Evaluation of Remedial Actions for Groundwater Pollution by Organic Solvents

R&D Technical Report P9

A Whittome, J Hodgson and P Rowland

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This report will be disseminated to Groundwater Protection staff at Regional and Area offices to use as a guidance document to ensure best practice when dealing with groundwater pollution investigations and remediation involving organic solvents.

Research contractor
This document was produced under R&D Project i598 by:

Geraghty & Miller International, Inc.
Conqueror House Vision Park
Histon
Cambridge
CB4 4ZR

Tel: 01223 236950 Fax: 01223 236242

Environment Agency's Project Manager
The Environment Agency's Project Manager for R&D Project i598 was:
Peter Ord - Anglian Region

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EXECUTIVE SUMMARY

Chlorinated solvents are amongst the most frequently occurring organic contaminants in British aquifers. The physical and toxicological properties of these compounds prescribe them as extremely insidious and difficult to characterise within the subsurface. Hence remediation of impacted aquifers can be a complicated and sometimes impossible task.

The objective of this research project was to provide guidance to the Environment Agency on the evaluation of remedial actions for groundwater pollution by chlorinated solvents (specifically DNAPL compounds). The document describes the most useful methodologies and reference guides for each sequential phase of a remedial investigation.

The project focused on a few specific organic solvent compounds known as DNAPLs (dense non aqueous phase liquids) and their associated degradation products. A concise description of the important physical and chemical properties controlling the migration of the relevant contaminants is provided as section 3. For a more detailed explanation of the behaviour of organic solvent contaminants in the Chalk and Triassic Sandstone aquifers, the reader is referred to Environment Agency R&D Notes 46 and 47.

The remedial evaluation process is divided into phases, briefly; Site characterisation, setting of remedial objectives and the selection of an appropriate remedial technology.

Site characterisation includes the iterative process between data collation (field investigation) and the interpretation and decision making process (refining the conceptual model). Field methodologies and techniques specific to DNAPL contamination incidents are described and references to more detailed information provided.

Remedial objectives are defined once groundwater pollution is recognised and quantified which often leads to further site investigations. The definition of site specific remedial objectives is a stepped process involving consideration of prescriptive clean up criteria standards and site specific risk assessment methodologies.

The selection of an appropriate remedial alternative takes into account the results of the site characterisation and remedial objective developments. The selection process involves an initial screening stage where all relevant remedial technologies are evaluated in terms of the site specific conditions followed by a feasibility study. Details of thirty two in situ and ex situ remedial technologies, applicable to DNAPL contaminants, are provided as section 6. of this report to aid in the initial screening phase. The feasibility study is a detailed analysis of the short list of suitable remedial technologies. The study includes treatability studies involving both pilot and bench scale tests. Details of applicable feasibility study methodologies and references are provided as section 7.

Finally, to demonstrate the performance and selection of applicable remedial technologies, twelve case histories selected from European and North American literature are presented as section 8.

KEYWORDS

Groundwater, Remediation, Pollution, Chlorinated Solvents, DNAPL (Dense Non Aqueous Phase Liquid), Solvents.

GLOSSARY

Adsorption	Adherence of ions or molecules in solution to the surface of solids
Air sparging	Injection of air below the water table to strip volatile contaminants from the saturated zone
Biodegradation	Biologically mediated conversion of a compound to more simple products
CERCLA	Comprehensive Environmental Response Compensation and Liability Act (1988). Established a national programme in the US to respond to past releases of hazardous substances to the environment
DNAPL	Dense Non Aqueous Phase Separated Liquid, an immiscible organic phase with a relative density >1
EOR	Enhanced Oil Recovery; EOR refers to processes such as cosolvent or steam flushing
Free Phase NAPL	Immiscible liquid existing in the aquifer
Halogenated Solvents	Organic chemicals in which one or more hydrogen atoms have been replaced by a halogen atom
Imbibition	Process during which the saturation of the wetting fluid is increasing and the saturation of the non wetting fluid is decreasing
PCE	Tetrachloroethene: tetrachloroethylene: perchloroethylene: PERC
Plume	Zone of dissolved contaminants
RCRA	Resources Conservation and Recovery Act (USA); regulates monitoring, investigation and corrective action activities at all hazardous waste sites.
Risk Assessment	Evaluation of the potential for exposure to contaminants and the associated hazards
Soil flushing	Forced circulation of water, steam, cosolvents or surfactants to enhance the recovery of contaminants
Sorption	Equilibration of a component between a solid phase surface and a gas or liquid phase

Solidification/ Stabilisation	Processes which utilise cementing agents to mechanically bind subsurface contaminants, thereby reducing their rate of release
TCA	1,1,1-Trichloroethane: methyl chloroform
TCE	Trichloroethene: trichloroethylene
Vacuum extraction	Forced extraction of gas and volatile contaminants from the vadose zone
VC	Vinyl chloride: 1-chloroethene
Volatilisation	Transfer of a chemical from the liquid to the gas phase
Water wet	Media that are preferentially wetted by water relative to another immiscible fluid
Wettability	Relative degree to which a fluid will spread on a solid surface in the presence of other immiscible fluids

1. INTRODUCTION

This report is written as a guidance document for the Environment Agency, on the implementation of remedial action at sites contaminated by organic solvents, in particular dense non aqueous phase liquid (DNAPL) contaminants.

The report is divided into sections relevant to the sequential steps of a remedial implementation procedure. Each step is described and guidance on the major factors involved and information sources is provided.

The specific objectives of the document are as follows:

- To provide a broad strategy for the selection of remedial objectives.
- To provide information on suitable site investigation techniques pertinent to contamination by DNAPL compounds.
- Collate information on applicable in-situ and ex-situ remedial technologies and develop a screening methodology (feasibility study) to aid the selection of a remedial alternative.
- Present a selection of case histories which critically demonstrate a variety of remedial technologies applicable to DNAPL organic solvent contaminants at sites in Europe and the USA.

Chlorinated organic solvents are amongst the most commonly occurring groundwater contaminants in British aquifers, so much so that the quality of our groundwater supplies is being increasingly affected. The toxicological and physiochemical characteristics of organic solvents and particularly those present as DNAPLs cause them to be extremely insidious contaminants and very difficult to characterise in the subsurface. This document details current research and methodologies focused on organic solvent pollution incidents, providing guidance to the Environment Agency on conducting remedial investigations and implementation procedures.

2. USE OF REPORT

The layout of the report is intended to follow the sequential stages of the development and implementation of a remedial action plan. These are presented in the form of a flow chart as Figure 2.1, that highlights major milestones in the remedial action plan and major decision times for the Environment Agency. Each section contains guidance on the decisions, methodologies and references showing where further information can be obtained.

This guide contains eight sections:

1. INTRODUCTION
2. USE OF REPORT
3. DNAPL CHARACTERISTICS AND PROPERTIES
4. SITE CHARACTERISATION
5. REMEDIATION OBJECTIVES
6. REMEDIATION TECHNOLOGIES
7. REMEDIATION FEASIBILITY STUDIES
8. CASE STUDIES

Section 1. Introduction
The Introduction presents the objectives and background information to the report.

Section 2. Use of Report
Presents guidance on how to use this document.

Section 3. DNAPL Characteristics and Properties
This is a reference section detailing the physical, chemical and toxicological properties of selected DNAPL organic compounds and the factors controlling their migration in the subsurface.

Section 4. Site Characterisation
This section includes the methodologies involved in the initial review of existing data and development of a conceptual model, followed by the iterative process between data collection (field investigation stage) and the interpretation and decision making processes (refining the conceptual model).

Section 5. Remedial Objectives
This stage involves two sections; a complete risk assessment stage (following a preliminary risk assessment before the site characterisation stage), and options available for defining remedial objectives.

Section 6. Remediation Technologies
The section is intended to be used as a screening matrix for selecting the most technically appropriate remedial technologies based on the remedial objectives and site specific hydrogeological conditions. Thirty two technologies suitable for DNAPL contaminated sites are presented; a brief outline of each technology including a description and notes on applicability, limitations, data needs, performance data, costs and case studies. References are provided.

Section 7. Remedial System Feasibility Studies

The remediation feasibility study is the methodology for selecting the most appropriate remedial technology. It provides guidance on remedial technology assessment criteria, performance of treatability and pilot tests, evaluation of performance and comments on completion and validation procedures. It should provide a means for evaluating remedial options based on all the necessary technical, logistical and cost considerations.

Section 8. Case Studies

Case histories are provided for reference and document the sequential steps in the flow chart for twelve existing sites. The sites were selected from European and North American literature and demonstrate a variety of remedial technologies.

The remaining steps in the flow chart are site and technology specific and are not discussed within the scope of this work. Guidance on where to find design, implementation and monitoring information on specific technologies is given in section 6.

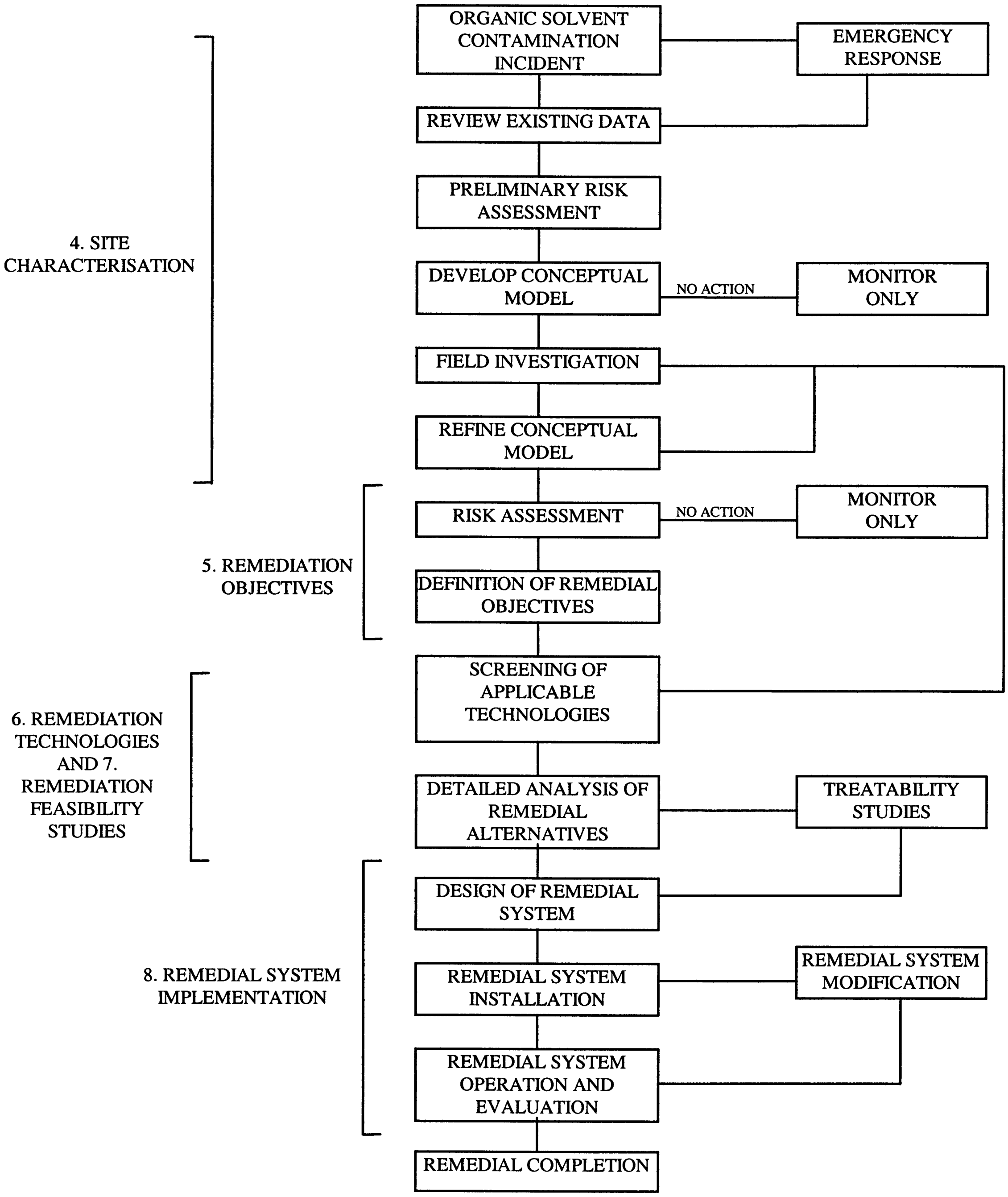


Figure 2.1 **Flow Chart of Remedial Action Implementation**

3. DNAPL MIGRATION CHARACTERISTICS AND PROPERTIES

3. DNAPL MIGRATION CHARACTERISTICS AND PROPERTIES

3.1 Introduction

The definition of a DNAPL (Dense Non Aqueous Phase Liquid) is a compound that occurs in the subsurface as an immiscible phase which is more dense and less viscous than water. Many halogenated organic solvents can be described as DNAPL compounds.

Section 3. briefly describes the major factors controlling the migration and occurrence of DNAPL organic solvent contaminants in the subsurface, with particular reference to the following compounds:

Tetrachloroethene (PCE)
Trichloroethene (TCE)
Tetrachloroethane (TCA)
1,1,1-Trichloroethane (1,1,1-TCA)
Carbon Tetrachloride
Dichloroethene (1,2-DCE)
Chloroethane
Vinyl Chloride (VC)

The chapter is in two sections:

Section 3.2 DNAPL Migration Characteristics in the Subsurface
Factors controlling the migration of free phase DNAPL in the subsurface are described. A number of conceptual models of DNAPL subsurface migration are presented.

Section 3.3 Properties of Fluid and Media Controlling Migration
Important properties of the DNAPL compound and the aquifer affecting DNAPL migration are described. A complete set of physical, chemical and toxicological properties of the contaminants listed above are presented in tabular form at the end of this section.

3.2 DNAPL Migration Characteristics in the Subsurface

Several factors control the subsurface migration of free phase DNAPL and the phase partitioning of DNAPL in the subsurface (Feenstra and Cherry, 1988; Cohen and Mercer, 1993; Domenico and Schwartz, 1990). DNAPL migration in the subsurface is influenced by:

- volume of DNAPL released
- area of infiltration
- time duration of release
- properties of the DNAPL
- properties of the media
- subsurface flow conditions

After DNAPL release at the surface transport mechanisms include immiscible subsurface flow, dissolution and solute transport, volatilisation and vapour transport.

Three distinct forces act upon subsurface DNAPL and each force may have a different principal direction of action. The subsurface movement of DNAPL is determined by the interaction of these forces:

- pressure due to gravity (also referred to as buoyancy or hydrostatic pressure)
- capillary pressure
- hydrodynamic pressure (also referred to as the hydraulic or viscous force)

Figure 3.1 presents conceptual models of migration routes of DNAPL in several subsurface situations.

3.2.1 DNAPL in the Unsaturated Zone

When released to the subsurface, DNAPL migrates downwards under the force of gravity through the unsaturated zone as a phase separated liquid. Water is the wetting fluid and therefore occupies the smaller pores and capillary channels in the unsaturated zone. The DNAPL migrates through the larger pores, which initially have water coating the grains and air filling the remainder of the pore. The DNAPL displaces the air and the pore becomes filled with the DNAPL and residual water coating the grain surface.

The unsaturated zone permeability for the DNAPL is greater than for water, when the two fluids exist simultaneously in the unsaturated zone, because the pores through which the DNAPL, as the non-wetting fluid, migrates are larger than the pores through which the water, as the wetting fluid, migrates.

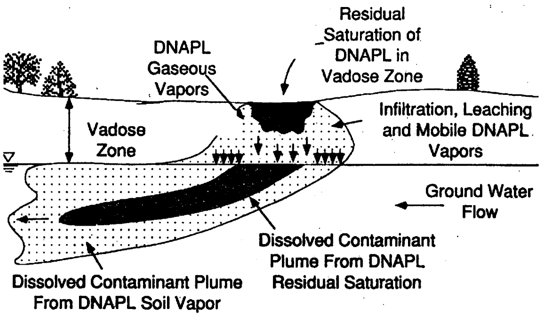
Capillary forces and the variable permeability of the impacted medium induce lateral spreading whilst the DNAPL is migrating vertically (Schwille, 1988; Cohen and Mercer, 1993). Small differences in soil water content and grain size can provide sufficient capillary contrast to cause lateral DNAPL spreading in the unsaturated zone. Alternatively, downward movement will be enhanced, and lateral spreading limited, by dry conditions and the presence of transmissive vertical pathways for DNAPL transport, i.e. root holes, fractures, uniform coarse-grained materials and bedding planes with high-angle dip.

As it sinks through the unsaturated zone, a significant proportion of DNAPL is trapped in the porous media at residual saturation, due to interfacial tension effects. This entrapment depletes the migrating DNAPL volume and, given a sufficiently small release or thick unsaturated zone, may exhaust the mobile DNAPL body above the water table. Residual saturation values for NAPLs in variably saturated soils typically range from 0.05 to 0.20 where flow is through the matrix, however residual saturation will be significantly less where movement is along fissures.

For a given DNAPL release volume, the depth of infiltration will be influenced by the area over which the release occurs and the release rate. Experimentation using PCE has shown that a continuous drip release over a small area will infiltrate the subsurface to a greater depth than an instantaneous spill occurring over a larger area (Poulsen and Kueper, 1992).

Case 1: DNAPL Release to Unsaturated Zone Only

After release on or near the surface, DNAPL moves vertically downward under the force of gravity and soil capillarity. Because only a small amount of DNAPL was released, all of the mobile DNAPL is eventually trapped in pores and fractures in the unsaturated zone. Infiltration through the DNAPL zone leaches soluble organic constituents from the residual DNAPL and transports them to the water tables, thereby producing a dissolved organic contaminant plume in the aquifer. Migration of gaseous vapours by diffusion and density flow also act as a source of dissolved organics to groundwater. Contaminated vapours are leached by infiltration which recharges the water table and sink to contact the saturated zone.



After Waterloo Centre for Groundwater Research, 1989.

Case 2: DNAPL Release to the Unsaturated and Saturated Zone

If enough DNAPL is released at or near the surface, it can migrate through the unsaturated zone, overcome the capillary resistance provided by the water saturated pores at the capillary fringe and sink into the saturated zone because it is heavier than water. DNAPL penetration is often resisted by the capillary fringe which leads to lateral spreading. DNAPL migration will continue until the mobile DNAPL is trapped at residual saturation by capillary mechanisms and/or in pools above stratigraphic traps. Groundwater flowing past the trapped DNAPL leaches soluble components from the DNAPL, thereby creating a dissolved contaminant plume down groundwater gradient from the DNAPL zone. As with case 1, water infiltrating from the source zone also carries dissolved chemicals to the aquifer and contributes further to the dissolved plume. Within the saturated zone, lateral spreading of DNAPL is promoted just above finer layers and generally increases with decreasing permeability and grain size. DNAPL saturation typically increases at the base of coarser layers overlying finer layers. The rate of dissolved chemical migration with groundwater increases with layer permeability.

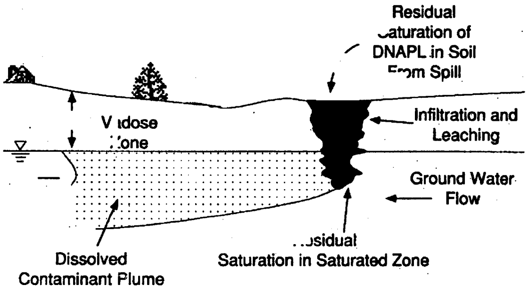


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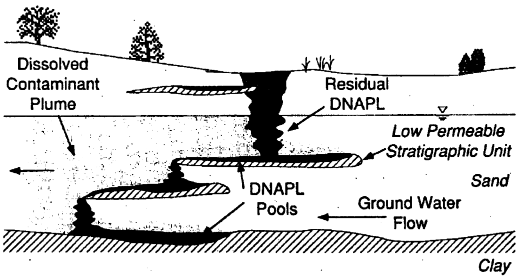
Figure 3.1: Conceptual Models of DNAPL Subsurface Migration (USEPA, 1992)

Case 3: DNAPL Pools and the Effect of Low Permeability Capillary Barriers

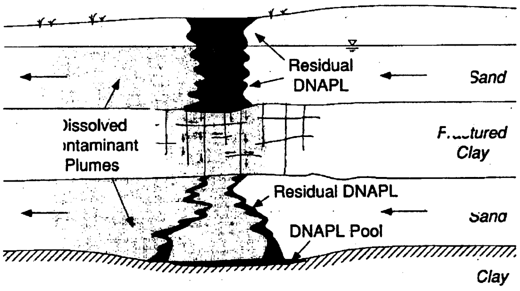
Mobile DNAPL will continue to sink downward until it is trapped at residual saturation (cases a and b) or until low permeability stratigraphic units are encountered which create capillary barriers upon which DNAPL pools. It is possible for a perched DNAPL pool to fill up and then spill over the low permeability lens. The spill over point (or points) can be some distance away from the original source, greatly complicating the process of tracking the DNAPL migration.



After Waterloo Centre for Groundwater Research, 1989.

Case 4: Composite Aquifer Site

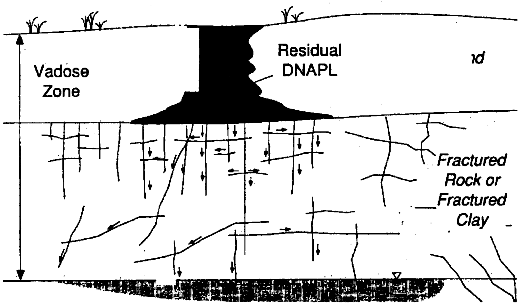
In this case for example, sand overlies fractured clay, overlying a permeable sand above an impermeable clay layer. Mobile DNAPL migrates downward through the unsaturated zone, producing a dissolved chemical plume in the upper aquifer. Although a DNAPL pool is formed on the fractured clay unit, the fractures are large enough to permit vertical migration downward to the deeper aquifer. DNAPL may pool in a surface depression on the underlying capillary barrier and a second dissolved chemical plume is formed.



After Waterloo Centre for Groundwater Research, 1989.

Case 5: Fractured Rock or Fractured Clay System

DNAPL introduced into a fractured rock or fractured clay system follows a complex pathway based on the distribution of fractures in the original matrix. The number, density, size and direction of the fractures often cannot be determined due to the heterogeneity of the fractured system and the lack of economical formation characterisation technologies. Relatively small volumes of DNAPL can penetrate deeply into the fractured systems due to the low retention capacity of the fractures and the ability of some DNAPLs to migrate through very small, less than 20 micron fractures. Many clayey units act as fractured media with preferential pathways for vertical and horizontal DNAPL migration. DNAPL contained in fractures will dissolve and be transported through the fracture network with groundwater and will also diffuse into and sorb onto the porous inter fracture matrix. Residual saturation and adsorbed chemicals both provide long term sources for groundwater contamination.



After Waterloo Centre for Groundwater Research, 1989.

Figure 3.1: Cont'd. Conceptual Models of DNAPL Subsurface Migration (USEPA, 1992)

DNAPL is retained at residual saturation as films, wetting rings, wedges and as non-wetting globules, in the presence of water within the unsaturated zone. This residual DNAPL will dissolve slowly into infiltrating precipitation and will be a long term source for groundwater contamination. DNAPL immobilised within the unsaturated zone can result in continuous or repeated incidents related to each recharge event of dissolved contaminant releases to groundwater.

Most dense organic solvents have high vapour pressures and, where DNAPL exists in the unsaturated zone, a plume of solvent vapour develops in the soil air surrounding the DNAPL source. These vapours can condense on soil water and the water table causing additional groundwater contamination. Field experiments involving TCE show that significant groundwater plumes may form over a period of weeks from solvent vapour in a thin unsaturated zone. Vapour transport can cause shallow groundwater contamination in directions opposite to groundwater and/or DNAPL flow. The resulting groundwater contamination plumes can have high dissolved chemical concentrations, but tend to be very thin in vertical extent, and occur close to the water table (Cohen and Mercer, 1993).

3.2.2 DNAPL in the Saturated Zone

After free phase DNAPL has migrated vertically to the capillary fringe, the DNAPL will spread laterally and accumulate until the gravitational pressure developed exceeds the threshold entry pressure of the underlying water saturated medium. When this occurs, DNAPL will displace water and continue its migration under pressure and gravity forces. Where DNAPL encounters relatively permeable layers, fractures or other pathways that present lower capillary resistance to entry than underlying less permeable strata, lateral spreading will occur (Cohen and Mercer, 1993).

In some situations a light non aqueous phase liquid (LNAPL), such as a hydrocarbon, may be present floating on the water table. It is important to note that solvents may preferentially partition into the LNAPL and vertical migration in the saturated zone may be impeded.

In the saturated zone the DNAPL will migrate vertically until it reaches a barrier layer upon which it may continue to flow laterally under pressure and gravity forces. DNAPL may be immobilised as a reservoir of continuous immiscible fluid, if the capillary barrier forms a bowl shaped stratigraphic trap, or may migrate laterally by gravity and down the slope of the barrier layer. DNAPL may therefore move in a different direction to groundwater flow and solute transport. Determining the slope and location of low permeability layers can be critical to evaluating DNAPL migration potential.

Many fine grained layers are inadequate capillary barriers to DNAPL migration due to the presence of preferential pathways which allow spreading DNAPL to sink into lower formations. As DNAPL spreads above a fine grained layer, it may encounter and enter fractures, root holes, stratigraphic windows, burrow holes, inadequately sealed wells or borings etc. DNAPL migration may occur through hairline fractures as small as ten microns in diameter.

A finite DNAPL source will eventually be immobilised by residual saturation and/or in stratigraphic traps. Mobile and immobile DNAPL in the saturated zone will dissolve in groundwater and thereby act as a long term source of groundwater contamination.

3.3 Properties of Fluid and Media Controlling Migration

Multifluid flow involving DNAPL, water and air in the unsaturated and saturated zones is considerably more complex than single fluid flow and several different concepts must be applied when evaluating the subsurface flow system. These are explained briefly below. Further information can be found in Cohen and Mercer (1993), Fetter (1993), Domenico and Scwartz (1990) and Wilson (1990). Tables 3.1 and 3.2 presents the physical and toxicological properties of the nine most frequently occurring subsurface DNAPL contaminants.

3.3.1 Saturation

Saturation describes the ratio of the volume fraction of a fluid and the total void volume of the media occupied by that fluid. Saturation ranges from zero to one and the saturations of all fluids, including air, sum to one. Saturation defines the volumetric distribution of DNAPL, properties such as relative permeability and capillary pressure are functions of saturation.

3.3.2 Interfacial Tension

The characteristics of DNAPL movement are largely derived from tension which exists at the interface between immiscible fluids (NAPL, air and water). Interfacial tension can be defined as the energy resulting from the difference between the greater mutual attraction of like molecules within each fluid and the lesser attraction of dissimilar molecules across the immiscible fluid interface. The unbalanced energy draws molecules along the interface inward, resulting in a tendency for contraction of the fluid-fluid interface to attain a minimum interfacial area. This phenomenon is related directly to the capillary pressure across a water-NAPL interface and is a factor controlling wettability. The fluid on the concave side of the interface is at higher pressure than the fluid across the interface and the pressure difference is proportional to the interface curvature. It is as a result of interfacial tension that non wetting DNAPLs tend to form globules in water and water saturated media. The interfacial tension between a liquid and its own vapour is called surface tension.

3.3.3 Wettability

Wettability is dependent upon interfacial tension and affects relative permeability, capillary pressure and residual DNAPL saturation. Within a two fluid system, the term refers to one fluid spreading and coating solid surfaces in preference to a second fluid. Whereas the wetting fluid (usually water in a DNAPL water system) tends to coat solid surfaces and occupy smaller openings in porous media, the non wetting fluid will tend to be constricted to the larger openings, i.e. fractures and relatively large pore bodies.

Contact angle at the fluid-solid interface is the simplest measure of wettability. The porous medium is considered water wet if the contact angle is less than 70°, NAPL wet if the contact is greater than 110° and neutral if the angle is between the two figures. Contact angle measurements are only qualitative indicators of wettability because they do not account for physical properties of the medium such as heterogeneity, roughness and pore geometry. Other factors that must be taken into consideration include water chemistry, NAPL chemistry, media mineralogy, the presence of organic matter or surfactants and media saturation history. Most natural porous media, except organic matter and anhydrites, are strongly water wet if not contaminated by NAPL.

Few wettability studies have been conducted on DNAPLs but given the heterogeneous nature of subsurface media and the factors that influence wettability, some investigators have concluded that the wetting of porous media by NAPL can be heterogeneous or fractional rather than uniform.

Aquifers are naturally water wet because they contain water before any NAPLs are discharged to them. The unsaturated zone may be either water wet or NAPL wet, depending upon whether the soil is moist or dry when the NAPL is discharged. However, even soil in the unsaturated zone that appears to be dry will have water held to it by capillary pressures.

3.3.4 Capillary Pressure

Capillary pressure is a function of interfacial tension, contact angle and pore size. The capillary pressure increases as pore size and contact angle decrease and interfacial tension increases. Capillary pressure causes porous media to draw in the wetting fluid and repel the non wetting fluid. This is due to the dominant adhesive force between the wetting fluid and media solid surfaces. As a result of contact angle a meniscus, with a radius of curvature that is proportional to the pore radius, exists at the interface between two immiscible fluids within a pore. The pressure drop across the curved interface is the capillary pressure, which is equal to the difference between the non wetting fluid pressure and the wetting fluid pressure.

Before NAPL can penetrate a water saturated porous medium, the NAPL pressure head must exceed the resistance of the capillary forces. Once the threshold, or displacement entry pressure has been overcome, a non wetting NAPL can enter the largest pores, which offer the least capillary pressure resistance. Capillary forces can restrict the migration of NAPL into water saturated media, so that fine grained layers with a small pore size can be capillary barriers.

Capillary pressure effects explain much of the distribution and behaviour of subsurface DNAPL. Penetration of the unsaturated zone is influenced by the distribution of water content and pore openings. Upon reaching the capillary fringe above the water table, sinking DNAPL will tend to be obstructed and spread laterally until sufficient DNAPL thickness has accumulated to exceed the threshold entry pressure at the capillary fringe. Similarly in the saturated zone, DNAPL will tend to spread laterally over fine grained capillary barriers and sink through fractures and coarser materials where possible.

Once DNAPL enters a vertical fracture, it will readily invade finer and finer fractures with depth due to the increase in DNAPL column height with fracture depth.

Where DNAPL encounters a coarser underlying medium, capillary pressure will work to squeeze the DNAPL into the larger openings. This effect can be demonstrated by upward rather than downward DNAPL movement after placing DNAPL in a silt layer beneath a very coarse sand with a much lower DNAPL saturation. Capillary pressure will cause a portion of the DNAPL in the silt to rise into the coarser medium against the force of gravity. Therefore unless exhausted by residual saturation or prevented by hydraulic pressure, downward DNAPL movement will occur readily in homogeneous media or from finer to coarser layers.

There is no unique relationship between capillary pressure and saturation. Changes depend on whether the medium is undergoing wetting (imbibition) or drainage of the wetting fluid. This capillary hysteresis results from non-wetting fluid entrapment and differences in contact angles during wetting and draining that cause different drying and wetting curves to be followed. During drainage, the larger pores drain the wetting fluid quickly while the smaller pores drain slowly, if at all. As a result of this capillary retention, capillary pressure corresponds to higher saturations on the drainage curve. During wetting, the smaller pores are filled first and the larger pores are least likely to fill with the wetting fluid, thereby leading to a lower capillary pressure curve with saturation. Significant errors can occur by overlooking hysteretic effects during the simulation of some immiscible flow problems. Hysteresis is typically ignored, however, during simulation studies because its significance is considered minor compared to uncertainties associated with other parameter estimates.

3.3.5 Residual Saturation

Beneath the water table, residual saturation of NAPL is the saturation at which NAPL is immobilised by capillary forces, usually as discontinuous globules, under ambient groundwater flow conditions. In the unsaturated zone, however, residual NAPL may be more or less continuous depending on the extent to which NAPL films develop between the water and gas phases and thereby interconnect isolated NAPL globules. A significant portion of NAPL is retained in porous media, depleting and eventually exhausting the mobile NAPL body.

Residual saturation for the wetting fluid is conceptually different from that for the non wetting fluid. The non wetting fluid is discontinuous at residual saturation, whereas the wetting fluid is a continuous film. The controlling factor is capillary forces but residual saturation for both fluids also depends on: (1) the media pore size distribution, (2) wettability, (3) fluid viscosity ratio and density ratio, (4) interfacial tension, (5) gravity/buoyancy forces and (6) hydraulic gradients. Unless residual NAPL is replenished by continued contaminant releases it will be slowly reduced in volume by dissolution, volatilisation and in some situations biodegradation.

3.3.6 Relative Permeability

During simultaneous flow of two immiscible fluids, part of the available pore space will be filled with one fluid and the remainder will be filled with the other fluid. Because the two fluids must compete for space in which to flow, the cross sectional area of the pore space available for each fluid is less than the total pore space. This can be quantified by multiplying the intrinsic permeability by a dimensionless ratio, known as relative permeability. Relative permeability is the ratio of the effective permeability of a fluid at a fixed saturation to the intrinsic permeability. As such, it varies with saturation from one to zero. Unfortunately, relative permeability data are generally unavailable for DNAPLs found at contamination sites.

Three phase relative permeabilities are required to describe the simultaneous movement of NAPL, water and air at a point. However, given the difficulty and expense of measurement, site specific data and the functional form of the three phase permeability are generally not available, particularly for DNAPLs.

3.3.7 Solubility

Aqueous solubility refers to the maximum concentration of a chemical that will dissolve in pure water at a particular temperature. Factors affecting solubility include temperature, cosolvents, salinity and dissolved organic matter. Although the aqueous solubility of most organic chemicals rises with temperature, the direction and magnitude of this relationship is variable. Similarly, the effect of cosolvents (multiple organic compounds) on chemical solubility depends on the specific mix of compounds and concentrations. Increasing salinity leads to a general decline in aqueous solubility of organic chemicals.

Many sites contaminated by DNAPLs are composed of multiple chemicals with varying individual solubilities. At these sites, preferential and sequential loss of the relatively soluble and volatile NAPL components leaves behind a less soluble residue. This weathering causes the ratios of chemicals in the NAPL and dissolved plume to change with time and space.

Results of laboratory dissolution experiments show that chemical concentrations approximately equal to aqueous solubility values are obtained in water flowing at 0.1-1 md^{-1} through NAPL contaminated sands. However, it is widely reported that organic compounds are commonly found in groundwater at concentrations less than 10 percent of NAPL solubility limits, even where NAPL is known or suspected to be present. The discrepancy between field and laboratory measurements is probably caused by heterogeneous field conditions, such as non uniform groundwater flow, complex NAPL distribution and mixing of stratified groundwater in a well. Various studies suggest that dissolution may be rate limited when NAPL is present as large complex globules, groundwater velocities are high, NAPL concentrations are low and/or the mass fraction of soluble species in a NAPL mixture is low. For halogenated solvents in particular, these chemical and hydrodynamic processes promote the creation of large plumes of groundwater with low chemical concentrations, which may still be in excess of drinking water standards.

3.3.8 Volatilisation

Volatilisation refers to mass transfer from liquid to the gaseous phase. Soil vapour contaminants may be derived from the presence of free NAPL, dissolved chemicals or adsorbed chemicals. The process is controlled by the vapour pressure of the organic solvent or solute. The vapour pressure of a liquid or solid is the pressure of the gas in equilibrium, with respect to the liquid or solid, at a given temperature. It indicates the tendency to evaporate of a specific compound and is essentially the solubility of an organic solvent in a gas. Other factors influencing volatilisation rate are: aqueous solubility, concentration in soil, soil moisture content, soil air movement, sorptive and diffusive characteristics of the soil, soil temperature and bulk properties of the soil such as organic-carbon content (foc), porosity, density and clay content.

Volatile organic compounds (VOCs) in soil gas can: 1) migrate and ultimately condense, 2) sorb onto soil particles, 3) dissolve in groundwater, 4) degrade and/or 5) escape to the atmosphere.

Volatilisation of dissolved organic solutes from water is described by Henry's law, which states that, at low vapour pressures, there is a linear relationship between the vapour pressure of a solute above its aqueous solution and the concentration in the solution. The proportionality constant between the two is called Henry's law constant and is equal to the vapour pressure in atmospheres divided by the solubility of the compound in water (moles m^{-3}).

Recent studies have examined soil gas advection due to gas pressure and gas density gradients. Density driven gas flow can be an important transport mechanism in the unsaturated zone that may result in contamination of the underlying groundwater and significant depletion of the residual NAPL below the detection limits.

3.3.9 Viscosity

Viscosity is the internal friction derived from molecular cohesion within a fluid that causes it to resist flow. A low viscosity NAPL will migrate more rapidly in the subsurface than a high viscosity NAPL assuming all other factors. This is because hydraulic conductivity is inversely related to absolute (or dynamic) fluid viscosity. Absolute viscosity divided by fluid density is referred to as kinematic viscosity. At sites with multiple DNAPL types, therefore, more distant free phase NAPL migration is usually associated with the less viscous liquids. Subsurface NAPL viscosity can change with time, typically becoming thicker as the more volatile, thinner components evaporate and dissolve from the NAPL mass.

The NAPL water viscosity ratio is part of a term used in the petroleum industry known as the mobility ratio. In a water flood scenario, the mobility ratio is defined as the mobility of the displacing fluid (relative permeability/viscosity for water) divided by the mobility of the displaced fluid (relative permeability/viscosity for NAPL). Mobility ratios greater than one favour the flow and recovery of NAPL.

During immiscible fluid displacement in a porous medium, the interface between the two fluids may become unstable. Known as viscous fingering, this instability typically arises when a less viscous fluid moves into a more viscous fluid. This phenomenon causes fingers of the driving fluid to penetrate the displaced fluid. The location of viscous fingering is also influenced by heterogeneities in the impacted media. As a result of viscous fingering, NAPL may not occupy the complete cross sectional area through which it moves, thus permitting water to flow through and increase dissolution. Additionally, for a given NAPL volume, viscous fingering will promote deeper NAPL penetration than would occur in its absence.

3.3.10 Degradation of Organic Solvents in the Subsurface

Chlorinated solvents are generally persistent contaminants in the subsurface. “Most DNAPL compounds are halogenated solvents which are resistant to degradation and involve transformations to equally undesirable compounds” according to Feenstra and Cherry (1988). However, under certain circumstances in the subsurface, degradation of the compounds can occur and a wide range of new compounds, the degradation products and intermediates, are produced. Degradation can occur through both biotic and abiotic processes under aerobic and anaerobic conditions. Most abiotic transformations are generally slow, however biotic transformations may be rapid if the required environmental conditions prevail (Hinchee et al., 1994).

Environmental conditions influencing the type and rate of the degradation reactions described below include pH, temperature, state of oxidation or reduction, micro organisms and nutrients present, and other chemicals present. Reaction kinetics also play an important role in the determination of the abiotic and biotic fate of organic contaminants. Theoretically, the end products of the abiotic reactions are ethane and ethene, which should be amenable to further biodegradation. However, under field conditions such a favourable outcome might require many years to occur, and a variety of toxic degradation products may form in the process. When considering remedial strategies it is important to note the range of degradation products present in the contaminated subsurface and not just the initially spilled solvent.

