Minor disparities will exist if compounds other than benzene are the major contaminants; however, these differences are generally insignificant relative to the larger error associated with analytical data.

Constants:

Mass ratio of benzene to electron acceptor for complete mineralization:

Benzene/Oxygen = 1/3.1 = 0.32

Benzene/Nitrate = 1/4.8 = 0.21

Benzene/Sulfate = 1/4.6 = 0.22

Mass ratio of benzene to respiratory products for complete mineralization:

Benzene/Iron (Fe II) = 1/15.7 = 0.064

Benzene/Methane = 1/0.8 = 1.25

The assimilative capacity of the aquifer (the amount of contaminant that can be biodegraded) is determined by the general equation:

$$O_c + N_c + + I_c + S_c + M_C = T_c$$

Where:

O_c = assimilative capacity of dissolved oxygen
N_c = assimilative capacity of nitrate

Example Calculation 6-6. Biodegradation potential of an aquifer.

Example Calculation 6-6 (continued)

I_c = assimilative capacity of iron based on the amount of ferric iron (Fe II) converted to Fe II
S_c = assimilative capacity of sulfate
M_c = assimilative capacity of methane based on the amount of methane produced

The assimilative capacity of each electron acceptor or respiratory product is calculated by:

$$\frac{B}{O_2}\,[C] = O_C$$

Where:

B/O_2 = the benzene-to-nitrogen mass ratio
[C] = background concentration of nitrate

$$\frac{B}{N}\,[C] = N_c$$

The assimilative capacity of each electron acceptor or respiratory product is calculated in like manner. The total assimilative capacity is calculated by summing the assimilative capacities of each individual electron acceptor or product. If the total assimilative capacity is greater than the maximum contaminant concentration, intrinsic biodegradation has the potential to remediate the aquifer. On the other hand, if the total assimilative capacity is less than the maximum contaminant concentration, intrinsic biodegradation is less likely to be successful.

biodegradation and are important aspects for evaluating the potential of successful intrinsic bioremediation at a site. Because of the energy derived from each substrate, they are preferentially used in the order shown in Figure 6-3. In addition to preferential utilization, respiration tends to be exclusive. For example, in the presence of oxygen, other respiratory substrates are not used. Similarly, when oxygen is depleted and nitrate is available, denitrification will prevail with no iron and sulfate reduction or methanogenesis. This pattern of respiratory exclusion continues as high energy respiratory substrates are expended.

Oxygen Consumption

Groundwater undergoing intrinsic bioremediation will usually contain much less dissolved oxygen than a nearby "clean" groundwater. An area of oxygen depleted groundwater usually coincides with the dissolved contaminant plume and it often extends beyond the contaminant plume in the downgradient direction. The difference in dissolved oxygen between "clean" and contaminated groundwater is a useful indicator of intrinsic biodegradation. Three to 3.5 pounds of oxygen are required to completely biodegrade one pound of hydrocarbon (Wiedemeier et al., 1994).

Nitrate Reduction

The nitrate content of groundwater varies with local land use practices. Agricultural areas, groundwater downgradient of land fills, and industrial areas often have elevated nitrate concentrations in the groundwater. However, within areas with measurable nitrate, the groundwater within a contaminant plume will often have a much lower nitrate concentration than surrounding "uncontaminated" groundwater. This concentration change indicates nitrate reducing activity. The absence or much lower rate of nitrate reduction in clean groundwater indicates that the presence of contaminant is required to support nitrate reduction. About four pounds of nitrate are required to biodegrade one pound of hydrocarbon (Ehrlich, 1981, Kuhn et al., 1988, Major et al., 1988, and Wiedemeier et al., 1994).

Iron Reduction

Oxidized iron is insoluble and its presence is indicated by the red coloration of oxidized soil. Soil within contaminant plumes is often reduced. The biological conversion of oxidized iron, Fe(III), to reduced iron, Fe(II), can support hydrocarbon biodegradation. Iron reduction is not an efficient biochemical process requiring about 42 pounds of Fe(III) per pound of hydrocarbon degraded. Nevertheless, iron reduction is an important process because of the abundance of iron in the soil. Unfortunately, the speciation and analysis of Fe(III) and Fe(II) is very challenging and usually not accurate. Field measurement of Fe(II) in groundwater samples using colorimetric test kits usually yields satisfactory results (Ehrlich, 1981, Lovely, 1991, and Wiedemeier et al., 1994).