Following are brief descriptions of the main degradation reactions (Fetter, 1993):

a) **Substitution** - Water reacts with the halogenated compound to substitute a hydroxide (OH^-) ion for a halogen ion, creating an alcohol. Also known as hydrolysis this reaction can occur in water without inorganic or biological catalysts. Substitution reactions proceed most rapidly for monohalogenated compounds, which have half lives of approximately one month. However, as the number of halogen ions increases, the half life for reactions increases rapidly into the range of years to hundreds of years.

b) **Dehydrohalogenation** - A reaction where an alkane loses a halide ion from one carbon atom and then a hydrogen atom from an adjacent carbon. The result is the formation of a double bond between the carbon atoms, thus creating an alkene. For example transforming 1,1,1 trichloromethane to 1,1 dichloroethene. The rate of dehydrohalogenation increases with increasing numbers of halogen ions; hence compounds that undergo substitution slowly undergo dehydrohalogenation rapidly.

c) **Oxidation** - The addition of an OH^- radical to an alkane in place of an H atom on a carbon leads to the formation of chlorinated alcohol e.g. 1,1-dichloroethane forms 1,1-dichloroethanol. Oxidation of a carbon-carbon double bond results in the formation of an epoxy. The epoxy is short lived and under neutral pH conditions can be oxidised to a carboxylic acid.

d) **Reduction** - Reduction reactions can take two forms when considering the degradation of organic solvents: (i) **Hydrogenolysis** - The removal of a halide ion by a reduced species, such as a reduced transition metal or a transition metal complex. The reduced species is thus oxidised. The alkyl radical thus formed can react with a H^+ ion which substitutes for the departed halide ion. (ii) **Dehaloelimination** - Reductions can also occur if there are halides on adjacent carbon atoms. In this case the loss of a halogen from each carbon atom creates an alkene by the formation of a double bond between the carbon atoms. This process leads to the transformation of chlorinated alkanes to chlorinated alkenes, e.g. hexachloroethane goes to tetrachloroethene which may then further degrade to chlorethene by hydrogenolysis

Table 3.1 Toxicological Properties of DNAPL Compounds (adapted from Cohen and Mercer, 1993)

DNAPL	RCRA or NJ Action Level Water (mg/l)	RCRA or NJ Action Level Soil (mg/kg)	ACGIH TWA (ppm)	ACGIH STEL (ppm)	NIOSH IDLH (ppm)	High Odour Threshold (ppm)	Toxicity	Acute Symptoms	Chronic Symptoms
Carbon tetrachloride	3.00E-04	5.00E+00	Ca 5 (31)		Ca 300	238	LC50 for mice = 9528ppm. Poisoning by inhalation, ingestion or skin absorption.	Nausea, vomiting, diarrhoea, headache, stupor, renal damage leading to anuria and azotenia, liver injury. Can be fatal.	Primarily liver damage but kidney damage and visual disturbance can also occur. Skin contact can lead to dermatitis through defatting action. Alcohol intensifies action. Substance may reasonably be anticipated to be a carcinogen.
1,1-Dichloroethene (1,1-DCE)	7.00E-03	1.00E+01	Ca 5 (20)	Ca 20 (79)		1009			Irritant to skin, mucous membranes, narcotic in high concentrations. Has caused liver and kidney injury in experimental animals.
1,2-Dichloroethene(1,2-DCE)	1.00E-01		200 (793)		4000	498	LD50 in rats 1ml/kg orally, 60 ml/kg intrapertoneal. LD50 in mice 3.2ml/kg intraperitoneal. Soluble in alcohol, ether and most other organic solvents, under these conditions LD50 in mice 2150 mg/kg.		May cause respiratory irritation, narcosis.
1,1,2,2-Tetrachloroethane	2.00E-03	4.00E+01	Ca 1 (6.9)			5	LD50 orally in rats 0.20 ml/kg		Powerful narcotic, liver poison. For symptoms see Carbon Tetrachloride
Tetrachloroethene (PCE)	7.00E-04	1.00E+01	Ca 50 (339)	Ca 200 (1357)	Ca 500	69	LD50 orally in mice 8.85 g/kg. LC for mice in air 5925 ppm.		Narcotic in high concentrations, defatting action on skin can lead to dermatitis.
1,1,1-Trichloroethane (1,1,1-TCA)	3.00E+00	7.00E+03	350 (1910)	450 (2460)	1000	696			Irritating to eyes, mucous membranes and in high concentrations narcotic.
Trichloroethene (TCE)	5.00E-03	6.00E+01	Ca 50 (269)	Ca 200 (1070)		402	LD50 orally in rats 4.92 ml/kg. LC (4hrs) in rats 8000 ppm	Deaths occurring after heavy exposure attributed to ventricular fibrillation. Found to induce hepatocellular carcinomas in U.S. National Cancer Institute tests on mice.	Moderate exposures cause symptoms similar to alcohol inebriation. Higher concentrations can have a narcotic effect. Liver injury is not definitely established in occupational exposures.
Chloroethane									Mildly irritating to mucous membranes. High concentrations of vapour causes narcosis, unconsciousness.
Vinyl Chloride								Has been listed as known carcinogen.	Causes "Vinyl chloride disease". Maybe narcotic in high concentrations. Consult latest Government regulations on allowable concentrations in air. If spilled on skin, rapid evaporation can cause local frostbite.

3.4 References

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4. SITE CHARACTERISATION

4. SITE CHARACTERISATION

4.1 Introduction

This section of the document discusses the methods of characterising a site contaminated by organic solvents. Site characterisation is the term applied to the procedure for defining the nature of the subsurface and the extent of contamination, i.e. developing a conceptual model of the subsurface and contamination.

Site characterisation should be conducted in a phased, evolutionary manner starting with a review of all available information. The development of a conceptual model is continued until sufficient information is obtained to assess adequately the risks associated with the specific subsurface contamination and to select the appropriate remedial measures. As the extent and complexity of subsurface contamination and the associated risks vary widely so do the requirements of site characterisation.

A step-by-step methodology for generic site characterisation cannot be defined due to the site specific nature of subsurface contamination incidents. This section describes techniques available for the characterisation of DNAPL solvent contaminated sites and the data provided by each investigative technique. However, the judgement of the environmental scientist must be applied when selecting techniques in order to characterise a particular site most efficiently.

The contents of each sub-section are described briefly below:

Section 4.2 Objectives of Site Characterisation - The key objective of site characterisation is to define the conceptual model to such an extent that risk can be assessed and the appropriate remedial measures can be selected. This section of the report discusses the principle site characterisation objectives and includes a flow chart to assist technique selection.

Section 4.3 Site Identification and Initial Site Evaluation - At the outset of an investigation into subsurface contamination all existing site specific data should be obtained to enable development of the initial conceptual model.

Section 4.4 Non invasive Site Characterisation Techniques - This section describes the application of surface geophysics and soil vapour surveys to aid the characterisation of solvent contaminated sites.

Section 4.5 Invasive Site Characterisation Techniques - Drilling and sampling geological materials and the associated risks when drilling in DNAPL contaminated ground are discussed. The design and installation of monitoring wells, groundwater sampling techniques, equipment decontamination and borehole geophysics are also reviewed.

Section 4.6 Numerical Modelling - Numerical groundwater flow modelling and contaminant transport modelling are tools which are in widespread use in hydrogeology and can be applied to predict impacts of groundwater contamination and assess remedial system design.

4.2 Objectives of Site Characterisation

The ultimate objective of characterising a contaminated site is to obtain sufficient data to be able to assess risk and select appropriate remedial measures. Site characterisation of contaminated sites has become an increasingly complex process as a result of rapid developments in 1) methods of observing the physical, chemical and biological characteristics of the subsurface, and 2) methods for remediation of soil and groundwater. Consideration of the possible methods that may be used to clean up contaminated soil and groundwater early in the site characterisation process can ensure the data collected are appropriate and may reduce the time it takes to initiate subsurface remediation (Cohen and Mercer, 1993).

The initial phase of site characterisation involves the development of a conceptual model of contaminants present, their migration pathways and fate using all available information on the site and the processes that control contaminant distribution in the subsurface. Conceptual models of DNAPL compound distribution in the subsurface are included in Section 3.2 of this report. The potential presence of free phase DNAPL should be considered as part of this early hypothesis.

The difficulty in evaluating contaminant presence, migration and risk, and remediation of DNAPL contaminated sites is complicated by the following:

- DNAPL behaviour is only loosely related to that of groundwater. The relative importance of the forces that control the rate and direction of flow of DNAPL is different from that controlling dissolved phase flow.

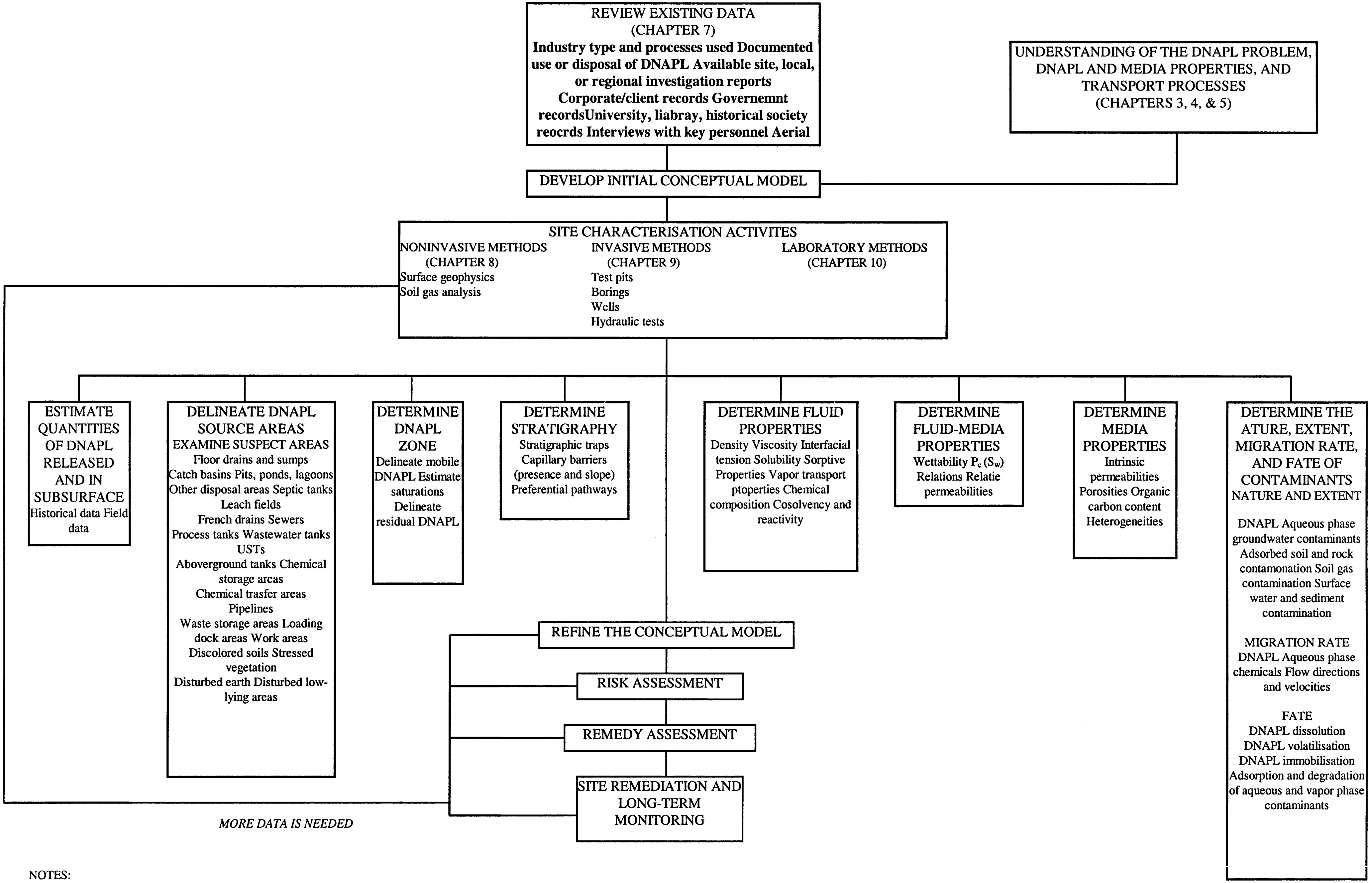
- Obtaining an accurate delineation of DNAPL location is extremely difficult and conventional site investigation techniques are not always suitable for the investigation of DNAPL contamination and can occasionally lead to re mobilisation of DNAPL.

- DNAPL in fractured media poses problems for both site investigation and remediation because of the complexity of fracture networks and the potentially great depths of penetration in fractured media.

- The absence of direct evidence of DNAPL at a site does not necessarily mean that DNAPL is not present.

- DNAPLs all have a density greater than water. However they can have viscosity greater or less than water, solubility and Henry's Constant, increasing the complexity of characterisation and remediation.

- Site characterisation is a continuous iterative process, requiring reappraisal of the conceptual model after each stage of the site investigation. The complexity of DNAPL fate and transport dictates that most decisions regarding site investigation and remedial techniques depend on site-specific conditions.



NOTES:
Characterisation should be conducted in a phased, evolutionary manner starting with review of available data. Early field work should focus on areas beyond the DNAPL zone and use non invasive methods in the DNAPL zone. Each characterisation activity should be designed to test conceptual model in a manner that will increase the capacity to preform risk and remedy analysis. To limit the potential for promoting contaminant migration avoid: (1) Conducting unnecessary field work; (2) Drilling through capillary barriers beneath DNAPL zones; (3) Pumping from beneath DNAPL zones; and, (4) using invasive characterisation or remediation without due consideration for the potential consequences.

Figure 4.1: DNAPL site characterisation flow chart (adapted from Cohen and Mercer, 1993)

Specific objectives of site characterisation are presented in the flow chart, Figure 4-1 (from Cohen and Mercer, 1993). Site characterisation data are ultimately used for the evaluation and selection of remedial technologies. Specific data requirements vary between available remedial technologies and therefore data acquisition from the site characterisation should become more focused with respect to clean up selection as the site conceptual model becomes more refined.

The investigative procedures to be undertaken to characterise the site cannot be precisely defined prior to the investigation and require assessing after each step of the investigation. It is important to define the information required from the investigation but the specific techniques for data collection can only be selected as the conceptual model is refined and data deficiencies are identified. Therefore it is very difficult to define the cost of site characterisation at the outset. The various techniques of characterisation of halogenated solvent contaminated sites are described below. The implementation of these techniques, however depends on the continual review and reassessment of the conceptual model and the targeting of data deficiencies.

4.3 Site Identification and Initial Site Evaluation

The first stage of any investigation into subsurface contamination should involve collection of existing information on geology, hydrogeology, historical land use, and other site specific data that may assist in developing the preliminary conceptual model. The initial conceptual model is then used as a guide for further site investigations, identifying data deficiencies and targeting potential contaminant hot spots.

Determining the presence of free phase DNAPL at a site should be a priority at the commencement of the site investigation as this will have major implications for subsequent investigative methodologies. If DNAPL presence is suspected, special consideration must be given to devising an effective site investigation strategy and preventing inducement of further DNAPL chemical migration due to the investigative techniques applied. Table 4-1 (Newell and Ross, 1992) lists the implications for site assessment of suspected DNAPL presence.

DNAPL presence may be inferred from historical site information on usage, disposal and release of DNAPLs at a particular site or by direct observation of subsurface DNAPL during excavations. However, the conceptual models of DNAPL migration in the subsurface presented in Section 3. identify the complexities of subsurface DNAPL distribution and at some sites determination of DNAPL presence may be difficult. Two USEPA documents discuss in detail methodologies for the determination of the presence of DNAPL at contaminated sites, 1) Dense Non Aqueous Phase Liquids - A Workshop Summary (USEPA, 1992), and 2) Subsurface Characterisation and Monitoring Techniques (USEPA, 1993).

4.3.1 Historical Site Use

DNAPL contamination is associated with industries that manufacture or utilise DNAPL chemicals and with waste disposal sites used by these industries. Industries which use DNAPL compounds and where there is a high probability of historical DNAPL release are listed in Table 4-2. The Department of Environment has issued a series of industry profiles which include descriptions on those industries that use DNAPL compounds (DOE 1995, 1996). The potential for DNAPL release increases with the size and active period of operation for a site, industrial process or waste disposal facility (USEPA, 1992). However, relatively small and short term releases from ruptured pipelines, overfilled tanks, or other sources can also cause significant DNAPL contamination in some cases. Assessment of the potential for DNAPL contamination at a particular site based on historical site data requires consideration of; land use since site development, site operations and processes, types and volumes of chemicals used and manufactured on the site, DNAPL handling and disposal practices. Possible sources of information for the desk top study include:

- Site plans; to provide information on site layout, location of subsurface pipelines, tanks etc., and details of previous alterations.
- Material safety data sheets; provide information on the physical and chemical nature of the products stored on-site and the health and safety environmental hazards associated with them.
- Ordnance survey (OS) maps; County 6” and 25” series to provide information on the historical uses of the site surrounding areas together with surface water flow.
- British Geological survey (BGS); geological and hydrogeological survey.
- Utility companies and site owners/operators to provide information on the layout of drains, sewers, water, gas and electricity mains.
- Photographs, ground and aerial; useful in defining potential source areas; also facilitate analysis of waste disposal practices and locations, drainage patterns, signs of vegetative stress and large scale geological features such as fractures.
- Long serving employees with experience of the site operation and knowledge of spills, leakages and on-site waste disposal to provide information on:
    1. How products are stored, transported and monitored.
    2. Spills and leakages.
    3. Decommissioning work and previous site alterations.
    4. Complaints during the operation of the site from either the authorities or public.
- Authorities other than the Environment Agency:
    - Local authorities who may have information on past/current waste disposal operations and past uses of adjacent land.
    - Environmental Health; historical experience of nuisances at the site.

4.3.2 Initial Site Characterisation Data

Some site characterisation data may be available at the outset of the investigation which may assist the evaluation of potential DNAPL presence, for example, groundwater analyses indicating the presence of dissolved DNAPL. DNAPL presence can be determined from the direct visual examination of a soil or groundwater sample, inferred from chemical analyses of soil, groundwater or soil vapour, and suspected from anomalous field conditions such as increasing concentrations in groundwater with depth. Table 4-3 lists the various techniques for determining presence of DNAPL from initially available site characterisation data.

Table 4.1 Implications of DNAPL presence on site assessment (adapted from Newell and Ross, 1992)

Category	Implications For Site Assessment
I CONFIRMED OR HIGH POTENTIAL FOR DNAPL AT SITE	• The risk of spreading contaminants increased with the proximity to a potential DNAPL zone. Special precautions should be taken to ensure that drilling does not create pathways for vertical migration of free phase DNAPLs. In DNAPL zones, drilling should be suspended when a low permeability unit or DNAPL is first encountered. Wells should be installed with short screens (=10 feet). If required, deeper drilling through known DNAPL zones should be conducted only by using double or triple-cased wells to prevent downward migration of DNAPL. As some DNAPLs can penetrate fractures as narrow as ten microns, special care must be taken during all grouting, cementing and well sealing activities conducted in DNAPL zones. In some hydrogeologic settings, such as fractured crystalline rock, it is impossible to drill through DNAPL with existing technology without causing vertical migration of DNAPL down the borehole, even when double or triple casing is employed. The subsurface DNAPL distribution is difficult to delineate accurately at some sites. DNAPL migrates preferentially through selected pathways (fractures, sand layers, etc.) and is affected by small-scale stratigraphic changes. Therefore, the ultimate path taken by DNAPL can be very difficult to characterise and predict. In most cases, fine grained aquitards (such as clay or silt units) should be assumed to permit downward migration of DNAPL through fractures unless proven otherwise in the field. At some sites, it can be exceptionally difficult to prove otherwise even with intensive site investigation. • Drilling in areas known to be DNAPL free should be performed before drilling in DNAPL zones in order to form a reliable conceptual model of site hydrogeology, stratigraphy, and potential DNAPL pathways. In areas where it is difficult to form a reliable conceptual model, an "outside-in" strategy may be appropriate: drilling in DNAPL zones is avoided or minimised in favour of delineating the outside dissolved-phase plume. Many fractured rock settings may require this approach to avoid opening further pathways for DNAPL migration during site assessment.
II MODERATE POTENTIAL FOR DNAPL AT SITE	• Due to the potential risk of exacerbating groundwater contamination problems during drilling through DNAPL zones, the precautions described for Category I should be considered during site assessment. Further work should focus on determining if the site is a DNAPL site.
III LOW POTENTIAL FOR DNAPL AT SITE	• DNAPL is not likely to be a problem during site characterisation, and special DNAPL precautions are probably not needed. However, floating, less-dense-than-water non aqueous phase liquids (LNAPLs), sorption, and other factors can complicate site assessment and remediation activities.

Table 4.2 Industries and industrial processes using DNAPLs and some DNAPL chemicals (modified from Newell and Ross, 1992) also see DOE, (1995, 1996).

Industries/Businesses using DNAPL	Processes involving DNAPLs	DNAPL Chemicals
Chemical manufacturing	Metal cleaning/degreasing	Aniline
Solvent manufacturing, reprocessing, and/or packaging	Storage of solvents (and other DNAPLs) in drums in uncontained areas	Carbon tetrachloride Chlordane Chlorobenzene
Commercial dry cleaning operations	Tool-and-die operations	Chloroform
Electronic equipment manufacturing	Paint removing/stripping	2-Chlorophenol
Computer component manufacturing	Metal machining	Chlorotoluene
Metal parts/products manufacturing	Loading and unloading of solvents (and other DNAPLs)	Dibutyle phthalate 1,2-Dichlorobenzene
Aircraft automotive manufacturing, maintenance, and repair operations	Solvent storage in underground and above ground tanks	1,3-Dichlorobenzene 1,1,-Dichloroethane
Machine shops and metals works	Textile cleaning operations	1,2-Dichloroethane
Tool-and-die-plants	Dry plasmas etching of semi conductor chips	1,1-Dichloroethene trans-1,2-Dichloroethene
Musical instrument manufacturing		cis-1,2-Dichloroethene
Photographic film manufacturing and processing		1,2-Dichloropropane cis-1,3-Dichloropropene
Plastics manufacturing		trans-1,3-Dichloropropene
Pharmaceutical manufacturing		Diethyl phthalate
Illicit drug manufacturing		Dimethyl phthalate
Flame retardant materials manufacturing		Ethylene dibromide
Refrigerants manufacturing		Hexachlorobutadiene
Military equipment manufacturing and maintenance		Hexachlorocyclopentadiene Malathion
Manufacturing/processing of septic system/plumbing cleaners		Methylene Chloride Nitrobenzene
Manufacturing of typewriters, printers and copiers		Parathion Polychlorinated Biphenyls
Printing presses and publishing operations		1,1,2,2-Tetrachloroethane
Textile processing, dying and finishing operations		Tetrachloroethene 1,2,4-Trichlorobenzene
Pesticide and herbicide manufacturing		1,1,1-Trichloroethane
Wood preservation/treating plants		1,1,2-Trichlorofluoromethane
Manufactured gas plants (prevelant between the mid-1800s to mid-1900s)		1,1,2-Trichlorotrifluoroethane Coal tar
Steel industry coking operations		Creosote
Asphalt processing and distribution plants		
Coal tar distillation plants		
Transformer/capacitor oil production, reprocessing and disposal operations		
Waste disposal sites		

Table 4.3 Determinant, inferential, and suggestive indications of DNAPL presence based on examination of subsurface, samples and data (based on Newell and Ross, 1992; Cherry and Feenstra, 1991; and Cohen et al, 1992).

Determining DNAPL Presence by Visual Examination of Subsurface Samples	Inferring DNAPL Presence by Interpreting Chemical Analyses	Suspecting DNAPL Presence based on Anomalous Field Conditions
Methods to detect DNAPL in wells: • NAPL water interface probe detection of immiscible phase at base of fluid column • Pumping from bottom of fluid column and inspecting retrieved sample • Retrieving a transparent, bottom-loading bailer from the bottom of a well and inspecting the fluid sample • Inspecting fluid retrieved from the bottom of a well using a mechanical discrete-depth sampler • Inspecting fluid retained on a weighted cotton string that was lowered down a well. **Methods to enhance inspection of fluid samples for DNAPL presence:** • Centrifuge sample and look for phase separation • Add hydrophobic dye (such as Sudan IV or Red Oil) to sample, shake, and look for colouration of DNAPL fraction • Examine UV fluorescence of sample (many DNAPLs will fluoresce) • Assess density of NAPL relative to water (sinkers or floaters) by shaking solution or by using a syringe needle to inject NAPL globules into the water column **Methods to detect DNAPL in soil and rock samples:** • Examine UV fluorescence of sample (many DNAPLs will fluoresce) • Add hydrophobic dye and water to soil sample in a polythene bag or jar, shake, and examine for colouration of the NAPL fraction • Conduct a soil-water shake test without hydrophobic dye (can be effective for NAPLs that are neither colourless nor the colour of the soil) • Centrifuge sample with water and look for phase separation • Perform a paint filter test, in which soil is placed in a filter funnel, water is added, and the filter is examined for separate phases	**Chemical analysis results from which DNAPL presence can be inferred (with more or less certainty depending on the strength of the overall data):** • Concentrations of DNAPL chemicals in groundwater are greater than 1% of the pure phase solubility or effective solubility (refer to Worksheet 7.1) • Concentrations of DNAPL chemicals on soils are greater than 10,000 mg/kg (equal to 1% soils mass) • Concentrations of DNAPL chemicals in groundwater calculated from water/soil partitioning relationships and soil samples are greater than pure phase solubility or effective solubility (refer to Worksheet 7.2) • Organic vapour concentrations detected in soil gas exceeds 100-1000 ppm	**Field conditions that suggest DNAPL presence:** • Concentrations of DNAPL chemicals increase with depth in a pattern that cannot be explained by advective transport • Concentrations of DNAPL chemicals increase up the hydraulic gradient from the contaminant release area (apparently due to contaminated soil gas migration and/or DNAPL movement along capillary and/or permeability interfaces that slope counter to the hydraulic gradient) • Erratic patterns of dissolved concentrations of DNAPL chemicals in groundwater which are typical of DNAPL sites due to heterogeneity of (1) the DNAPL distribution, (2) the porous media, (3) well construction details, and (4) sampling protocols • Erratic, localised, very high contaminant concentrations in soil gas, particularly located just above the water table (where dense gas derived from DNAPL in the vadose zone will tend to accumulate) • Dissolved DNAPL chemical concentrations in recovered groundwater that decrease with time during a pump-and-treat operation, but then increase significantly after the pumps are turned off (although complexities of contaminant desorption, formation heterogeneity, and temporal and spatial variations of the contaminant source strength can produce similar results) • The presence of dissolved DNAPL chemicals in groundwater that is older than potential contaminant releases (using tritium analysis for age dating) suggests DNAPL migration (Uhlman, 1992) • Deterioration of wells and pumps (can be caused by DNAPL; ie, chlorinated solvents degrade PVC)

4.4 Non invasive Site Characterisation Techniques

4.4.1 Introduction

Non invasive techniques of site characterisation can frequently be applied in the early stages of field investigation and in many cases can provide a cost effective method of increasing knowledge of DNAPL contamination at a site and refining the conceptual model. The two main techniques of non invasive characterisation are surface geophysics and soil vapour surveys.

Non invasive techniques are considerably less expensive than invasive methods of investigation where excavation is required. However, subsurface data acquired non invasively is indirect and therefore, also less definitive. As a result, non invasive techniques are usually followed by some form of invasive investigation to confirm the findings of the non invasive investigation.

The applicability of non invasive techniques must be assessed on a site specific basis as there are many criteria that must be met before surface geophysics or soil vapour surveys can be successfully implemented.

4.4.2 Surface Geophysics

Geophysical surveys can provide relatively rapid and inexpensive information on subsurface conditions over a wide area of potentially DNAPL contaminated land.

At contaminated sites geophysical surveys are usually conducted to:

- assess geological stratigraphy and hydrogeological conditions
- locate subsurface utilities and buried wastes
- delineate electrically conductive contaminants
- optimise the location of boreholes and trial pits
- facilitate interpolation of subsurface conditions between borehole locations.

Surface geophysical methods most commonly applied include ground penetrating radar, electromagnetic (EM) conductivity, electrical resistivity, seismic reflection and refraction, magnetometer surveys and metal detectors. Table 4-4 presents each of these techniques, describing the principles, applicability, advantages and disadvantages and provides references for further information. The USEPA (1993) document “Subsurface Characterisation and Monitoring Techniques” describes all surface geophysical techniques applied to subsurface characterisation investigations and provides references for further reading. CIRIA (Construction Industry Research and Information Association) is currently conducting two research projects in the UK on the use of geophysical techniques for site investigation and demonstration of remediation (Proposal 1298 *Civil Engineering Applications of Geophysical Investigation Techniques*, inaugural seminar June 1996).

Subsurface DNAPL is generally a poor target for conventional surface geophysical methods. Although ground-penetrating radar, EM conductivity and complex resistivity techniques have been applied to identify NAPL presence at several sites (e.g. Davis, 1991; Olhoeft, 1986) direct detection and mapping of non-conductive DNAPL plumes using surface geophysical techniques is an unclear and currently limited investigative technique. The value of geophysics at most DNAPL sites is in aiding characterisation of waste disposal areas, stratigraphic conditions and potential routes of DNAPL migration. Inferences derived from geophysical surveys can be used to optimise the cost effectiveness of subsequent invasive investigations.

Table 4.4 Summary of various surface geophysical survey methods (modified from Cohen and Mercer, 1993)

Method And Targets	Operating Principles / Description	Operating Parameters and Advantages and Disadvantages
GROUND PENETRATING RADAR • stratigraphy (layering and lateral variations) • water table in coarse media • metallic and non-metallic buried drums, tanks and pipes • bedrock surface • fracture zones • very limited capacity to delineate NAPL presence	High frequency electromagnetic (<100 - 1000 MHz radio) waves transmitted from a radar antenna at the ground surface are reflected from interfaces between subsurface materials with contrasting dielectric properties back to a receiving antenna. The reflections are amplified, processed, and displayed in real time on a recorder and/or colour video monitor. Such contrasts are due to changing clay content, fluid content, dielectric constants, porosity, fracture density, bedding, cementation, the presence of manmade objects, the bedrock surface, etc. The depth of penetration (and measurement of reflected waves) is proportional to the receiving antenna response time.	• Provides a continuous visual profile of shallow subsurface objects, structure and lithology in real time. • The graphic output can often be interpreted in the field; thereby facilitating direction of the survey. • Traverse rates range from 600 - 6000ft/hr for detailed studies and up to 10mph for low-resolution reconnaissance work. • Depth of penetration is site-specific; typically between 6 and 30ft. Radar penetration increases in coarse, dry, sandy or massive rock; and decreases with increasing clay content, fluid content, and fluid conductivity. • Approximate and relative depths are calculated using simple interpretative methods and assumptions. Depth calibrations, however, require careful onsite work and are often non-linear. • Depending on the frequency used, GPR provides very high resolution from an inch to a few feet. • The survey can be optimised to local conditions by changing antennas (frequency). High frequency provides the best resolution; lower frequency provides deeper penetration. • GPR can be used in fresh water and through ice to obtain profiles of sediment depth. • Access is limited due to bulkiness of GPR equipment. • Limited use during wet weather. • A variety of processing options can be used to enhance data interpretation and presentation. • Quantitative interpretation is difficult. The data can be affected by various sources of system noise.
ELECTRO-MAGNETIC CONDUCTIVITY • detection and mapping of conductive contaminant plumes • stratigraphy (layering and lateral variations) • waste disposal areas containing metallic and non-metallic buried drums • USTs and buried pipes • fracture zones • very limited capacity to delineate NAPL presence	Electromagnetic methods measure changes in the bulk subsurface electrical conductivity (also referred to as terrain conductivity). A transmitter induces circular eddy current loops in the subsurface. The magnitude of the induced current is proportional to and altered by the terrain conductivity in the vicinity of the loop. Each current loop generates a magnetic field which is proportional to the current magnitude. A portion of the generated magnetic field is measured by the EM receiver and results in an output voltage that is proportional to terrain conductivity. Terrain conductivity generally increases with increasing (1) subsurface fluid conductivity, (2) clay content, (3) fluid content, and, (4) porosity (including fracture porosity). Interpretation is typically	• Profiling or vertical sounding data can be acquired from various depths between 2 and 200ft by combining measurements from various common EM systems and by varying the coil orientation and/or spacing between the EM transmitter and receiver. Compared to the resistivity method, however, EM has reduced vertical sounding resolution due to the limited number of transmitter-receiver spacings available. • The influence of subsurface materials on the measured EM conductivity decreases with depth; a confounding factor that must be considered when interpreting EM data. • Continuous EM profiling can be obtained from 2.5 to 50ft providing increased survey speed, density, and resolution. Data can be recorded on an analog strip chart or digital data logger. • Spatial variability and anomalies can be caused by several factors, thereby confounding unique interpretation of conductivity measurements. • Various objects emit noise and interfere with EM surveys including natural atmospheric noise, power lines, buried metal objects, radio transmitters, buried pipes and cables, fences, vehicles, and buildings. • Limited use in wet weather. Frequency-domain EM systems measure changes in continuously transmitted current. Time-domain EM systems measure in-phase and out-of-phase components of EM conductivity. The in-phase component responds to magnetic susceptibility and can be used to detect metals. The out-of-phase component measures electrical conductivity.

Table 4.4 Contd Summary of various surface geophysical survey methods (modified from Cohen and Mercer, 1993)

Method And Targets	Operating Principles / Description	Operating Parameters and Advantages and Disadvantages
	qualitative based on consideration of spatial variability, anomalies, and the aforementioned factors.	
ELECTRICAL RESISTIVITY • detection and mapping of conductive contaminant plumes • stratigraphy (layering and lateral variations) • waste disposal areas containing non-metallic buried drums • fracture zones • very limited capacity to delineate NAPL presence	Electrical resistivity methods measure the bulk electrical conductivity of the subsurface in a manner different from the EM Conductivity method. Electrical current is transmitted into the ground from a pair of surface electrodes and the voltage drop due to bulk subsurface resistivity is measured at the surface between a second pair of electrodes. The depth of measurement increases with, but is generally less than, the electrode spacing. Of the various electrode spacing geometries used, the Wenner array, with four electrodes equally spaced along a line and the two transmitting electrodes at each end, is the simplest. As the reciprocal of conductivity, electrical resistivity generally decreases with increasing (1) subsurface fluid conductivity, (2) clay content, (3) fluid content, and, (4) porosity (including fracture porosity).	• Survey speed is slower than with EM methods because of need with resistivity to drive electrodes into the ground. Station measurements are made; continuous measurements are not possible. • Profiling or vertical sounding data can be acquired from various depths by using different electrode spacings. Because the current electrodes can be spaced at any distance (assuming site access), resistivity is capable of providing better vertical resolution of subsurface conductivity than EM methods (which rely on fixed intercoil lengths). • The vertical sounding technique, however, requires that subsurface conditions be relatively consistent laterally. • Results are amenable to qualitative interpretation based on observed spatial variability and anomalies. However quantitative interpretation of stratigraphic layering can be made based on vertical soundings. • Spatial variability and anomalies can be caused by several factors, thereby confounding unique interpretation of resistivity measurements. • The influence of subsurface materials on the measure resistivity decreases with depth; a confounding factor that must be considered when interpreting EM data. • Resistivity is affected less than EM methods by noise associated with power lines, buried metal objects such as pipes and cables, fences, vehicles, and buildings. This, resistivity can be used to provide reliable measurements in some locations near metal objects where EM is of little use. • Limited use in wet weather.
SEISMIC REFRACTION AND REFLECTION • bedrock surface • depth to water table • locate fractures, faults, and buried bedrock channels • characterise rock type and degree of weathering	The subsurface transmission of seismic waves emitted from a point source are measured using geophones implanted in the ground along a straight line and recorded digitally by a seismograph. The seismic source may be the impact of a sledge or mechanical hammer on a steel plate, or an explosive device. Compressional, shear, and surface seismic waves radiate from the energy source. The compressional waves are refracted and reflected as they pass through media with different	• Seismic refraction is generally used for shallow investigations (< 200ft depth). A refraction survey may require a maximum source; to geophone distance of up to five times the depth of investigation. • Given sufficient velocity contrast between adjacent horizontal layers, as many as three or four layers can be delineated using seismic refraction. A lower velocity layer under a higher velocity layer and thin layers, however, cannot be resolved using the refraction method. • Geophone spacing can be varied from a few to hundreds of feet depending on the desired measurement depth and resolution. For shallow investigations, 12 or 24 geophones may be positioned at equal spacings as close as 5 to 10ft and seismic waves may be initiated separately at each end of the line. • Seismic reflection can be used for much deeper investigations (to >1000ft). It is similar to GPR in that the depth of measurement is as a function of wave reflection travel time. • Seismic data is collected as station measurements and surveying is slow

Table 4.4 Contd Summary of various surface geophysical survey methods (modified from Cohen and Mercer, 1993)

Method And Targets	Operating Principles / Description	Operating Parameters and Advantages and Disadvantages
• stratigraphy (layering and lateral variations) depth of landfills, trenches, and disturbed zones	seismic velocities (densities). Refracted and/or reflected compressional wave travel times associated with different source-to-geophone wave paths are interpreted using analytical models to determine the depth to one or more geologic units.	• measurement methods. • Data interpretation is confounded by heterogeneous subsurface conditions. • Use may be limited during wet and very cold weather. Seismic methods are subject to interference from vibrations noise associated with various natural and cultural sources (ie, walking, machinery)
MAGNETICS • buried ferrous metal objects (drums, pipelines, USTs etc.) • waste zones containing ferrous metal	Magnetometers are used to measure the strength of the earth's magnetic field and respond to ferrous metals perturb the earth's natural magnetic field. Two common types of magnetometers are available; the total field magnetometer and the gradiometer. Typically, a hand held magnetometer is used to measure total magnetic field intensity along a grid allowing detection of anomalies associated with shallow buried ferrous metal objects. A nearby base station can be used during the survey to record background diurnal variations in the earth's magnetic field.	• Magnetometers respond only to ferrous metals (iron or steel). • Magnetometers provide greater depth range than metal detectors; single drums and drum masses can be detected at depths to 20 and 60ft, respectively, using a total field magnetometer. • The total field magnetometer response is proportional to the ferrous target mass and inversely proportional to cube of the distance to the target. Gradient measurements using a gradiometer are inversely proportional to the fourth power of the distance to the target and thus minimise interference's but are less sensitive than total field measurements. • Magnetometers can be used to provide continuous or station measurements, and can be mounted to vehicles for coverage of large sites. • Magnetometer response is subject to interference noise from many sources including steel fences, buildings, vehicles, iron debris, utilities, ferrous soil minerals, vehicles, etc. • Data interpretation may be confounded by heterogeneous subsurface conditions and/or the presence of iron-rich geologic media (such as greensands and red hematitic soils). • Magnetometry may also be used to study regional geologic conditions, and occasionally to map the bedrock surface.
METAL DETECTORS • shallow buried metal objects (drums, pipelines, USTs, etc.) • shallow waste zones containing metal	Metal detectors sense ferrous and nonferrous metals. The area of detection is typically 1 to 3ft (equal to the detector coil size or spacing). The depth of detection is commonly limited to < 10ft because the response is proportional to the target cross-section and inversely proportional to the sixth power of the distance to the target.	• Metal detectors are routinely used to locate buried cables and pipes. • Quart-size metal objects and drum masses can be detected to depths of 3 and 10-25ft, respectively. • Buried and above ground metal objects (cars, fences, buildings etc.) can interfere with measurements.

4.4.3 Soil Vapour Surveys

During the 1980s soil vapour surveys became a widely used tool for detecting volatile organic contaminants in the vadose zone (Marrin and Kerfoot, 1988; Marrin and Thompson, 1984; Marrin and Thompson, 1987; Devitt et al., 1987). Soil vapour surveys generate extensive chemical distribution data at a fraction of the cost of invasive techniques.

Consideration should be given to the use of soil vapour surveying during the early stages of site characterisation to assist delineation of DNAPL in the vadose zone, contaminant source areas and contaminated shallow groundwater. Soil vapour survey results are of great value in guiding the location of further invasive investigations, such as the location of groundwater monitoring boreholes or trial pits, and in optimising the number of samples sent to the laboratory for confirmatory analyses.

Many DNAPLs have high vapour pressures and will volatilise in the vadose zone to form a vapour plume around the DNAPL source zone. Dissolved volatile organic compounds can also volatilise to soil vapour. However, experiments conducted at the Borden DNAPL research site in Ontario suggest that soil vapour contamination is usually from contaminant sources in the vadose zone rather than from groundwater and that the upward transport of VOCs from groundwater is probably limited to the uppermost saturated zone only (Rivett and Cherry, 1991; Rivett et al., 1991). Therefore soil vapour surveys do not provide an accurate indication of the distribution of groundwater contamination at depth below the water table.

Although advective processes due to density flow effects or high vapour pressure gradients may influence VOC migration, gaseous diffusion is considered the predominant vapour transport mechanism at most sites (Marrin and Kerfoot, 1988).

Soil Vapour Sampling Methods

Soil gas sampling methodologies have been described by Devitt et al. (1987), Marrin and Kerfoot (1988) and Tillman et al. (1989a and 1989b) and a standard methodology has been produced (ASTM, 1991a). The following list of tasks can be used to assist in the organisation of a soil vapour survey.

- Develop site conceptual model of contaminant sources and distributions.
- Select Tracer gases.
- Select sampler type and sampling methods.
- Select analytical method(s).
- Prepare QA sampling plan.
- Conduct pilot test of sampling and analysis procedures in an area of known contamination. Sample at several depths to determine the vertical profile of soil gas concentrations and select a sampling target depth.
- Evaluate pilot test results and modify sampling and analysis methods as necessary.
- Consider sampling grid based on the site conceptual model and investigation objectives.
- Conduct soil gas survey.
- Modify/augment sampling grid based on real-time data aquisition (if possible).
- Plot and contour data and make interpretations.
- Consider value of additional soil gas surveying.

Each soil vapour survey should be customised to match the requirements of a particular site. Factors such as the size of the affected area, permeability of subsurface materials, presence of perched groundwater, and depth to groundwater should be considered. This information affects the horizontal and vertical spacing of soil vapour sampling and corresponding installation methods of the soil gas probes.

The most widely implemented soil vapour sampling technique, known as grab sampling, has been well documented due to its extensive application to the investigation of subsurface hydrocarbon contamination (USEPA, 1991; Marrin and Thompson, 1987, Marrin and Kerfoot, 1988). Grab sampling typically involves driving a hollow probe with a conical tip to a depth of one to three metres through unconsolidated formations, pumping gas from the probe and collecting a sample from the moving soil vapour. Samples are usually taken from a depth of at least one metre to minimise effects of surface contamination, changes in barometric pressure, temperature, rainfall and airborne pollution. Transient meteorological interferences can be minimised by conducting the soil vapour survey in as short a time as possible. Vertical soil vapour profiles can be obtained by sampling soil vapour from different depths as the probe is driven in.

Primary advantages of grab sampling during a soil vapour survey include: its low cost relative to drilling, the quick acquisition and analysis of samples (in the order of 40 to 70 samples per day), its non invasive nature and its documented reliability (Tillman et al., 1989a & b). On site analysis of soil vapour using a portable photoionisation detector, for example, allows increased efficiency and accurate targeting of the survey locations. Potential disadvantages of the technique include: possible collection of unrepresentative samples due to excessive pumping, disturbance of the vadose zone, clogging of the probe screen with cohesive soils and misinterpretation of results due to complex chemical or hydrogeological conditions.

Passive soil vapour sampling provides an integrated measure of VOC concentrations over the sampling period. The method involves placing a sorbent material such as activated carbon below ground within a hollow probe or sampling chamber for an extended period to trap VOCs that diffuse through soil vapour. The sorbent material is then retrieved after a specified time and submitted to a laboratory for analysis. Passive soil vapour sampling is used infrequently at contaminated sites, mainly because of the inconvenience of the long duration sampling time required (Kerfoot and Barrows, 1987).

Table 4.5 Advantages and limitations of soil vapour analytical methods (from Devitt et al., 1987)

Method	Advantages	Limitations
Portable VOC Detectors	Easy to transport Minimum operator training required Elimination of sample collection steps minimises uncertainties and expense of sample collection Immediate analysis provides guidance for additional sampling	Limited sensitivity due to lack of an analyte concentration step, typical detection limit 1ppm Limited selectivity and interference problems because of lack of a separation step, variable response to different compounds Limited accuracy because of inability to calibrate adequately for chemical mixtures Relatively large sample volumes required
Portable FID Analyser (e.g. Century OVA)	Flame ionisation detectors use hydrogen fed flame to ionise organic gases and generate current that is proportional to concentration Capable of detecting all organic compounds Sensitivity is to <1ppm (methane) Less susceptible to high humidity interference than PIDs The Gas Chromatograph option included in FIDs allows identification and quantification of individual organic compounds to low ppb levels	High humidity will reduce relative response Significant operator training required to use the GC mode Approximate cost of Century System OVA-128 FID is $6,800 (1992)
Portable PID Analyser (e.g. HNU, Photovac TIP)	A UV light is used to ionise gas or vapour molecules which are then collected and produce a current which is proportional to the concentration Capable of monitoring many organic and some inorganic gases and vapours Sensitivity to 0.1ppm (benzene); detection range approx. 0.1ppm to 2000ppm With the 10.2eV lamp, alcohols, halogenated alkanes, and most inorganic gases have no response and alkenes, aromatics, organo sulphur compounds and carbonyl compounds have a high response With the 11.2eV lamp all organic compounds except methane produce instrument response	The energy generated by the lamp must exceed the ionisation potential of the target chemical for detection The instrument's response to different chemicals varies UV intensity declines slowly with age Airborne dust can interfere with UV light transmission and reduce readings High humidity can condense on lamp and reduce light transmission PIDs cannot detect light hydrocarbons such as methane Approx. cost of HNU meter is $4,300 (1992)
Portable Hot-Wire Detector (Bacharach TLV Sniffer)	Vapours are catalytically combusted using a hot wire Similar advantages to FID Sensitive to approximately 2ppm, detection range 2-10,000ppm	Similar advantages to FIDs Approx. cost of Bacharach TLV Sniffer is $2,000 (1992)
Portable and field GC Units with various detectors	GC units can be used to separate a mixture of gaseous compounds prior to detection Several portable VOC analysers have GC options including the Photovac PID and the Century FID allowing individual compounds to be quantified in the ppb range Portable GCs are most effective on samples with large concentrations on easy-to-separate VOCs Field GC units contain temperature controlled ovens and a variety of injectors and detectors facilitating better precision and accuracy	No temperature control for the portable GC column hinders high resolution compound separation Reproducible retention times are difficult to replicate in the field using portable GCs due to temperature variation Estimated cost for GC units without a detector is from $2,500 to >$30,000 (1992)
Lab-grade GC Units	Fast analytical response with better controlled analytical conditions; typically processes 50-70 samples per day Produces highest quality data Provides significantly lower detection limits for a wider range of compounds than possible using portable GC Detection limits can be in ppt range Can be mounted in van or mobile laboratory	Requires significant operator training Lab grade GC units are extremely expensive

Soil Vapour Analytical Techniques

Selection of an analytical technique for soil vapour depends on the required sensitivity and detection limits, degree of compound specificity, and immediacy of analytical results required from a particular survey. Devitt et al. (1987) and USEPA (1993) provide a detailed review of alternative techniques of analysis including: portable VOC analysers (i.e. Flame Ionisation Detectors (FIDs), Photoionisation Detectors (PIDs)), portable gas chromatographs (GCs) and laboratory grade GCs which can be used in a mobile laboratory. Table 4-5 describes commonly available soil vapour analytical techniques and presents advantages and limitations of each method. Table 4.6 lists typical analytes and products identifiable by a soil vapour survey.

The gas chromatograph is the most well developed and accurate field analytical technique for organic vapour when used with the appropriate detector, usually the photoionisation detector.

Value of Soil Vapour Surveys at DNAPL Sites

During the 1980s several studies indicated the utility of soil vapour surveying in delineating VOC contaminated soil and groundwater (Marrin and Thompson, 1987; Thompson and Marrin, 1987). Many case studies have been published that describe the applicability of soil vapour surveying to site characterisation at DNAPL contaminated sites. Examples from the UK include Bishop et al (1990) and Eastwood et al (1991) and examples from the USA and Canada include Rivett and Cherry (1991), Hughes et al (1990a), Marrin and Thompson (1987).

At the Borden DNAPL research site in Ontario controlled releases of TCE to both the vadose zone and beneath the water table were made in order to study the behaviour and distributions of TCE in soil vapour. The studies are well documented (Rivett and Cherry, 1991; Hughes et al. 1990a), one of the main conclusions being that soil vapour contamination derived from a vadose zone source is considerably greater than that derived from a groundwater source. The process of upward transport of VOCs from groundwater to soil gas is probably only really important for the partitioning of very shallow water table contamination to the soil gas (Rivett and Cherry, 1991).

Rivett and Cherry (1991) describe several conceptual models of soil vapour contamination derived from different DNAPL release scenarios. These models are presented in Figure 4.3 and illustrate that soil vapour surveying can be generally useful in delineating VOC contamination in the vadose zone and in shallow groundwater but may fail to identify areas of deeper groundwater contamination that are not coincident with shallow soil gas contamination due to vapour transport (Cohen and Mercer, 1993; Kerfoot, 1988). However, soil vapour surveying can provide misleading results if the subsurface conditions are not understood adequately and interpretation must be performed carefully (Marrin, 1988; Silka, 1988). Thus interpretations of subsurface VOC distribution derived from soil vapour surveys should be confirmed by analysis of soil and groundwater samples taken at depth during invasive site investigations.

Table 4.6 **Typical analytes and products detectable by soil gas surveys (modified from Tillman et al, 1990a).**

Analytes	Products
Acetone	Cleaning fluids
Benzene	Coal tar
1-Butane	Creosote
n-Butane	Degreasers
Carbon Tetrachloride	Diesel fuel
Chloroform	Gasoline
1,1-Dichloroethane (1,1-DCA)	Heating oil
1,1-Dichloroethene (1,1-DCE)	Jet fuel
Ethane	Solvents
Ethylbenzene	Turpentine
Isopropyl Ether (DIPE)	
Methane	
Methylene Chloride (Dichloromethane)	
Methyl Ethyl Ketone (MIBK)	
Methyl-Isobutyl Ketone (MTBK)	
Methyl-Tert Butyl Ether (MTBE)	
Propane	
Tetrachloroethene (PCE)	
Toluene	
1,1,1-Trichloroethane (1,1,1-TCA)	
1,1,2-Trichloroethane (1,1,2-TCA)	
Trichloroethene (TCE)	
1,1,2-Trichlorotrifluoroethane (Freon-113)	
Xylenes	

4.5 Invasive Site Characterisation Techniques

4.5.1 Introduction

Following the generation and subsequent refinement of the conceptual model from information gathered during the site identification and non invasive stages of the site characterisation investigations, invasive techniques will generally be required to confirm the existing conceptual model. Invasive methods should be used in a phased manner to test and advance the site conceptual model and will be selected on a site specific basis. However, their purpose in general, will be to:

- delineate DNAPL source areas
- define the geologic and hydraulic controls on the movement and distribution of DNAPL, contaminated groundwater and contaminated soil gas
- characterise the fluid and fluid media properties that affect DNAPL migration and the feasibility of alternative remedies
- determine the nature and extent of contamination and the rates and directions of contaminant transport
- evaluate exposure pathways
- design monitoring and remedial system.

Invasive techniques include drilling and test pit excavation to characterise subsurface solids and groundwater and/or DNAPL in addition to monitoring well installation to sample groundwater and/or DNAPL and to conduct fluid level surveys, hydraulic tests and borehole geophysical surveys.

The choice of characterisation strategy depends on the conceptual model of the site and the physical properties of the contaminants. Immiscible liquids with relatively high densities and low viscosities will be relatively more mobile than less dense, more viscous liquids. More mobile liquids present a greater risk for spreading contamination to greater depths within the aquifer during site investigation. In addition these liquids may have migrated considerably farther from DNAPL entry location than less dense, more viscous liquids (USEPA, 1992).

The techniques of invasive site investigation have been thoroughly documented and are not discussed in detail in this report. Table 4.7 presents a description of the most commonly used drilling methods in site investigation and discusses the applications and limitations of each technique. References that discuss selection and application of drilling techniques in site investigation include a) “Subsurface Characterisation and Monitoring Techniques” USEPA (1993), b) “Practical Handbook of Groundwater Monitoring” edited by Nielsen (1991), c) “Handbook of Suggested Practices for the Design and Installation of Groundwater Monitoring Well” from USEPA (1991) and d) “Groundwater and Wells” by Driscoll (1986). However, only those points pertinent to DNAPL contaminated site characterisation are discussed in this report.

4.5.2 Risks Associated with Invasive Techniques

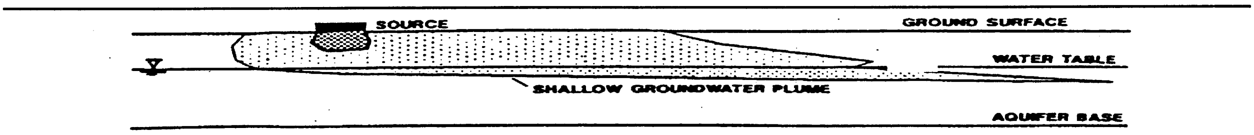
The risk of enlarging the extent of subsurface contamination by use of invasive site characterisation techniques must be considered during DNAPL site investigation. DNAPL migration induced by site investigation activities may increase the risk to receptors, increase the complexity and cost of site remediation and generate misleading data leading to an incorrect conceptual model (USEPA, 1992). Drilling, well installation and pumping activities present the greatest risk of promoting DNAPL migration during site investigation.

Specific conditions that may promote vertical DNAPL migration include:

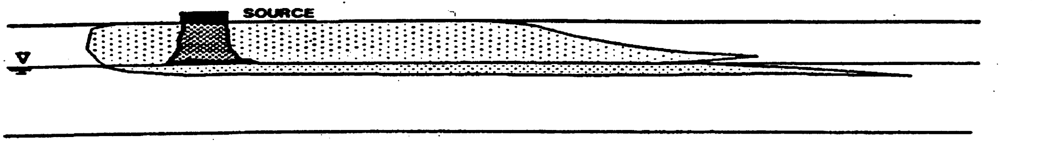
- an open borehole during drilling or left open prior to monitoring well installation
- an inadequately sealed borehole that allows DNAPL to migrate through: a) the well grout interface, b) the grout, c) the grout formation interface, d) vertical fractures in the disturbed zone adjacent to the well
- a well screen that spans a geological horizon impermeable to DNAPL
- degradation of grout or well casing due to chemical effects of DNAPL or groundwater environment
- pumping from beneath or adjacent to the DNAPL zone, therefore inducing vertical migration, particularly in fractured media.

To minimise the risk of inducing further DNAPL migration by site investigation activities the site investigators should:

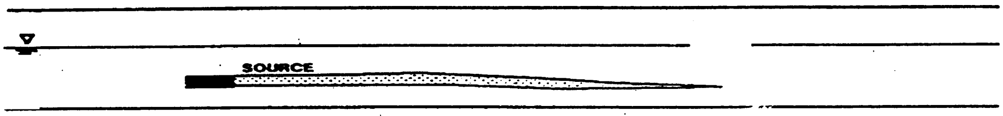
- avoid unnecessary drilling in the DNAPL zone
- minimise time during which the borehole is left open and uncased and minimise the length of time the borehole is open at any time during drilling
- use telescopic casing techniques to seal off overlying horizons during drilling
- examine all drill cuttings carefully for any indication of DNAPL and constantly update the conceptual model during drilling in order to avoid penetrating a horizon impermeable to DNAPL
- select well materials and grouting materials based on site specific chemical compatibility and consider layering different types of grout to increase the anticipated life of the seal.



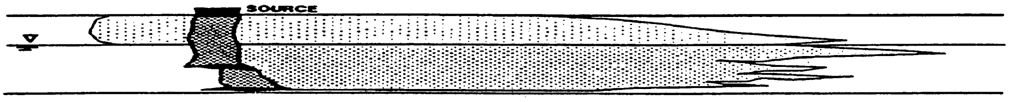
(a) A VOC vapour plume develops around NAPL in the vadose zone and contaminates shallow groundwater in the area larger than the NAPL source area. The shallow groundwater VOC plume moves down gradient hydraulically and repartitions to the soil gas; thus forming a zone of shallow groundwater and soil gas contamination wider than the NAPL source area. Soil gas monitoring near the NAPL source detects direct VOC vapour transport from the NAPL source. At some distance down gradient hydraulically, soil gas monitoring detects VOCs that have diffused from the shallow groundwater VOC plume.



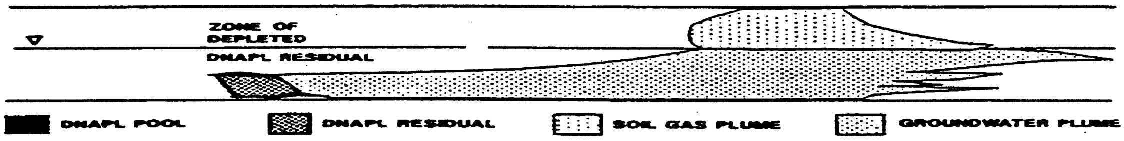
(b) If NAPL does not substantially penetrate the water table, soil gas and groundwater concentrations patterns will be similar to case (a).



(c) For the unusual case where NAPL has been injected or emplaced below the water table without being present in the vadose zone, or where VOC transport in groundwater at depth has advanced far beyond the vapour plume that has migrated from the NAPL source, upward diffusion of VOCs from groundwater to soil gas may be negligent, particularly where recharge causes a downward component of groundwater flow.



(d) Where DNAPL has sunk below the water table a vapour plume will develop around the residual DNAPL in the vadose zone and a dissolved plume will emanate from the DNAPL in the saturated zone. Vapour transport will contaminate shallow groundwater over an area wider than the DNAPL source. The deeper dissolved chemical plumes will generally be narrower and more concentrated than the shallow groundwater plume that results from vapour transport. If the hydrogeologic conditions are complex, several distinct dissolved plumes may migrate at different rates and in different directions. Thus soil gas monitoring will provide information on the extent of shallow groundwater contamination, but may not be a reliable indicator of deeper groundwater contamination.



(e) DNAPL trapped in pools below the water table may continue to dissolve in groundwater after the residual DNAPL in the vadose zone has been completely depleted. For this case soil gas contamination may be limited to the area above where the shallow groundwater plume has migrated to, or where the deeper groundwater plume reaches the water table. Note however that several processes will work to prolong soil gas contamination in the zone of depleted DNAPL, including adsorption / desorption, and the slow movement of water and dissolved chemicals in relatively low permeability portions of the vadose and saturated zones.

Figure 4.2 **Conceptual models (longitudinal sections) of soil gas and groundwater contamination resulting from NAPL releases (modified from Rivett and Cherry, 1991).**

Table 4.7 Drilling methods, applications, and limitations (modified from Cohen and Mercer, 1993; USEPA, 1987).

Method	Applications/ Advantages	Limitations
HAND AUGERS - A hand auger is advanced by turning it into the soil until the bucket or screw is filled. The auger is then removed from the hole. The sample is dislodged from the auger, and drilling continues. Motorised units are also available.	• Shallow soil investigations (0 to 15ft) • Soil samples collected from the auger cutting edge • Water bearing zone identification • Contamination presence examination; sample analysis • Shallow, small diameter well installation • Experienced user can identify stratigraphic interfaces by penetration resistance differences as well as sample inspection • Highly mobile, and can be used in confined spaces • Various types (ie, bucket, screw, etc.) and sizes (typically 1 to 9 inches in diameter) • Inexpensive to purchase	• Limited to very shallow depths (typically <15ft) • Unable to penetrate extremely dense or rocky or gravely soil • Borehole stability may be difficult to maintain, particularly beneath the water table • Potential for vertical cross contamination • Labour intensive
SOLID FLIGHT AUGERS - A cutter head (=2 inch diameter) is attached to multiple auger flights. As the augers are rotated by a rotary drive head and forced down by either a hydraulic pulldown or a feed device, cuttings are rotated up to ground surface by moving along the continuous flighting.	• Shallow soils investigations (<100ft) • Soil samples are collected from the auger flights or using split spoon or thin walled samplers if the hole will not cave upon retrieval of the augers • Vadose zone monitoring wells • Monitor wells in saturated, stable soils • Identification of depth to bedrock • Fast and mobile; can be used with small rigs • Holes up to 3ft diameter • No fluids required • Simple to decontaminate	• Low quality soil samples unless split spoon or thin wall samples are taken • Soil sample data limited to areas and depths where stable soils are predominant • Unable to install monitor wells in most unconsolidated aquifers because of borehole caving upon auger removal • Difficult penetration in loose boulders, cobbles, and other material that might lock up auger • Monitor well diameter limited by auger diameter • Cannot penetrate consolidated materials • Potential for vertical cross contamination
HOLLOW STEM AUGERS Hollow stem augering is done in a similar manner to solid flight augering. Small diameter drill rods and samplers can be lowered through the hollow augers for sampling. If necessary, sediment within the hollow stem can be cleaned out prior to inserting a sampler. Wells can be completed below the water table using the augers as temporary casing.	• All types of soil investigations to <100ft below ground • Permits high quality soil sampling with split spoon or thin wall samplers • Water quality sampling • Monitor well installation in all unconsolidated formation • Can serve as a temporary casing for coring rock • Can be used in stable formations to set surface casing • Can be used with small rigs in confined spaces • Does not require drilling fluids	• Difficulty in preserving sample integrity in heaving (running sand) formations • If water or drilling mud issued to control heaving will invade the formation • Potential for cross contamination of aquifers where annular space not positively controlled by water or drilling mud or surface casing • Limited auger diameter limits casing size (typical augers are: 6¼-in OD with 3¼-in ID and 12-in OD with 6-in ID) • Smearing of clays may seal off interval to be monitored

Table 4.7 contd. Drilling methods, applications, and limitations (modified from Cohen and Mercer, 1993; USEPA, 1987).

Method	Applications/ Advantages	Limitations
DIRECT MUD ROTARY - Drilling fluid is pumped down the drill rods and through a bit attached to the bottom of the rods. The fluid circulates up the annular space bringing cuttings to the surface. At the surface, drilling fluid and cuttings are discharged into a baffled sedimentation tank, pond or pit. The tank effluent overflows into a suction pit where drilling fluid is recirculated back through the drill rods. The drill stem is rotated at the surface by top head or rotary table drives and down pressure is provided by pull down devices or drill collar.	• Rapid drilling of clay, silt and reasonably compact sand and gravel to great depth (>700ft) • Allows split spoon and thin wall sampling in unconsolidated materials • Allows drilling and core sampling in consolidated rock • Abundant and flexible range of tool sizes and depth capabilities • Sophisticated drilling and mud programmes available • Geophysical borehole logs	• Difficult to remove drilling mud and wall cake from outer perimeter of filter pack during development • Bentonite or other drilling fluid additives may influence quality of groundwater samples • Potential for vertical cross contamination • Circulated cutting samples are of poor quality; difficult to determine sample depth • Split spoon and thin wall samplers are expensive and of questionable cost effectiveness at depths >150ft • Wireline coring techniques for sampling both unconsolidated and consolidated formations often not available locally • Drilling fluid invasion of permeable zones may compromise integrity of subsequent monitor well samples • Difficult to decontaminate pumps
AIR ROTARY - Air rotary drilling is similar to mud rotary drilling except that air is the circulation medium. Compressed air injected through the drill rods circulates cuttings and groundwater up the annulus to the surface. Typically, rotary drill bits are used in sedimentary rocks and down-hole hammer bits are used in harder igneous and metamorphic rocks. Monitor wells can be completed as open hole intervals beneath telescoped casings.	• Rapid drilling of semi consolidated and consolidated rock to great depth (>700ft) • Good quality/reliable formation samples (particularly if small quantities of drilling fluid are used) because casing prevents mixture of cuttings from bottom of hole with collapsed material from above • Allows for core-sampling of rock • Equipment generally available • Allows easy and quick identification of lithologic changes • Allows identification of most water-bearing zones • Allows estimation of yields in strong water-producing zones with short "down-time"	• Surface casing frequently required to protect top of hole from caving • Drilling restricted to semi consolidated and consolidated formations • Samples reliable, but occur as small chips that may be difficult to interpret • Drying effect of air may mask lower yield water producing zones • Air stream requires contaminant filtration • Air may modify chemical or biological conditions; recovery time is uncertain • Potential for vertical cross contamination • Potential exists for hydrocarbon contamination from air compressor or down hole hammer bit oils
AIR ROTARY WITH CASING DRIVER - This method uses a casing driver to allow air rotary drilling through unstable unconsolidated materials. Typically the drill bit is extended six to twelve inches ahead of the casing, the casing is driven down, and then the drill bit is used to clean material from within the casing.	• Rapid drilling of unconsolidated sands, silts and clays • Drilling is alluvial material (including boulder formations) • Casing supports borehole, thereby maintaining borehole integrity and reducing potential for vertical cross-contamination • Eliminates circulation problems common with direct mud rotary method • Good formation samples because casing (outer wall) prevents mixture of caving materials with cuttings from bottom of hole • Minimal formation damage as casing pulled back (smearing of silts and clays can be anticipated)	• Thin, low pressure water bearing zones easily overlooked if drilling not stopped at appropriate places to observe whether or not water levels are recovering • Samples pulverized as in all rotary drilling • Air may modify chemical or biological conditions; recovery time is uncertain

Table 4.7 contd. Drilling methods, applications, and limitations (modified from Cohen and Mercer, 1993; USEPA, 1987).

Method	Applications/ Advantages	Limitations
DUAL WALL REVERSE ROTARY - Circulating fluid (air or water) is injected through the annulus between the outer casing and drill pipe, flows into the drill pipe through the bit, and carries cuttings to the surface through the drill pipe. Similar to rotary drilling with the casing driver, the outer pipe stabilises the borehole and reduces cross-contamination of fluids and cuttings. Various bits can be used with this method.	• Very rapid drilling through both unconsolidated and consolidated formations • Allows continuous sampling in all types of formation • Very good representative samples can be obtained with reduced risk of contamination of sample and/or waterbearing zone • Allows for rock coring • In stable formations, wells with diameters as large as six inches can be installed in open hole completions	• Limited borehole size that limits diameter of monitor wells • In unstable formations well diameters are limited to approximately four inches • Equipment available more common in the Southwest US than elsewhere • Air may modify chemical or biological conditions; recovery time is uncertain • Unable to install filter pack unless completed open hole
CABLE TOOL DRILLING - A drill bit is attached to the bottom of a weight drill stem that is attached to a cable. The cable and drill stem are suspended from the drill rig mast. The bit is alternatively raised and lowered into the formation. Cuttings are periodically removed using a bailer. Casing must be added as drilling proceeds through unstable formations.	• Drilling in all types of geologic formations • Almost any depth and diameter range • Ease of monitor well installation • Ease and practicality of well development • Excellent samples of coarse grained media can be obtained • Potential for vertical cross contamination is reduced because casing is advanced with boring • Simple equipment and operation	• Drilling is slow and frequently not cost-effective as a result • Heaving of unconsolidated materials must be controlled • Equipment availability more common in central, north central and south east sections of the US
ROCK CORING - A carbide or diamond tipped bit is attached to the bottom of a hollow core barrel. As the bit cuts deeper, the rock sample moves up into the core tube. With a double-wall core barrel, drilling fluid circulates between the two walls and does not contact the bore allowing better recover. Clean water is usually the drilling fluid. Standard core tubes are attached to the bottom of a drill rod and the entire string of rod must be removed after each core run. With wireline coring, an inner core barrel is withdrawn through the drill string using an overshot device that is lowered on a wireline into the drill string.	• Provides high quality, undisturbed core samples of stiff to hard clays and rock • Holes can be drilled at any angle • Can detect location and nature of rock fracture • Can use core holes to run a complete suite of geophysical logs • Variety of core sizes available • Core holes can be utilised for hydraulic tests and monitor well completion • Can be adapted to a variety of drill rig types and operations	• Relatively expensive and slow rate of penetration • Can lose a large quantity of drilling water into permeable formations • Potential for vertical cross contamination

Table 4.7 contd. Drilling methods, applications, and limitations (modified from Cohen and Mercer, 1993; USEPA, 1987).

Method	Applications/ Advantages	Limitations
CONE PENETROMETER - Hydraulic rams are used to push a narrow rod (e.g. 1.5 inch diameter) with a conical point into the ground at a steady rate. Electronic sensors attached to the test probe measure tip penetration resistance, probe site resistance, inclination and pore pressure. Sensors have also been developed to measure subsurface electrical conductivity, radioactivity, and optical properties (fluorescence and reflectance). Cone penetrometer tests (CPT) are generally performed using a special rig and computerised data collection, analysis and display system. To facilitate interpretation of CPT data from numerous tests, CPT data from at least one test per site should be compared to log of continuously sampled soil at an adjacent location Referenced: Robertson and Campanella (1986), Lurk et al. (1990), Smolley and Kappmeyer (1991), Cristy and Spradlin (1992), Edge and Cordry (1989), and Chiang et al. (1992).	• Efficient tool for stratigraphic logging of soft soils • Measurement of some soil/fluid properties (e.g. tip penetration resistance, probe side fraction, pore pressure, electrical conductivity, radioactivity, fluorescence (with proper instrumentation can be obtained continuously rather than at intervals; thus improving the detectability of thin layers (ie, subtle DNAPL capillary barriers) and contaminants • There are vitually no cuttings brought to the ground surface, thus eliminating the need to handle cuttings • Process presents a reduced potential for vertical cross contamination if the openings are sealed with grout from the bottom up upon rod removal • Porous probe samplers can be used to collect groundwater samples with minimal loss of volatile compounds • Soil gas sampling can be conducted • Fluid sampling from discrete intervals can be conducted using special tools (e.g. the "Hydropunch" manufactured by QED Environmental Systems of Ann Arbor, Michigan)	• Unable to penetrate dense geologic conditions (ie hard clays, boulders, etc.) • Limited depth capability • Soil samples cannot be collected for examination or chemical analyses unless special equipment is utilised • Only very limited quantities of groundwater can be samples • Limited well construction capability • Limited availability

The risk of causing DNAPL migration generally increases where there is fractured media, heterogeneous strata, multiple release locations, large DNAPL release volumes and subtle horizontal barriers to DNAPL migration (Cohen and Mercer, 1993).

There are two basic approaches to invasive characterisation of contaminated sites, referred to as the outside-in and inside-out strategies. The outside-in strategy defines the extent of DNAPL contamination by initially drilling outside suspected DNAPL areas and gradually working towards the source. The main advantage of the outside-in technique is the ability to acquire considerable geological and hydrogeological information on the site at low risk of inducement of further DNAPL migration. The inside-out approach involves drilling initially in the areas suspected to be most contaminated and subsequently drilling in more remote areas to define the extent of contamination and is the traditional approach to contaminated site investigation. The main advantage of the inside-out approach is that fewer boreholes are generally required to define the extent of DNAPL contamination, although the risk of inducing DNAPL migration is high using this strategy. The relative time and cost advantages of the inside-out approach may be offset by the additional cost of investigation and remediation if DNAPLs are mobilised to greater depths during site characterisation (USEPA, 1992). However the correct methodology to be applied must be assessed on a site specific basis.

4.5.3 Sampling Unconsolidated Geological Material

Subsurface explorations permit direct measurement of stratigraphic, hydrogeologic and contaminant conditions. Locations of trial pits and borings are selected to test and verify the site conceptual model. The numbers and locations of excavations and borings required during site characterisation investigation depend on site specific conditions and investigation objectives.

The value of subsurface exploration relies on the quality of measurements recorded during the investigation. In addition to recording soil characteristics such as texture, particle size and moisture, it is crucial to note visual and olfactory observations that may identify the presence of DNAPL.

Trial Pits and Trenches

Excavation of trial pits can be an extremely rapid and cost effective technique to a) evaluate shallow overburden stratigraphy and structure, b) identify and delineate contaminated areas, c) locate and examine buried structures, tanks and pipelines, and d) acquire samples for chemical and physical analyses. Guidelines for trial pit and trench excavation, sampling and backfilling are provided in "A Compendium of Superfund Field Operations" USEPA (1987) and "Subsurface Characterisation and Monitoring Techniques" USEPA (1993).

Trial pits and trenches allow the observation of a continuous subsurface section and as a result can reveal stratigraphic relations, soil fracture patterns, heterogeneous DNAPL distributions etc. The risk of inducing further DNAPL migration is low due to the limited depth of excavation to a maximum of approximately four metres with a backhoe.

Disadvantages related to trial pit excavation include the limited depth of excavation, disturbance of surface materials such as concrete or tarmac, possibility of trial pit collapse near underground utilities, potential airborne release of contaminated vapours, potential increased waste handling problems, and potential subsidence problems after backfilling of the trench or trial pit.

Drilling in Unconsolidated Geological Material

Boreholes and groundwater monitoring wells are installed to evaluate subsurface stratigraphic, hydrogeologic and contaminant conditions. Selection of drilling locations, technique and depth is based on the conceptual model of subsurface contamination and site specific factors limiting location. Drilling methods applicable to contaminated site investigation have been widely documented and several key references are given above. The most commonly used methods of drilling in unconsolidated media at contaminated sites are presented in Table 4.7 and each technique's applicability is discussed in USEPA (1993).

The additional risks associated with drilling at a DNAPL site mean that special consideration should be given to drilling methods which allow for continuous, high quality sampling to facilitate a) identification of DNAPL presence and potential barriers to vertical DNAPL flow and b) highly controlled well construction and borehole abandonment. Some potential for causing vertical DNAPL migration is associated with all drilling methods, however the risk can be minimised by careful consideration of drilling strategy. Selection of drilling technique is discussed in Davis et al (1991) and USEPA (1991). The USEPA (1991) document presents a series of matrices that aid the selection of drilling technology by considering site specific objectives of the investigation and the hydrogeological situation.

Drilling in unconsolidated media in the UK is most commonly undertaken using the cable tool percussion technique, also known as the shell and auger method.

Soil or waste samples brought to the surface during drilling are typically examined and observations logged. At sites potentially contaminated with DNAPL compounds, samples are generally routinely screened using an organic vapour analyser such as a photionisation detector (PID). Methods for visual identification of DNAPL in soil and groundwater samples are described below. Samples are also collected for submission to the laboratory for detailed chemical analyses and for physical property testing.

Unconsolidated media sampling methods are widely documented, for example in Davis et al (1991), USEPA (1993) and Driscoll (1986), and all those sampling techniques that are applicable to standard site investigations are generally applicable to DNAPL investigations. However, particular care must be taken to reduce loss of VOCs during sample storage and handling. Studies have shown that storing soil samples in jars containing methanol and subsequent analysis of the solvent can reduce loss of VOCs (WCGR, 1991). Storing samples in jars with air can cause significant under estimation of VOC concentrations. Volatile loss from core barrel samplers, such as 'U100' samples, can be significantly reduced by rapid sealing of the ends of the core barrel (Cheery and Feenstra, 1991). Samples should be kept refrigerated wherever possible, submitted to laboratory quickly and agitation should be kept to a minimum to reduce volatile loss.

4.5.4 Sampling Consolidated Geological Material

Drilling in consolidated material is primarily undertaken to characterise the nature and extent of contamination in bedrock, either in the vadose or saturated zone. The main techniques of drilling in consolidated material are briefly described in Table 4.7 and are discussed in detail in USEPA (1991), USEPA (1993) and Driscoll (1986). The USEPA (1991) document "Handbook of Suggested Practices for the Design and Installation of Groundwater Monitoring Wells" discusses criteria for selection of drilling technology applicable to a particular hydrogeological and contaminant situation, and includes matrices to aid technique selection.

Drilling in rock typically poses a significantly greater risk of inducing vertical migration of DNAPL than drilling in unconsolidated media. When evaluating the presence of DNAPL in bedrock fractures, the following should be considered: a) fracture orientations, spacings and apertures, b) DNAPL density, viscosity and interfacial tension, c) DNAPL release volume, d) DNAPL head driving density flow, and e) groundwater hydraulic gradients. Drilling through bedrock containing DNAPL should be avoided, wherever possible. Where drilling through DNAPL is necessary the risk minimisation measures discussed in Section 4.4.2 should be implemented.

An example drilling protocol for characterising DNAPL contaminated sites in fractured bedrock is included in Cohen and Mercer (1993), taken from a site investigation at S-Area Landfill, Niagara Falls, New York. The example describes the drilling of an initial investigation borehole minimising the potential for cross contamination and induced DNAPL migration. The borehole involved drilling through unconsolidated drift using large diameter hollow stem auger and taking continuous split spoon samples. The shallow aquifer was sealed from the underlying Lockport Dolomite by installing permanent casing and pressure grouting. The Lockport Dolomite was drilled in five metre sections using a rotary coring rig with continuous coring facility. The core was retained in sealed core boxes. The drilling fluid was spiked with a tracer. After drilling five metres of the dolomite, the aquifer was packer tested to define hydraulic parameters and formation water was sampled. Analysis of groundwater samples for the drilling fluid tracer allowed estimation of influence of drilling on the aquifer. Each five metre section was cased and pressure grouted and the drilling diameter reduced prior to drilling the next five metre section.

4.5.5 Groundwater Monitoring Well Construction

Monitoring wells are installed to characterise immiscible fluid distributions, groundwater and NAPL flow directions and rates, groundwater quality and aquifer hydraulic properties. The locations and design of monitoring wells are based on the site conceptual model and the site specific data collection objectives.

Design and installation of groundwater monitoring wells has been widely documented, for example Nielsen and Schalla (1991), USEPA (1991) USEPA (1993) and Driscoll (1986), and only those aspects pertinent to DNAPL contamination are discussed in this report.

The design and construction of wells at DNAPL contaminated sites require special consideration of 1) the effect of well design and location on immiscible fluid movement, 2) the compatibility of well materials with NAPLs and dissolved chemicals, and 3) well development and sampling technique.

Inadequate well design can increase the potential for causing vertical DNAPL migration and misinterpretation of DNAPL elevation and thickness. Several factors may cause the elevation and thickness of DNAPL in the monitoring well to differ from that in the formation, and/or lead to DNAPL migration, and include the following:

- If the well screen or casing extends below the top of the DNAPL barrier layer (impermeable to vertical DNAPL flow) the measured DNAPL thickness may exceed that in the formation
- If the well base is located above the base of the DNAPL pool in the formation the measured DNAPL thickness will be less than the formation DNAPL thickness
- If the screened interval is across a formation impermeable to vertical DNAPL flow the DNAPL will flow vertically along the well and enter the deeper permeable formation
- DNAPL which enters a well filter pack may sink through the well pack rather than flow through the screen
- Filter packs should generally be coarser than the aquifer material to induce flow of DNAPL into the well; screen or sand pack that is too fine may act as a capillary barrier to DNAPL flow
- If the screen is located entirely within a DNAPL pool and water is pumped from the well upconing of DNAPL in the well will occur to maintain the hydrostatic equilibrium
- DNAPL will not flow into a well where it is present at or below residual saturation or at negative pressure
- The elevation of DNAPL in a well may exceed that in the adjacent formation by a length equivalent to the DNAPL-water capillary fringe height where the top of the pool is under drainage conditions

Therefore, the construction of the well screen should intercept the water DNAPL interface and the lower end of the screen should be placed as close as possible to the impermeable stratigraphic unit underlying the DNAPL .

The compatibility of well materials with NAPL compounds and highly contaminated groundwater should also be evaluated during well design (Nielsen and Schalla, 1991; USEPA, 1991; USEPA, 1993; Driscoll, 1986). Table 4-8 summarises the advantages and disadvantages of different screen and casing materials. Steel well materials are generally recommended where DNAPLs may be present because of its strength and chemical resistance to solvents. However the cost effectiveness and suitability of each material must be assessed on a site specific basis. PVC and ABS thermoplastics should not be used where there is potential for contact with halogenated solvents as casing and screen material will degrade.

Monitoring well annular seals are composed of several different stable and low hydraulic conductivity materials. The composition and characteristics of various grouts are given in Table 4-9 and are discussed further in Edil et al (1992), USEPA (1991), USEPA (1993), Nielsen and Schalla (1991) and Driscoll (1986). Hydrophobic liquids may cause bentonite grouts to shrink and fracture and are therefore unsuitable for use where DNAPL is present.

After construction monitoring wells are usually developed to remove fine grained particles and drilling residues from the well screen, filter pack and aquifer in the vicinity of the well. Standard well development techniques such as over pumping, surging, backwashing and jetting are not applicable to monitoring wells where DNAPL is present as these techniques may induce further DNAPL migration or produce a DNAPL-water emulsion. Well development should be limited to gentle pumping and removal of fines to minimise DNAPL redistribution. Measurements should be made of NAPL stratification before and after development.

4.5.6 Determination of DNAPL Thickness and Mobility

Measurements of the elevation of air-LNAPL-water-DNAPL interfaces, and determination of NAPL thicknesses are made in monitoring wells to assist determination of flow directions (NAPL and groundwater) and immiscible fluid distributions. DNAPL migration can be assessed by integrating the conceptual model with measurements of DNAPL thickness from monitoring wells.

Techniques for acquiring water level data, including wetted tape method, air line method, electrical and ultrasonic techniques, pressure transducers, floats etc., are discussed in USEPA (1993) and are not covered further in this report.

When measuring fluid levels and thicknesses, care should be taken to not disturb immiscible fluids. Measurements of fluid thicknesses should be made before and after purging and sampling activities. The cost of decontamination of measuring devices, should be considered before selecting a particular technique.

Interface Probes

Most interface probes operate using an optical device to determine the air fluid interface and a conductivity sensor to determine NAPL water interfaces (Sanders, 1984). These probes are typically 25-40mm in diameter, 225mm long and attached to an incrementally marked tape. Interface probes should be operated by gently lowering to the base of the well and slowly raising through the well. Different audible signals indicate the location of the various interfaces. At maximum sensitivity interface probes can identify a NAPL layer thickness to within 3mm. However spurious results can occur when electrically conductive NAPL, emulsified NAPL or viscous NAPL coats the probe.

Table 4.8 Advantages and disadvantages of some common well casing materials (modified from Driscoll, 1986; Geotrans, 1989; and Nielsen and Schalls, 1991).