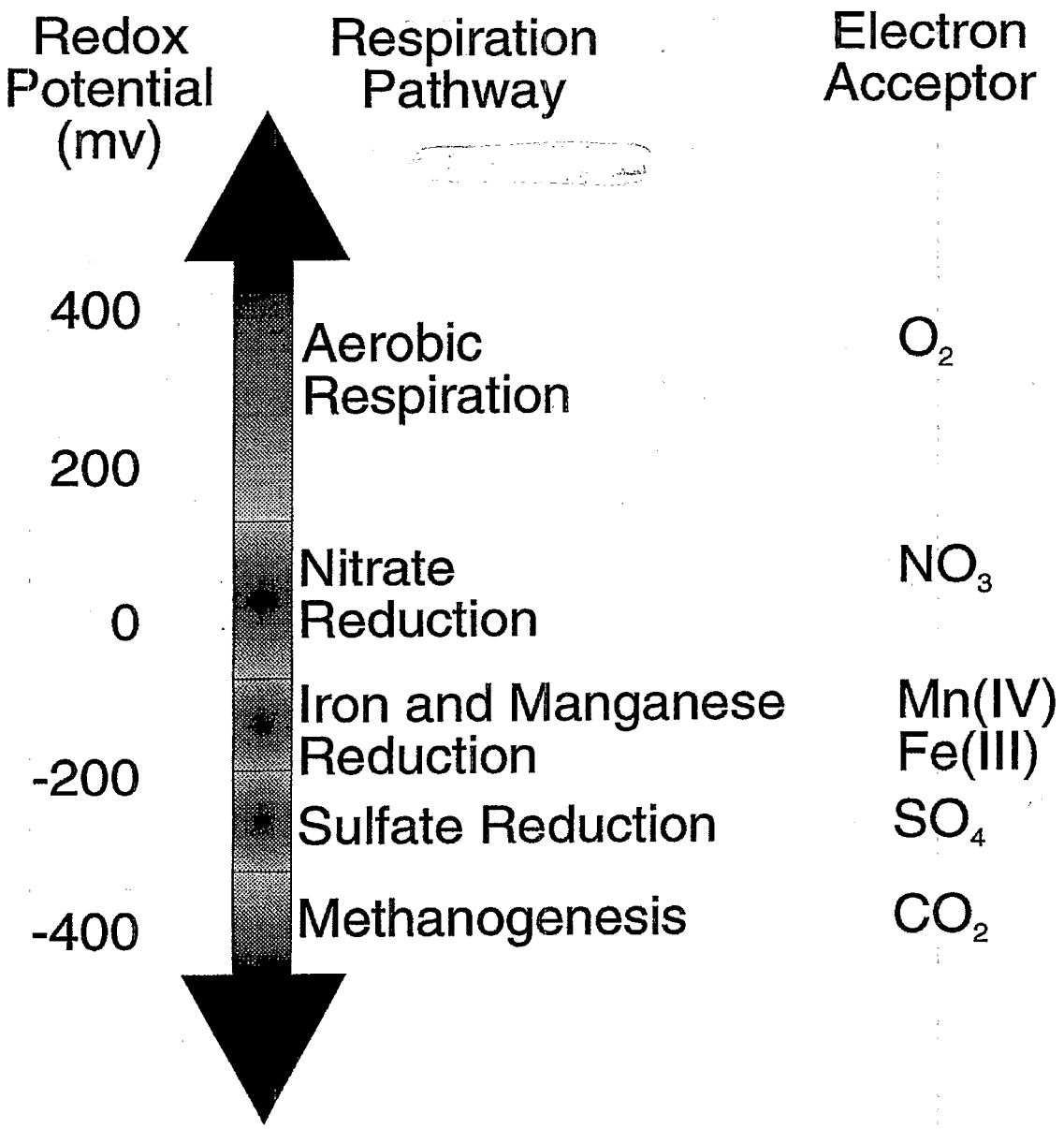

Figure 6-3. Electron acceptors for common microbial respiration pathways and approximate oxidation/reduction potential (Redox or Eh) where each pathway occurs. (Atlas and Bartha, 1981)

Sulfate Reduction
Sulfate reduction can contribute to hydrocarbon biodegradation in the absence of oxygen, nitrate, and iron [Fe(III)]. Sulfate reducing conditions are characterized by a low oxidation reduction potential and the presence of sulfide. Approximately 4.8 pounds of sulfate are required to biodegrade one pound of hydrocarbon (Ehrlich, 1981, Edwards et al., 1992, and Wiedemeier et al., 1994).

Methanogenesis
Under strictly anaerobic conditions and low redox, biodegradation of hydrocarbon leads to the production of methane. About 0.8 pounds of methane are produced during the biodegradation of one pound of hydrocarbon (Wiedemeier et al., 1994, Wilson et al., 1993, Grbic-Galic and Vogel, 1987).