Type	Advantages	Disadvantages
FLUOROPOLYMERS such as polytetrafluoroethene (PTFE), tetrafluoroethylene (TFE), and fluorinated ethylene propylene (FEP)	• Excellent chemical resistance to organic chemicals and corrosive environments; practically insoluble in all organic liquids except a few fluorinated solvents. • Lightweight • High impact Strength	• Lower tensile strength and wear resistance compared to other plastics, iron or steel • Expensive relative to steel and other plastics
THERMOPLASTICS: POLYVINYLCHLORIDE (PVC) AND ACRYLONITRILE BUTADIENE STYRENE (ABS)	• Lightweight • Easy workability (with threaded couplings) • Inexpensive compared to fluoropolymers and steel • Resistant to alcohols, aliphatic hydrocarbons, weak and strong alkalies, oils, strong mineral acids and oxidising acids • Completely resistant to galvanic and electrochemical corrosion • High strength to weight ratios and resistent to abrasion	• More reactive than PTFE • Poor chemical resistance to aromatic hydrocarbons, esters, ketones and organic solvents • Much lower tensile compressive and collapse strength than steel or iron • May adsorb to elute trace organics • PVC glues, if used, may contribute organic chemicals to well water
STAINLESS STEEL such as Type 304 and Type 316	• Stronger more rigid and less temperature sensitive than plastic materials • Good chemical resistence to organic chemicals • Resistant to corrosion and oxidation • Readily available	• Expensive • May catalyse some organic chemical reactions • May corrode if exposed to long term corrossive conditions and leach chromium • Heavy
CARBON STEEL	• Stronger more rigid and less temperature sensitive than plastic materials • Less expensive than stainless steel or teflon	• Expensive • Rusts easily, providing high sorptive and reactive capacity for many metals and organic chemicals • Subject to corrosion (under conditions of low pH, high dissolved oxygen, H2S presence, > 1000 mg/l total dissolved solids, > 50 mg/l CO2 or 500 mg/l Cr • Heavy
GALVANIZED STEEL	• Stronger more rigid and less temperature sensitive than plastic materials	• Expensive • Will rust if galvanised coating is scratched • Resistance to corrosion provided by zinc coating may be short lived • May be a source of zinc • Heavy

Table 4.9 Borehole and well annulus grout types and considerations (modified from Aller et al. 1989; Edil et al., 1992)

1. BENTONITE AND BENTONITE-CEMENT GROUTS:	Bentonite is a hydrous aluminium silicate comprised primarily of montmorillinite clay. The volume of hydrated bentonite in water is typically 10 to 15 times greater than that of dry bentonite because water is incorporated within the expanding grey lattice. The low permeability and expansion of bentonite in water are desirable properties for sealing abandoned boreholes and well annular spaces. Bentonite grouts are best prepared using mechanical mixers and should be pumped under pressure in place from the base of the interval to be grouted through a tremie pipe. Bentonite grouts should be mixed in batches so that they can be pumped before becoming too viscous. Bentonite grout should not be placed in the vadose zone because it will dry, shrink and fracture. Bentonite grout should also shrink and fracture in the presence of hydrophobic NAPLs. Several available bentonite grouts are described below:
Bentonite Slurry Grout	Bentonite slurry grout is commonly prepared by mixing dry powder in fresh water at a ratio of 15 lbs of bentonite to seven gallons of water to make 1ft^3 of slurry. Thick slurries may gel prematurely and be impossible to emplace. Due to their low solid content, bentonite slurries tend to settle as liquid bleeds off, requiring the emplacement of more slurry.
Quick Gell® Bentonite	Quick Gell® Bentonite Drilling Mud Grout is a slurry of sodium bentonite and water that is marketed primarily as a drilling mud. Grouts of varying viscosity and strength can be obtained by mixing different proportions of Quick Gell®, water and sand. Slurries containing sand appear more stable than pure Quick Gell®. Edil et al. (1992) found that Quick Gell® slurries of different sand content and viscosity form poorer annulus seals than neat cement, cement-bentonite and Benseal® -bentonite slurry grouts.
Benseal® Bentonite slurry grout	Benseal® Bentonite slurry grout is a mixture of Benseal®, a granular nondrilling mud grade bentonite developed for use in sealing and grouting well casings, and bentonite powder with water. Edil et al. (1992) mixed 30lbs of natural gell® (a natural unaltered bentonite powder) with 100 gallons of water, and then used a venturi pump to mix 125lbs of Benseal® to the slurry. They found that this grout adheres to steel and PVC casing and has low permeability, good swelling characteristics and flexibility, and is an excellent sealant.

Table 4.9 cont.d **Borehole and well annulus grout types and considerations (modified from Aller et al., 1989; Edil et al., 1992)**

Benseal® Bentonite slurry grout	Benseal® Bentonite slurry grout is a mixture of Benseal®, a granular nondrilling mud grade bentonite developed for use in sealing and grouting well casings, and bentonite powder with water. Edil et al. (1992) mixed 30lbs of natural gell® (a natural unaltered bentonite powder) with 100 gallons of water, and then used a venturi pump to mix 125lbs of Benseal® to the slurry. They found that this grout adheres to steel and PVC casing and has low permeability, good swelling characteristics, and flexibility, and is an excellent sealant.
Bentonite-Cement Grout	Bentonite-Cement Grout is a slurry incorporating 5 to 6 gallons of water and 2 to 6 lbs of bentonite powder for each 94 lbs (ft^3) of Portland cement. Bentonite improves the workability of the cement slurry, reduces slurry density, and reduces grout shrinkage during setting. Edil et al. (1992) found the addition of 5 lbs of bentonite to 94 lbs of cement forms a rigid well annulus seal with low permeability and high durability: and the grout adheres to steel casing, but appeared to allow some infiltration along the grout-PVC casing interface.
Bentonite pellets	Bentonite pellets can be used to seal borehole or well annulus intervals. Well pellets, however, tend to stick to well casing and borehole walls and bridge high above their intended placement depth. A tamper can be used to break up bridges, but this technique becomes ineffective at depths greater than approximately 20ft. Pellets can be frozen using refrigeration or liquid nitrogen to increase their fall distance.

Table 4.9 cont.d Borehole and well annulus grout types and considerations (modified from Aller et al., 1989; Edil et al., 1992)

2. PORTLAND CEMENT	Neat cement is a mixture of Portland cement (ASTM C-150) and water in the proportion of five to six gallons of clean water per bag (94lbs or 1ft^2) of cement. Five types of Portland cement are produced. Type I for general use; Type II for moderate sulphate resistance of moderate heat of hydration; Type III for high early strength; Type IV for low heat of hydration; and Type V for high sulphate resistance. Type I is most widely used in well construction or hole abandonment. A typical 14 lb/gallon neat cement slurry with a mixed volume of 1.5 ft^3 will have a set volume of 1.2 ft^3, reflecting a 17% shrinkage. The setting time ranges from 48 to 72 hours depending primarily on water content. Common additives include: (1) 2 to 6% bentonite to reduce shrinkage, improve workability, reduce density and produce a lower cost volume of grout; (2) 1 to 3% calcium chloride to accelerate the setting time and thereby create higher early strength of particular value in cold climates; (3) 3 to 6% gypsum to produce a very hard quick setting cement that expands upon setting; (4) <1% aluminium power to produce a quick setting strong cement that expands upon setting; (5) 10 to 20% flyash to increase sulphate resistance and provide early compressive strength; (6) hydroxylated carboxylic acid to retard setting time and improve workability without compromising set strength; and (7) diatomaceous earth to reduce slurry density, increase water demand and thickening time, and reduce set strength. Edil et al. (1992) found neat cement grout forms a rigid seal with low permeability and high durability that adheres fairly well to steel and PVC casing. Kurt and Johnson (1982), however report that neat cement seals are subject to channeling between the casing and the grout due to temperature changes during curing, swelling and shrinkage during curing, and poor bonding between the grout and casing. Cement shrinkage can produce fractures, thereby degrading the integrity of the grout seal. Cement slurries can infiltrate the well sandpack, particularly if well development occurs prior to when the cement has completely set. Thus a minimum of 1 to 2 ft of filter pack is usually extended above the annulus, above the top of the well screen. The high heat content of cement hydration can compromise the integrity of thermoplastic casing. Cement is a highly alkaline substance with a pH that ranges from 10 to 12. This can alter groundwater pH.

Hydrocarbon Detection Paste

Hydrocarbon detection paste changes colour within seconds upon contact with liquid hydrocarbons. It can be used to measure DNAPL thickness by applying a thin film to a tape and lowering it to the base of a monitoring well where DNAPL is present. Upon retrieval the length of tape with colour changed paste represents the thickness of the DNAPL. This technique is not widely used although it is relatively inexpensive and can produce measurements of layer thickness accurate to within 3mm. Measurement errors can occur if LNAPL is floating on the water table and this technique is of no value where the DNAPL is non hydrocarbon.

Transparent Bailers

Transparent bottom loading bailers can be used to measure NAPL thickness in a well. For DNAPL thickness measurement the bailer is gently lowered to the bottom of the monitoring well and then raised to the surface. The thickness of the DNAPL layer can be determined to within 50mm if the DNAPL thickness is less than the length of the bailer. If the DNAPL thickness is greater than the length of the bailer, then the bailer must be lowered several more times, not to the base of the well, to identify the elevation of the upper surface of the DNAPL layer.

Assessing DNAPL Mobility

Determination of the extent and mobility of DNAPL is a crucial part of site characterisation as it has implications for remedial options. Monitoring DNAPL elevations in wells over a period of time may provide an indication of DNAPL mobility. However migration pathways can also be assessed based on 1) measurements and observations of DNAPL saturation in subsurface media samples, such as locations of residual saturation and source, 2) measurement of DNAPL elevations before, during and after DNAPL pumping experiments.

DNAPL migration will cease when all the DNAPL spilled has been distributed at residual saturation through the subsurface or when the DNAPL has been immobilised in a stratigraphic trap. DNAPL with low viscosity and DNAPL in low permeability media will migrate slowly and therefore remain mobile for a longer period. Long term mobility is also promoted by larger release volumes and where there is an on-going release, for example from a pipeline. Increased hydraulic gradients and a fluctuating water table may cause remobilisation of DNAPL.

4.5.7 DNAPL and Groundwater Sampling

Sampling of groundwater from monitoring wells is routinely undertaken to identify aquifer contamination and sampling methods and protocols have been described in numerous references. General references describing sampling protocols include 1) Subsurface Characterisation and Monitoring Techniques, USEPA (1993), 2) Practical Handbook of Groundwater Monitoring, edited by Nielsen (1991), 3) Site Characterisation for Subsurface Remediation, USEPA (1991), and 4) Practical Guide for Groundwater Sampling, USEPA (1985).

A groundwater sampling programme must begin with a quality assurance/quality control plan, that defines the site specific requirements of the sampling programme. Key elements of the QA/QC plan include: 1) development of a statistically sound sampling plan for spatial and temporal characterisation of groundwater quality, 2) installation of a sampling network which allows collection of representative samples from the subsurface, 3) use of sampling devices that minimise disturbance of the chemistry of the formation water, 4) use of decontamination procedures for all sampling equipment, 5) collection of QA/QC samples such as field rinsate samples, trip blanks and field duplicates, 6) bottling, preservation and handling of samples to maximise sample integrity (USEPA, 1993).

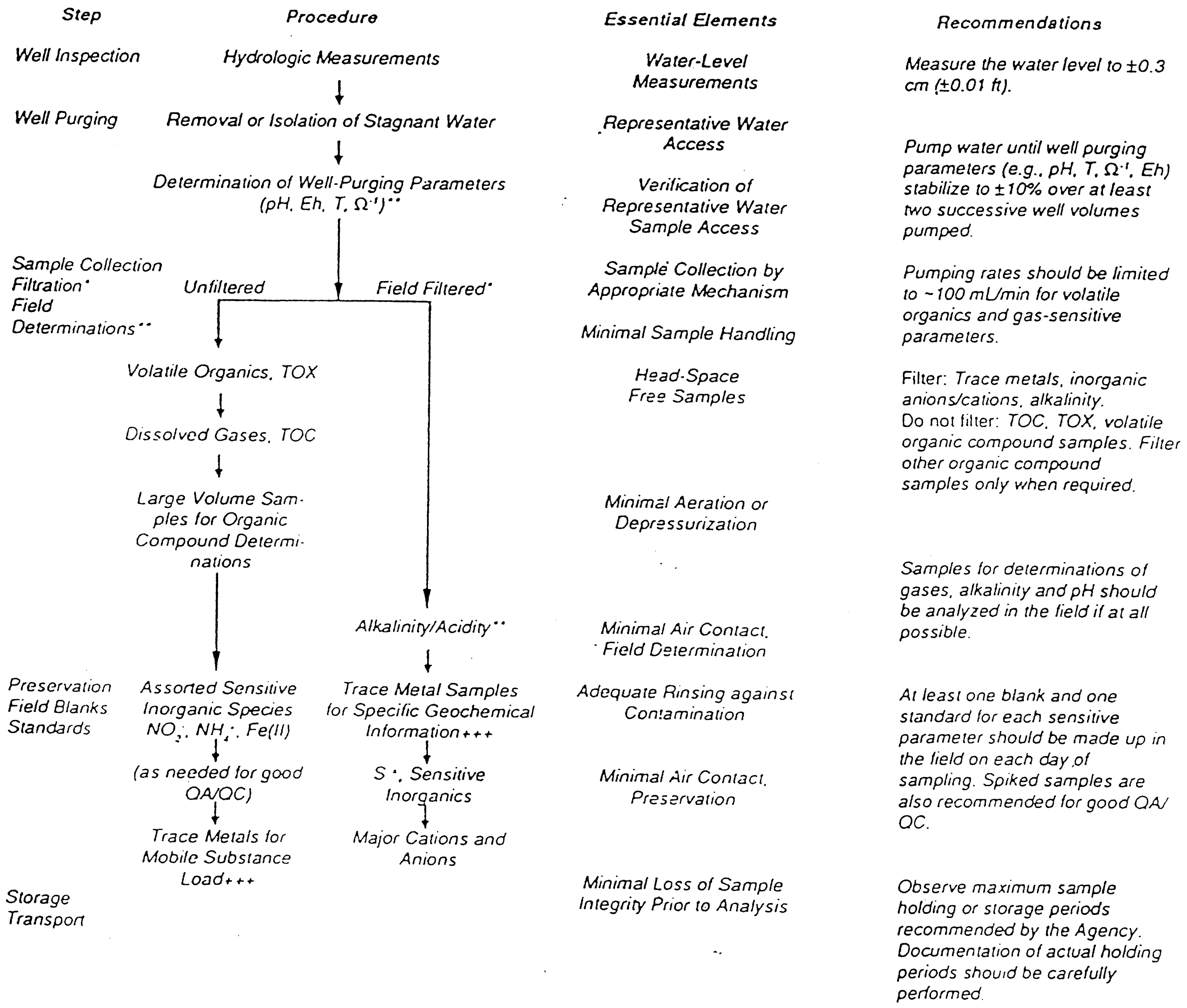
A flow chart indicating the procedures of groundwater sampling is included in Figure 4.4. Table 4.10 is a matrix to aid selection of a groundwater sampling device and each device is described in USEPA (1993). Table 4.11 shows recommended sampling handling and preservation procedures (USEPA, 1993).

Those aspects of monitoring well sampling relevant to DNAPL or dissolved DNAPL presence are discussed below.

Three of the most widely used techniques to retrieve a DNAPL sample from a monitoring well are the peristaltic pump, the inertial pump and the bailer. A peristaltic pump can be used to collect a sample if the depth to groundwater fluid to be sampled is not beyond the lift of the pump, approximately eight metres. At greater depths an inertial pump, such as the Waterra series of pumps, can be implemented. An advantage of the peristaltic and inertial pumps is that fluid contact is limited to the inexpensive tubing, thereby reducing decontamination requirements since the tubing is discarded after use. The most commonly used sampling apparatus where DNAPL compounds are present is the teflon bailer, a relatively cheap, simply operated and easily decontaminated item. A double check valve bailer has been cited as the ideal technique to sample free phase DNAPL from a monitoring well (Huling and Weaver, 1991). Decontamination requirements should be considered before selecting sampling technique as decontamination costs can comprise a large proportion of total sampling costs.

4.5.8 Equipment Decontamination

It is of paramount importance that subsurface samples collected during site characterisation investigations and therefore field and laboratory data are truly representative of site conditions. Equipment decontamination is a very important component of most subsurface contamination investigations. However, it is often poorly planned and documented. Decontamination procedures are not widely documented and as yet USEPA procedures have not been produced. Decontamination programme design is discussed in "Practical Handbook of Groundwater Monitoring" edited by Nielsen (1991), and "Subsurface Characterisation and Monitoring Techniques" USEPA (1993).



Measure the water level to ±0.3 cm (±0.01 ft).

Pump water until well purging parameters (e.g., pH, T, Ω⁻¹, Eh) stabilize to ±10% over at least two successive well volumes pumped.

Pumping rates should be limited to ~100 mL/min for volatile organics and gas-sensitive parameters.

Filter: Trace metals, inorganic anions/cations, alkalinity.
Do not filter: TOC, TOX, volatile organic compound samples. Filter other organic compound samples only when required.

Samples for determinations of gases, alkalinity and pH should be analyzed in the field if at all possible.

At least one blank and one standard for each sensitive parameter should be made up in the field on each day of sampling. Spiked samples are also recommended for good QA/QC.

Observe maximum sample holding or storage periods recommended by the Agency. Documentation of actual holding periods should be carefully performed.

* Denotes samples that should be filtered to determine dissolved constituents. Filtration should be accomplished preferably with in-line and pump pressure or by N_2 pressure methods. Samples for dissolved gases or volatile organics should not be filtered. In instances well development procedures do not allow for turbidity free samples and may bias analytical results, split samples should be spiked wi standards before filtration. Both spiked samples and regular samples should be analyzed to determine recoveries from both types of handlin

** Denotes analytical determinations that should be made in the field.

+++ See Puls and Barcelona (1989).

Figure 4.3 Generalised flow diagram of groundwater sampling procedures (adapted from Barcelona et al., 1985)

Table 4.10 Generalised groundwater sampling device selection matrix (adapted from USEPA, 1991)

						Groundwater Parameters													
						Inorganic							Organic				Radioactive		Biol.
		Device	Approximate Maximum Sample Depth	Minimum Well Diameter	Sample† Delivery Rate or Volume	EC	pH	Redox	Major Ions	Trace Metals	Nitrate, Fluoride	Dis-solved Gasses	Non-volatile	Volatile	TOC	TOX	Radium	Gross Alfa & Beta	Coli-form Bacteria
PSD*	Grab	Open bailer	No Limit	1/2 in	Variable	√			√	√	√		√				√		√
		Paint-source bailer	No Limit	1/2 in	Variable	√	√	√	√	√	√		√	√	√	√	√		√
		Syringe sampler	No Limit	1 1/2 in	0.01-0.2 gal	√	√	√	√	√	√		√				√	√	√
	PD	Gear-drive	200 ft	2 in	0-0.5 gpm									√					
		Bladder pump	400 ft	1 1/2 in	0.2 gpm	√	√	√	√	√	√	√	√	√	√	√	√	√	√
		Helical rotor	160 ft	2 in	0-1.2 gpm	√	√	√	√	√	√	√	√	√	√	√	√	√	
		Piston pump (gas-drive)	500 ft	1 1/2 in	0-0.5 gpm	√			√	√	√		√				√	√	
		Centrifugal	Variable	3 in	Variable	√			√		√						√	√	
	SL	Peristaltic	26 ft	1/2 in	0.01-0.3 gpm	√			√		√		√				√		√
	GC	Gas-lift	Variable	1 in	Variable														
		Gas-drive	150 ft	1 in	0.2 gpm	√			√		√		√				√		
In Situ Sampling Devices*		Pneumatic	No Limit	Not Applicable	0.01-0.13 gal	√	√	√	√	√	√		√				√	√	√

** Sampling devices on this chart are divided into two categories: (1) portable devices for sampling existing monitoring wells; and (2) in situ monitoring devices (often multi-level) that are permanently installed. Sampling device construction materials (including tubing, haul lines etc) should be evaluated for suitability in analysing specific groundwater parameters. It is assumed on this chart that existing monitoring wells are properly installed and constructed of materials suitable for detection of the parameters of interest. See references for additional information.*

†Sample delivery rates and volumes are average ranges based on typical field conditions. Actual delivery rates are a function of diameter of monitoring installation, size and capacity of sampling device, hydrogeologic conditions, and depth to sampling point. For all devices, delivery rate should be carefully controlled to prevent aeration or degassing of the sample.

√ Indicates device is generally suitable for application (assuming device is cleaned and operated properly and is constructed of suitable materials.

Key: PSD - Portable Sampling Devices*, PD - Positive Displacement (submersible), SL - Suction Lift, GC - Gas Contact.

Most larger equipment, such as drilling rigs, should be cleaned between sampling locations using a high pressure, hot water power washer. This system frequently employs an initial soapy wash and scrubbing with brushes to remove larger soil particles from surface areas, followed by a high pressure water wash to remove soap and contaminants. Equipment is usually allowed to air dry before use.

Larger equipment items can also be cleaned by the application of high pressure steam to remove contaminants and soil. The primary advantage of steam cleaning is that the volume of waste water produced by decontamination is reduced. However, it may be difficult generating a sufficient source of high pressure steam on site.

Decontamination of smaller items of equipment, such as groundwater sampling equipment, is often defined by specific analytes. To generalise, for sampling devices used to sample for inorganics, the more frequently used decontamination protocol involves a) tap water and soap water wash, b) rinse with dilute acid solution (10% hydrochloric or nitric acid), followed by c) rinses with distilled or deionised water. When sampling devices are used to sample for organics the following procedure is commonly used: a) initial wash water and lab grade detergent, b) solvent rinse (acetone, isopropyl alcohol or methanol, followed by c) distilled water or deionised water rinses. For practical purposes the decontamination procedure is satisfactorily simplified to using an initial rinse with water, followed by a wash and scrub with lab grade detergent (for example Alconox, Liquinox or Detergent 8) followed by three rinses with deionised or distilled water (Nielson, 1991).

Field rinsate blanks produced by rinsing equipment with deionised water should be used as a standard procedure to identify any carry over of compounds and to check adequacy of the decontamination procedure.

4.5.9 Borehole Geophysics

Borehole geophysical surveys are conducted to characterise lithologies, correlate stratigraphy between boreholes, identify fracture zones, estimate formation properties such as porosity and identify intervals containing conductive dissolved contaminants. As such, they can be useful in developing the site conceptual model. The utility of the various borehole geophysical techniques is discussed in Table 4.12 and the application of borehole geophysical methods to groundwater investigations is described in USEPA (1987), USEPA (1993) and Driscoll (1986).

Two references discuss the application of borehole geophysics to DNAPL contaminated aquifers, Annan et al (1991) and Waterloo Centre for Groundwater Research (1991). Following the controlled release of PCE at the Borden DNAPL research site, geophysical logging successfully traced the infiltration of PCE into the shallow sand aquifer using EM induction, resistivity, and neutron logging. However, in most cases of DNAPL contamination baseline surveys will not be available, and subsurface conditions will be considerably more complex than at the Borden site. In general, the value of using borehole geophysics to delineate NAPL presence is limited.

Table 4.11 Recommended sample handling and preservation procedures for a detective monitoring program (USEPA, 1991).

Parameters (Type)	Volume Required (mL) 1 Sample[a]	Containers (materials)	Preservation Method	Maximum Holding Period
Well purging				
pH (grab)	50	T, S, P, G	None; field det.	<1 hr[b]
Ω^{-1} (grab)	100	T, S, P, G	None: field det.	<1 hr[b]
T (grab)	1,000	T, S, P, G	None: field det.	None
Eh (grab)	1,000	T, S, P, G	None: field det.	None
Contamination indicators				
pH, Ω^{-1} (grab)	As above	As above	As above	As above
TOC	40	G, T	Dark, 4°C	24 hr[d]
TOX	500	G, T	Dark, 4°C	5 days
Water Quality				
Dissolved gases (O_2, CH_4, CO_2)	10 mL minimum	G, S	Dark, 4°C	< 24 hr
Alkalinity/acidity	100	T, G, P	4°C/None	<6 hr[b] 24 hr
	Filtered under pressure with appropriate media			
(Fe, Mn, NA^+, K^+, Ca^{++}, Mg^{++})	All filtered 1,000 mL[1]	T, P	Field acidified to pH <2 with HNO_3	6 months[c]
(PO_4, Cl, Silicate)	@50	(T, P, G glass only)	4°C	24 hr/ 7 days[e], 7 days
NO_3	100	T, P, G	4°C	24 hr[d]
SO_4	50	T, P, G	4°C	7 days[e]
OH_4^+	400	T, P, G	4°C/H_2SO_4 to pH <2	24hr/ 7 days
Phenols	500	T, G	4°C/H_2PO_4 to pH <4	24 hours
Drinking Water suitability As, Ba, Cd, Cr, Pb, Hg, Se, Ag	Same as above for water quality cations (Fe, Mn, etc)[1]	Same as above	Same as above	6 months
F	Same as chloride above	Same as above	Same as above	7 days
Remaining organic	As for TOX/TOC, except where analytical parameters method calls for acidification of sample			24 hours

T = Teflon; S = stainless steel; P = PVC, polypropylene, polyethylene; G = borosilicate glass

[a] It is assumed that at each site, for each sampling date, replicates, a field blank, and standards must be taken at equal volume to those of the samples.

[b] Temperature correction must be made for reliable reporting. Variations greater than ± 10% can result from a longer holder period.

[c] In the event the HNO_3 cannot be used because of shipping restrictions, the sample should be refrigerated to 4°C, shipped immediately, and acidified on receipt at the laboratory. Container should be rinsed with 1:1 HNO_3 and included with sample.

[d] 28-day holding time if samples are preserved (acidified).

[e] Longer holding times in U.S. EPA (1986b).

[1] Filtration is <u>not</u> recommended for samples intended to indicate the mobile substance lead. See Puls and Barcelona (1989a) for more specific recommendations for filtration procedures involving samples for disolved species.

Table 4.12 Utility limitations of borehole geophysical methods for site characterisation (modified in Cohen and Mercer, 1993 from Benson, 1991).

Method	Utility	Can Method Be Used In The Following Conditions?		
		Casing Uncased/Pvc/Steel	Saturated / Unsaturated	Radius Of Measurement
Temperature	Provides a continuous record of fluid temperature with depth. Preferential inflow zones may be indicated by an increase or decrease in groundwater temperature.	Y/N/N	Y/N	Within borehole
Fluid Conductivity	A specific conductance probe is used to record fluid conductivity with depth. This data is used to assess groundwater conductivity, inflow zones, contamination zones, etc.	Y/N/N	Y/N	Within borehole
Flow	Fluid movement logging utilises impeller flow meters, thermal flow meters and various tracer detection systems to measure the groundwater inflow rate as a function of boring depth. Variation in groundwater inflow rate may derive from well construction details, hydraulic head differences, and/or variable hydraulic conductivity. Most frequently an impeller flow meter is used to identify zones of preferential inflow.	Y/N/N	Y/N	Within borehole
Caliper	Spring loaded 'feelers' extend from the caliper logging tool, follow the borehole wall and continuously measure the hole diameter. Calipers can be used to locate fractures, cavities or wash out zones in an open borehole. Caliper logs are also used to calculate correction factors for other measurements influenced by borehole diameter.	Y/Y/Y	Y/Y	To limit of sensor, typically one metre

Table 4.12 cont.d Utility limitations of borehole geophysical methods for site characterisation (modified in Cohen and Mercer, 1993 from Benson, 1991).

Method	Utility	Can Method Be Used In The Following Conditions?		
		Casing Uncased/Pvc/Steel	Saturated / Unsaturated	Radius Of Measurement
Video	Small diameter video cameras can be lowered down a borehole to inspect for casing corrosion, well condition, fracture zones etc.	Y/Y/Y	Y/Y	Within borehole
Electrical Resistivity	Electrical resistivity logs record apparent electrical resistivity as a function of depth in the saturated zone. High resistivity in porous sands may reflect NAPL presence.	Y/Y/N	Y/N	0.25-1.5 metres
Spontaneous Potential	Spontaneous potential logs measure natural potential differences between the borehole fluid and adjacent media. SP logs are used to help characterise and correlate stratigraphy.	Y/N/N	Y/N	Near borehole surface
Natural Gamma	Natural gamma logs measure the amount of natural gamma radiation emitted along the length of the borehole. Natural gamma emitting radioisotopes are preferentially adsorbed in clay particles and the natural gamma log is therefore primarily used to reveal the presence of clay and shale layers.	Y/Y/Y	Y/Y	0.1-0.3 metres
Gamma-Gamma (Density)	Gamma-gamma logs measure the response of media adjacent to the boring to gamma radiation that is emitted from a radiation source in the logging tool. The amount of radiation detected is inversely proportional to the formation density.	Y/Y/Y	Y/Y	0.1 metres

Table 4.12 cont.d Utility limitations of borehole geophysical methods for site characterisation (modified in Cohen and Mercer, 1993 from Benson, 1991).

Method	Utility	Can Method Be Used In The Following Conditions?		
		Casing Uncased/Pvc/Steel	Saturated / Unsaturated	Radius Of Measurement
Neutron-Neutron (Porosity)	The neutron logging tool contains a radiation source and detector. The detector output is proportional to the water content of the borehole environment. Neutron logs can provide estimates of the moisture content in the vadose zone and total porosity in the saturated zone.	Y./Y/Y	Y/Y	0.1-0.3 metres
EM Induction	EM induction logs record the bulk electrical conductivity of the near borehole environment and are used to identify lithology and correlate stratigraphy. Highly conductive zones of contaminated groundwater can be identified, as can thick intervals with high organic NAPL saturation.	Y/Y/N	Y/Y	0.75 metres

4.5.10 Identification of DNAPL in Soil and Groundwater Samples

Significant cost savings can be made during a site investigation if DNAPL presence can be determined by direct visual identification rather than by costly laboratory techniques. Techniques for identification of DNAPL in samples in the field are discussed fully in Cohen and Mercer (1993) and Cohen et al (1992). Techniques include:

- Organic Vapour Analyser measurement (e.g. PID)
- Unaided visual examination
- UV fluorescence analysis
- Soil water shake test
- Centrifugation
- Hydrophobic dye soil water shake test
- Centrifugation of hydrophobic dye shake test suspension

NAPL presence can be inferred by indirect observations and measurements where:

- groundwater concentrations exceed 1% of the pure phase or effective aqueous solubility of a NAPL chemical;

- NAPL chemical concentrations in soil exceed 10,000mg/kg (>1% of soil mass);

- NAPL chemical concentrations in groundwater calculated from soil-water partitioning relationships and soil sample analyses exceed their effective solubility;

- organic vapour concentrations detected in soil gas (or sample headspace) exceed 100 to 1000 ppm; or

- observed chemical distributions suggest NAPL presence.

4.6 Numerical Modelling

The application of numerical modelling is becoming increasingly popular as a tool used to aid characterisation and prediction of impacts of contamination in both intergranular flow aquifers and fissured (dual porosity) aquifers. The complexity of the modelling problem is increased where dissolved phase transport is to be modelled, rather than groundwater flow alone. Further complexities arise when considering DNAPL migration in the saturated zone and DNAPL as a source of dissolved phase contamination.

Data requirement to successfully model these situations increases with hydrogeological complexity and therefore data shortage is frequently the main impediment to numerical modelling. Numerical modelling of groundwater flow in intergranular and fractured aquifers is discussed in depth in Anderson and Woessner (1992).

Solute transport modelling requires the consideration of advection (groundwater flow), dispersion and chemical reaction. Several solute transport models are commercially available for modelling heterogeneous aquifers and their utility has been widely proved. Finite element models include SEFTRAN (GeoTrans, 1988), CFEST (Gupta et al., 1987), HST3D (Kipp,

1987) and SUTRA (Voss, 1984). A particle tracking solution is frequently applied to avoid the numerical problems associated with finite difference and finite element solution of the advection-dispersion equation (Anderson and Woessner, 1992). The USGS MOC model (Konikow and Bredehoeft, 1978) combines particle tracking for advection with a finite difference solution for dispersion. The model MT3D (Zheng, 1990) is a particle tracking code with dispersion that is compatible with the widely used USGS advection model MODFLOW (McDonald and Harbaugh, 1988).

Multiphase flow models for simulating DNAPL flow in the saturated zone of heterogeneous aquifers are still at the research and development stage due to the complexities of the flow equations (Anderson and Woessner, 1992). However, several applications have been reported, including Kueper and Frind (1991a&b).

A recent development in numerical modelling is the application to remedial feasibility studies, see Section 7. The model AIRFLOW/SVE, by Waterloo Hydrogeologic Software, is a three phase multicomponent numerical model for simulation of soil vapour extraction systems in areas contaminated by NAPL. Soil vapour extraction as a remedial technique is discussed in Section 6.

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5. REMEDIAL OBJECTIVES

5. REMEDIAL OBJECTIVES

5.1 Definition of Remedial Objectives

Remedial objectives are quantitative goals which define the extent of remediation required to achieve site specific initial clean up aims.

The development of the remedial objectives is an iterative process which occurs throughout the site characterisation and feasibility study phases. The initial objectives are set in the primary stages of the investigation procedure, however continual reappraisal and alteration is necessary as site information and remedial alternative data is collated.

The development of the remedial objectives is summarised in Figure 5.1. The important stages are described below.

5.2 Definition of Response Objectives

Response objectives are site specific initial clean up aims, based on the nature and extent of the contamination, the resources that are currently and potentially threatened, and the potential for human and environmental exposure. The USEPA has recognised four major response objectives for contaminated groundwater (USEPA, 1988). These are summarised in Table 5.1.

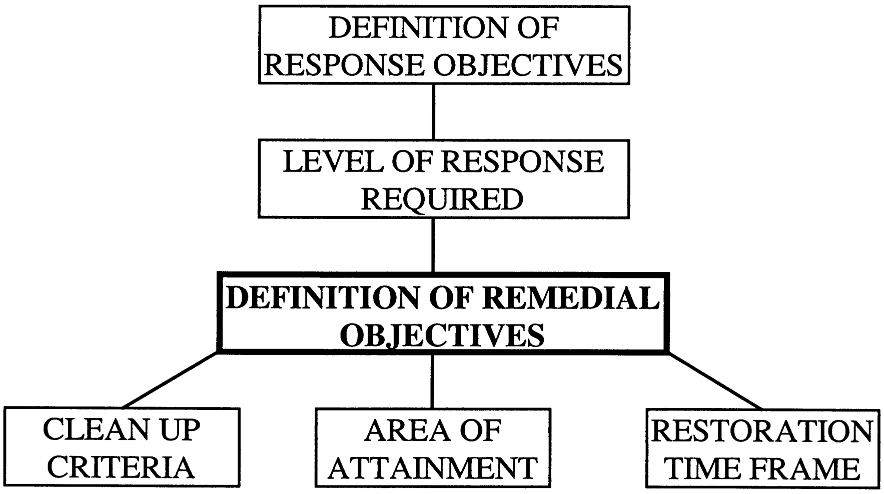

Figure 5.1 Factors involved in defining remedial objectives

Table 5.1 Potential response objectives for groundwater (USEPA, 1988)

- Prevent Exposure to contaminated groundwater
  - Provide an Alternative water supply for the population that has existing wells affected by the contaminant plume
  - Establish institutional controls to restrict access to the contaminant plume

- Protect uncontaminated ground and surface water for current and future use
  - Prevent contamination of existing wells that could be affected by the plume and in adjacent groundwater
  - Minimise migration of contaminants within the ground and surface water
  - Minimise migration of contaminants to adjacent ground and surface water

- Restore contaminated groundwater for future use
  - Reduce contaminant concentrations within the area of the plume to levels that are safe for drinking

- Protect environmental receptors
  - Reduce contaminant concentrations in the plume to levels that are safe for biological receptors that may be affected at the groundwater discharge point

5.3 Level of Response

The level of response action varies on a site specific basis. For any contamination incident the level of response is related to either protection of the entire resource, or protection of individual source points. The following remedial objectives are listed in decreasing order of response:

- On site remediation - Clean up is aimed at the on site contamination, i.e. the source of the contaminant plume.

- Off site Remediation - Clean up is aimed at the contaminant plume which has migrated away from the source area.

- Wellhead Treatment - Treatment and removal of contaminants from contaminated water which is pumped to the surface. This may require specialised equipment involving an upgrade at substantial expense.

- No Remedial Action - The no remedial action objective could encompass the following two actions:

  a) Point-of-use Treatment - Installation of special treatment units at the point-of-use. This is usually implemented when private abstraction wells become contaminated. There are two main problems to the approach; maintenance requirements and high costs incurred. Often it may be more economical to install new water mains than individual treatment units at all impacted abstraction points.

  b) Development of Alternative Water Supplies - If there is no readily available alternative existing water supply an alternative source must be developed.

5.4 Development of Clean up Criteria

There are two principle categories of clean up criteria, which illustrate two approaches for setting remedial objectives; *non site specific risk based clean up levels* and *site specific corrective action target levels*. These are described below, followed by a review of the risk assessment methodology, RBCA (Risk Based Corrective Action) developed by the American Society for Testing of Materials (ASTM), which is commonly used to define clean up criteria.

5.4.1. Non Site Specific Risk Based Screening Levels (RBSLs)

These are generally conservative corrective action goals based on Maximum Concentration Limits (MCLs). For example, UK standards for drinking water limits for potable groundwater or surface water courses, or environmental quality standards (EQSs) in surface water courses receiving groundwater discharge. Prescriptive RBSLs set in other countries can also be used as reference values. These include Dutch, Canadian and US (Independent State) standards. The Department of the Environment (DoE) is currently funding the development of prescriptive RBSLs for the UK. Soil and groundwater policy regulations in England and Wales that are pertinent to the potential contamination of groundwater are listed in Table 5.3.

Table 5.2: Various RBSLs for common DNAPL contaminants

	UK Drinking Water Standards (μg/l)	Dutch Target Levels for Groundwater (μg/l)	Guidelines for Canadian Drinking Water Quality (1978) (μg/l)	RCRA NJ* Action Level Water (μg/l)
Tetrachloroethene (PCE)	10	0.01	0.26	0.7
Trichloroethene (TCE)	30	0.01	ID	5
Tetrachloroethane (TCA)	3	ns	ID	2
1,1,1-Trichloroehthane (1,1,1-TCA)	ns	ns	ID	3000
Carbon Tetrachloride	ns	ns	ID	0.3
Dichloroethane (DCE)	ns	ns	ID	70 NJ
1,2-Dichloroethene (1,2-DCE)	ns	0.01	ID	0.03
Chloroethane	ns	ns	ID	ns
Vinyl Chloride (VC)	ns	0.7 IV	ID	ns
Trichloromethane	ns	0.01	ID	6

Notes:
ns - Not specified
ID - Insufficient data to produce guidelines
IV - Intervention value
NJ - Guidelines specific to New Jersey State US
* RCRA NJ Action level - Proposed chemical concentrations in groundwater which would trigger conduct of a corrective measures study under the Resource Conservation and Recovery Act (RCRA). (US Federal Register 7/27/90; NJDEP, 10/14/91).

Table 5.3 Soil and Groundwater Policy and Regulations in England and Wales

Water Resources Act (1991)	Gives the Environment Agency legal responsibility to prevent the pollution of groundwater. Provides Environment Agency with 1) Statutory power to declare water source protection zones; 2) powers to require pollution prevention methods; 3) powers to take remedial actions to prevent pollution from occurring or continuing; 4) power to fine polluter.
National Rivers Authority Policy and Practice for the Protection of Groundwater (1992)	Sets out a groundwater classification system and lays out policies on contaminated land and unacceptable activities in inner source protection zone.
Environmental Protection Act (1990)	S.I. gives the Environment Agency power to impose its own conditions on authorisations. S.79-82 Note provisions on statutory nuisance. S.143. Registers of land that may be contaminated (may or may not affect the site in question; see recent DoE publications).
Inter departmental Committee on the Redevelopment of Contaminated Land guidelines (ICRCL 59/83)	UK guidance on contaminant levels in soils for a limited range of contaminants
DoE Circulars 4/82 and 20/90	Policy on the protection of groundwater against pollution caused by certain dangerous substances.
DoE Circular 7/89	Policy on the implementation of EC directives on pollution caused by certain dangerous substances discharged to the aquatic environment.

Table 5.4 Relevant EC Soil and Groundwater Policy Regulation

Framework Directive Dangerous Substances in Water (76/464/EEC)	Sets out the principles and philosophy of EC's water quality management strategy
Directive on Groundwater (80/68/EEC)	All groundwater regardless of use should be afforded protection; prohibits the discharge of List I substances to aquifers; limits the discharge of List II substances.

5.4.2. Site Specific Corrective Action Target Levels (SSTLs)

SSTLs are implemented at appropriate points of compliance and are generally less conservative clean up criteria, which take account of contaminant concentrations, extent, fate and transport processes, contaminant toxicity and receptor exposure. SSTLs are developed using risk assessment methodologies and can be divided into two categories; simple SSTLs based on site data and conditions, and complex SSTLs based on complex mathematical procedures and computer simulations. A number of software systems and methodologies providing guidance for the selection of appropriate SSTL criteria exist. These include:

- **DSS - Decision Support System, API 1994**. A software package developed by the American Petroleum Institute (API) to assist environmental professionals in estimating human exposure and risk from contaminated sites. The package has the capability to; estimate site specific risks, identify the need for site remediation, develop and negotiate site specific clean up levels with regulatory agencies, and evaluate efficiently and effectively the effect of parameter uncertainty and variability on estimated risk (API, 1994).

- **HESP - Human Exposure to Soil Pollutants, Shell International 1994**. A software package which estimates the exposure of humans to contaminants in soil (Veerkamp and ten Berge, 1994).

- **USEPA - Superfund Risk Assessment Procedure**. Guidelines set by the USEPA for the risk assessment of superfund sites (USEPA, 1989).

A number of methodologies for determining clean up standards based on risk exist. Of these, the most commonly used is the Risk Based Corrective Action (RBCA) Methodology developed by the American Society for Testing of Materials (ASTM).

The UK Environment Agency (Environment Agency) is currently (1996) developing a risk based methodology for clean up of contaminated groundwater in this country (Environment Agency R&D Project A08(95)02B). The study is part of a national R&D project due for completion in mid 1996 and aims to provide a recommended methodology for production of site specific clean up objectives for use by the Environment Agency. It is intended that the methodology will provide reference concentrations (background), target concentrations and intervention concentrations.

The American RBCA methodology (ASTM, 1994) is briefly described here by way of an example of a risk based methodology. Future references, however, should be made to the EA's methodology.

Example: RBCA Methodology

The RBCA methodology follows a three tiered approach, each tier representing an increasingly detailed analysis, requiring additional information and expertise. The three tiers are illustrated in Figure 5.2 and described below:

TIER 1

- **Data Evaluation**: Available site data is evaluated in terms of sampling and analytical protocols and Quality Assurance / Quality Control (QA/QC) procedures.

- **Comparison with RBSL Thresholds**: Measured concentrations are compared to relevant RBSLs which signify an acceptable level of risk. The RSBLs are used to develop a worst case scenario. In the absence of suitable RBSL values, the background soil concentrations can be used.

TIER 2

- **Conceptual Site Model and Development of Simple SSTLs**: An evaluation of how chemical sources at the site could contribute to increased levels of health risk in potentially exposed individuals. This includes a quantitative evaluation of the contaminant source(s), exposure pathways and receptors relevant to each of the chemicals which exceed the RBSL threshold values ("chemicals of potential concern").

- **Screening Exposure Assessment**: Estimation of potential human doses of chemicals of potential concern in exposed individuals via the pathways identified in the conceptual model. This screening process is conducted with reference to a hypothetical individual known as the "Maximally Exposed Individual" (MEI). The process estimates long term 'chronic' dose levels as well as short term 'acute' effects. The exposure for each pathway is characterised as the maximum daily intake (MDI) and chronic daily intake (CDI). These can then be used to estimate carcinogenic and non carcinogenic risks.

- **Toxicity Assessment**: Development of toxicity criteria (human doses of hazardous chemicals which are without adverse health effects). Toxicity criteria for non carcinogenic effects are referred to as Tolerable Daily Intakes (TDIs), Reference Doses (RfDs) and Acceptable Daily Intakes (ADIs). Toxicity criteria for carcinogens are set using a TDI approach which involves assigning an exposure threshold representing an "exceedingly small risk to health", accompanied by a lower target level for genotoxic carcinogens.

- **Risk Characterisation**: Estimation of the risk present at a site is qualified in terms of the new SSTLs developed through the exposure and toxicity assessments.

TIER 3

- **Refined Analysis and the Development of Complex SSTLs**: This stage may involve:
  - Changing the "worst case" scenario based on the RSBLs, to more reasonable values, based on site specific considerations.
  - Collection of additional data.

- Use of sophisticated statistical and computer modelling techniques (e.g. Monte Carlo analysis, biokinetic modelling, numerical fate and transport simulations).

The refined analysis stage often results in lower risk estimates that are within the previously derived limits of acceptability. In these cases the recommendation is that no action is required. However if the risk estimates are still outside these limits, remediation to site specific risk based clean up levels is recommended.

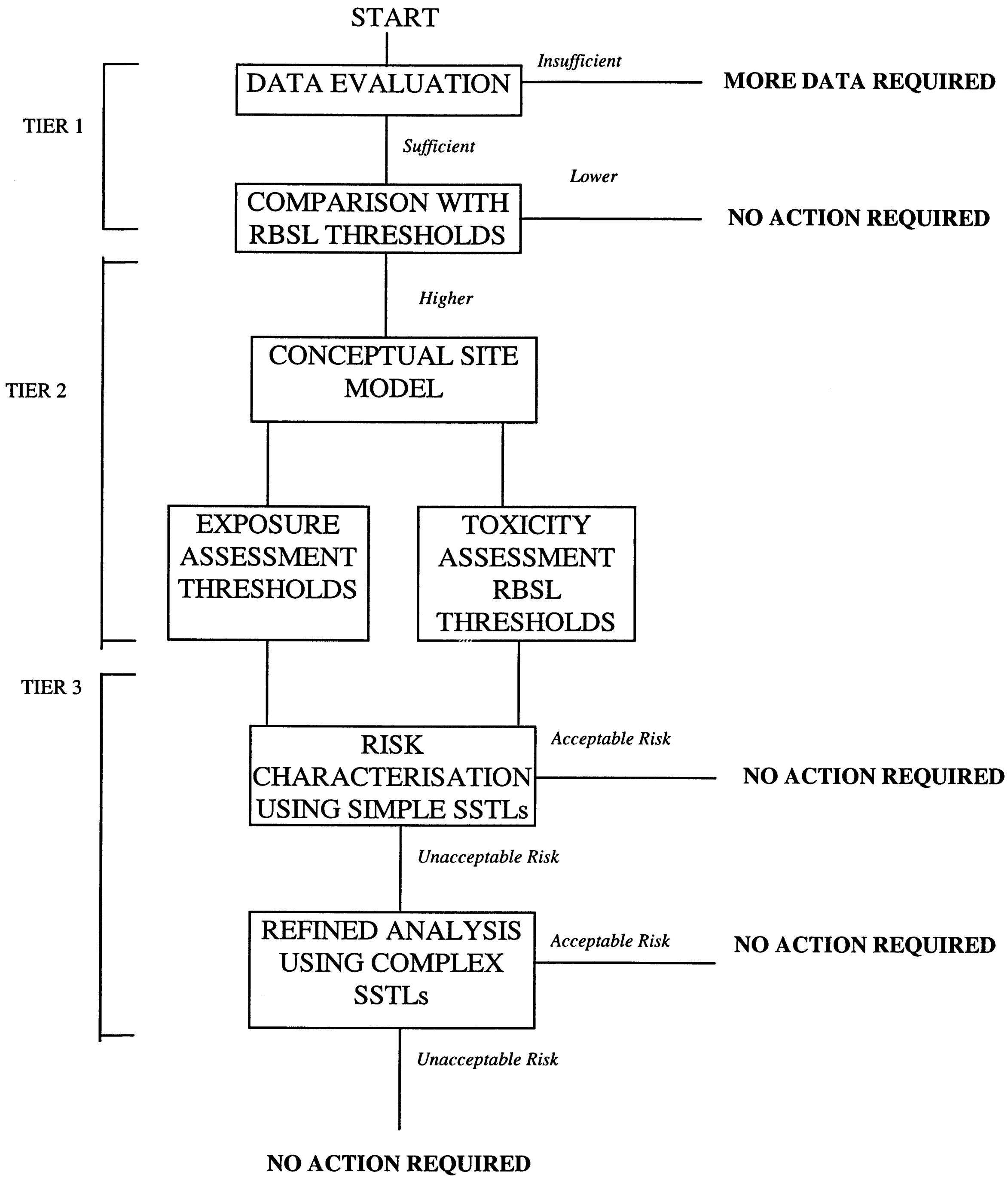

Figure 5.2: Risk Based Corrective Action Assessment Approach

5.5 Establishing Area of Attainment

The area of attainment is the area of groundwater over which the clean up criteria will be met. Typically it encompasses the area outside the site boundary (or boundary of remaining waste) up to the boundary of the contaminant plume. Establishing the area of attainment is crucial as it defines the area within which the remedial objectives are operational. Usually the boundary of the waste is defined by the source control remedy. For example, if the source is removed, the entire plume is within the area of attainment. On the other hand if waste is managed or contained on-site, the groundwater beneath the waste management area is not within the area of attainment (USEPA 1988).

5.6 Estimating the Restoration Time Frame

The restoration time frame is defined as the period of time required to achieve selected clean up levels in the groundwater at all locations within the area of attainment. Important factors which affect the restoration time frame include:

Technical limits to extracting contaminants - This factor must be evaluated first to define a restoration time frame that is practical for the site. The presence of DNAPLs can significantly lengthen the time frame, as points of accumulation are difficult to identify and unless the well screen is located within the non-aqueous liquid phase, the contaminant will only be abstracted slowly as it dissolves into groundwater.

The feasibility of providing an alternate water supply - A readily accessible water supply of sufficient quality and yield may reduce the importance of rapid remediation, providing more flexibility to select a response action and remedial alternative.

The potential use and value of the groundwater - Successively higher classes of groundwater should be remediated more rapidly.

The effectiveness and reliability of institutional controls - If there is adequate certainty that institutional controls will be effective and reliable, there is more flexibility to select a response action that has a longer restoration time frame.

5.7 References

ASTM (1994) *Guide for Risk Based Corrective Action Applied at Petroleum Release Sites.* American Society for Testing of Materials, Philadelphia, USA.

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6. REMEDIATION TECHNOLOGIES

6.1 Introduction

6.2 Remediation Technology Descriptions

Non Technological Remedial Measures

1 Excavation, Retrieval and Off Site Disposal
2 Natural Attenuation and Intrinsic Bioremediation

Containment and Isolation Technologies

3 Hydraulic Containment
4 Containment by Physical Barriers
5 Stabilization and Solidification
6 In Situ Vitrification (ISV)
7 Permeable Treatment Walls

In Situ Remediation Technologies

8 Aerobic Biodegradation
9 Anaerobic Biodegradation
10 Water Flooding and Groundwater Extraction
11 Hot Water or Steam Flushing/Stripping
12 Alkali Soil Flushing
13 Cosolvent Soil Flushing
14 Surfactant Soil Flushing
15 Air Sparging
16 Vacuum Vapour Extraction
17 Soil Vapour Extraction
18 Steam Enhanced Extraction
19 Radio Frequency Heating
20 Dual Phase Extraction

Ex Situ Remediation Technologies

21 Controlled Ex Situ Aerobic Biodegradation
22 Controlled Ex Situ Anaerobic Biodegradation
23 Liquid Phase Carbon Adsorption
24 Soil Washing
25 Solvent Extraction
26 Air Stripping
27 Ex Situ Soil Vapour Extraction
28 Dehalogenation base catalyzed desorption
29 Dehalogenation glycolate
30 UV oxidation
31 High temp. thermal desorption
32 Incineration

6. REMEDIATION TECHNOLOGIES

6.1 Introduction

This section of the document is intended to be used to screen and evaluate candidate clean up technologies for remediation of DNAPL contaminants in the subsurface. The individual remedial technologies are listed in Table 6.1 (Remedial selection table). Table 6.1 is a summary table allowing comparisons between the relevant remedial technologies.

This section comprises an overview of each technology as a two to three page summary. The main factors included in the overview of each technology are as follows; Description, applicability, limitations, data needs, performance data, costs, case studies and references.

Description
A brief description of the technology is presented, including the theoretical background of the process, field implementation and the scale of demonstration.

Applicability
Applicability refers to the suitability of the technology for removing and/or treating the different phases (gas, dissolved, adsorbed and free phase) of DNAPL compounds. The section also refers to the aquifer media in which the technology is most effective.

Limitations
The major theoretical and practical limitations encountered in applying the technology to a variety of aquifer medias contaminated by DNAPL compounds are documented.

Data Needs
The data needs are the physical and chemical site specific conditions to be obtained during the site characterisation stage prior to assessing the feasibility of potential remedial options. The section describes the important data requirements needed for the individual technologies, in addition to those stated below:

1. Soil characteristics: particle size distribution, homogeneity and isotropy, bulk density, particle density, permeability, soil moisture content, pH, Eh, Kow, humic content, total organic carbon BOD and COD.
2. Groundwater chemistry: pH, BOD, COD, TOC and suspended solid concentrations.
3. Hydrogeological conditions: hydraulic gradient, rate of groundwater flow, effective porosity, hydraulic conductivity, safe aquifer yields and boundary conditions.

For more details on these parameters the reader is referred to USEPA 1994. Acquisition of further information regarding the actual design of a remedial system is usually obtained by means of a pilot test, these are discussed in more detail in Section 7.

Performance Data
This section provides information on time scales and contaminant removal efficiencies obtained by each remedial technology. New innovative techniques' data are scarce and only available in the form of results from the few reported pilot and bench scale tests conducted to date.

Costs

The major factors affecting capital and operating costs for the individual technologies are stated.

Case Studies

A number of case studies are referenced including, where applicable, those summarised in Section 8. of this document. A brief description of the contaminant problem and the remedial technology employed is given with the relevant references. References of pilot and bench scale tests are provided where the technology has not been developed on a full scale.

References

A selection of references relevant to the theory, design and operation of the individual technologies, as well as those pertaining to the case studies are provided at the end of each section. These are intended to give the reader guidance on where to find more detailed information on the range of technologies described.

Table 6.1 Remedial Technology Selection

NON-TECHNOLOGICAL REMEDIAL SOLUTIONS

METHOD	APPLICATION/PROCESS	EFFECTIVENESS/ADVANTAGES/LIMITATIONS	EXPERIENCE
1. Excavation	Conventional excavating methods are used to remove contaminated materials from the subsurface for subsequent ex situ treatment methods and/or disposal.	Excavation can be a very effective site remedy where contaminant penetration is limited to shallow soils and where shallow contamination hot spots are identified. The cost and difficulty of excavation increases with the depth of contaminant migration and generally becomes prohibitive in bedrock. Additional concerns include potential fugitive dust, liquid and gas emissions caused by excavating contaminated materials, and the possibility that DNAPL may have migrated beneath the excavation limit, thereby reducing the effectiveness of excavation of a remedy.	Excavation of contaminated materials is a widely used remedy of proven value in appropriate situations.
2. Natural Attenuation	Natural subsurface processes are left to reduce contaminant concentration to acceptable levels.	Natural attenuation is most suitable at sites where contaminants are strongly sorbed to deep subsurface soils and are not migrating. It may be the only effective solution at sites where removal of DNAPL has been determined infeasible and where active remedial measures would be unable to speed up remediation time scales. Natural attenuation is not a “do nothing” option it involves extensive site characterisation and modelling of the site. The process is limited when applied to halogenated VOCs (many DNAPLs) due to their high toxicity and persistence.	The approach has been widely used in Europe and the States. Performance is extremely variable depending heavily on site specific conditions.

Table 6.1 Contd. Remedial Technology Selection

CONTAINMENT / ISOLATION TECHNOLOGIES

METHOD	APPLICATION/PROCESS	EFFECTIVENESS/ADVANTAGES/LIMITATIONS	EXPERIENCE
3. Hydraulic containment	Hydraulic containment of DNAPL and dissolved chemicals can be achieved by pumping groundwater from wells and/or drains.	The effectiveness of a hydraulic containment system depends on the adequacy of the design and operation of the system. Long term hydraulic containment at DNAPL sites is required as residual and trapped pools of DNAPL are long term sources of groundwater contamination. Containment is eased where there is a continuous barrier layer preventing downward migration. Vertical hydraulic containment has not been demonstrated in the field to date. The main draw backs are the cost and the need for long term operation.	Hydraulic containment is a generally proven migration control technology, however its success depends largely on adequate design and implementation.
4. Containment using physical barriers	Low permeability barrier walls can be constructed to impede the lateral migration of non wetting DNAPL below the water table. Where possible barrier walls should be keyed into a low permeability, capillary barrier layer beneath the DNAPL contamination zone.	Barrier walls can provide a cost effective control over NAPL migration in favourable settings. Barrier walls have not been tested to determine their capacity for long term impedance of NAPL migration. Small fractures or openings will facilitate DNAPL breakthrough. Consideration must be given to the compatibility of barrier wall materials with subsurface chemicals, potential for inducing migration during construction and changes to the hydrologic system affected by the wall emplacement.	Cut off walls have been installed as part of containment systems at many sites.
5. Containment by solidification / stabilisation	S/S technologies immobilise contaminants in the subsurface by either mechanically binding them to the soil or converting them to less soluble, less mobile and less toxic forms.	Obtaining complete and uniform mixing of the solidifying/stabilising agents with the contaminated soil is a critical factor for determining the success of S/S systems. Successful application of these methods becomes more difficult with increasing depth and costs are high. Mobilisation and migration of contaminants may be caused by these processes. The long term stability and leaching characteristics of the materials produced is unknown.	Pilot and full scale demonstrations of S/S technologies have been conducted.
6. Containment by In situ Vitrification	In situ vitrification utilises electrical power to melt contaminated soils. Organic contaminants are pyrolized and vapours are captures at the surface for treatment	Successful application of this method becomes more difficult with increasing depth and costs are high. Mobilisation and migration of contaminants may be caused by these processes. The long term stability and leaching characteristics of the materials produced is unknown.	In situ vitrification has been tested on PCB wastes and other solid combustibles and liquid chemicals. To date it has not been applied to DNAPL compounds.
7. Permeable treatment walls	In situ treatment walls are reactive structures constructed of granular materials which allow groundwater flow through the wall.	Granular backfills consist of a variety of additives or surface coatings; nutrients and bacteria for in situ biodegradation, redox controls and or metal catalysts to aid in metal precipitation and chemical dehalogenation, organic carbon for enhanced denitrification, and selective adsorbents. Since most DNAPL is immobile once in place, the intended use of this technology is the management and treatment of dissolved phase in aquifers. The active amendments must be reactive, non toxic and soluble enough to supply ample reagent and persist for a long enough period of time.	No full scale applications are known to exist although the technology has been successfully demonstrated on a pilot scale.

Table 6.1 Contd. Remedial Technology Selection

IN SITU REMEDIAL TECHNOLOGIES

METHOD	APPLICATION/PROCESS	EFFECTIVENESS/ADVANTAGES/LIMITATIONS	EXPERIENCE
8, 9. Aerobic/ Anaerobic Bioremediation	Bioremediation involves enhancement of natural processes to degrade hazardous chemicals. Highly chlorinated solvents are degraded by anaerobic processes only to a less chlorinated state where they are more susceptible to aerobic degradation. The process is most applicable to high permeability, granular aquifers.	Adequate characterisation of the hydraulic conductivity is necessary to achieve efficient delivery of oxygen, nutrients and/or microbes to the contaminated zone. NAPLs may be toxic to micro organisms as a result biodegradation is limited to the periphery of the NAPL contaminated zone. Degradation may generate other undesirable chemicals. Bench and pilot scale studies are recommended. Bioremediation is commonly used as a "polishing" step following the application of other chemical recovery and treatment processes.	Efforts to stimulate biodegradation have been employed at full field scale at numerous contamination sites with varying degrees of success and documentation.
10. Soil Flushing ; by flooding with water	The contaminated zone is flooded with flushing solutions to sweep the contaminants to recovery wells or drains. It can be used to enhance recovery of NAPLs, adsorbed and dissolved chemicals from the unsaturated and saturated zones.	Soil flushing is most effective in permeable, uniform media. Heterogeneous or reduced permeability soils will generally result in reduced sweep efficiency, longer project duration and less successful recovery. It will generally not be possible to remove NAPL from sites with substantial NAPL presence but it can reduce residual saturation levels. The movement of contaminants mobilised by the flood must be carefully controlled to prevent detrimental migration. Site specific bench and pilot scale tests are recommended.	The technology has been extensively used in the oil industry. The application of soil flushing technologies to remediation of contaminated sites is at a pilot stage and the effectiveness is relatively unknown.
11. Steam injection to enhance soil flushing	Steam is injected into the contaminated zone where it condenses into a zone that acts as a hot water flood.	Napl recovery is enhanced because: (1) NAPL becomes less viscous and more mobile on heating. (2) NAPL solubility may be increased by higher temperatures. (3)Volatile NAPL vapours move ahead of the hot water and then condense to form a NAPL bank. (4) The bank results in increased NAPL transmissivity and results in a snowball effect. Costs may be high due to heat loss and the need to heat large volumes of subsurface materials. Consideration must also be given to the toxicity, nature and fate of the flushing solution.	Soil flushing using thermal techniques has been widely used in the oil industry. The displacement of NAPLs at contamination sites has been evaluated in a few laboratory and pilot field studies.
12. Alkali injection to enhance soil flushing	Used to increase NAPL recovery during a flood operation Inexpensive caustics added to injection water raise the pH of the flood and react with organic acids present.	The reaction leads to improved recovery of NAPL due to (1) greatly reduced interfacial tension, (2) emulsification effects and (3) wettability reversals, which can mobilize entrapped NAPL ganglia. NAPLs must have acidic components to react with alkali agents to form surfactants. Alkali flooding is relatively cheap, but consumption of alkali due to reaction with porous media may be a limiting factor.	Alkali soil flushing accomplishes permanent removal of contaminants from the soil .The removal rate and clean up times depend very much on site specific conditions

Table 6.1 Contd. Remedial Technology Selection

METHOD	APPLICATION/PROCESS	EFFECTIVENESS/ADVANTAGES/LIMITATIONS	EXPERIENCE
13. Cosolvent injection to enhance soil flushing	Used to increase the dissolution and recovery of NAPL and adsorbed chemicals from the subsurface. The addition of co solvents to the soil flushing fluid mobilizes the DNAPL by overcoming the capillary forces. Continued flooding of the contamination zone drives the solvent amended NAPL to production wells or drains.	Co solvent soil flushing is most effective in permeable, uniform media. Heterogeneous or reduced permeability soils will generally result in reduced sweep efficiency, longer project duration and less successful recovery. It will generally not be possible to remove NAPL from sites with substantial NAPL presence but it can reduce residual saturation levels. The movement of contaminants mobilised by the flood must be carefully controlled to prevent detrimental migration. Site specific bench and pilot scale tests are recommended.	Miscible flooding with CO_2 and/or hydrocarbon solvents has been tested at numerous sites by the oil industry Several bench and pilot scale studies have been conducted using in situ co solvent flushing technology with variable success.
14. Surfactant injection to enhance soil flushing	Used to increase NAPL recovery during a flood operation. Surfactant solution, injected as a slug, decreases the interfacial tension between NAPL and water by several orders of magnitude.	Low interfacial tension improves the NAPL displacement efficiency of water flushing, promotes the coalescence of NAPL ganglia and the development of a NAPL bank in front of the surfactant flood. This results in increased NAPL recovery and reduced NAPL residual saturation. The process may also increase NAPL wetting, solubilisation and emulsification. Using surfactant solutions may be the only practical way to enhance NAPL recovery at some contamination sites, even allowing for high cost.	The use of surfactant flooding to enhance NAPL recovery at contamination sites is in its infancy. The process has been used to boost DNAPL recovery.
15. Air sparging	Air stripping can be applied below the water table to remove dissolved volatile contaminants from the saturated zone. Vaporised volatiles move with the air to the unsaturated zone and are recovered using a vacuum extraction system.	In situ air injection will be most effective removing low molecular weight volatile compounds.	The application of in situ air stripping of groundwater is very limited.
16. UVB wells. (vacuum vapour extraction)	Air stripping can be applied below the water table to remove dissolved volatile contaminants from the saturated zone. The contaminated groundwater is stripped by air at negative pressures in a special filtered well.	In situ air injection will be most effective removing low molecular weight volatile compounds.	The UVB well method is currently in use at several sites in Germany.

Table 6.1 Contd. Remedial Technology Selection

METHOD	APPLICATION/PROCESS	EFFECTIVENESS/ADVANTAGES/LIMITATIONS	EXPERIENCE
17. Soil Vapour Extraction	Vapour extraction can be used to remove volatile chemicals from the unsaturated zone and to prevent the uncontrolled migration of volatile chemicals in soil gas. Air forced through soils generates advective vapour fluxes that change the vapour liquid equilibrium, inducing volatilisation of contaminants.	Soil vapour extraction is most effective removing low molecular weight, volatile chemicals (Henry's law constant $>10^5$ atm-m^3/mol) from homogeneous, permeable media. Vapour extraction is less effective at removing volatile chemicals from heterogeneous and low permeability soils and is ineffective removing volatile chemicals from the saturated zone. Vapour extraction can result in groundwater contamination where chemicals are located just above the water table because the process induces upwelling in the water table. Lowering the water table to allow volatile chemical recovery may promote DNAPL demobilisation and sinking.	In situ Vapour extraction processes have been employed at more than 100 contamination sites in the USA
18. Steam injection to enhance soil vapour extraction	Vapour extraction in the unsaturated zone can be enhanced by steam injection. Heating and increased soil gas movement, caused by steam injection, raises the vapourisation rate of volatile and some semi volatile compounds. Additionally contaminated soil water and low viscosity NAPLs can be physically displace by condensate that forms in front of the steam zone.	In general, steam injection will increase the effectiveness of a vapour extraction system. Heating will reduce the viscosity and interfacial surface tension of residual or trapped DNAPL in the unsaturated zone which may result in uncontrolled migration. Similarly, accumulation of the DNAPL at the steam condensate front may result in uncontrolled downward or lateral migration of the DNAPL.	
19. Radio frequency heating (RFH) to enhance soil vapour extraction	Vapour extraction of chemicals that volatilise between 80°C and 300°C can be enhanced by using radio frequency heating of contaminated soil. Electromagnetic energy (in the range 6.7 Mhz to 2.5 Ghz) is transmitted to the zone targeted for decontamination via electrodes placed in an array of boreholes. Volatilised chemicals are recovered with soil gas for treatment by applying a vacuum to selected hollow electrodes.	The technology is only applied to the unsaturated zone and its use is precluded where buried metal objects are present. The method is best suited to sites where volatile chemicals are present at shallow depth in homogeneous, coarse grained soils. Heating will reduce the viscosity and possibly the interfacial surface tension of residual or trapped DNAPL in the unsaturated zone, which may result in uncontrolled migration. The technology may result in more uniform decontamination than achieved using steam injection methods and may make this method more applicable to heterogeneous soils.	Several bench and pilot scale tests and limited field testing have been conducted using RFH to remove 70% to 90% of various solvents from shallow soils.

Table 6.1 Contd. Remedial Technology Selection

METHOD	APPLICATION/PROCESS	EFFECTIVENESS/ADVANTAGES/LIMITATIONS	EXPERIENCE
20. Dual Phase Extraction	Dual phase extraction utilises a high vacuum to simultaneously remove liquid and gas from low permeability or heterogeneous formations. The technology is applicable for removal of LNAPL compounds and VOC contaminants.	Dual phase extraction/vacuum enhanced extraction is limited to low permeability formations. Treatment of both groundwater and vapours is required.	
EX SITU REMEDIAL TECHNOLOGIES			
21, 22. Aerobic/Anaerobic Bioremediation	Bioremediation involves enhancement of natural processes to degrade hazardous chemicals. Highly chlorinated solvents are degraded by anaerobic processes only to a less chlorinated state where they are more susceptible to aerobic degradation. The process is most applicable to high permeability soils.	Excavation of contaminated soils (needing large amounts of space) may lead to the uncontrolled release of VOCs. Degradation may generate other undesirable chemicals. However, these may be alleviated by the implementation of fluctuating aerobic/anaerobic conditions. High concentrations of highly chlorinated organics are likely to be toxic to micro organisms.	The method is commonly used as a treatment technique to remove TPH but, as yet, has not been applied to VOCs.
23. Liquid Phase Carbon Adsorption	Groundwater is pumped through a series of vessels containing activated carbon to which dissolved contaminants adsorb. The process is effective for removing contaminants at low concentrations and is often used to 'polish' discharges from other remediation technologies to attain regulatory compliance	The presence of multiple contaminants can impact process performance. Costs are high if the process is used as the primary treatment on waste streams with high contaminant concentration levels. The type and pore size of the carbon used, as well as the operating temperature, will impact performance. Water soluble compounds are not adsorbed well. Costs are dependent on waste stream flow rates, type of contaminant and site and timing requirements.	The technology has a long history of use in treating municipal, industrial and hazardous wastes and may be used in conjunction with other remedial technologies for treating VOCs
24. Soil Washing	Soil washing removes contaminants by dissolving or suspending them in the wash solution or by concentrating contaminants into a smaller volume of soil through attrition scrubbing, particle size and gravity separation. The process is best suited to sandy and sandy loam soils.	Soil washing can be used as a relatively cost effective way to reduce the volume of material needed to be disposed of or treated by a more energy intensive process. Removal efficiencies depend on the type of contaminant and washing fluid. Fine soil particles may require the addition of a polymer to remove them from the washing fluid. Complex waste mixtures make formulating washing fluid difficult. High humic content in soil may require pretreatment. The aqueous waste stream will require treatment.	The technology is in the early stages of field use. Bench tests conducted by USEPA have achieved greater than 99.7% clean up for selected solvents.

Table 6.1 Contd. Remedial Technology Selection

METHOD	APPLICATION/PROCESS	EFFECTIVENESS/ADVANTAGES/LIMITATIONS	EXPERIENCE
25. Solvent Extraction	Solvent extraction is a means of separating hazardous contaminants from soils, sludges and sediments. Solvent, passed through an extractor containing waste, dissolves contaminants to leave decontaminated water and solids which can be treated. The solvent including organic contaminants is passed through a separator to produce concentrated contaminants and recyclable solvent.	In general, solvent extraction is effective in treating primarily organic contaminants such as PCBs, VOCs and petroleum wastes. Organically bound metals can be extracted along with the target organic pollutants, which may restrict handling of the residuals. The presence of detergents and emulsifiers can unfavourably influence the extraction performance. Traces of solvent may remain in the treated solids, depending on the toxicity, and the process is least effective on very high molecular weight organic and very hydrophilic substances. Some soil types and moisture content levels will adversely impact process performance. Costs are dependent on waste volume, number of extraction stages and operating costs.	Although not used for halogenated solvents, the technology has been used to remediate soils contaminated by PCBs and achieved clean up greater than 99%.
26. Air Stripping	Air stripping is a technology in which volatile organics are partitioned from groundwater by greatly increasing the surface area of the contaminated water exposed to air. The process involves forcing air through contaminated water either in a packed tower or aeration tank.	Air stripping is effective for organic compounds with Henry's law constants > 10^5 atm-m^3/mol. The process becomes less effective if inorganic or biological fouling of the equipment or packing occurs. Compounds with low volatility at ambient temperature may require preheating of the groundwater. Off gases may require treatment based on mass emission. The major operating cost is the electricity necessary for the groundwater pump, sump discharge pump and air blower which in turn are dependent on the size of the tower or tank.	Air stripping is commonly used for the removal of VOCs from groundwater. Removal efficiencies of 99% have been achieved for towers with approx. 4.5-6m of packing.
27. Soil Vapour Extraction (SVE)	Vapour extraction can be used to remove volatile chemicals in excavated soil. Air forced through soils generates advective vapour fluxes that change the vapour liquid equilibrium, inducing volatilisation of contaminants.	Soil vapour extraction is most effective removing low molecular weight, volatile chemicals (Henry's law constant >10^5 atm-m^3/mol) from homogeneous, permeable media. The advantages over in situ SVE are that; excavation of the soil leads to an increase in the number of passageways in the soil; shallow groundwater no longer limits the process and leachate collection is more uniform and easily monitored. However; the process does require a large amount of space, air emissions occurring during excavation and materials handling may require treatment. As a result of air emission treatment, SVE may require the treatment of residual liquid and spent activated carbon, increasing the project cost.	SVE has been successfully used to remediate jet fuel, but has not yet been used to remediate chlorinated solvent contaminated soil

Table 6.1 Contd. Remedial Technology Selection

METHOD	APPLICATION/PROCESS	EFFECTIVENESS/ADVANTAGES/LIMITATIONS	EXPERIENCE
28. Dehalogenation, Base-catalyzed decomposition (BCD)	Dehalogenation of chlorinated aliphatic compounds occurs through an elimination reaction and the formation of a double or triple carbon-carbon bond. This converts toxic compounds into less toxic compounds. Contaminated soil is screened, processed with a crusher and pug mill, and mixed with sodium bicarbonate. Then decomposed and volatilised in a rotary reactor.	The target groups for BCD are halogenated SVOCs and pesticides. The technology can be used to treat halogenated VOCs but will generally be more expensive than alternative technologies. Wastewater produced may require treatment prior to discharge and air emissions can be controlled by condensation and/or activated carbon adsorption. High clay or moisture content may raise the treatment cost.	Dehalogenation (BCD) has been shown to be effective on DNAPL's such as carbon tetrachloride and dichloromethane at laboratory scale. To date no field scale studies using dehalogenation to treat DNAPL's have been conducted
29. Dehalogenation, Glycolate	Contaminated soils mixed with a reagent (alkaline polyethylene glycol aka APEG) produce a reaction in which the APEG replaces a halogen molecule, leading to a reduction in toxicity.	The target groups for glycolate are halogenated SVOCs and pesticides. The technology can be used to treat halogenated VOCs but will generally be more expensive than alternative technologies. Wastewater produced may require treatment prior to discharge and air emissions can be controlled by condensation and/or activated carbon adsorption. The process is generally not cost effective for large waste volumes, media water content above 20% requires excessive reagent volume and concentrations of organics greater than 5% require large volumes of reagent.	Dehalogenation has successfully treated DNAPL's such as carbon tetrachloride and dichloromethane at Lab. scale. To date no field studies using dehalogenation to treat DNAPL's have been conducted
30. Ultraviolet (UV) Oxidation	UV oxidation is a destruction process that oxidizes organic constituents in wastewaters by the addition of strong oxidisers and irradiation with UV light. Oxidation reactions are achieved through the synergistic reaction of UV light in combination with ozone (O_3)and/or hydrogen peroxide (H_2O_2)	A wide variety of organic contaminants are susceptible to destruction by UV oxidation including chlorinated solvents. Organic compounds with double carbon bonds (e.g., TCE, PCE and vinyl chloride) are rapidly destroyed in UV oxidation processes. The aqueous stream being treated must provide good transmission of UV light, high turbidity causes interference. When UV/O_3 is used on volatile organics, such as TCA, the contaminants may be volatilised rather than destroyed. They then have to be removed from the off gas by activated carbon adsorption or catalytic oxidation. Costs may be higher than competing technologies because of energy requirements. The main advantage of UV oxidation is that it is a destruction process, as opposed to air stripping or carbon adsorption for which contaminants are extracted and concentrated in a separate phase.	UV oxidation has been successfully used to treat groundwater contaminated with chlorinated solvents. Clean up consistently meets required targets and clean up of > 99.95% has been achieved.
31. High Temperature Thermal Desorption (HTTD)	HTTD systems are physical separation process and as such are not designed to destroy organics. Bed temperatures (320°C - 560°C) and typical residence times will cause selected contaminants to volatilise but not to be oxidised.	HTTD is frequently used in combination with incineration, depending on site specific conditions, but may be less cost effective than other treatments. Dewatering may be necessary to reduce the amount of energy required to heat the soil. Clay/silty soils and soils with high humic content increase reaction time as a result of binding contaminants. Feed particle size greater than 5cm can impact applicability or cost at specific sites, highly abrasive feed can potentially damages the processor unit.	HTTD has been used to treat chlorinated solvents such that clean-up greater than 99% has been achieved.

Table 6.1 Contd. Remedial Technology Selection

METHOD	APPLICATION/PROCESS	EFFECTIVENESS/ADVANTAGES/LIMITATIONS	EXPERIENCE
32. Incineration	High temperatures (870°C - 1,200°C) are used to volatilise and combust organic contaminants to leave non combustible organics. Solid is passed through a primary chamber in a rotary kiln (540C - 980C) to partially combust and volatilise organic components. A second chamber (870C - 1,200C) is used to ensure adequate destruction of the partially combusted gases.	Incinerators can be used to remediate soils contaminated with hazardous wastes particularly chlorinated solvents. Feed size and materials handling equipment can impact applicability or cost at specific sites. Heavy metals, within the waste, can produce a bottom ash that requires stabilisation. Incinerator off gas requires treatment by an air pollution control system to remove particulates and to neutralize and remove acid gases. Fixed costs are relatively independent of site size whilst operating costs vary significantly depending on the type of waste treated and site size.	Incineration has been used effectively in the USA to achieve 99.99% removal of carbon tetrachloride from contaminated soil.

TECHNOLOGY 1 - EXCAVATION, RETRIEVAL AND OFF SITE DISPOSAL

Description: Contaminated material is removed and transported to permitted off site treatment and/or disposal facilities. Some pre-treatment of the contaminated media may be required in order to meet land disposal restrictions.

Applicability: Excavation and off site disposal is applicable to the complete range of contaminant groups, including DNAPLs (in all phases), and aquifer media materials. Although excavation and off-site disposal alleviates the contaminant problem at the site it does not treat the contaminants.

Limitations: Major factors that limit the effectiveness and applicability of the process include:

- Generation of fugitive emissions (dust, liquid, gas) may be a problem during operations.
- The distance from the contaminated site to the nearest disposal facility will affect cost.
- Depth and composition of the media requiring excavation must be considered.
- Transportation of the soil through populated areas may affect community acceptability.

Data Needs: The range and diversity of contamination across the site must be established in order to delineate the potential area of excavation. The proximity of the water table to the surface may require a dewatering system to be implemented. The type of contaminant and its concentration will impact off-site disposal requirements. Soil characterisation as dictated by land disposal restrictions are required.

Performance Data: Excavation and off-site disposal is a well proven and readily implemented technology. Excavation is the initial component of all ex situ soil treatment technologies. As a consequence the remediation consulting community is very familiar with this option. Disposal of the contaminated media is dependent on the availability of adequate containers to transport the hazardous waste.

Costs: Cost estimates for excavation depend heavily on the transportation distance and disposal charges (dependent on the quantity and quality of the waste material).

Case Studies:

- Pintsch Waste Oil Refinery, Hanau, Germany (Case Study 7, Section 8.) - Soils from the unsaturated zone were excavated and treated by soil washing to remove a combination of hydrocarbon and solvent contaminants.
- McColl Superfund Site - Demonstration of a trial excavation (USEPA, 1992).

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TECHNOLOGY 2 - NATURAL ATTENUATION AND INTRINSIC BIOREMEDIATION

Description: Natural attenuation in the subsurface includes processes such as dilution, volatilisation, biodegradation, adsorption and chemical reactions with subsurface materials which eventually reduce contaminant concentrations to acceptable levels. Intrinsic bioremediation refers only to the biological natural attenuation processes. Consideration of this option usually requires modelling and evaluation of contaminant degradation rates and pathways. The primary objective of site modelling is to demonstrate that the natural processes of contaminant degradation will reduce contaminant concentrations below regulatory standards before potential exposure pathways are affected.

Sampling and sample analysis must be conducted throughout the process to confirm that degradation is proceeding at rates consistent with meeting clean up objectives.

Applicability: Natural attenuation is selected at sites where contaminants are strongly sorbed to deep subsurface soils and are not migrating; where removal of DNAPL has been determined to be technically impractical; and where it is determined that active remedial measures would be unable to speed up significantly remediation time frames.

Halogenated VOCs and SVOCs are less responsive to natural attenuation than other contaminants.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Large quantities of data must be collected to determine model input parameters and highly skilled modellers are required.
- Intermediate degradation products may be more mobile and more toxic than the original contaminant.
- Natural attenuation should only be used where there are no impacts on potential receptors.
- Contaminants may migrate before they are degraded.
- If source material exists it may have to be removed.

Data Needs: Extensive site characterisation is required in all cases. Important information to be obtained during the data review includes: Three-dimensional distribution of the residual, free and dissolved phase contaminants, groundwater and soil geochemical data, chemical and physical characteristics of the contaminants, potential for biodegradation of the contaminants, lithology and stratigraphic relationships, grain size distribution, flow gradient, preferential flow paths, interaction between groundwater and surface water and location of potential receptors.

Performance Data: Performance of natural attenuation can be extremely variable and the potential for use must be carefully evaluated on a site specific basis. The approach has been widely used in the US and in Europe.

Costs: The major factors affecting costs are the extent of the site characterisation and the amount of skilled labour hours required during confirmation monitoring.

Case Study:

- Textile factory, Ontario, Canada (Fiorenza et al., 1994, Case study 8.10) - Evidence of natural anaerobic degradation of chlorinated solvents in glacial till and fractured shale limestone bedrock.

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TECHNOLOGY 3 - HYDRAULIC CONTAINMENT

Description: Isolation and containment mechanisms include passive systems such as impermeable barriers, and active systems such as hydraulic controls. These are used to either contain or isolate a dissolved plume or source area. Active groundwater controls are often used in conjunction with impermeable barriers to minimise the potential for advective transport of contaminants across an impermeable barrier.

Groundwater extraction and recharge by arrays of wells and trenches facilitate hydraulic gradient control, create capture zones and permit redirection of local groundwater flow.

Hydraulic controls have a long history of use as containment mechanisms on sites where contaminated groundwater is present. The technology is generally a proven migration control although its success depends on adequate design and implementation.

Applicability: Hydraulic controls may be utilised for containment and partial recovery of DNAPL. Containment and isolation options are required on many DNAPL sites since residual and trapped pools of DNAPL are long term sources of groundwater contamination. Containment requirements are perhaps less where there is a continuous barrier that prevents downward migration of DNAPL migration. Downward migration has been arrested by creating upward hydraulic gradients in the DNAPL zone that exceeds the density difference between DNAPL and water. Vertical hydraulic containment of DNAPL, however, has yet to be demonstrated in the field.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Long term containment is often required, resulting in slow remedial time scales and high operating costs.

- Hydraulic control is only a containment mechanism and further treatment of the extracted groundwater is also required.