Manganese Reduction
Oxidized manganese (Mn^{+4}) can be reduced by microbial respiration (Ehrlich, 1981, Lovely, 1991, and Wiedemeier et al., 1994). As seen in Figure 6-2, manganese reduction occurs under conditions similar to those that support iron reduction. There is some evidence that manganese reduction can support hydrocarbon biodegradation (reference); however, the difficulty in speciating manganese ions usually precludes any serious attempts to evaluate the effect of manganese on intrinsic biodegradation. A practical approach to dealing with manganese reduction is to evaluate the other (easy to analyze) respiratory substrates or products. If contaminant degradation appears to be occurring but can not be accounted for using more common respiratory substrates, manganese should be considered as a possible substrate supporting biodegradation.

Biodegradation Rates
Biodegradation rates may be determined using field data or laboratory data. Biodegradation rates are usually calculated with satisfactory results using a first order rate equation (Example Calculation 6-7). Laboratory data have the unfortunate disadvantage of usually overestimating biodegradation rates. Collection of biodegradation rate data in the field with the accuracy to calculate a degradation rate in the absence of other physical loss mechanisms is challenging. The calculation of biodegradation rates corrected for physical loss using a conserved compound that does not biodegrade anaerobically is shown in Example Calculation 6-2. Laboratory derived biodegradation rates may also be used to define the percentage of the overall loss that can be attributed to biological activity.

Physical/Chemical Monitoring Parameters
Physical/chemical monitoring parameters reveal abiotic processes that can result in contaminant dissipation. Unless these parameters are accounted for in the overall contaminant mass balance, biodegradation may be credited for more contaminant loss than actually occurs. Because most of the physical loss mechanisms do not result in contaminant degradation, these processes may not be acceptable approaches for site

Site-Specific Data:

Groundwater velocity -- determines the minimum time required for dissolved contaminants to travel between two points.

Contaminant concentration data -- contaminant concentration must be determined in monitoring wells positioned along a vector in the direction of groundwater flow. Contaminant concentration data from two or more points is required. The points may be temporal or spatial. Selecting useful data can be difficult. Sequential analytical data for the same well or data from two wells separated by a known groundwater travel time may provide useful data, depending on site conditions described below.

Speciation of dissolved contaminants -- contaminants monitored should include target compounds as well as one or two compounds that do not readily degrade anaerobically. For refined petroleum products, 2,3-dimethyl pentane, trimethylbenzenes, and tetramethylbenzenes have been used to evaluate the rate and magnitude of nonbiological contaminant loss. The choice of an appropriate conserved chemical is determined by conducting gas chromatography and mass spectroscopy on groundwater samples near or in the source and at a few locations downgradient. Chemicals that persist in the groundwater at elevated levels--presumably due to poor anaerobic biodegradability--and that have chemical properties similar to target compounds can serve as conserved indicators of contaminant dispersion, dilution, volatilization, and sorption.

Sequential contaminant data covering several months to several years

Distance between monitoring wells -- used to calculate hydraulic retention time between wells

Seasonal groundwater elevation in each monitoring well -- seasonal fluctuations can cause significant changes in groundwater flow direction and velocity.

A first-order decay equation is usually an accurate model for contaminant biodegradation:

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

Example Calculation 6-7. Biodegradation rate and target compound half-life.

Example Calculation 6-7 (continued)

Where:

C_t = concentration of contaminant at time "t"
C_o = concentration of contaminant at time "zero"
t = lapsed time from C_o to C_t
-k = biodegradation rate constant

From the biodegradation rate constant "k", the half-life of a contaminant can be calculated:

$$t_{1/2} + \frac{ln2}{k}$$

Where:

$t_{1/2}$ = contaminant half-life, the time required for the concentration of the contaminant to decline by one-half

Calculation of "t" when contaminant concentration data are collected from two wells located along a downgradient flow vector:

$$t = \frac{x}{v}$$

Where:

x = distance between the two monitoring wells (sample collection points)
v = groundwater velocity or seepage velocity. Groundwater velocity can be a tricky variable to calculate. The hydraulic gradient may change dramatically with the season. Some aquifers actually change flow direction. Such changes in the hydraulic gradient seriously affect groundwater velocity calculations and must be considered when calculating the groundwater retention time between two points.

NOTE: When NAPL is present and contributing dissolved contaminant to the groundwater, the use of groundwater data collected from the same well, but at different times, is not useful for calculating biodegradation rates, because the groundwater is continually replenished by newly dissolved contaminant. If NAPL is the present, this type of analytical data can be used to calculate biodegradation rates, because all of the groundwater should be experiencing approximately the same conditions without the input of fresh contaminant.

remediation. Chemical processes usually do not result in contaminant degradation; however, abiotic chemical reactions in soil and groundwater may convert a contaminant into another compound. Chemical transformations may be beneficial if they result in a compound that is less hazardous or more biodegradable.

In addition to accounting for abiotic contaminant loss mechanisms, chemical monitoring is the ultimate parameter that determines when a site is remediated. Therefore, monitoring to determine contaminant concentration reduction, contaminant mass loss, and possibly the appearance of degradation products is critical to define the success of natural attenuation.

Dilution by Diffusion and Dispersion

Dilution is an inevitable physical event. The significance of dilution is site dependent and difficult to predict with certainty; therefore, a measure of the dilution rate is useful for defining physical changes in contaminant concentration. Dilution affects the concentration of a contaminant, not the mass of contaminant. Diffusion and dispersion are the most common mechanisms of contaminant dilution; however, in shallow aquifers, infiltrated rain water can also be a significant contributor.

Diffusion is a minor component of dissolved contaminant dilution because the tortuosity of soil greatly reduces the diffusion of rate. Although diffusion is usually insignificant in the dilution of dissolved contaminant (Freeze and Cherry, 1979), it may be one of the principle factors in the dissolution of contaminant from NAPL into the groundwater. The rate of dissolution depends on the major rate limiting components of natural attenuation, namely, how long is required to expend the source of dissolved contaminant in separate phase contaminant. Example Calculation 6-4 shows one approach for defining diffusion-limited contaminant dissolution.

Dispersion is a more significant physical process resulting in contaminant dilution. It is the movement of contaminant in a direction that is not the flow vector of groundwater. Dispersion commonly results in the side-to-side spread of a contaminant plume along the downgradient flow path. Like diffusion, dispersion does not result in a change of contaminant mass; although it does result in a concentration change. Dispersion is often estimated by examining plume dimensions in the downgradient and cross-gradient directions. The ratio (cross gradient movement versus downgradient movement) represents the dispersion coefficient. Dispersion can be directly measured using an in situ tracer; however, this approach is time consuming and expensive. Dispersion can also be approximated using published values for defined aquifer conditions. The approximated value can be further refined by adjusting it iteratively in a groundwater transport model until the model matches the in situ condition.

The net result of both diffusion and dispersion is a reduction in contaminant concentration. The combined effect of dilution and dispersion can be measured using the

single procedure. The contribution of each to contaminant concentration reduction does not need to be segregated; therefore, a single measurement is used to describe the effect of diffusion and dispersion on the movement of dissolved contaminant.

Volatilization

Volatilization results in a decrease in contaminant mass from one matrix and an increase in another matrix. For example, loss of volatile compounds from groundwater is the movement of volatile compounds from the water into unsaturated soil and possibly the atmosphere. Volatilization is controlled by the Henry's Law Constant, octanol-water partition coefficient, solubility, and density of the contaminant. Volatilization is most prominent in the capillary fringe and the groundwater fluctuation space when the contaminant is less dense than water or moves along the saturated/unsaturated soil boundary.

The contribution of volatilization is difficult to predict during natural attenuation, since multiple conditions interact during volatilization. Volatilization is probably a minor contaminant loss mechanism, unless a soil gas or vadose zone soil treatment technology is used in conjunction with natural attenuation. An example is the operation of a bioventing or soil vapor extraction system in the vadose zone above a contaminated aquifer.

Sorption and Retardation

"Sorption" is a general term used to describe adsorptive and absorptive processes that result in the partitioning of contaminant from the aqueous or dissolved phase to the solid phase or soil (Freeze and Cherry, 1979). In simple terms, contaminants stuck to soil are no longer dissolved in the groundwater. An adsorption coefficient can be estimated using the octanol-water partition coefficient and contaminant solubility. The adsorption coefficient can also be determined experimentally by observing the amount of contaminant in the soil and water. This type of experimental information usually fits a Freundlich adsorption isotherm which can be used to calculate the adsorption coefficient.

The sorption and desorption of dissolved contaminant results in contaminant migration that is slower than the groundwater velocity. The retardation coefficient describes the movement of dissolved contaminant relative to groundwater (Freeze and Cherry, 1979). Example Calculation 6-6 further discusses the retardation coefficient and shows how to estimate it. The retardation coefficient is important because it more accurately defines the retention time of a contaminant between two points along a flow vector. This information is central to the calculation of anaerobic biodegradation rates.

Contaminant Mass Loss

Determining the mass of contaminant lost during natural attenuation is a challenging but important activity. One of the greatest obstacles associated with measuring contaminant mass loss is accurately determining the original mass of contaminant.