- Vertical hydraulic containment of DNAPLs has not been demonstrated.

- The effectiveness of the system is largely controlled by site specific parameters and implementation of the technology requires extensive site characterisation and ongoing monitoring.

Data Needs: The hydrogeological characterisation of the site is of major importance and accurate estimates of the parameters stated in the introduction (section 6.1) are vital (e.g hydraulic gradient and conductivity, aquifer yields and boundary conditions) data pertaining to the nature and extent of the contaminant in the aquifer is also required.

Performance Data: Hydraulic containment and physical isolation of the contamination is employed as a source control mechanism. Therefore time scales and removal efficiencies depend on the contaminant removal technologies implemented. Hydraulic containment does result in removal of dissolved phase contamination from the aquifer, however complete remediation is a slow process and dependent on site specific conditions.

Costs: Hydraulic containment can be expensive depending on site specific conditions and time scales.

Case Study:

- Tyson's dump, King of Prussia, Pennsylvania (EPA, 1992, Case study 8.9) - Extensive dissolved and pure phase DNAPL contamination is present in the fractured aquifer below the site. Due to the extent and depth of the contamination it has been concluded that DNAPL can not be effectively recovered and will continue to act as a source for dissolved contaminants in the groundwater. The clean-up remedy is a containment system to prevent further discharge of dissolved contaminants to a nearby river.

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TECHNOLOGY 4 - CONTAINMENT BY PHYSICAL BARRIERS

Description: Isolation and containment mechanisms include passive systems such as impermeable barriers and active systems such as hydraulic controls. These are used either to contain or isolate a dissolved plume or source area. Active groundwater controls are often used in conjunction with impermeable barriers to minimise the potential for advective transport of contaminants across an impermeable barrier.

Impermeable barriers can consist of; grout curtains, geomembranes, in-situ soil mixed zones, clay slurry walls, caps and liners. The configuration of a containment barrier depends on two different approaches; 1) completely encompass the source area and dissolved plume with a continuous barrier, 2) locally arrest or stall dissolved plume migration using discrete barrier sections.

Hydraulic controls and cut off walls have a long history of use as remedial options. The technology is generally a proven migration control although its success depends on site conditions, adequate design and implementation.

Applicability: Impermeable barriers are generally used to isolate and contain dissolved phase contaminants. The actual remediation of pure and dissolved phase DNAPL requires other techniques.

Barrier wall resistance to the subsurface conditions and contaminant type must be evaluated, to avoid possible break through of the DNAPL.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Long term integrity of engineered subsurface barriers is poorly documented. Small fractures or openings in the wall will facilitate DNAPL break through.
- There is a potential for inducing contaminant migration during wall construction and changes in the hydrogeological system may be affected by wall emplacement.
- It is often difficult to seal the base of vertical walls effectively.

Data Needs: In addition to the parameters discussed in the introduction to this section, the following factors must be assessed prior to designing a low permeability barrier: maximum allowable permeability, anticipated hydraulic gradients, required wall strength, availability and grade of bentonite (for bentonite slurry walls), boundaries of contamination, compatibility of wastes with respect to wall materials, characteristics of the subsurface, site terrain and physical layout.

Performance Data: Physical isolation of the contamination is employed as a source control mechanism. Time scales and removal efficiencies depend on the contaminant removal technologies employed. Implementation of walls requires a hydraulic containment system to control the flow of groundwater. Hydraulic containment results in removal of dissolved phase contamination from the aquifer. However, complete remediation is a slow process and very much dependent on site specific conditions.

Costs: Passive isolation and containment systems usually cost less than other remedial alternatives.

Case Study:

- Industrial Facility, Liguria, Italy (Manassero and Viola, 1992) - Installation of a 3km long high density polyethylene (HDPE) slurry wall in a high permeability sand and gravel aquifer underlain by marl. The contaminants were unspecified.

References:

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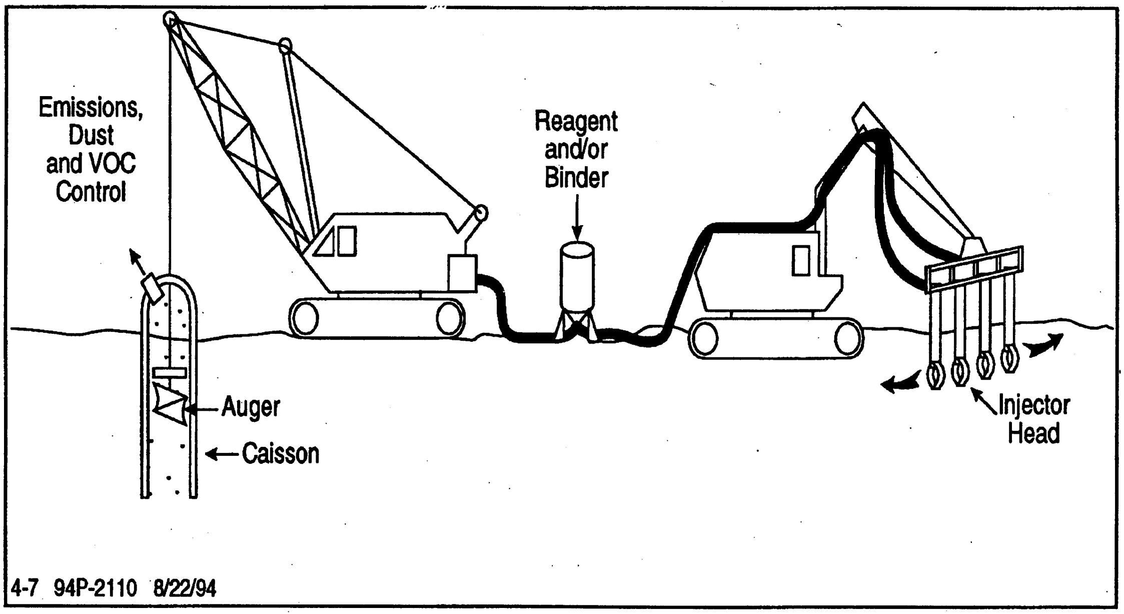
TECHNOLOGY 5 - STABILISATION AND SOLIDIFICATION

Description: Stabilisation and solidification (S/S) techniques are intended to immobilise dissolved contaminants and in some cases DNAPLs. Stabilisation refers to techniques that reduce contaminant hazard potential by converting the contaminants to less soluble, mobile or toxic forms. Solidification refers to techniques which encapsulate the contaminant in a monolithic solid of high structural integrity. These two ends may be achieved by a variety of means and often occur simultaneously.

In situ S/S techniques use auger/caisson systems and injector head systems to apply S/S agents to in situ soils. S/S techniques can be used alone or combined with other treatment and disposal methods.

S/S or soil mixing technologies were developed in the US in the 1950s, but has since been used for a variety of construction related purposes, mostly in Japan. Most environmental applications involve treatment of inorganics. However, one case study documents S/S application to soils contaminated with DNAPLs (PCBs).



4-7 TYPICAL AUGER/CAISSON AND REAGENT/INJECTOR HEAD IN SITU SOLIDIFICATION/STABILIZATION SYSTEMS

Figure 6.1: Auger/Caisson and reagent/injector head in situ S/S systems (USEPA, 1988).

Applicability: S/S has not been specifically used for DNAPLs to date, and it is not clear whether migration from the treatment zone can be prevented. Metals and organics can be treated simultaneously. Dissolved phase plumes and DNAPLs in fractured rocks are better addressed by other techniques.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Depth of contamination may limit some types of application process.
- Future use of the site may weather materials and affect ability to maintain immobilisation of contaminants.
- Some processes result in a significant increase in volume (up to double the original volume).
- Certain wastes are incompatible with variations of this process. Treatability studies are generally required.
- Reagent delivery and effective mixing are more difficult than for ex situ applications.
- Quality assurance is problematical.

Data Needs: The following characteristics need to be determined in addition to the parameters specified in the introduction to this section: particle size, Atterberg limits, moisture content, metal concentrations, sulphate concentrations, organic content, density, permeability, unconfined compressive strength, leachability, pH and microstructure analysis. Treatability tests are vital as the process is highly site specific (USEPA, 1989a).

Performance Data: In situ S/S projects have demonstrated the capability to reduce mobility of contaminated waste by greater than 95%. However, the effects of long term weathering can significantly affect the integrity of the stabilized mass. The application of the technology to DNAPL contaminants is in a developmental stage.

Costs: Costs vary widely according to materials or reagents used, their availability, site size and the chemical nature of the contaminants. S/S processes require potentially large quantities of bulk reagents and additives. Transportation costs can quickly dominate remedial economics.

Case Study:

- Hialeah, Florida (USEPA, 1989b, Jasperse and Ryan, 1992) - S/S techniques were successfully tested on a site comprising sands, silty sands and karstic limestone rock contaminated by PCBs.

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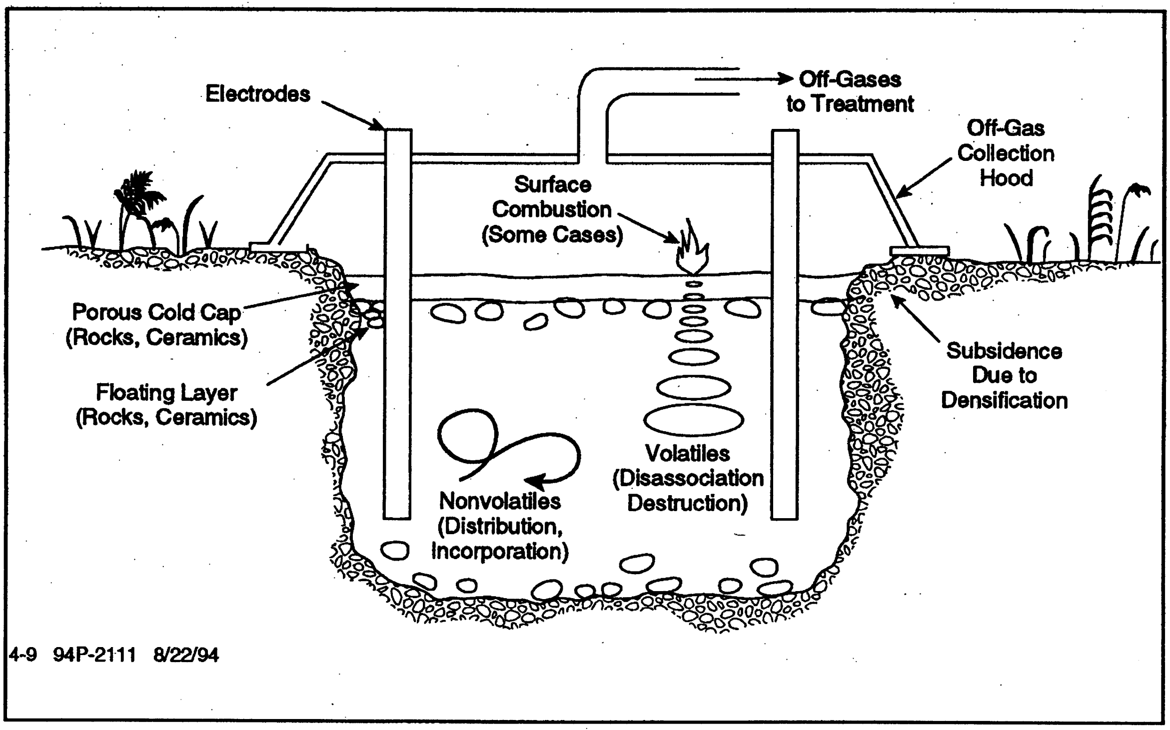
USEPA (1994) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, Oct 1994.

TECHNOLOGY 6 - IN SITU VITRIFICATION (ISV)

Description: In situ vitrification (ISV) uses an electric current to melt soil and other materials at extremely high temperatures (1600 to 2000°C) and thereby immobilise most inorganics and destroy organic pollutants by pyrolysis. Water vapour and organic pyrolysis combustion products are captured in a hood which draws the contaminants into an off gas treatment system that removes particulates and other pollutants from the gas.

High temperatures are achieved using a square array of four graphite electrodes. The process is initiated using a path of conducting material (graphite) on the surface of the soil to heat the soil to melting point. The molten zone grows downward and outward. The vitrification product is chemically stable, leach resistant, glass and crystalline, like.

Since 1980 the technology has been employed on both pilot and full scale applications. However there have been few, if any, commercial applications. None of these applications have included DNAPL compounds. Testing with NAPL compounds has occurred on the engineering test scale using soil quantities of less than one tonne.



4-9 TYPICAL IN SITU VITRIFICATION SYSTEM

Figure 6.2: In situ vitrification system (USEPA, 1994).

Applicability: The ISV process was originally developed for sites contaminated by heavy metals and radionuclides, where there are few options for treatment and treatment costs are high. The ISV process can theoretically destroy DNAPLs by pyrolysis and this has been demonstrated in small scale tests. ISV is therefore, a potentially attractive technology for sites containing mixed inorganic and organic wastes.

The ISV process is essentially applicable to the unsaturated zone only unless dewatering, containment or other hydraulic controls are engaged. Fine grained, clay saturated soils may be more easily treated due to their low hydraulic conductivity and higher electrical conductivity than coarser soils. However the amount of DNAPL contained within clay soils is likely to be low compared to that of coarser media.

Limitations: Factors that limit the applicability and effectiveness of the process include:

- Waste content limitations; Rubble exceeding 20 wt%, combustible organic content limits of 5-10 wt%, general metals concentration limits of 5-16wt%.
- Heating of the soil may cause subsurface migration of contaminants into clean areas.
- Solidified material may hinder future site use.
- Processing of contamination below the water table may require some means to limit recharge.
- The achievable depth is limited under certain heterogeneous conditions.

Data Needs: A minimum alkali content in soil of 1.4 wt% is required to form glass. The composition of most soils is well within the range of processibility.

Performance Data: The time scales are small due to the intensive nature of the treatment. Removal efficiencies of greater than 99% have been achieved for a range of volatile and semi volatile DNAPL compounds.

Costs: Process costs are affected by the following major factors: cost of electrical power, initial moisture content of soil and amount of recharged water to be removed, depth of treatment and analytical requirements associated with process control and permit compliance.

Case Study:

- No case studies involving the remediation of solvent/DNAPL contaminated sites are available. ISV testing at private, Superfund and DOE sites are summarized in USEPA, 1992.

References:

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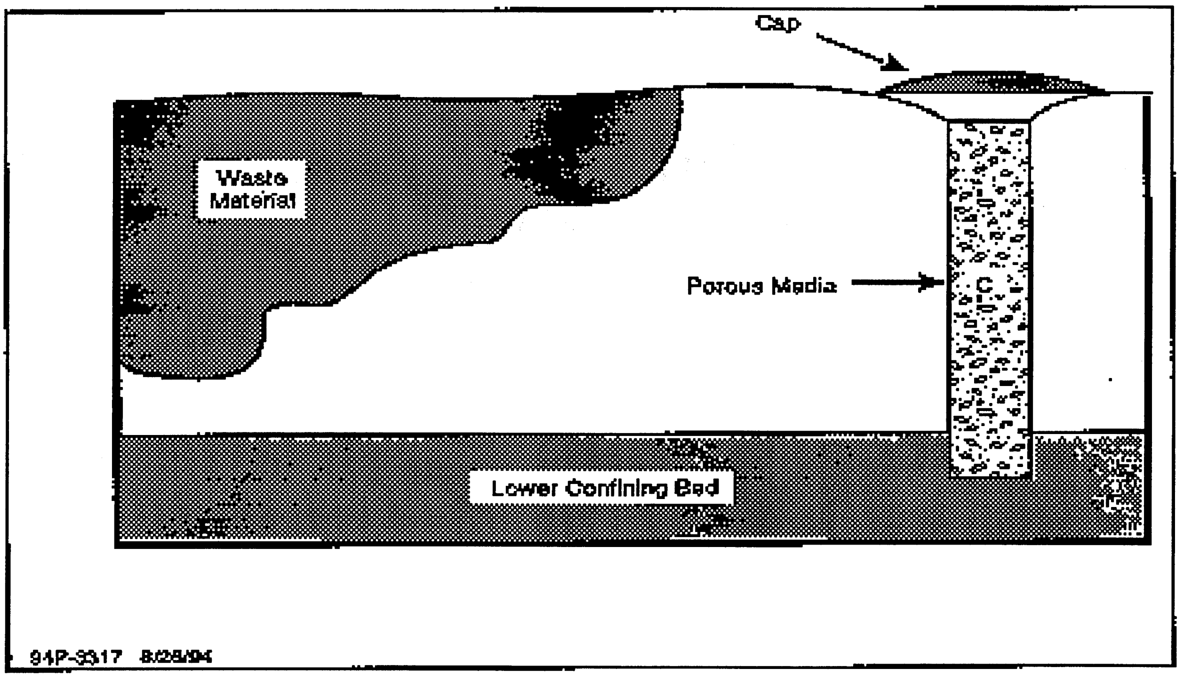
TECHNOLOGY 7 - PERMEABLE TREATMENT WALLS

Description: In situ treatment walls are permeable, reactive structures constructed of granular materials to allow groundwater flow through the wall. Treatment is achieved by using a granular backfill of a variety of additives or surface coatings such as: nutrients and bacteria for in situ biodegradation, redox controls and/or metal catalysts to aid in metals precipitation and chemical dehalogenation; organic carbon for enhanced denitrification; and selective adsorbents to increase the retardation capacity of the in situ wall.

Installation of in situ treatment walls depends on the desired wall configuration and its composition. Hydraulic feed controls can be installed to deliver gaseous or liquid phase amendments.

No full scale applications are known to exist, although a pilot test at the Canadian Air Force Base, Borden, was completed in 1991; treating a dissolved plume of TCE and PCE with a reactive wall containing iron grindings and sand.



4-40 TYPICAL PASSIVE TREATMENT WALL (CROSS-SECTION)

Figure 6.3: Cross section of a passive treatment wall (USEPA, 1994).

Applicability: Since most DNAPL has low mobility once emplaced, the intended use of this technology is the management and treatment of the dissolved phase in aquifers, extension to fractured media is unlikely.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Passive treatment walls may lose their reactive capacity, requiring replacement of the reactive medium. The active amendments must be reactive, non toxic and both soluble enough to supply ample reagent mass for reactions and stationary enough to persist for long periods of time.

- The system requires consistent control of pH levels. When pH levels within the wall rise reaction rate is reduced and can inhibit the effectiveness of the technology.

- Depth and width of barrier.

- Volume cost of treatment medium.

- Biological activity may limit the permeability of the passive treatment wall.

- Inorganic catalysts that promote organic compound reduction can also foster anaerobic degradation which may potentially occur within the wall or down gradient. Formation of toxic intermediate and end products is then possible.

Data Needs: In addition to those parameters specified in the introduction (Section 6.1) the following parameters need to be defined: groundwater flow rate and direction, soil permeability and buffering capacity.

Performance Data: Degradation of dissolved contaminants has been shown on a pilot scale only (Canadian Air Forces Base, Borden), where reductions of 91% and 95% for PCE and TCE concentration in a dissolved plume were recorded as groundwater passed through a reactive wall. Time scales obviously depend on the groundwater velocity through the wall.

Costs: Capital costs are likely to be high although life cycle costs for operational systems are expected to be 5 or 10 times less than pump and treat.

Case Study:

- Canadian Forces Base, Borden (Gillham and O'Hannesin, 1992; Gillham et al., 1993) - A permeable reactive wall of iron grindings (22wt%) and sand (78wt%) was successfully used to reduce concentrations of PCE and TCE in a shallow dissolved plume.

References:

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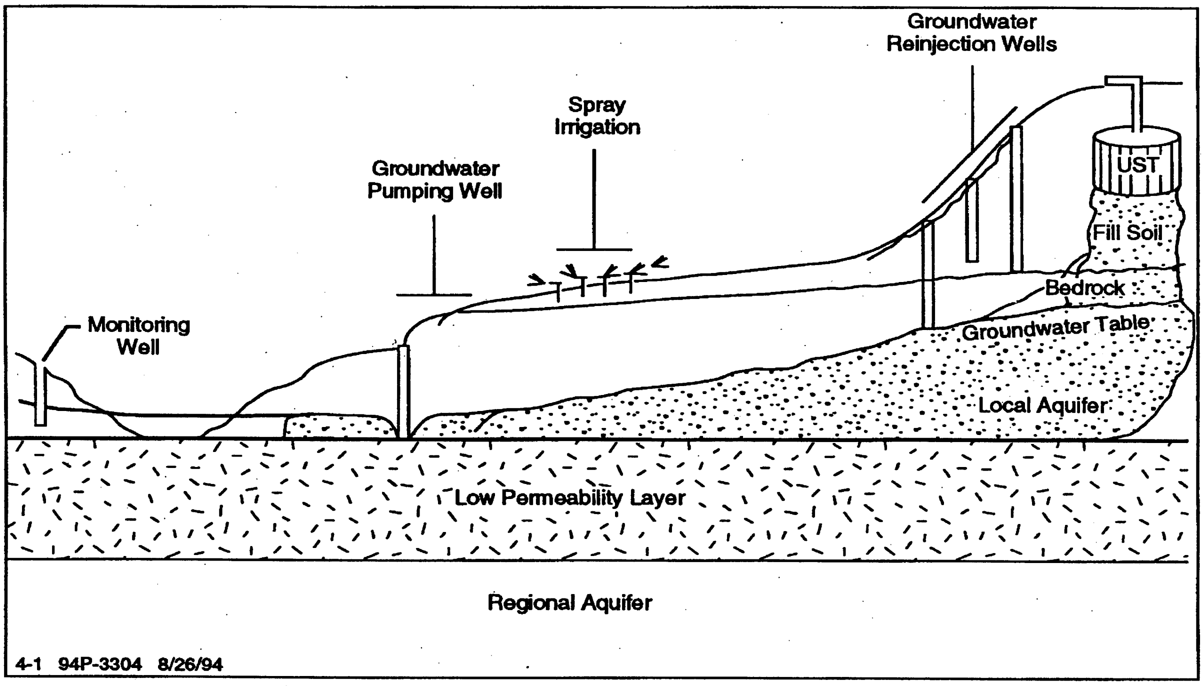
TECHNOLOGY 8 - AEROBIC BIODEGRADATION

Description: Aerobic biodegradation is a process in which indigenous or inoculated micro organisms degrade organic contaminants found in soil and/or groundwater. In the presence of sufficient oxygen the micro organisms will ultimately convert many organic contaminants to carbon dioxide, water and microbial cell mass.

The in situ bioremediation of soil and groundwater typically involves the percolation or injection of water mixed with nutrients and saturated with dissolved oxygen. Acclimated micro organisms and other oxygen sources (e.g. hydrogen peroxide) may also be added. Wellhead injection and infiltration galleries are two commonly used configurations for supplying these materials to the subsurface.

Efforts to stimulate aerobic bio degradation have been employed at numerous contaminated sites with varying degrees of success and documentation. Confirmation of targeted DNAPL compound destruction by microbial degradation has only been provided in a few studies (Madsen 1991, Alvarez-Cohen, 1993).



4-1 TYPICAL IN SITU BIODEGRADATION SYSTEM

Figure 6.4: Typical in situ biodegradation system (USEPA, 1994).

Applicability: Highly chlorinated solvents do not appear to undergo aerobic degradation. However if dechlorination occurs under anaerobic conditions a less chlorinated, often more aerobically degradable product is produced. Less chlorinated solvents can be degraded by aerobic processes alone.

In situ bioremediation applies only to the remediation of contaminants in the dissolved and adsorbed phase. Aquifers containing the separate phase cannot be fully treated as the large compound concentrations result in toxicity to microbes.

Aerobic bioremediation is most suited to high permeability, granular aquifers with a moderate amount of organic matter. It is not well suited for low permeability and fractured media.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Degradation pathways for more complex aliphatics and aromatics may involve recalcitrant and/or toxic intermediates and end products.
- Clean up goals may not be attained if the soil matrix prohibits contaminant-micro-organism contact.
- The circulation of water based solutions through the soil may increase contaminant mobility and necessitate treatment of underlying groundwater.
- Preferential colonisation by microbes may occur causing clogging of nutrient and water injection wells.
- Preferential flow paths may severely decrease contact between injected fluids and contaminants throughout the contaminated zones. The system should not be used for clay, highly layered, or heterogeneous subsurface environments because of other electron acceptor transfer limitations.
- High concentrations of highly chlorinated organics and NAPLs are likely to be toxic to micro organisms.
- Bioremediation slows at low temperatures.

Data Needs: Site characterisation of parameters directly related to in situ biological activity is required. These include redox potential, dissolved oxygen concentrations, pH, temperature, ionic strength, presence or absence of heavy metals and potential electron acceptors. Laboratory tests that evaluate microbial activity and potential toxicity for a given site determine the potential for natural bioremediation. Bench and pilot scale test are recommended.

Performance Data: Remediation time scales depend on the degradation rates of specific contaminants, site characteristics and climate.

Costs: Natural unaided bioremediation imposes little or no costs other than the time for natural processes to proceed.

Variables affecting the cost of enhanced bioremediation are the nature and depth of the contaminants, use of bioaugementation and/or hydrogen peroxide addition and groundwater pumping rates. Ex situ hardware will include nutrient feed stocks, air strippers and granular activated carbon.

Case Study:

- Moffet Field Naval Air Station in Mountain View, California (1986 - 1988), (Roberts et al. 1990, Semprini et al. 1990, 1991, Semprini and McCarty, 1991, 1992) - In situ aerobic biodegradation studies illustrating the successful biotransformation of chlorinated aliphatics.

References:

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TECHNOLOGY 9 - ANAEROBIC BIODEGRADATION

Description: Anaerobic degradation involves complete or partial metabolisation of aqueous phase organic compounds by non oxygen utilising micro organisms. Reduction of halogenated hydrocarbons occurs through two generalised dehalogenation mechanisms; hydrogenolysis, entailing the substitution of halogen atoms by hydrogen atoms, and dihalo-elimination which results in the substitution of two adjacent halogen atoms by an ethene bond.

The field implementation process is analogous to aerobic processes with the exception of electron acceptor delivery. Anaerobic acceptors are extremely water soluble, therefore delivery of primary substrates, electron acceptors, nitrogen and phosphorous amendments is easily facilitated by aqueous phase injection. In anaerobic systems wellhead injection is the usual configuration.

Anaerobic biodegradation processes naturally occur in situ. Field studies have been conducted but no full scale engineering applications are known to exist. Anaerobic mineralisation of halogenated hydrocarbons is not well understood, full scale application of anaerobic biodegradation is generally discouraged due to the formation of potentially toxic end products. A typical in situ biodegradation system is presented in figure 6.8.

Applicability: Anaerobic bioremediation is suitable for degradation of the highly chlorinated organic solvents. Optimum degradation rates may be achieved by a combination of anaerobic and aerobic processes.

In situ bioremediation applies only to the remediation of contaminants in the dissolved and adsorbed phase. Aquifers containing the separate phase cannot be fully treated as the large compound concentrations result in microbial toxicity.

Anaerobic bioremediation is most suited to high permeability, granular aquifers with a moderate amount of organic matter. It is not well suited for low permeability and fractured media.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Depending on the environmental conditions and the contaminant chemistry, the end products exuded by the anaerobic consortia may be recalcitrant, toxic or undesirable. This issue may preclude the stimulation of anaerobic processes as a remedial option at certain sites.
- Consideration of the chemical condition of the aquifer post remediation is also of some concern. It will be anaerobic and possibly very reduced (characterised by high concentrations of Fe, Mn, H_2S and CH_4).
- Clean up goals may not be attained if the soil matrix prohibits contaminant micro organism contact.

- The circulation of water based solutions through the soil may increase contaminant mobility and necessitate treatment of underlying groundwater.

- Preferential colonisation by microbes may occur causing clogging of nutrient and water injection wells.

- Preferential flow paths may severely decrease contact between injected fluids and contaminants throughout the contaminated zones. The system should not be used for clay, highly layered, or heterogeneous subsurface environments because of other electron acceptor transfer limitations.

- High concentrations of heavy metals, highly chlorinated organics, long chain hydrocarbons, or inorganic salts are likely to be toxic to micro organisms.

- Bioremediation slows at low temperatures.

Data Needs: Parameters directly related to in situ biological activity are required. These include redox potential, dissolved oxygen concentration in the groundwater, pH, temperature, ionic strength, presence or absence of heavy metals and potential electron acceptors. Laboratory tests that evaluate microbial activity and potential toxicity can determine the potential for natural bioremediation.

Performance Data: Remediation time scales depend on the degradation rates of specific contaminants, site characteristics and climate. In general higher molecular weight compounds take longer to degrade. Much remains unknown about the anaerobic mineralisation of halogenated hydrocarbons in situ and the lack of full scale demonstration sites involving this technology make it difficult to speculate on the contaminant removal efficiency.

Costs: The cost is affected by the nature and depth of the contaminants, the use of bioaugementation and groundwater pumping rates. Ex situ hardware includes nutrient feed stocks, air strippers and granular activated carbon.

Case Studies:

- St. Louis Park, Minnesota, (Ehrlich et al., 1982) - In situ anaerobic degradation of creosote constituents was evaluated within a 20m thick aquifer of glacial deposits.

- Moffett Field Naval Air Station in Mountain View, California, (Semprini et al., 1992) - The successful biotransformation of chlorinated aliphatics was illustrated in a confined sand and gravel aquifer.

- Pinsch Waste Oil Refinery, Hanau, Germany (Case study 8.7) - An enhanced, sequential aerobic/anaerobic remedial system is being used to clean up a sand and gravel aquifer contaminated with waste oil products.

References:

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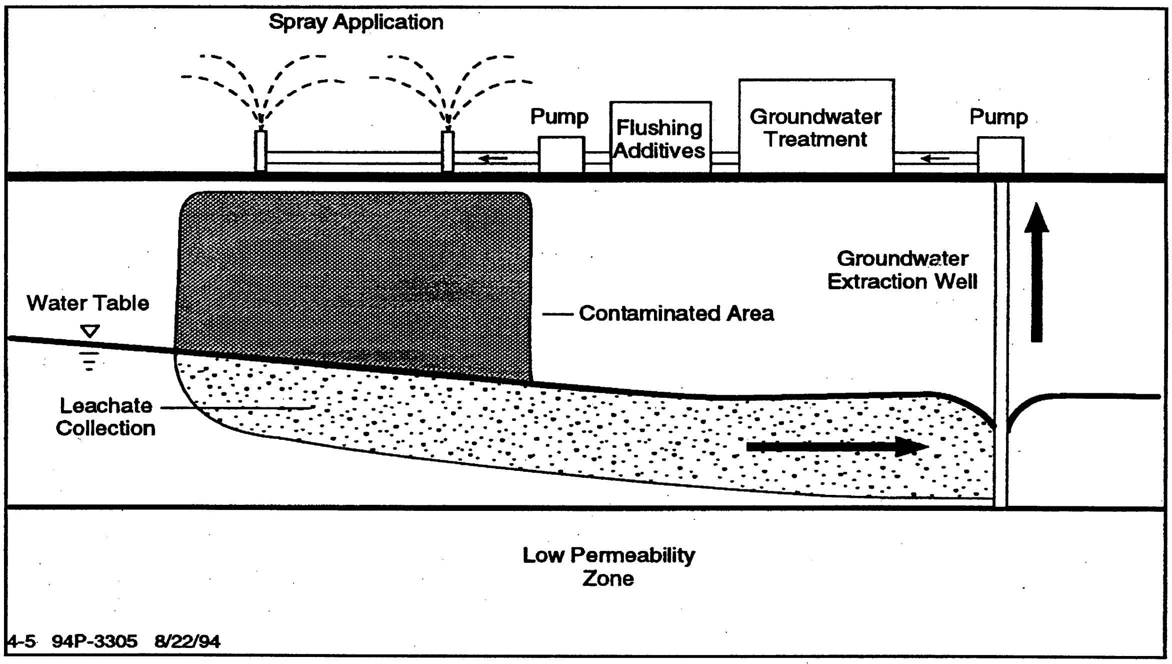
TECHNOLOGY 10 - WATER FLOODING AND GROUNDWATER EXTRACTION

Description: Water flooding and or groundwater extraction uses groundwater injection or reinjection and pumping to remove contaminants. The primary mechanisms involved are: increased recovery of the DNAPL as it responds to pumping stress in the aqueous phase, dissolution of DNAPL components into the aqueous phase and containment of the dissolved plumes.

Depending on the properties of the NAPL, conventional injection and extraction well construction equipment is applicable. Both vertical and horizontal well configurations have been successfully used. DNAPL recovery wells are placed as close to the base of the DNAPL pool as possible. Water recovery wells are nested directly above the DNAPL recovery wells at an elevation which accommodates upconing of the DNAPL interface. The water recovery wells are pumped continuously and at a higher rate than the DNAPL recovery wells, which are pumped intermittently.

There are at least two published accounts which emphasise the use of upconing and pumping response strategies to enhance DNAPL recovery. The hardware required for in situ water flooding is readily available and the requisite expertise to design such systems exists within the environmental community.



4-5 TYPICAL SOIL FLUSHING SYSTEM

Figure 6.5: Typical soil flushing system (USEPA, 1994).

Applicability: At extensively contaminated sites (where sufficient separate phase is present) DNAPL flow may be induced simply by gravity or the application of groundwater gradients. However, interfacial and viscous effects between water and DNAPLs may preclude the use of such a simplified approach. DNAPL recovery is seen to be a function of thickness of the DNAPL pool, capillary pressure and the buoyant density and viscosity of the separate phase.

Based on theoretical calculations (McWorter and Sunada, 1990) it is anticipated that DNAPL recovery can be maximized by utilizing low pumping rates.

Pump and treat systems are most applicable to homogenous, single layer aquifers where the contaminant is present only in the dissolved phase. Remediation of heterogeneous, fractured (dual porosity) aquifers where contaminants are present in the separate phase is inherently difficult.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- This treatment is suitable only as a precursor to other in situ clean up measures since the residual concentrations of DNAPLs will remain significant (approx. 5 - 20 wt%).
- Thus far, only relatively light DNAPLs (S.G<1.1) are known to have been recovered by this technique.
- A large volume of liquid may be pumped to the surface but a relatively small contaminant yield is achieved.
- Significant problems may be encountered as a result of chemical attack on down hole equipment.

Data Needs: Definition of the horizontal and vertical extent of contamination in all phases is required. Feasibility studies will include pumping and recovery tests.

Performance Data: Clean up times can be estimated by considering the number of pore volumes that must be pumped from the contaminated zone to attain the clean up goals. Theoretical clean up times can range from years to hundreds of years depending on the hydrogeology and contaminant characteristics. Systems often become "diffusion limited" which tends to lengthen the treatment period.

The removal efficiencies of the technology depend on the division of the contaminant between the different phases (dissolved, adsorbed and separate).

Costs: Capital costs should be comparable to pump and treat. Operation and maintenance costs (including labour, materials, electrical power, analytical work and waste disposal) are likely to be high.

Case Studies:

- Coal Gasification Facility, East Stroudsburg, Pennsylvania, (Villaume et al., 1983, Villaume, 1985) - Contamination at the site involved the presence of 35,000 gallons of coal tar pooled in a stratigraphic depression at the base of a silty sand aquifer. Using a water flushing technique more than 8,000 gallons of coal tar was recovered within nine months of operation.

- Wood Treating Facility, Laramie, Wyoming. (Sale et al., 1988) - As a precursor to in situ surfactant/alkali soil flushing water flooding was conducted.

References:

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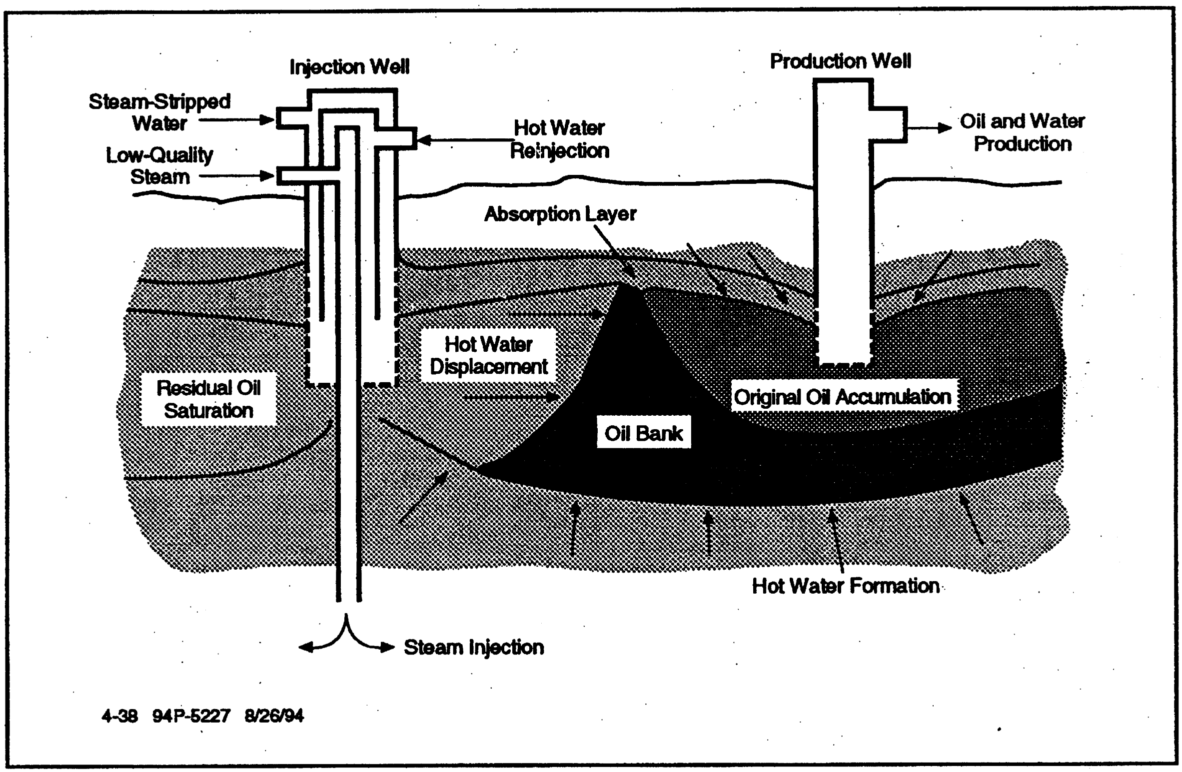
TECHNOLOGY 11 - HOT WATER OR STEAM FLUSHING/STRIPPING

Description: Hot water or steam are forced into the aquifer to vapourise volatile and semivolatile contaminants. The vapourised components rise to the unsaturated zone where they are removed by vacuum extraction and treated. NAPL recovery is enhanced because: (1) NAPL becomes less viscous and more mobile on heating. (2) NAPL solubility may be increased by higher temperatures. (3)Volatile NAPL vapourises, moves ahead of the hot water and then condenses to form a NAPL bank. (4) The bank results in increased NAPL transmissivity and results in a snowball effect.

Hot water or steam based techniques include; the contained recovery of oily wastes (CROW®), Steam injection and vacuum extraction (SIVE®), in-situ steam enhanced extraction (SEE®) and steam enhanced recovery process (SERP®). The injection of hot water/steam along the periphery of the contamination serves the dual purpose of lateral containment and displacement of DNAPL towards the extraction well. In situ biological treatment may follow the displacement.

The field implementation includes a series of hot water/steam injection wells around the limits and below the contaminant plume and a series of production wells to remove the groundwater and contaminants.



4-38 CROW™ SUBSURFACE DEVELOPMENT PROCESS

Figure 6.6: Hot water/steam flushing, CROW™ system (USEPA, 1994).

Applicability: Hot water/steam flushing is applicable to separate phase DNAPL contamination, providing the DNAPL becomes less dense than water under applied temperatures. The application of this technology has so far been to sites contaminated by compounds with densities within 10-25% of water at 20°C, such as coal tar and creosote. Application of the technology to much denser DNAPLs (e.g. TCE and PCE) is currently being investigated. Hot water/steam injection will have the highest impact on source areas.

Depth application and soil type will dictate allowable steam and hot water injection pressures and well spacing.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Soil type, geology and hydrogeology which significantly impact the process effectiveness.

- Residual saturations on the order of 0.1 - 5% may persist after application of the technology therefore it must be augmented by another form of in situ treatment. An attractive option for this treatment is in situ biological treatment although to date this has not been used in conjunction with hot water/steam flushing.

- The cost of this treatment is relatively high in comparison to other applicable technologies.

Data Needs: A detailed discussion of the data needs is provided in the introduction.

Performance Data: Of the four vendors promoting hot water/steam flushing system the CROW^{TM} (Contained Recovery of Oily Wastes) system is the most developed. The CROW^{TM} system was tested in the US on both laboratory and pilot scales under the EPA SITE Emerging Technology Programme. The programme showed the effectiveness of the hot water displacement and displayed the benefits from the inclusion of chemicals with the hot water (USEPA, 1991).

Costs: Costs of thermal technologies are inherently higher than other remedial options. All these methods are sampling and monitoring intensive, therefore operating and maintenance costs are also high.