This estimate is made by determining the volume of groundwater in the contaminated area, the contaminant concentration, the three dimensional contamination distribution, soil porosity, soil contaminant concentration, and the depth of contaminated soil. Mass loss is determined by comparing the initial mass to the mass remaining at the time of subsequent contaminant mass estimates. The Thiessen Method discussed above is a potentially useful and relatively simple approach for tracking mass loss (Dupont, 1995).

Contaminant Concentration Reduction

Reduction in contaminant concentration is the simplest measurement to make when evaluating natural attenuation, because all the widely accepted analytical methods are designed to report contaminant as a concentration. Accepted methods are available for most common groundwater contaminants. Analytical methods specific for target contaminants should be used. General analyses such as Total Petroleum Hydrocarbon (TPH or TRPH) (U.S. EPA Method 418.1) should be avoided, because the results do not provide data for individual contaminants and the methods are prone to interferences and ambiguities.

The use of typical monitoring wells tend to give artifactual results that do not represent the actual conditions in the aquifer. The long screened intervals in most monitoring wells and the non-uniform flow of groundwater into a monitoring well during bailing often result in samples that poorly reflect actual aquifer water quality. Groundwater monitoring points positioned in contaminated zones or narrowly screened monitoring wells are better alternatives to typical monitoring wells, because they are installed to provide information within the vertical limits of the contaminated area.

Appearance of Degradation Products

Organic contaminants degrade through a series of steps, with each step resulting in a intermediate product that is not the original compound nor the final product (Atlas, 1983, Rochkind-Dubnisky, 1987). Sometimes these intermediates are so transient that they can not be detected or they do not accumulate to a detectable level. After the first few degradation steps, the products are usually common to several biodegradation pathways and cannot be correlated to contaminant degradation.

Quantitation of intermediate biodegradation products is analytically challenging, because the compounds are typically more hydrophilic than the parent contaminant and are, therefore, more difficult to extract and analyze. Fatty acids are potentially quantifiable intermediates of petroleum biodegradation.

Defining an Efficient and Cost-Effective Monitoring Plan for Natural Attenuation

Several approaches can be taken to minimize the cost of long term monitoring of natural attenuation based corrective action plans. Once the plume has been delineated and its behavior has been evaluated, the following issues are important for long term monitoring:

- "Sentry wells" may be installed in an intermediate point between the current downgradient edge of the plume and the nearest receptor, property boundary, or "point of compliance" well. Sentry wells are "clean" groundwater monitoring wells that are used to indicate movement of the contaminant plume. If sentry wells become contaminated, more aggressive remedial technologies are invoked to deal with the contamination; otherwise, natural attenuation continues to be the environmental management strategy.

- The contaminant concentration must be periodically evaluated; however, since plume migration is limited, the sentry wells are protecting downgradient receptors, and plume dimension and concentration is well documented, the frequency of contaminant analysis can be minimized. Similarly, the number of samples can be reduced to the minimum number that will confirm satisfactory performance of the natural attenuation remedial plan. There is no need to remap the entire contaminant plume at each sampling event. Sampling events should be used to confirm treatment with a negotiated confidence level.

- In addition to contaminant concentrations, groundwater parameters should be monitored. The choice of which parameters to monitor should be determined from the initial site assessment. For example, if no nitrate was detected in the groundwater during the site assessment, nitrate would be a useless monitoring parameter. Similar arguments can be made for each groundwater chemistry parameter. If the parameter was not initially useful in defining the natural attenuation process, it need not continue to be analyzed. Field data on water table elevation is an important parameter that should always be included in the monitoring program.

Modeling Natural Attenuation

Predicting the long-term results of natural attenuation relative to aquifer restoration, plume migration, further groundwater contamination, and projected remediation time is often a critical component in a defining a natural attenuation remedial action plan that is acceptable to regulatory agencies and the public. Two general approaches are usually taken to model the future performance of natural attenuation. These are analytical and numerical modeling.

Analytical Modeling

Analytical modeling relies on relatively simple calculations of groundwater flow, contaminant dispersion, adsorption, retardation, partitioning into groundwater, biodegradation, and abiotic transformations of the contaminant. Site specific values for each of the above parameters are used to define the likely migration and attenuation of the contaminant plume. The accuracy of the prediction is dependent on the accuracy of the

defining parameters. Attenuation rates are often modeled using chemical-specific data one chemical at a time.

In at least one case, multivariate statistical analysis was used to model intrinsic biodegradation of BTEX in an aquifer (Tan, 1994). The benefit of this approach is that it can evaluate all pertinent site data as a whole and derive an overall degradation rate for a multicomponent contaminant plume. Further refinements of this and other statistical approaches may lead to a new generation of analytical tools for evaluating and predicting natural attenuation.

If enough site data are available to directly calculate abiotic contaminant losses and a biodegradation rate, most of the other parameters become unimportant since they contribute to abiotic loss. The octanol-water partition coefficient and the diffusion mass flux are of particular value because the continued addition of contaminant to the groundwater from NAPL is an important process governing the rate of remediation. As long as more contaminant is being added to the aquifer from a source area, the remediation cannot be completed although plume dimensions should reach an equilibrium based on the biodegradation rate and the dissolution rate or mass flux into the groundwater.

The mass flux is controlled by the diffusion coefficient and the partition coefficient of the contaminant. Example Calculation 6-4 shows how the mass flux can be estimated. As suggested above, aquifer restoration cannot be completed until all the separate phase (NAPL) contaminant has been physically removed or dissolved into the water.

Numerical Modeling

Numerical modeling employs computer programs to simulate the behavior of an aquifer. The most widely used numerical model for aquifer bioremediation is BIOPLUME II (Rice University). This computer model requires the input of many of the parameters discussed above. In addition to simulating current conditions, the model also predicts what will happen to the contaminant plume in the future. This aspect of the numerical model is extremely valuable for weighing the benefits and risks of natural attenuation, defining the location of sentry wells, and approximating the time required to complete the aquifer remediation.

Computer models are constantly evolving to include more features, improve their accuracy, and expand their flexibility. A major revision of BIOPLUME II is underway that will permit much more precise definition of anaerobic processes within the dissolved contaminant plume. Other aquifer bioremediation computer models include BIO1D (GeoTrans, Inc., Washington, D.C.) and BIOTRANS (Environmental Systems & Technologies, Inc., Blacksburg, VA) (Rafai, 1993). Each model has useful features and may be pertinent for a given site. Because of the subtleties of computer modeling, potential modelers are referred to software user's manuals for detailed instructions on how to use each model. Novice users are strongly encouraged to seek the guidance of an

experienced groundwater modeler. Incorrectly applied or inaccurately calibrated computer models will provide faulty output that can lead to false expectations for natural attenuation.

Data Presentation

Integrating monitoring data into clear and concise figures and tables is very useful for showing the interrelationships between various data and the attenuation process. Particularly important items include:

- The ratio of compounds not subject to anaerobic biodegradation to degradable ones
- Time versus concentration comparisons
- Calculated biodegradation rates and mass biodegraded based on conserved marker concentrations
- Plume movement, size, and contaminant concentration
- Groundwater flow rate and direction, especially seasonal fluctuations
- Groundwater chemistry
  - Dissolved oxygen
  - Nitrate
  - Sulfate and sulfide
  - Methane

Numerous other parameters, calculations, and observations may be included in natural attenuation reports.

One of the most convincing ways to display natural attenuation data employs superimposed contour maps showing the following relationships:

- Change in contaminant concentration with time
- Relationship between contaminant concentration and electron acceptor or respiratory product concentration such as dissolved oxygen, nitrate, sulfate, or methane concentration superimposed on the contaminant contour map
- Relationship between the conserved marker compound and a target compound

- Superimposed contour maps of various target compounds.

A simple way to express monitoring well data is to use pie charts positioned on a site map at each well location. The pie chart shows the relative chemical composition of the groundwater sample. Shifts in relative concentration are easily visualized as the slices of the pie change in size. The magnitude or level of contamination in each well is conveyed by the diameter or area of the pie. During natural attenuation, the size of the pie is expected to decrease with distance from the source and the chemical composition should shift to favor compounds that have a slower anaerobic biodegradation rate. Figure 6-4 is a simplified example of this type of chart.

Regardless of how results are conveyed, the data presentation should accurately portray the natural attenuation process. Important decisions supporting, rejecting, or discontinuing natural attenuation will be made from site data. Inappropriate or erroneous interpretations of site data will have serious implications for the natural attenuation process as time passes and performance objectives are not met. Therefore, conservative, well-documented assessments of candidate sites are essential before decisions are made to proceed with natural attenuation. Armed with a thorough understanding of site conditions, a critical evaluation and presentation of site data, and an appreciation for public and regulatory sensitivities, natural attenuation can be embraced as a viable remedial alternative at many sites.

Rigorous evaluation of natural attenuation during aquifer remediation will provide assurance that the process is working. The final result is successful aquifer restoration and confidence that natural attenuation and intrinsic bioremediation are reliable remedial alternatives that economically protect human health and the environment.

Applying the Principles of Natural Attenuation for Environmental Management, Risk Reduction, and Remediation

Natural attenuation is a powerful process that can, with time, result in site remediation. Natural attenuation faces three obstacles that will hinder its use as a viable environmental risk management strategy. Recognition of these obstacles and conscious effort to avoid stumbling over them will assure responsible and reliable use of natural attenuation.