Case Studies:

- Former wood treatment plant (Fahy et al., 1992) - Pilot study to demonstrate hydraulic control of the hot water front as it propagated in the subsurface.

- Former wood treatment plant, Minnesota (Johnson, 1992) - Pilot Study

- Pennsylvania Power & Light (PP&L), Broadhead Creek Site, Stroudsburg (USEPA 1991) Pilot study and full application.

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TECHNOLOGY 12 - ALKALI SOIL FLUSHING

Description: Soil flushing relies on fluid-fluid displacement processes to enhance contaminant removal. The effectiveness of the displacement process is controlled by phase equilibria and the hydrodynamics of frontal propagation in porous media. In situ soil flushing involves two recovery phases: primary and secondary. In a successful primary recovery phase a very large concentrated "bank" of resident pore fluid is recovered prior to the breakthrough of the injected fluid. Secondary recovery occurs as a result of increased solubilisation after the break through of the injected fluid.

The addition of alkalis to the soil washing fluid saponifies the organic acid from the NAPL resulting in natural surfactant production and thus interfacial tension reduction. Alkalis also disrupt adsorption, precipitation and ion exchange processes between the pore fluids and porous media which reduces surfactant losses.

Conventional injection and extraction well construction equipment can be used for in situ alkaline soil flushing. Both horizontal and vertical configurations have been successfully used.

The USEPA has selected soil flushing as a source control remedy at ten superfund sites. Prior to this it had been demonstrated on only a few sites contaminated by petroleum hydrocarbons and TCE. To date, there has been little commercial success with this technology.

Applicability: In situ alkali soil flushing can be incorporated into almost any soil flushing treatment of DNAPLs. Although the selected compound must produce favourable bulk liquid properties and phase behaviour.

Multi component DNAPLs are not likely to contain acidic components, in these instances saponification is precluded and surfactant must be applied separately. The favourable influences of alkalis will still be realised with respect to optimal salinity, hardness precipitation, surfactant adsorption mitigation and interfacial tension reduction.

Alkali soil flushing is most suitable for use in granular, high permeability aquifers.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- A potential to spread the contamination if the water DNAPL interfacial tension is significantly reduced. Laboratory experiments have indicated rapid downward vertical migration of DNAPL after the interfacial tension is reduced to below five dynes/cm.

- Excessive alkali consumption and insufficient pHs may lead to poor NAPL recovery.

- Clayey soils may cause dispersion of the alkali and OH fronts which will delay and affect NAPL recovery, as well as potentially increasing alkali consumption and surfactant adsorption.

- The condition of the aquifer upon completion of the alkali soil washing is likely to be reduced with a high pH. Therefore it may be necessary to oxygenate or neutralise the groundwater.

Data Needs: In addition to the soil and contaminant characteristics described in the introduction to this section, the following parameters should be determined: pH buffering capacity, presence of heavy metals, total organic carbon content, cation exchange capacity and variable soil conditions.

Treatability tests to determine the most suitable flushing fluid, flushing fluid compatibility and changes of flushing fluids with changes in contaminants are required.

Performance Data: Soil flushing accomplishes permanent removal of contaminants from the soil; it proves most effective in permeable soils. The removal rate and clean up times depend very much on site specific conditions.

Costs: No cost information concerning in situ alkali soil flushing for environmental applications is available at this time. Major issues requiring consideration are surfactant costs, surfactant re cycling, tankage requirements and effect of field scale soil heterogeneity on displacement efficiency.

Case Study:

- To date, no field scale studies using in situ alkali soil flushing have been conducted.

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TECHNOLOGY 13 - COSOLVENT SOIL FLUSHING

Description: Soil flushing relies on fluid-fluid displacement processes to enhance contaminant removal. The effectiveness of the displacement process is controlled by phase equilibria and the hydrodynamics of frontal propagation in porous media. In situ soil flushing involves two recovery phases: primary and secondary. In a successful primary recovery phase a very large concentrated "bank" of resident pore fluid is recovered prior to the breakthrough of the injected fluid. Secondary recovery occurs as a result of increased solubilisation after the break through of the injected fluid.

The addition of cosolvents to the soil flushing fluid mobilizes the DNAPL by overcoming the capillary forces. A concentrated cosolvent slug will locally create a displacing front which is essentially one fluid phase composed of water cosolvent DNAPL free of surface tension effects.

Conventional injection and extraction well construction equipment can be used for in situ cosolvent soil flushing. Both horizontal and vertical configurations have been successfully used.

Cosolvents have been employed on a full scale in petroleum engineering applications. At present there is limited experience with this technology within the environmental community.

Applicability: Theoretically this technology can be applied to almost any DNAPL providing a cosolvent can be selected such that the phase behaviour and the resultant changes in bulk liquid properties are favourable.

Alkali soil flushing is most suitable for use in granular, high permeability aquifers. Displacement efficiency will be greatly affected by soil heterogeneity and cosolvent buoyancy.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Low permeability soils are difficult to treat.
- The potential of flushing the contaminant beyond the capture zone and the introduction of cosolvents to the subsurface concern regulators. The technology should be used only where flushed contaminants and soil flushing fluid can be contained and recaptured.
- Cosolvents are more effective for cleaning up LNAPLs rather than DNAPLs, due to density considerations.

Data Needs: In addition to the soil and contaminant characteristics described in the introduction to this section, the following parameters should be determined: pH buffering capacity, presence of heavy metals, total organic carbon content, cation exchange capacity and variable soil conditions.

Treatability tests to determine the flushing fluid required, flushing fluid compatibility and changes of flushing fluids with changes in contaminants are required.

Performance Data: Soil flushing accomplishes permanent removal of contaminants from the soil; it proves most effective in permeable soils. The removal rate and clean up times depend very much on site specific conditions.

Costs: No cost information concerning in situ cosolvent soil washing is available at this time. Major issues requiring consideration are cosolvent costs, cosolvent recycling, tankage requirements and effect of field scale soil heterogeneity on displacement efficiency.

Case Study:

- No known field applications of in situ cosolvent soil flushing have been reported in the environmental literature. Although many laboratory based experiments on chemical displacement and flooding have been conducted (Boyd and Farley, 1992, Wood et al., 1992).

References:

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TECHNOLOGY 14 - SURFACTANT SOIL FLUSHING

Description: Soil flushing relies on fluid-fluid displacement processes to enhance contaminant removal. The effectiveness of the displacement process is controlled by phase equilibria and the hydrodynamics of frontal propagation in porous media. In situ soil flushing involves two recovery phases: primary and secondary. In a successful primary recovery phase a very large concentrated "bank" of resident pore fluid is recovered prior to the breakthrough of the injected fluid. Secondary recovery occurs as a result of increased solubilisation after the break through of the injected fluid.

Addition of surfactants to the soil flushing fluid reduces interfacial tension and enhances hydrocarbon solubilisation which improves DNAPL recovery.

Conventional injection and extraction well construction equipment can be used for in situ surfactant soil washing. Both horizontal and vertical configurations have been successfully used.

Surfactant soil flushing has been demonstrated on the full scale in petroleum applications and environmental field applications of surfactant soil flushing have been completed.

Applicability: Theoretically in situ surfactant soil flushing can be applied to almost any immiscible hydrocarbon providing a surfactant can be selected such that the phase behaviour and resultant changes in bulk liquid properties are favourable. Surfactants are good candidates for aquifer remediation of DNAPLs when used in conjunction with alkalis, cosolvents and viscosofiers. Surfactants will have their largest impact on DNAPL source areas.

Alkali soil flushing is most suitable for use in granular, high permeability aquifers. Application within fine grained soils is not likely to be successful.

Limitations: Factors that limit the applicability and effectiveness of the process include:

- Low permeability soils are difficult to treat.
- Surfactants can adhere to soil and reduce effective soil porosity
- Reactions of flushing fluids with soil can reduce contaminant mobility.
- There is a potential to spread the contamination if the water DNAPL interfacial tension is significantly reduced. Laboratory experiments have indicated rapid downward vertical migration of DNAPL after the interfacial tension is reduced to below 5 dynes/cm.
- The potential of washing the contaminant beyond the capture zone and the introduction of surfactants to the subsurface concern regulators. The technology should be used only where flushed contaminants and soil flushing fluid can be contained and recaptured.

Data Needs: In addition to the soil and contaminant characteristics described in the introduction to this section, the following parameters should be determined: pH buffering capacity, presence of heavy metals, total organic carbon content, cation exchange capacity and variable soil conditions.

Treatability tests to determine the flushing fluid required, flushing fluid compatibility and changes of flushing fluids with changes in contaminants are required.

Performance Data: Soil flushing accomplishes permanent removal of contaminants from the soil and proves most effective in permeable soils. The removal rate and clean up times depend very much on site specific conditions. In Germany soil flushing was used to clean up a TCE spill. The technology was effective in reducing TCE concentrations by 50% within 18 months (USEPA, 1991).

Costs: No cost information concerning in situ surfactant soil washing is available at this time. Major issues requiring consideration are surfactant costs, surfactant recycling, tankage requirements and effect of field scale soil heterogeneity on displacement efficiency.

Case Studies:

- Wood Treating Facility, Laramie, Wyoming, (Sale et al., 1989) - A test cell was created using sheet piling in alluvial soils contaminated by wood treating wastes. Surfactants were used to reduce the contamination by 95% weight and 99% of the surfactant was recovered.

- Canadian Forces Base, Borden, Ontario, Canada, (Fountain et al., 1990, 1991; Wunderlich et al., 1992). A sheet piled test cell was deliberately contaminated by PCE. The effect of the surfactant soil flushing process was evaluated in terms of the amount of contaminant and surfactant recovered.

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TECHNOLOGY 15 - AIR SPARGING

Description: Air sparging is an in situ technology in which air is injected or "sparged" directly into the saturated zone of a contaminated aquifer. The sparged air removes contaminants by volatilisation. The air is then recovered in the unsaturated zone by a soil vapour extraction system (AS/SVE system). The region affected by a properly pressurised, vertical air sparger is assumed to be conical in shape.

Air sparging and vapour extraction wells can be designed in a horizontal or vertical configuration. Vertical placement of injection wells in favoured in coarser soils as they possess a low air entry pressure, creating a larger radius of influence. The screened intervals are usually limited to less than one metre.

Numerous sites in North America and Europe are reported to have been remediated by AS/SVE to concentrations in the range of 10 to 1000 ppb.

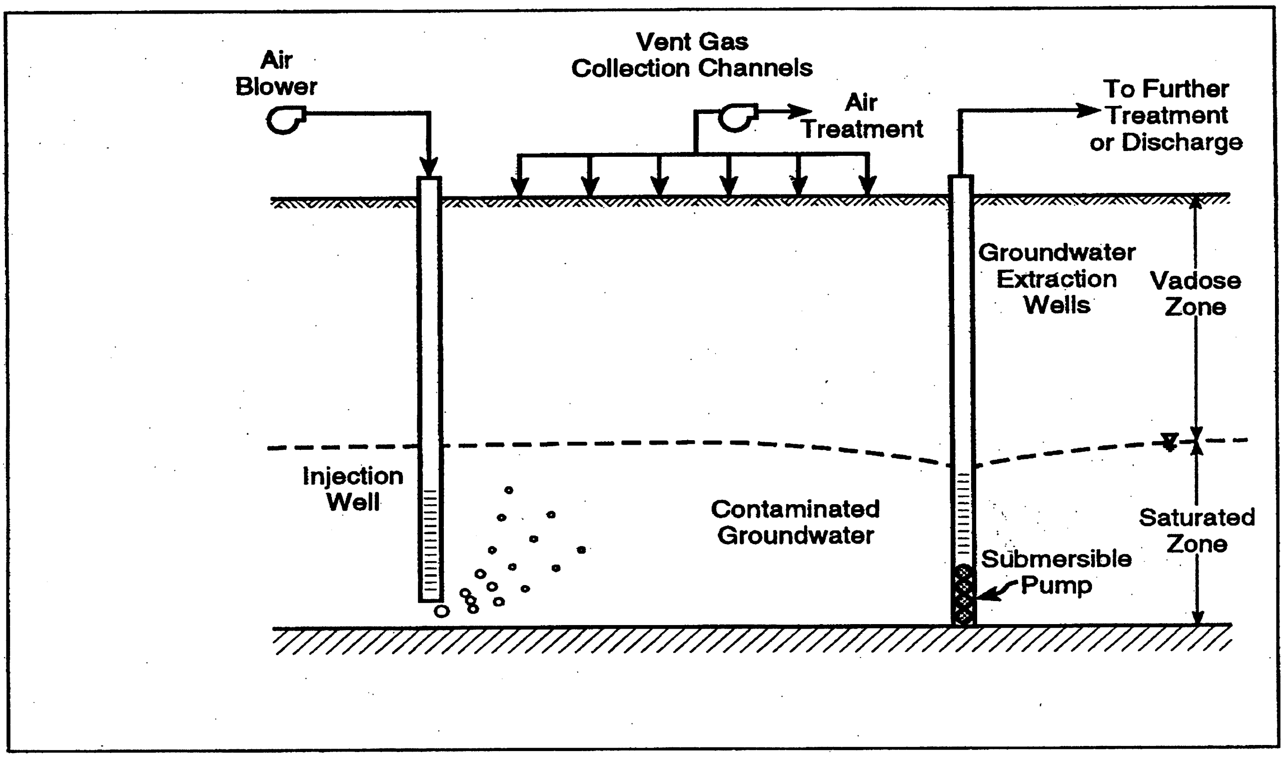

Figure 6.7: Typical air sparging system (USEPA, 1994).

Applicability: The technology applies to the recovery of volatile and semi volatile DNAPLs only. Contaminants possessing Henry's Law constants of greater than 10^5 atm-m^3/mole are good candidates for AS/SVE depending on subsurface conditions.

AS/SVE is used primarily to remediate the dissolved and adsorbed phases of the contaminants. Air sparging changes the pressure regime within the vicinity of the sparge well, NAPLs may be potentially mobilised laterally beyond the treatment zone or vertically downward below the sparge well.

Air sparging is most effective in coarse, high permeability soils. The process is strongly controlled by stratigraphic heterogeneities, therefore the presence of sand and silt lenses may affect the performance of the system.

Enhanced biostimulation in both the unsaturated and saturated zone may be a beneficial by product of both processes.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- The contaminant must be volatile, insoluble and/or biodegradable.
- Air flow through the saturated zone may not be uniform and air sparging is best suited to geologically homogenous and permeable sites.
- Depth of the contamination may preclude the effectiveness of the technology. A minimum depth of saturated aquifer above the contamination of approx. 1.5m and a maximum depth of approx. 10m is required, in order to contain the sparged air.
- The combination of sparging in the saturated zone and reduced air pressures in the unsaturated zone often leads to increases in groundwater table elevation in the vicinity of the sparge wells. As mentioned previously this may cause migration of phase separated liquid away from the site.
- The stimulation of in situ biological degradation through oxygenation of the subsurface may lead to biological fouling. Precipitation of metal carbonates and oxides can 'clog' the aquifer.
- Air emissions may require treatment. As a result residual liquids and spent activated carbon may require treatment and disposal.

Data Needs: In addition to those parameters described in the introduction to this section, the following characteristics should be determined; groundwater flow rate, aquifer permeability, presence of low permeability layers, presence of DNAPLs, depth of contamination, contaminant volubility and solubility, and groundwater chemistry in terms of possible fouling components (Fe and Mn).

Characteristics determined from a pilot test should include; unsaturated zone gas permeability and effective radius of influence of a single vapour extraction well.

Performance Data: ASP/SVE has been very successful in attaining negotiated Clean up goals relatively quickly. Typical time scales range between two months and three years.

Costs: The cost of a sparge system is dependent on the size of the site, degree of contamination, application depth and geology.

Case Studies:

- Air Sparge Pilot Test, Connecticut (Marley et al., 1992, Martin et al., 1992) - 4 week pilot study on a 2,000 sq. ft (186 m^2) test cell contaminated with TCE.
- Full scale AS/SVE system, Germany (Gudemann & Hiller, 1988) - In 8 months 4,000 kg of solvent was removed from a quaternary sand and gravel aquifer.
- Full scale AS/SVE system, USA (Brown et al., 1991) - A coarse sand aquifer contaminated by TCE, PCE, TCA, 1,2-DCE and petroleum hydrocarbons was successfully remediated using an AS/SVE system.

References:

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TECHNOLOGY 16 - VACUUM VAPOUR EXTRACTION

Description : Vacuum vapour extraction (also known as well air stripping) relies on the air stripping mechanism to recover volatile DNAPLs. Air is injected into a vacuum vapouriser well, lifting the contaminated water and allowing additional groundwater flow into the well. Once in the well, the VOC component in the water transfers to the vapour phase and is extracted through the water as air bubbles to a vapour extraction system in the top of the well. The partially treated groundwater is forced into the unsaturated zone and recirculated.

The vacuum vapourising wells (UVB in German: Unterdruck Verdampfer Brunnen) are divided into two segments; an extraction zone where groundwater is extracted, and a stripping region in which air stripping, vacuum extraction and groundwater recirculation occurs.

The technology is commercially available and has been implemented on a full scale in Europe. The UVB and GZB (Groundwater circulation wells - In German; Grundwasser Zirkulations Brunnen) have been patented by IEG mbH (Reutlingen, Germany).

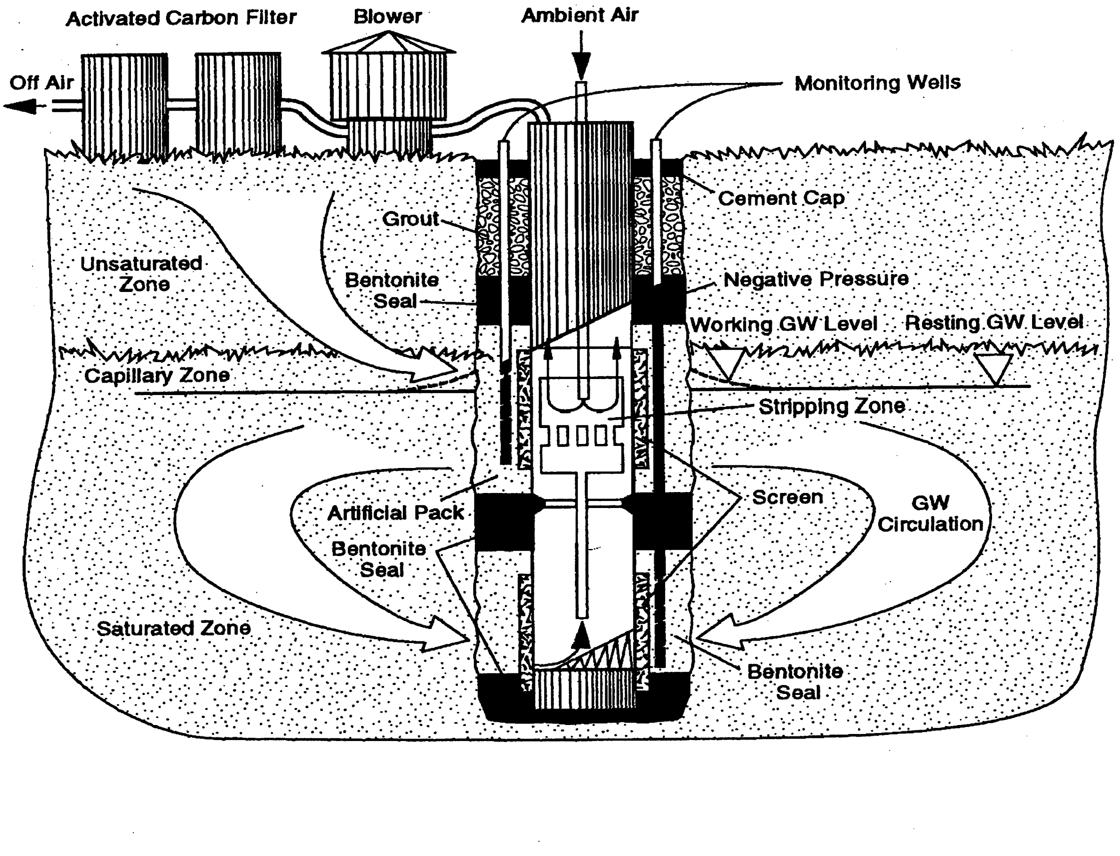

Figure 6.8: Vacuum vapour extraction well (USEPA, 1994).

Applicability: UVB can be applied to sites contaminated with aqueous phase volatile and semi volatile compounds having Henry's Law Coefficients greater than 10^5 atm-m^3/mole. It is not known whether separate phase liquids will be mobilised and the solubilisation process will be diffusion limited. Therefore, application to DNAPL contaminants is restricted.

Hydraulic conductivities at treated sites have been in the range of 10^{-3}m/s to 10^{-6}m/s, and ambient groundwater velocities that have been accommodated have been as high as 1 m/d.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- The contaminant must be volatile, insoluble and/or biodegradable.
- Shallow aquifers may limit process effectiveness.
- The stimulation of in-situ biological degradation through oxygenation of the subsurface may lead to biological fouling. Precipitation of metal carbonates and oxides can 'clog' the aquifer.
- Air emissions may require treatment. As a result residual liquids and spent activated carbon may require treatment and disposal.

Data Needs: Good site characterisation is required to avoid cross contamination of unconfined and confined aquifers. In addition the following characteristics should be determined; groundwater flow rate, aquifer permeability, presence of low permeability layers, depth of contamination, contaminant volubility and solubility, and groundwater chemistry in terms of possible fouling components (Fe and Mn).

Characteristics determined from a pilot test should include; unsaturated zone gas permeability, and effective radius of influence of a single vacuum vapourizer well.

Performance Data: Numerous sites within Europe containing immiscible compounds are reported to have been remediated to concentrations in the range of 10 to 1000 ppb. These include sites contaminated by PCE, TCE, TCA, 1,2-DCE, DCM and BTEX compounds in sandy to silty soils.

Costs: Cost estimates can be based on costs for AS/SVE and pump-and-treat systems due to the use of common elements. A breakdown of capital costs from one project indicated the following percentages: investigations planning etc. (22%), monitoring and field work (22%), analytical work (8%), borings and UVB installations (15%), vapour treatment and DNAPL disposal (24%) and energy cost (9%).

Case Studies:

- Steel Processing Plant, Rhine-Ruhr region of Germany, (Herrling et al. 1991) - UVB technology was used to remove TCE from a sand and gravel aquifer. After one month of operation the level of contamination was reduced by 98%.
- Field Experiments, Mannheim-Kaferetal area, Germany, (Herrling et al. 1992) - The effect of flow reversal in the UVB on efficacy of clean-up was investigated.

References :

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TECHNOLOGY 17 - SOIL VAPOUR EXTRACTION

Description : Soil vapour extraction (SVE) is an in situ, unsaturated zone soil remediation technology in which a vacuum is applied to the soil to induce the controlled flow of air and remove volatile and semi-volatile contaminants from the soil. The gas leaving the soil may be treated to recover or destroy the contaminants.

Vertical extraction vents are typically used at depths of 1.5m or greater. Horizontal extraction vents (installed in trenches or horizontal borings) can be used as warranted by contaminant zone geometry, drill rig access and site specific factors.

SVE is an accepted technology that has been operated commercially for several years. It is frequently selected as part of a treatment train for remediation at sites contaminated by VOCs.

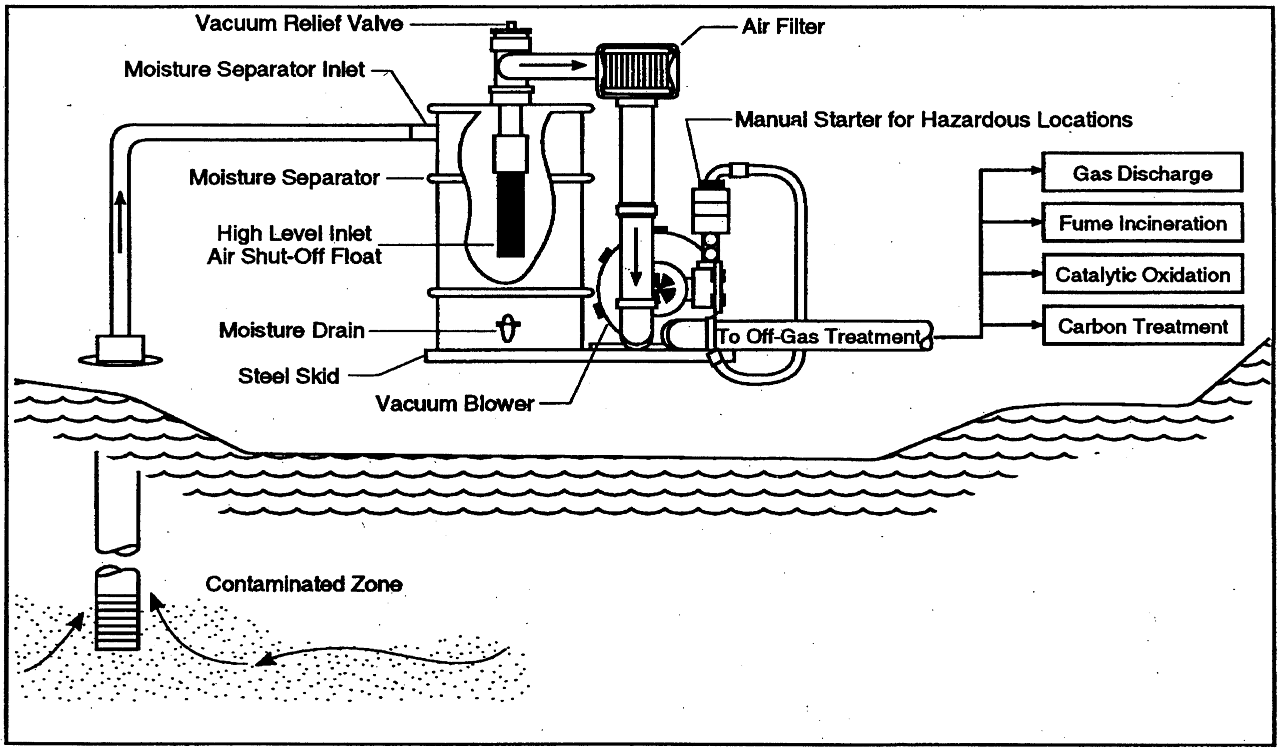

Figure 6.9: In situ soil vapour extraction (USEPA, 1994).

Applicability: SVE is applicable to VOC contaminants with a Henry's Law Constant of $>10^5$ atm-m^3/mole. The continuous flow of air through the soil can promote in-situ biodegradation of lower volatility organic contaminants that may also be present in the soil.

Soils must be well drained, contain low levels of organic materials and present relatively high pneumatic permeabilities ($>10^{-10}$ cm^2) for SVE to be successful.

Site heterogeneity may impede the implementation of SVE, however, the design and proper location of wells can overcome this problem.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- SVE is not effective in the saturated zone, however, lowering the water table can expose more media to SVE.
- Uneven gas flow through the contaminated regions and delivery at the extraction well may occur from soils with highly variable permeability.
- Soils with high moisture content and low air permeability require higher vacuums which can hinder the operation of SVE.
- Reduced removal rates result from soils that have a high organic content.
- Air emissions may require treatment. As a result, residual liquids and spent activated carbon may require treatment and disposal.

Data Needs: In addition to those parameters described in the introduction to this section, the following characteristics should be determined; soil pneumatic permeability, moisture and organic content in the soils, presence of low permeability layers, contaminant volubility and solubility.

Characteristics determined from a pilot test should include; extraction well radius of influence and gas flow rates, optimal applied vacuum and contaminant removal rates.

Performance Data: SVE remedial projects are typically completed within 18 months (depending on site condition). The technology is effective in reducing VOC concentrations in the unsaturated zone to below target levels, often removing between 98-100% of the contamination.

Costs: Capital costs cover well construction, vacuum blowers, vapour and liquid treatment systems, pipes, fittings and instrumentation. Operation and maintenance costs include labour, power, maintenance and monitoring activities.

Case Studies :

- San Fernando Valley Superfund Site, Area 1, Burbank, CA, (US EPA, 1991) - 98-99% removal of TCE and PCE contamination was achieved by in-situ SVE.
- Twin Cities Army Ammunitions Plant, MI (US EPA, 1991) - TCE concentrations of 2060mg/kg were reduced to 0.0085mg/kg by SVE.

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TECHNOLOGY 18 - STEAM ENHANCED EXTRACTION

Description : Steam enhanced extraction (SEE) is a form of thermally enhanced SVE. It uses steam injection to increase the mobility of volatile and semi-volatile contaminants. The process is otherwise identical to standard SVE treatment. As steam progresses through the porous media, it condenses and transfers its latent heat of vapourisation to the interstitial fluids; enhancing volatilisation and displacing the contaminants to the extraction point.

This remedial option is considered to be the most promising new technology for effectively treating and recovering DNAPL contaminants from source areas, pools and residually contaminated zones (USEPA, 1994a).

Pilot tests have been developed in the USA for its applications to DNAPL contaminats. However, full scale steam enhanced recovery systems (SERP) are in operation for the recovery of LNAPL hydrocarbons.

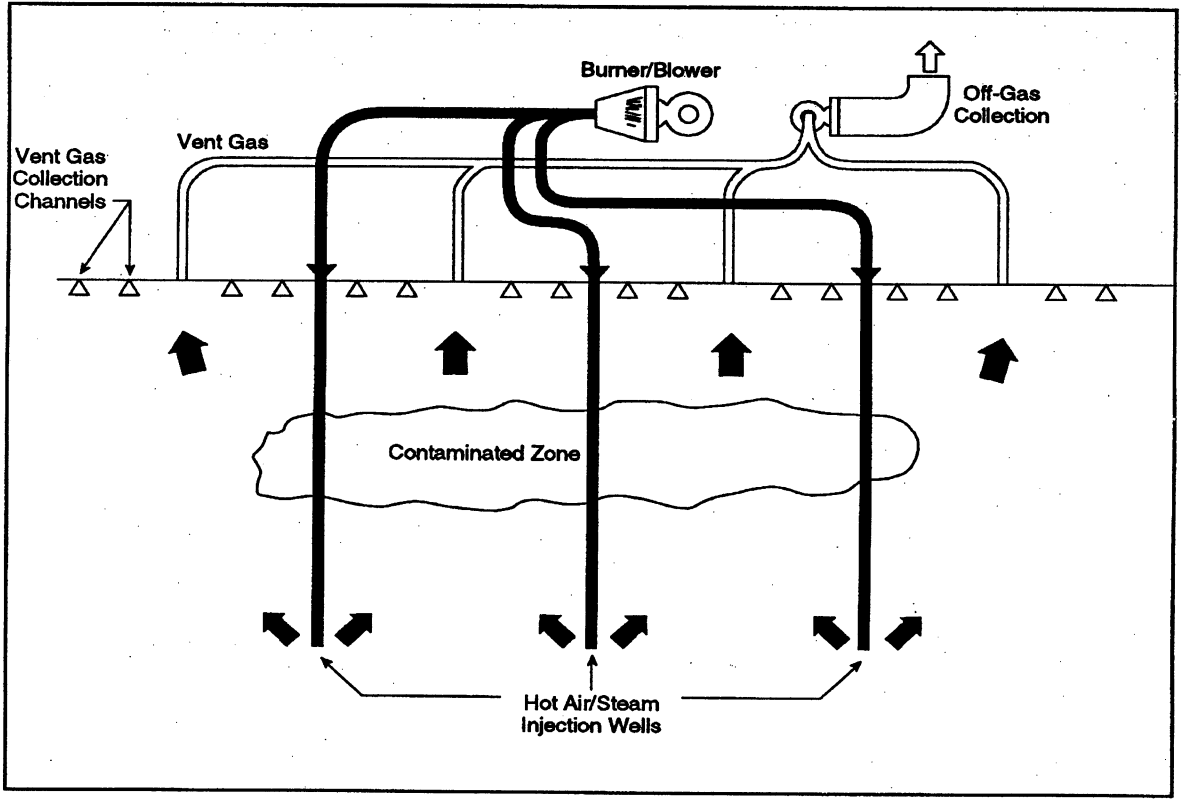

Figure 6.10: Thermally enhanced SVE system (USEPA, 1994b).

Applicability: Contaminants with low boiling points are completely removed from the steam zone and are displaced to the extraction point where they recondense to separate phase liquid. Contaminants with higher boiling points undergo enhanced volatilisation. This is proportional to the ratio of NAPL vapour pressures at the steam temperature. The NAPL vapours can be recovered in a gaseous form. Desorption of contaminants from the soil is also enhanced as the latent heat of adsorption is overcome.

SEE has been successfully conducted in a variety of saturated and unsaturated media; sand, ash, silty clays and gravels. Problems are encountered at sites dominated by silts and clays, however, SEE utilises both heat and mass transfer processes. The technology is therefore less susceptible to heterogeneity than other in-situ alternatives. To date, no applications of SEE in fractured rock have been developed.

At shallow depths, SEE treatment will leave the aquifer in a condition suitable for biodegradation. Thermally enhanced in situ biodegradation is regarded as a secondary benefit of SEE. Deeper applications of SEE may require greater injection pressures which could cause sterilisation of the aquifer media, biodegradation would then only occur after reacclimation or repopulation.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Performance in extracting certain contaminants varies depending on the maximum temperatures achieved by the system.
- The soil structure at the site may be modified.
- Soil that is tight or has a high moisture content has a reduced permeability to air, hindering the operation of SEE (because it requires more energy to increase the vacuum and temperature).
- Air emissions need to be regulated and possibly treated to eliminate possible harm to the public and the environment.

Data Needs: A detailed discussion of the data needs is provided in the introduction.

Performance Data: Evidence from preliminary estimates at the Livermore National Laboratory site indicate that contaminant removal by combined steam injection and vacuum extraction is forty times greater than that attainable by conventional SVE and groundwater pumping. A typical site consisting of 18,200 metric tonnes of contaminated media would require approximately nine months (USEPA, 1994b).

Costs: The factors of most influence to the treatment cost are: areal extent of treatment, depth of contamination, waste quantity and target clean-up goals, site preparation, ongoing surface activities and waste handling. SEE is anticipated to cost about US$40 - 100 per cubic metre, depending on site characteristics (Udell Technologies, 1991).

Case Studies:

- Pilot Study San Jose, California (Udell and Stewart, 1989) - 46 m^3 of unsaturated, silty soils contaminated by volatile and semi volatile LNAPLs and DNAPLs were treated. Initial contaminant concentrations of 2,065 mg/kg were reduced to 12mg/kg.

- Huntingdon Beach, California (USEPA, 1991a) - A full scale steam enhanced recovery process is being attempted to recover 135,000 gallons of diesel at depths of 40ft.

- Lawrence Livermore National Laboratory, Livermore (USEPA, 1991b) - Full scale SEE has been implemented to clean-up an aquifer contaminated by gasoline, to depths of 137ft.

References :

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USEPA (1994b) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, October.

TECHNOLOGY 19 - RADIO FREQUENCY HEATING

Description: Radio frequency (RF) heating is a form of thermally enhanced soil vapour extraction (SVE) that uses electromagnetic energy to increase the mobility of volatile and semi-volatile contaminants. The process is otherwise identical to standard SVE treatment and is based on the same principles as steam enhanced extraction (SEE). The process operates by enhancing volatilisation and displacing the contaminants to the extraction point.

Horizontal and vertical well configurations are possible. Full implementation of an RF heating system requires four major systems; RF energy deposition array, RF power generating, transmitting, monitoring and controlling, vapour barrier and containment, gas and liquid condensate handling and treatment. Any RF application must be designed to contain the electro-magnetic (EM) radiation within the specified soil treatment zone.

RF heating is a new technology for the clean up of hazardous waste sites, it has previously been used in the petroleum industry for oil recovery. For environmental application it is currently in the pilot and field-scale demonstration stage.

Applicability: Heating by RF is applicable to materials that typically volatilise in the temperature range 80°-300°C such as aliphatic and aromatic fractions of fuels and chlorinated solvents.

The technology is applicable to predominantly unsaturated sandy soils. The effect of soil stratigraphy on RF heating has yet to be evaluated.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- The soil water content greatly affects the viability of RF heating because of the large dielectric constant of water. It is therefore difficult to ascertain whether it is a suitable remedial technology for use in the saturated zone.
- The high temperatures involved may inhibit and destroy indigenous microorganisms, and could have an adverse impact on humic matter in the soil.
- Subsurface obstructions, such as buried utilities and abandoned foundations, appearing within the RF treatment zone may reduce the effectiveness of the process and potentially cause leakage of EM.
- Leakage of EM energy is a concern because of its interference with communications, navigation equipment and human health.
- Many of the effects of RF heating are unresolved at this time. Since the objective is to heat the subsurface, it is not clear as to whether RF heating has any distinct advantage over SEE.

Data Needs: A detailed discussion of the data needs is provided in the introduction.

Performance Data: The four major factors affecting performance of RF heating are: soil types (permeability), presence of metal drums/debris (disrupts current flow), contaminant type, and moisture content of the soil (increases energy requirements).

Costs: The estimated treatment costs vary according to the amount of native moisture present in the soil and the exact temperature of the treatment.

Case Study:

- Abandoned Fire Training Pit, Volk Air National Guard Base, Wisconsin (Dev and Downey, 1988; Dev et al., 1988, Sresty et al., 1992) - Sandy soils contaminated with numerous waste oils, fuels and solvents (concentrations of up to 4,000ppm) were treated. The technology demonstrated a 99% removal of volatile aromatics, aliphatics and semi volatile aromatics, and a 94% removal of semi volatile aliphatics.

References :

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TECHNOLOGY 20 - DUAL PHASE EXTRACTION

Description: A high vacuum system is applied to simultaneously remove liquid and gas from low permeability or heterogeneous formations. The vacuum extraction well includes a screened section in the zone of contaminated soils and groundwater. As the vacuum is applied to the well, soil vapour is extracted and groundwater is entrained by the extracted vapours. Once above grade, the groundwater and vapours are separated and treated.

Dual phase extraction is generally combined with bioremediation, air sparging and bioventing to help shorten the clean up time at a site.

Dual phase extraction is a full scale technology.

Applicability: The technology is applicable to VOC contaminants present in the dissolved and adsorbed phase. Dual phase extraction does not apply to the removal of separate phase compounds present below the water table surface. Therefore its relevance in remediation of DNAPL compounds is limited.

The technology is more effective than SVE for heterogeneous clays and fine sands.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Site geology and contaminant characteristics/distribution may limit effectiveness.

- Combination with complementary technologies (e.g. pump-and-treat) may be required to recover groundwater from high yielding aquifers.

- Dual phase extraction requires both treatment of groundwater and vapours.

Data Needs: In addition to those parameters described in the introduction to this section, the following characteristics should be determined; soil pneumatic permeability, moisture and organic content in the soils, presence of low permeability layers, contaminant volubility and solubility.

Characteristics determined from a pilot test should include; extraction well radius of influence and gas flow rates, optimal applied vacuum and contaminant removal rates.

Performance Data: Dual phase extraction systems are often used in combination with a number of technologies to shorten the clean up time (e.g. bioremediation air sparging, bioventing and pump-and-treat).

Costs: Costs are highly dependent on timescales and site characteristics.

Case Study:

- Lockheed Aeronautical Systems Co. Burbank, CA. - Dual phase extraction has successfully remediated soils and groundwater contaminated by dissolved and vapour phase PCE and TCE. The concentrations attained indicate 98-99.99% removal. (Contact: AWD Technologies, Inc. 49 Stevenson St, Suite 600, San Francisco, CA 94105).

References :

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TECHNOLOGY 21 - CONTROLLED EX SITU AEROBIC BIODEGRADATION

Description: Aerobic biodegradation is a process in which indigenous or inoculated microorganisms degrade organic contaminants found in soil and/or groundwater. In the presence of sufficient oxygen, the microorganisms will ultimately convert many organic contaminants to carbon dioxide, water and microbial cell mass.

Ex situ bioremediation typically involves excavated soil being deposited in lined beds, approximately 12 - 18 inches deep. The temperature, nutrient and oxygen supply is controlled and any leachate produced is collected. Variations of the technique include composting (thicker beds) and land farming (soil is spread thinly over a larger area and turned over repeatedly). Alternatively, the soil is mixed with water to form a slurry. It is then treated in a bioreactor where rate limiting factors can be controlled.

Aerobic biodegradation has, and is, being extensively used for petroleum hydrocarbon remediation. The technique has only just been extended to chlorinated solvents and first results are awaited.