- Overuse. Natural attenuation will effectively reduce the risk associated with contaminated groundwater and even result in aquifer restoration in some fraction of contaminated aquifers. Some of the suitable sites will also be easily and rapidly remediated using other technologies. When cost and timing do not favor natural attenuation, especially at small or geologically simple sites, other, more aggressive, technologies may be

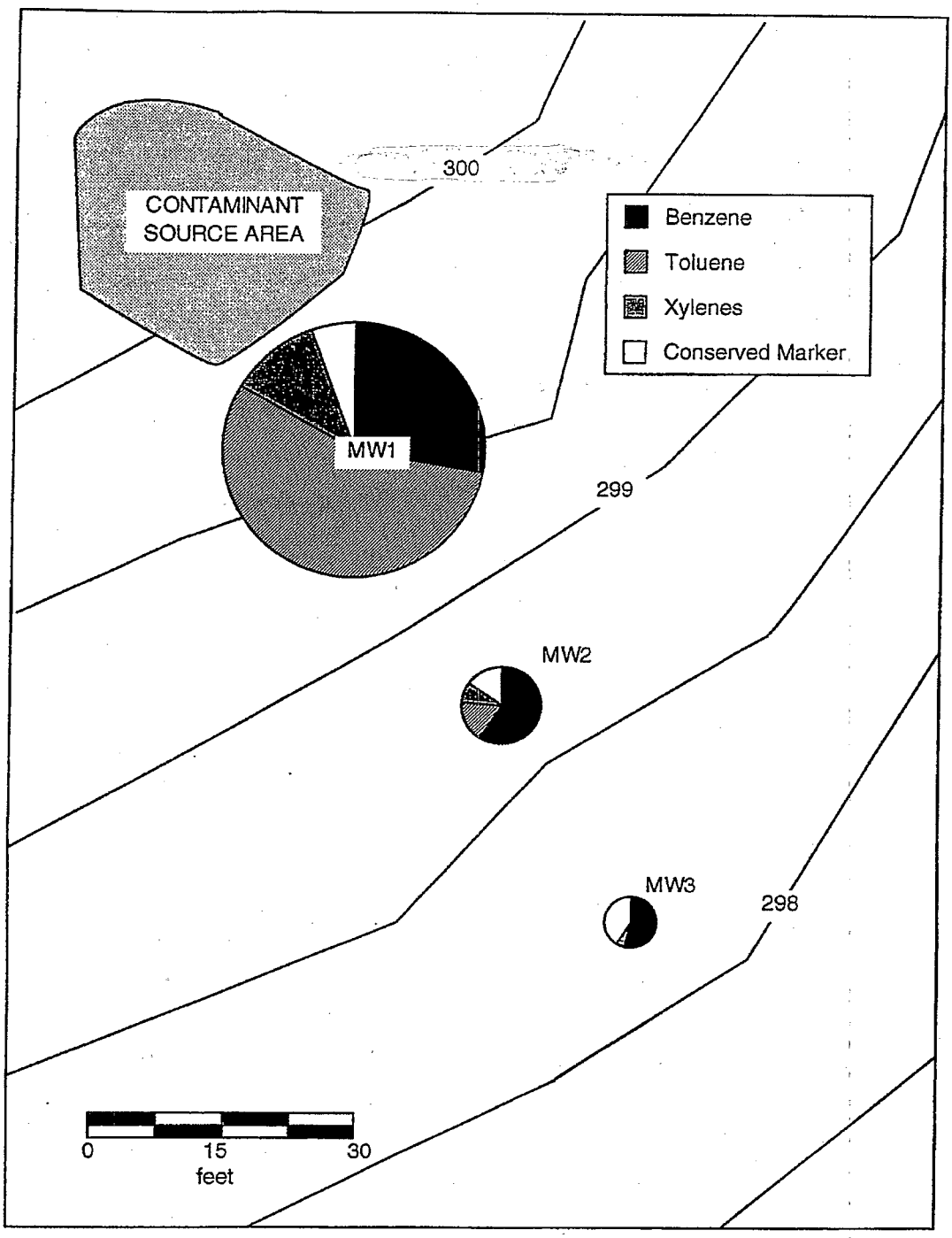

Figure 6-4. Simplified groundwater elevation and contaminant content and composition figure showing relative contaminant composition and content in three monitoring wells.

preferable to natural attenuation(GW citation). In such cases, natural attenuation is probably not the best environmental management choice.

- Misapplication. Emerging environmental technologies are often indiscriminately applied to every site as though the technology can handle any problem. This unfortunate practice has compromised the perception of many useful technologies including air sparging, soil vapor extraction, soil flushing, thermal desorption, and nearly every biological treatment technology. Because of the potential cost savings implied with natural attenuation, this approach will be particularly susceptible to misapplication.

- Skepticism. Skeptical, uninformed, or inflexible regulatory agencies can thwart the use of natural attenuation at ideal sites. Cooperation and flexibility among all involved parties and realization that even proven technologies were once innovative and unproven will help ease the way for applications of natural attenuation at suitable sites.

Evaluating, Selecting, and Monitoring Natural Attenuation for Site Remediation

The following outline suggests a logical progression of data collection, evaluation, and interpretation for quantifying and applying natural attenuation. The outline is intended to highlight some of the steps that are usually required to develop a working knowledge of the natural attenuation processes occurring on site. Site specific conditions, previous site activity, or regulatory and public involvement may result in significant deviation from the proposed outline.

Stepwise Process for Evaluating, Selecting, and Monitoring Natural Attenuation for Groundwater Remediation--

1. Collect and evaluate existing site data

2. Identify exposure points, water use practices, and receptors of the aquifer (RBCA)

3. Determine groundwater flow direction, velocity, and distance to nearest receptor

4. Define the risk associated with the current groundwater conditions (RBCA)

5. Assess potential for natural attenuation using existing data and preliminary risk evaluation

6. Construct a conceptual model for natural attenuation on site
   - 6.1 If preliminary site data provide evidence that natural attenuation is occurring proceed
   - 6.2 If risk of human exposure or further environmental damage is unacceptable or if adequate site data indicate the natural attenuation is not or cannot occur, evaluate other remedial strategies

7. Conduct site characterization to specifically support natural attenuation
   - 7.1 Contaminant mass
   - 7.2 Contaminant concentration
   - 7.3 Presence of source areas
   - 7.4 General groundwater monitoring parameters, e.g., electron acceptors, respiration products, pH, alkalinity, etc.
   - 7.5 Define abiotic mechanisms that result in change in concentration, e.g., dilution, dispersion, dissolution from a source area, retardation, etc.

8. Refine the conceptual model, incorporating new site data

9. Determine if supplemental treatment technologies (e.g. NAPL recovery/source removal) are required to insure successful and expedient natural attenuation

10. Project performance of natural attenuation using analytical or numerical methods
    - 10.1 Analytical modeling includes the application of the calculations presented in this document and other emerging analytical approaches such as multivariate statistical analysis
    - 10.2 Three numerical models are widely available for modeling natural attenuation
      - 10.2.1 BIO-1D, a commercially available one-dimensional computer simulation of biodegradation and contaminant migration
      - 10.2.2 BIOTRANS, a commercially available two-dimensional computer model that incorporates available electron acceptors
      - 10.2.3 BIOPLUME II, public domain computer code using the USGS Method of Characteristic (MOC) code to model oxygen and contaminant distribution. Biodegradation occurs in stoichiometric proportions when oxygen and contaminant coincide. BIOPLUME II is the most widely used model for oxygen enhanced

aquifer bioremediation and natural attenuation. (BIO-PLUME III is anticipated by May, 1995)

11. Compare natural attenuation model predictions with long-term risk
    - 11.1 If risk is acceptable, proceed
    - 11.2 If risk is unacceptable, evaluate a more protective remedial strategy

12. Develop a long-term monitoring plan
    - 12.1 Revise attenuation model as data become available
    - 12.2 Sampling and analysis to verify continuing site remediation
    - 12.3 Locate "sentry" wells to delimit the maximum allowable extent of contaminant migration before a contingency plan is executed
    - 12.4 Define a contingency plan in case natural attenuation does not meet expectations or otherwise fails to protect human health and the environment

13. Execute monitoring plan
    - 13.1 Sample and analyze sentry wells
    - 13.2 Sample and analyze groundwater from selected monitoring wells
    - 13.3 Evaluate results and compare with expectations
    - 13.4 Close site when clean-up goals are reached
    - 13.5 Default to contingency if sentry wells become contaminated, or if natural attenuation otherwise fails to protect human health and the environment.

Conclusion

This chapter has identified the basic tools currently used to define the natural attenuation process. Natural attenuation is a combination of physical, chemical, and biological processes that occur in a complex geological setting. Evaluation techniques for parameters affecting natural attenuation are still evolving. Each parameter contributes complexity and largely unknown error to evaluations of past performance and predictions of future performance. The negative impact of these errors can be minimized by a technically sound monitoring plan, attention to deviations from model predictions, and the use of conservative assumptions. Time and experience will improve our understanding of this phenomenon. This will lead to more accurate performance estimates and greater acceptance of natural attenuation as a viable, reliable, and satisfactory environmental risk management strategy.

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