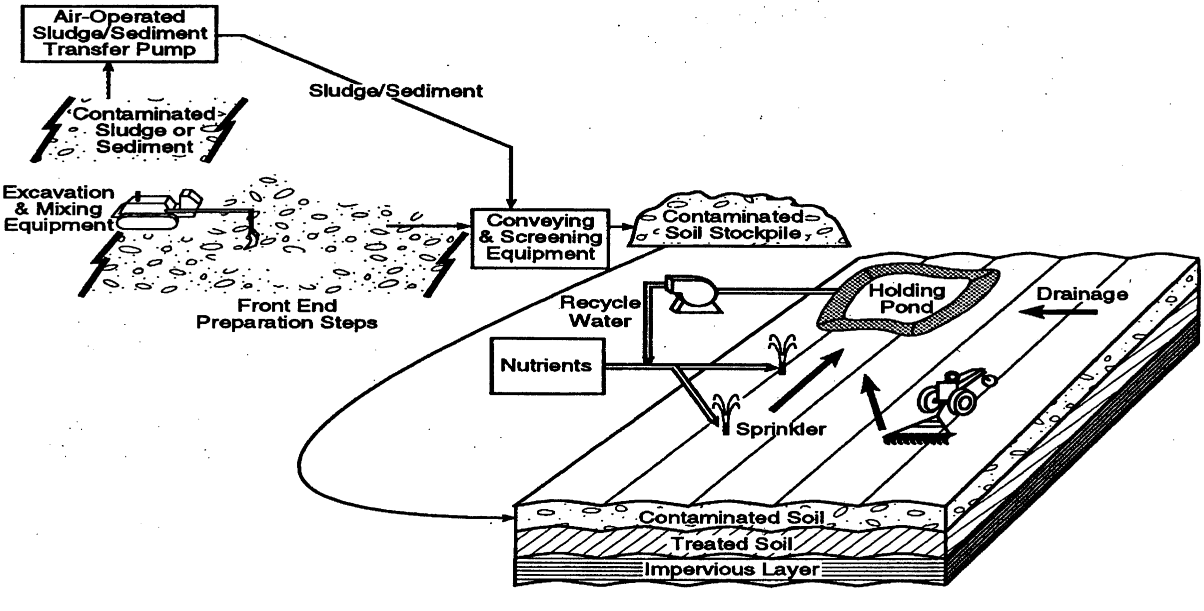

Figure 6.11: Typical controlled treatment unit for solid phase bioremediation (USEPA, 1994).

Applicability: Highly chlorinated solvents do not appear to undergo aerobic degradation. However, if dechlorination occurs under anaerobic conditions, a less chlorinated and often more aerobically degradable product, is produced. Less chlorinated solvents can be degraded by aerobic processes alone.

Ex situ bioremediation of soil applies only to the remediation of contaminants in the adsorbed phase.

Aerobic bioremediation is most suited to high permeability, granular soils with a moderate amount of organic matter. It is not well suited for low permeability media.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Large amounts of space are required.
- Degradation pathways for more complex aliphatics and aromatics may involve recalcitrant and/or toxic intermediates and end products.
- Excavation of contaminated soils is required which may lead to the uncontrolled release of VOCs.
- Clean up goals may not be attained if the soil matrix prohibits contaminant to microorganism contact.
- Increased concentrations of highly chlorinated organics are likely to be toxic to microorganisms.
- When using the slurry procedure, dewatering of soil fines after treatment can be expensive, and an acceptable method for disposing of non recycled wastewaters is required.

Data Needs: Site, soil and contamination characterisation are necessary to identify; amendment mixtures that best promote microbial activity, potential toxic degradation by-products, percent reduction and lower concentration limit of contaminant achievable, and potential degradation rates.

Performance Data: To date, ex situ controlled aerobic biodegradation has not been used to treat soils contaminated with chlorinated VOCs. Remediation timescales are likely to depend on the degradation rates of specific contaminants under controlled conditions.

The method has more commonly been used as a treatment technique to remove petroleum hydrocarbons.

Costs: Costs are dependent on the contaminant, the procedure employed, the need for additional treatment, and air emission control equipment.

References:

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USEPA (1994) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, Oct 1994.

TECHNOLOGY 22 - CONTROLLED EX SITU ANAEROBIC BIODEGRADATION

Description: Anaerobic degradation involves complete or partial metabolisation of organic compounds by non-oxygen utilising microorganisms. Reduction of halogenated hydrocarbons occurs through two generalised dehalogenation mechanisms; hydrogenolysis, entailing the substitution of halogen atoms with hydrogen atoms, and dihalo-elimination which results in the substitution of two adjacent halogen atoms by an ethene bond.

Implementation of controlled ex situ anaerobic degradation is not generally considered. However, the controlled ex situ aerobic degradation procedures may be modified to produce anaerobic conditions. Removing aeration systems and covering the soil piles will foster oxygen depletion by the microorganisms and result in the development of effective anoxic or anaerobic conditions (USEPA, 1994).

Applicability: Anaerobic bioremediation is suitable for degradation of the highly chlorinated organic solvents. Optimum degradation rates may be achieved, however, by a combination of anaerobic and aerobic processes.

Ex situ bioremediation of soil applies only to the remediation of contaminants in the adsorbed phase.

Similar to aerobic biodegradation, anaerobic bioremediation is most suited to high permeability, granular soils, with a moderate amount of organic matter. It is not well suited for low permeability media.

Limitations: Major factors that limit the applicability and effectiveness of the process include: :

- Large amounts of space are required.
- Excavation of contaminated soils is required which may lead to the uncontrolled release of VOCs.
- Clean up goals may not be attained if the soil matrix prohibits contaminant to microorganism contact.
- Increased concentrations of highly chlorinated organics are likely to be toxic to microorganisms.
- When using the slurry procedure, dewatering of soil fines after treatment can be expensive, and an acceptable method for disposing of non recycled wastewaters is required.
- Anaerobic conditions are potentially much harder to simulate and maintain in an ex situ environment.

Data Needs: Site, soil and contamination characterisation are necessary to identify; amendment mixtures that best promote microbial activity, potential toxic degradation by-products, percent reduction and lower concentration limit of contaminant achievable, and the potential degradation rate.

Performance Data: To date, ex situ controlled anaerobic biodegradation has not been used to treat soils contaminated with chlorinated VOCs. However, remediation timescales are likely to depend on the degradation rates of specific contaminants under controlled conditions.

The method has more commonly been used as a treatment technique to remove petroleum hydrocarbons. In the USA, a pilot study reduced Total Petroleum Hydrocarbons (TPH) from 1200 to 120 ppm after 2 months.

Much remains unknown about the anaerobic mineralisation of halogenated hydrocarbons. The lack of full scale demonstration sites involving this technology makes it difficult to judge the contaminant removal efficiency.

Costs: Costs are dependent on the contaminant procedure employed, the need for additional treatment and air emission control equipment.

Case Study:

- (No field applications of ex situ anaerobic degradation for removal of DNAPL compounds are known).

References:

Hinchee R.E., A. Leeson, L. Semprini, S.K.Ong (1994) *Bioremediation of Chlorinated and Polycyclic Aromatic Hydrocarbon Compounds.*

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USEPA (1993) *Bioremediation Resource Guide.* EPA/542/B-93/004.

USEPA (1994) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, Oct 1994.

TECHNOLOGY 23 - LIQUID PHASE CARBON ADSORPTION

Description: Groundwater is pumped through a series of vessels containing activated carbon to which dissolved contaminants adsorb. When the concentration of contaminants in the carbon bed exceeds a certain level, the carbon can be regenerated in place, removed and regenerated at an off-site facility or removed and then disposed.

Reactor configurations may either have a fixed bed or pulsed moving bed. The fixed bed configuration is the most widely used for adsorption from liquids. Carbon can be used in conjunction with steam reforming, a technology designed to destroy halogenated solvents adsorbed on the carbon. A reaction occurs with superheated steam in a commercial reactor.

Adsorption by activated carbon has a long history of use in treating municipal, industrial and hazardous wastes.

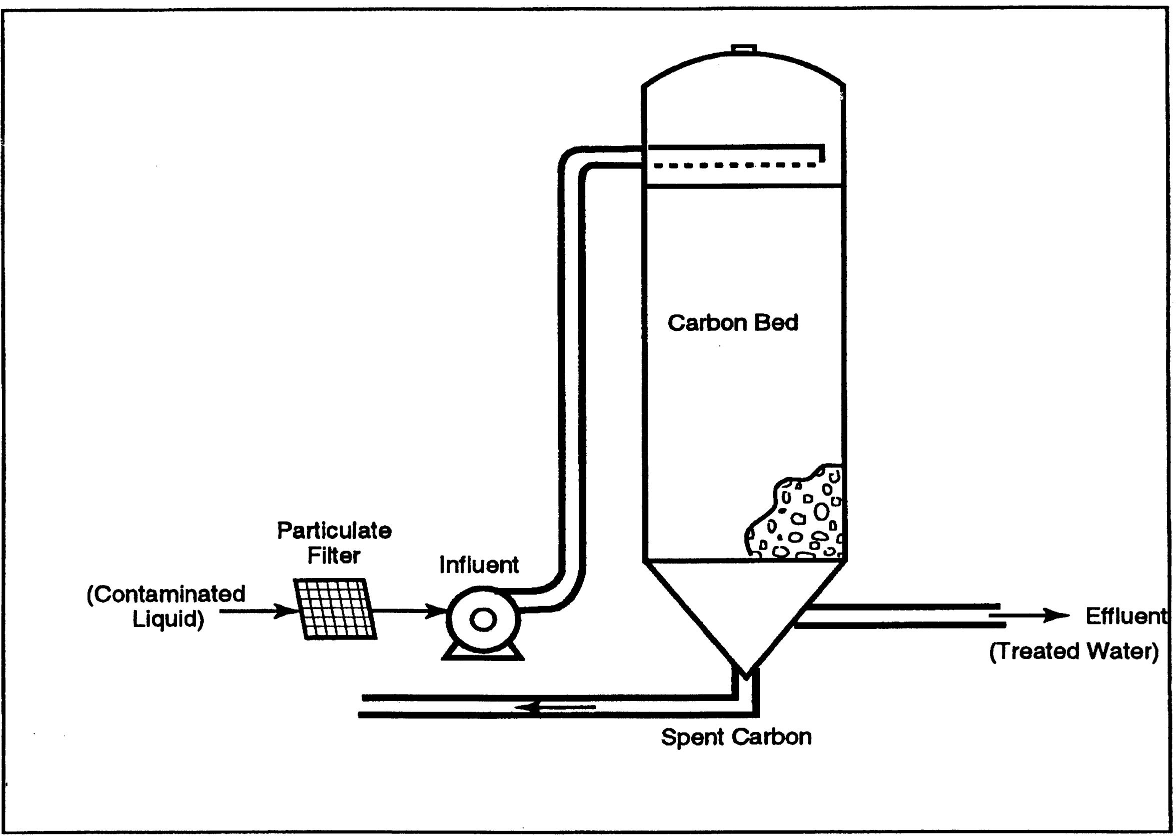

Figure 6.12: Fixed Bed Carbon Adsorption System (USEPA, 1994b).

Applicability: Liquid phase carbon adsorption is effective for removing contaminants at low concentrations (<10mg/l) from water at almost all flow rates, and for removing higher concentrations of contaminants from water at low flow rates. It is particularly effective for polishing water discharges from other remedial technologies to attain regulatory compliance.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- The presence of multiple contaminants can affect process performance.
- Metals can foul the system.
- Costs are high if used as the primary treatment on waste streams with high contaminant concentration levels.
- Type and pore size of the carbon, as well as the operating temperature, will affect process performance.
- Water soluble compounds and small molecules are not adsorbed well.

Data Needs : The major design variables for liquid phase carbon applications are empty bed contact time, usage rate and system configuration. Particle size and hydraulic loading are often chosen to minimise pressure drop and reduce (or eliminate) backwashing.

Performance Data : Adsorption by activated carbon has a long history of use in treating municipal, industrial and hazardous wastes. The concepts, theory and engineering aspects of the technology are well developed. It is a proven technology with documented performance data. Carbon adsorption is a relatively non specific adsorbent and is effective for removing many organic contaminants (liquid and gaseous).

Costs : Costs associated with the technology are dependent on waste stream flow rates, type of contaminant, concentrations and site and timing requirements.

Case Study:

- McClellan Air Force Base, California, USA (USEPA 1995). Activated carbon used to treat chlorinated solvents in conjunction with air stripping, an ongoing investigation.

References:

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Zappi, M.E., B.C. Fleming, C.L. Teetar (1992) *Draft Treatability of Contaminated Groundwater from the Lang Superfund Site.* USAE-WES.

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TECHNOLOGY 24 - SOIL WASHING

Description: Soil washing is an ex situ water based process for scrubbing soils to remove contaminants. The process removes contaminants from soils in two ways: by dissolving or suspending them in the wash solution or by concentrating them into a smaller volume of soil through particle size separation, gravity separation and attrition scrubbing. Additives such as surfactants, acids or chelating agents are used to increase separation efficiencies.

Soil washing systems that incorporate both techniques yield the greatest success for soils containing organic contaminants. The particle separation technique separates the silt and clay particles (to which contaminants preferentially bind) from the clean sand and gravel. The clay/silt fraction can then be further reduced through gravity separation (removing high and/or low specific gravity particles) or attrition scrubbing (removes adherent contaminant films from coarser particles). Alternatively, the particles are scrubbed and the soluble contaminants dissolve from the particle surfaces into the liquid phase.

Soil washing has been used extensively in Europe and to a lesser degree in the USA. Soil washing is a fully developed technology and has been operated commercially for several years.

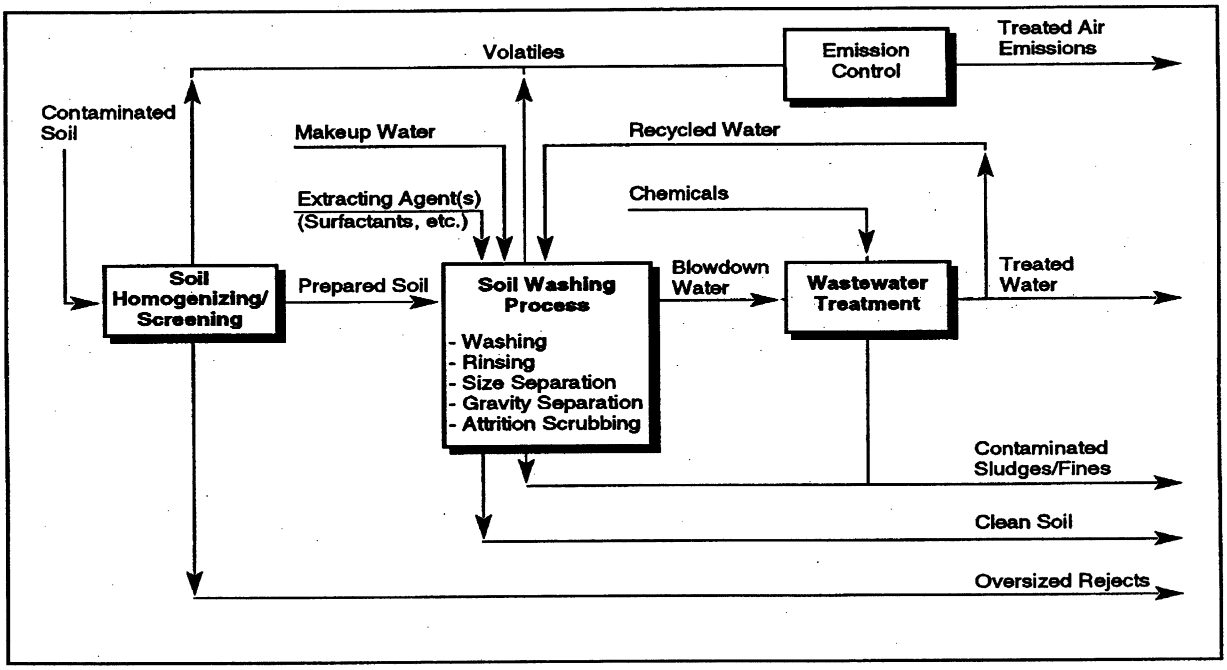

Figure 6.13: Soil Washing Process (USEPA, 1994a).

Applicability: Soil washing effectively treats a wide variety of wastes but is more effective at treating contaminants with high vapour pressures and water solubility quotients. The addition of surfactants, acids or chelating agents can improve the suitability of the process to some DNAPL contaminants.

The process is best suited for sandy and sandy loam soils that are low in organic matter and clay content. Soils with a high cation exchange capacity tend to bind pollutants more tightly. This can limit the effectiveness of the soil washing process to separate the pollutant from the soil.

Limitations: Major factors that may limit the applicability and effectiveness of the process include :

- Fine soil particles (e.g. silt and clays) may require the addition of a polymer to remove them from the washing fluid.
- Complex waste mixtures (e.g. metals with organics) make formulating a suitable washing fluid difficult and treatment may require sequential steps with different additives.
- High humic content limits the effectiveness of the process and soils may require pretreatment.
- Contaminated clay fines and sludge may require further treatment with other technologies, e.g. incineration, thermal desorption, solidification/stabilisation or bioremediation.
- The aqueous stream will require treatment.

Data Needs: The most important factors to identify are the specific blend of physical and chemical characteristics of the soil, and the spatial distribution of the contaminant within the soil. The key soil and contaminant properties that need to be measured are summarised in the introduction to this section.

Performance Data: Removal efficiencies for soil washing depend on the type of contaminant and washing fluid. Soil washing can be used as a relatively cost effective way to reduce the volume of material in need of disposal, or treated by a more energy intensive process.

Bench tests conducted by USEPA have found that more than 99.7% removal of contaminant can be achieved for selected chlorinated hydrocarbons.

Costs: Soil washing is a relatively low cost alternative for separating wastes and can be used as a relatively cost effective way of reducing the amount of contaminated material to be treated by more energy intensive processes. Costs are highly dependent on site specific soil characteristics and the amount of soil to be treated as well as the treatment of residuals required.

Case Study:

- Pintsch near Hanau Frankfurt, Germany (Case Study 7) - Soil washing used to remediate excavated, unsaturated loamy river deposits, contaminated by refinery waste oil containing dissolved organic solvents.

References:

Mann, M.J. et al. (1993) *Innovative Site Remediation Technology: Soil Washing/Soil Flushing*. Ed. W.C. Anderson. Prepared by WASTECH.

USEPA (1994a) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, Oct 1994.

USEPA (1994b) *Contaminants and Remedial Options at Solvent Contaminated Sites.* EPA/600/R-94/203, Nov. 94.

TECHNOLOGY 25 - SOLVENT EXTRACTION

Description: Solvent extraction is a physical separation process that removes contaminants from soils. The technology varies from soil washing in that it uses organic solvents to isolate contaminants rather than water improved by wash additives. There are three broad categories of solvent extraction; conventional, solution temperature fluid and subcritical fluid extraction.

Conventional solvent extraction uses organic solvents to selectively extract the contaminants of concern. Critical solution temperature fluid extraction uses solvents that are miscible with water at one temperature and insoluble at another. The solvents can then be recovered by steam stripping. Subcritical fluid extraction uses highly compressed gases to extract contaminants that generally resist extraction by conventional methods.

Excavated waste is prepared and placed in an extractor through which the solvent is passed. The solvent (including organic contaminants) is passed through a separator which produces concentrated contaminants and recyclable solvent.

Soil washing is a full scale technology and many commercial scale units are in operation in the USA.

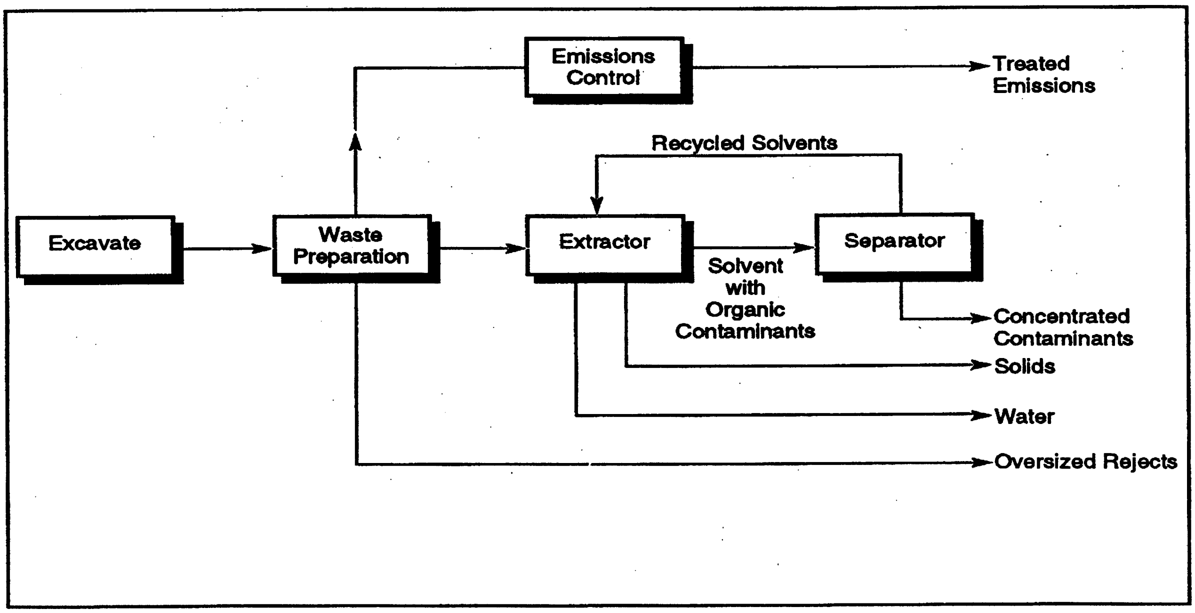

Figure 6.14: Solvent Extraction Process (USEPA, 1994a).

Applicability: Solvent extraction has been shown to be effective in treating soils containing primarily organic contaminants such as PCBs, VOCs and petroleum wastes. The technology is also thought to be effective for the removal of halogenated solvents.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Organically bound metals can be extracted along with the target organic pollutants. This restricts handling of the residuals.
- The presence of detergents and emulsifiers can unfavourably influence the extraction performance.
- Traces of solvent may remain in the treated solids; the toxicity of the solvent is an important consideration.
- Solvent extraction is generally less effective on organic substances which have very high molecular weights and are very hydrophilic.
- Some soil types and moisture content levels will limit process performance.

Data Needs: In addition to those parameters described in the introduction to this section, it is important to determine whether mass transfer or equilibrium will be the controlling factor. This is critical to the design of the unit and to the determination of whether the technology is appropriate for the waste.

Performance Data: System performance is influenced by the presence of detergents and emulsifiers, low pH materials and reactivity of organics with the solvent. The technology has been used to remove PCBs, PAHs, pesticides and herbicides from soils, and has been shown to remove greater than 99% of PCB's and PAH's found in river sediments.

Costs: Costs depend on waste volume, number of extraction stages and operating parameters (such as labour, maintenance, set up, decontamination and demobilisation).

Case Study:

To date there have been no recorded cases of solvent extraction technology in use to remediate DNAPL compounds. However, solvent extraction has been used to remediate soils contaminated by PCBs and other organics.

- Pinette Salvage Superfund Site, Washburn, Maine, USA - Solvent extraction used to remediate chlorobenzenes, dichlorobenzenes and trichlorobenzenes.

References

USEPA (1994a) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, Oct 1994.

USEPA (1994b) *Superfund Innovative Technology Evaluation Program.* EPA/540/R-94/526, Nov 1994.

USEPA (1994c) *Contaminants and Remedial Options at Solvent Contaminated Sites.* EPA/600/R-94/203, Nov, 1994.

TECHNOLOGY 26 - AIR STRIPPING

Description: Air stripping is a technology in which volatile organics are partitioned from groundwater by greatly increasing the surface area of the contaminated water exposed to air.

The process is typically conducted in a packed tower or an aeration tank. A typical packed tower sprays contaminated water over the packing in the column. The water falls to the base of the tower where it is collected in a sump. A blower at the base of the column forces air counter current to the water flow maximising the air/water contact. An aeration tank strips volatile compounds by bubbling air into a tank through which contaminated water flows. A forced air blower and a distribution manifold are designed to ensure air-water contact without the need for any packing materials.

Air stripping is a full scale technology that is commonly used both in the UK and abroad for the removal of VOCs from groundwater.

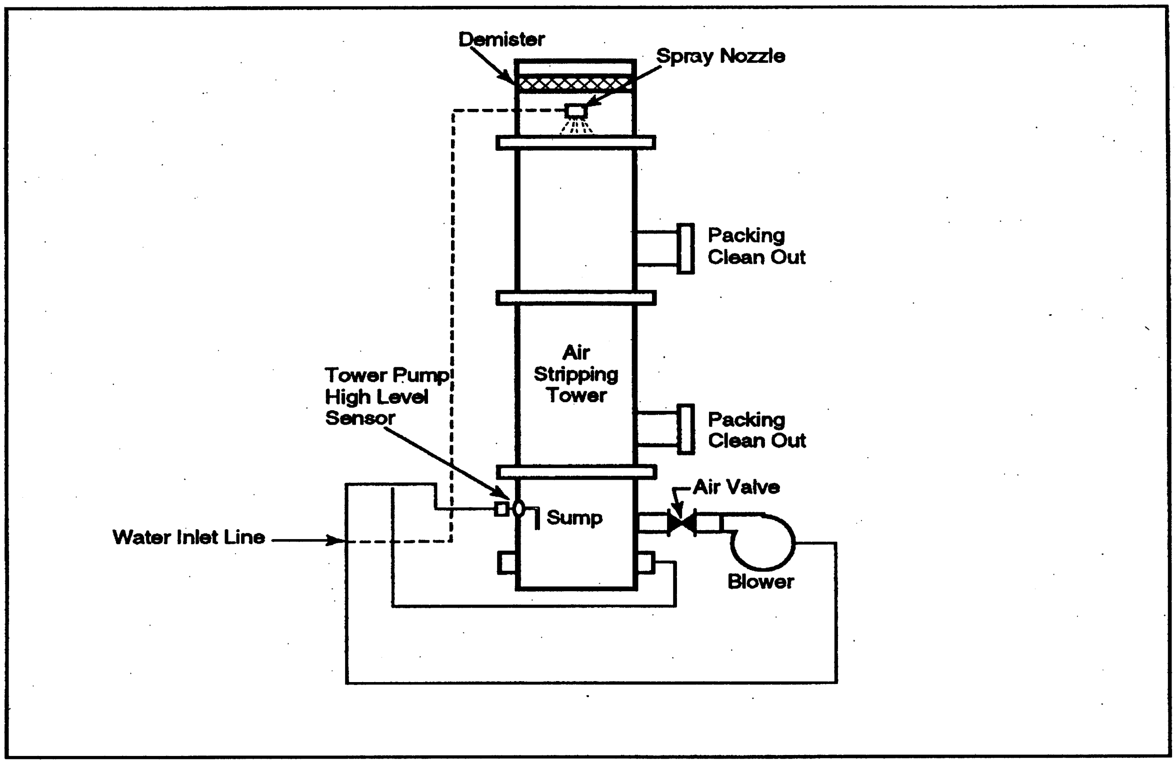

Figure 6.15: Air stripping tower (USEPA, 1994b).

Applicability: Air stripping is used to separate dissolved volatile contaminants from extracted groundwater. It is effective for organic compounds with Henry's Law Constant $>10^5$ atm-m^3/mol and has been used successfully to treat groundwater contaminated with TCE, DCE and PCE.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- The potential exists for inorganic or biological fouling of the equipment requiring pretreatment or periodic column cleaning.
- Consideration should be given to the Henry's Law Constant of the VOCs in the water stream and the type, and amount, of packing used in the tower.
- Compounds with low volatility at ambient temperature may require preheating of the groundwater.
- Off-gases may require treatment based on mass emission rate.

Data Needs: The following information is required to construct a properly sized tower to deal with a specific application: range of feedwater flow rates; range of water and air temperatures; whether the tower will operate continuously or intermittently; tower feed and discharge systems; height restrictions on the tower; influent contaminant identification and concentrations; mineral content; pH; requirements for effluent water contaminant concentrations; and restrictions on air discharge from the tower.

Performance Data: The removal efficiencies of air strippers can be improved by adding a second air stripper in series along with the first, heating the contaminated water, increasing the air/liquid ratio or heating the air. For aeration tanks, performance can be improved by adding chambers or trays or increasing the air supply.

Removal efficiencies of 99% have been commonly achieved using air stripping towers that have approximately 4.5 to 6m of packing.

Costs: Other than capital costs for the plant, the major operating cost is the electricity required for the groundwater pump, sump discharge pump and the air blower. Costs change with the size of the tower and the power required to operate the tower to the best of its ability.

Case Studies:

- US Department of Energy Savannah River Site, Aiken, South Carolina (USEPA 1995). Groundwater impacted with TCE and PCE was extracted and passed through an air stripper. The average removal efficiency for the air stripper was >99.9%. The process is ongoing and total costs are unavailable.
- Knitwear Manufacturers, Northumberland (Case Study 2) - Groundwater contaminated by PCE was extracted (via a private abstraction well) from a sand and gravel aquifer. The water was treated by air stripping before entering the factory supply system.

- Harwell Laboratory, Oxfordshire (Case Study 4) - A hydraulic containment system combined with air stripping and activated carbon adsorption was implemented to clean up a dissolved phase solvent plume in the Chalk aquifer.

(Case Studies 5, 8, 9 and 11 also document sites where ex situ air stripping has been used as a water treatment technology following groundwater extraction).

References :

Elliott, M.G., E.G. Marchand (1990) *USAF Air Stripping and Emissions Control Research.* In Proceedings of 14th Annual Army Environmental Synopsis, USATHAMA Report CETHA-TE-TR-90055.

Dietrich, C., D. Treichler, J. Armstrong (1987) *An Evaluation of Rotary Air Stripping for Removal of Volatile Organics from Groundwater.* USAF Environmental and Service Centre Report ESL-TR-86-46.

Shukla, H.M., R.E. Hicks (1990) *Process Design Manual for Stripping Organics.* Water General Corporation for EPA. EPA/600/12-84/139, NTIS PB 84 232628.

Singh S.P. (1989) *Air Stripping of Volatile Organic Compounds from Groundwater: An Evaluation of a Centrifugal Vapour Liquid Contractor.* USAF Environmental and Service Centre Report ESL-TR-86-46.

Wilson, J.H., R.M. Counce, A.J.Lucero, H.L. Jennings, S.P. Singh (1991) *Air Stripping and Emission Control Technologies:* Field Testing of Counter Current Packings, Rotary Air Stripping, Catalytic Oxidation and Adsorption Materials, ESL TR 90-51.

USEPA (1994a) *Superfund Innovative Technology Evaluation Program.* EPA/540/R-94/526, Nov 1994.

USEPA (1994b) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, Oct 1994.

USEPA (1995) *Abstracts of Remediation Case Studies.* EPA/542/R-95/001, Mar 1995.

TECHNOLOGY 27 - EX SITU SOIL VAPOUR EXTRACTION

Description: Ex situ soil vapour extraction (SVE) is analogous to in situ SVE in that a vacuum is applied to the soil to induce the controlled flow of air and remove volatile and semi-volatile contaminants from the soil. The gas leaving the soil may be treated to recover or destroy the contaminants.

Soil is excavated and placed over a network of above ground piping. A vacuum is then applied to encourage volatilization of organics. The process has advantages over in situ SVE in that: excavation of the soil leads to an increase in the number of passageways in the soil; shallow groundwater no longer limits the process; leachate collection is possible and treatment is more uniform and easily monitored.

SVE is an accepted technology that has been operated commercially for several years. It is frequently selected as part of a treatment train for remediation at sites contaminated by VOCs.

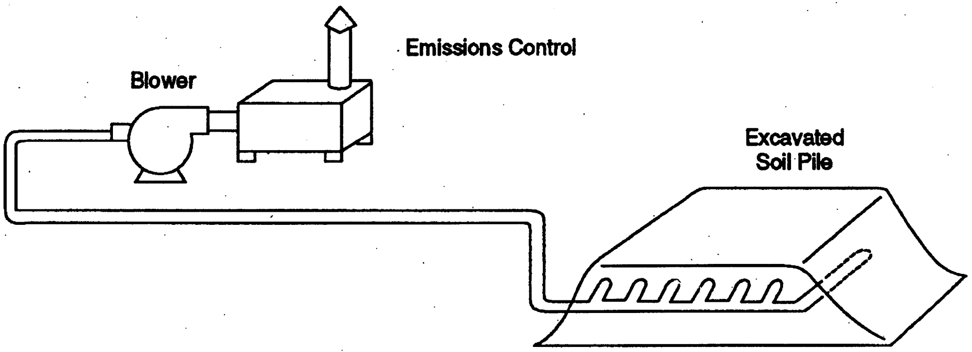

Figure 6.16: Ex situ SVE system (USEPA, 1994a).

Applicability: The target group for ex situ SVE is VOCs. SVE is applicable to VOC contaminants with a Henry's Law Constant of $>10^5$ atm-m^3/mole. The continuous flow of air through the soil can promote biodegradation of lower volatility organic contaminants that may also be present in the soil.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Air emissions occurring during excavation and materials handling may possibly require treatment.
- High humic content or compact soil inhibits volatilisation
- As a result of air emission treatment, SVE may require the treating of residual liquid and spent activated carbon, increasing the project cost.
- A large amount of space is required and the technology may be limited to sites with a relatively small amount of contaminated soil.

Data Needs: In addition to those parameters described in the introduction to this section, the following characteristics are particularly important; soil pneumatic permeability, moisture and organic content in the soils, contaminant volatility and solubility. Key operating parameters include air flow rate and vacuum pressure required. These are estimated by conducting a pilot test.

Performance Data: The time required to remediate a site using ex situ SVE is highly dependent on the specific soil and chemical properties of the contaminated media. Clean up of a typical site, consisting of approximately 20,000 tonnes of contaminated media, would require 12 to 36 months.

Costs: Capital costs cover plant construction, vacuum blowers, vapour and liquid treatment systems, pipes, fittings and instrumentation. Operation and maintenance costs include labour, power, maintenance and monitoring activities.

Case Study:

To date, no cases of ex situ soil vapour extraction being used to remediate DNAPL contamination have been recorded. However, the procedure has been used successfully at an Air Force Base in Utah, USA, to reduce levels of jet fuel from 410 mg/kg to 3.8 mg/kg.

References:

USEPA (1990) *State of Technology Review: Soil Vapour Extraction System Technology. EPA Hazardous Waste Engineering Research Laboratory.* Cincinnati, OH, EPA/600/2-89/024.

USEPA (1991) *AWD Technologies, Inc.-Integrated Vapour Extraction and Steam Vacuum Striping.* EPA RREL, series includes Applications, Analysis, EPA/540/A5-91/002, PB92-218379; and Demonstration Bulletin, EPA/540/M5-91/002.

USEPA (1992) *Proceedings of the Symposium on Soil Venting.* EPA/600/R-92/174, Sept 1992.

USEPA (1994a) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, Oct 1994.

USEPA (1994b) *Contaminants and Remedial Options at Solvent-contaminated sites.* EPA/600/R-94/203, Nov. 94.

USEPA (1994c) *Soil Vapour Extraction (SVE) Treatment Technology Resource Guide.* EPA/542/B-94/007, Sept 1994.

TECHNOLOGY 28 - DEHALOGENATION BASE CATALYZED DECOMPOSITION

Description: Dehalogenation or dechlorination of chlorinated aliphatic compounds occurs through an elimination reaction and the formation of a double or triple carbon-carbon bond. This converts the more toxic compounds into less toxic, more water soluble products that are more readily separated from the soil and treated.

Contaminated soil is screened, processed with a crusher and pug mill, and mixed with sodium bicarbonate. The mixture is heated to above 330°C in a rotary reactor to decompose and partially volatilise the contaminants. The contaminant is partially decomposed rather than being transferred to another medium. Washwater may require treatment prior to discharge and volatile air emissions can be controlled by condensation and/or activated carbon adsorption.

Dehalogenation Base Catalyzed Decomposition (BCD) has been used successfully at bench and pilot test levels to treat dioxin, PCB, chlorinated pesticides and PCP. At laboratory scale, dehalogenation has shown to be effective on DNAPL compounds such as ethene, tetrachloromethane and dichloromethane.

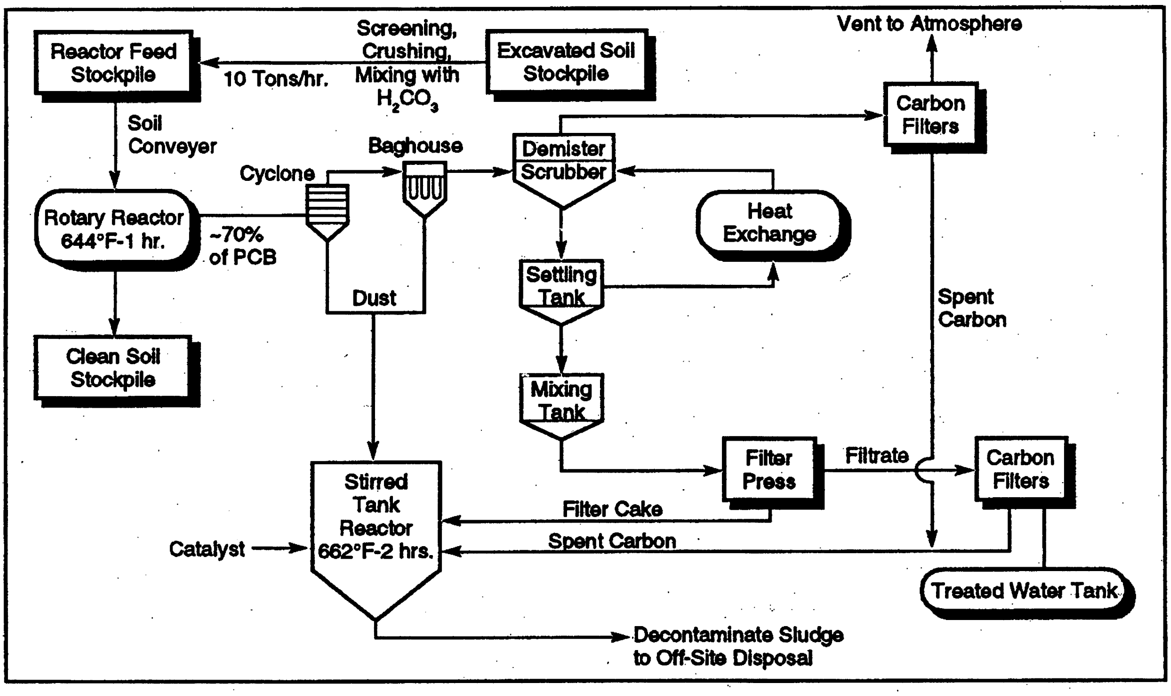

Figure 6.17: BCD Dehalogenation Process (USEPA, 1994a).

Applicability: BCD dehalogenation treats contaminated soil only. The target contaminant groups are halogenated SVOCs and pesticides. The technology can be used to treat halogenated VOCs but will generally be more expensive than alternative technologies.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- High clay and moisture content will increase treatment costs.
- Treatment is very expensive for large volumes of soil.

Data Needs: In addition to the soil and contaminant characteristics described in the introduction to this section, the following factors should be considered: treatability tests should be conducted to identify parameters (such as water, alkaline metals and humus content in the soils), the presence of multiple phases, pH, and total organic halides that could affect processing time and cost.

Performance Data: There have been no commercial applications of this technology to date. A successful test run with 15 tonnes of PCB soil was conducted in February 1994 by USEPA. Initial average levels of 2500 ppm PCB were reduced to less than 10 ppm. No time period was specified.

Costs: Factors such as high clay or moisture content may raise the treatment cost. Estimated costs in the USA are US$ 245 per tonnes but do not include excavation, refilling, residue disposal or analytical costs.

Case Study:

To date, no field scale studies using dehalogenation (BCD) to treat DNAPLs have been conducted.

References :

NCEL (1990) *Engineering Evaluation/Cost Analysis for the Removal of Treatment of PCB Contaminated Soils at building 3000 Site PWC Guam.*

NEESA and NCEL (1991) *Chemical Dehalogenation Treatment: Base Catalyzed Decomposition Process, Technical Data Sheet.*

NEESA and NCEL (1992) *Chemical Dehalogenation Treatment: Base Catalyzed Decomposition Process, Technical Data Sheet.*

USEPA (1991) *BCD: An EPA Patented Process for Detoxifying Chlorinated Wastes.* EPA, ORD.

USEPA (1994a) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, Oct 1994.

USEPA (1994b) *Physical/Chemical Treatment Technology Resource Guide.* EPA/542/B-94/008, Sept 1994.

TECHNOLOGY 29 - DEHALOGENATION (GLYCOLATE)

Description: Dehalogenation or dechlorination, of chlorinated aliphatic compounds occurs through an elimination reaction and the formation of a double or triple carbon-carbon bond. This converts the more toxic compounds into less toxic, more water soluble products that are more readily separated from the soil and treated.

Contaminated soils are mixed with a reagent (alkaline polyethylene glycol aka APEG) and heated in a treatment vessel. The reaction causes the polyethylene glycol to replace a halogen molecule and results in a reduction in toxicity. Washwater may require treatment prior to discharge and volatile air emissions can be controlled by condensation and/or activated carbon adsorption.

Dehalogenation has been used successfully at bench and pilot test levels to treat dioxin, PCB, chlorinated pesticides and PCP. At laboratory scale, a variation of the reagent (alkaline tetraethene glycol aka ATEG) has been shown to be effective when used on halogenated aliphatic (DNAPL) compounds such as ethene, tetrachloromethane and dichloromethane.

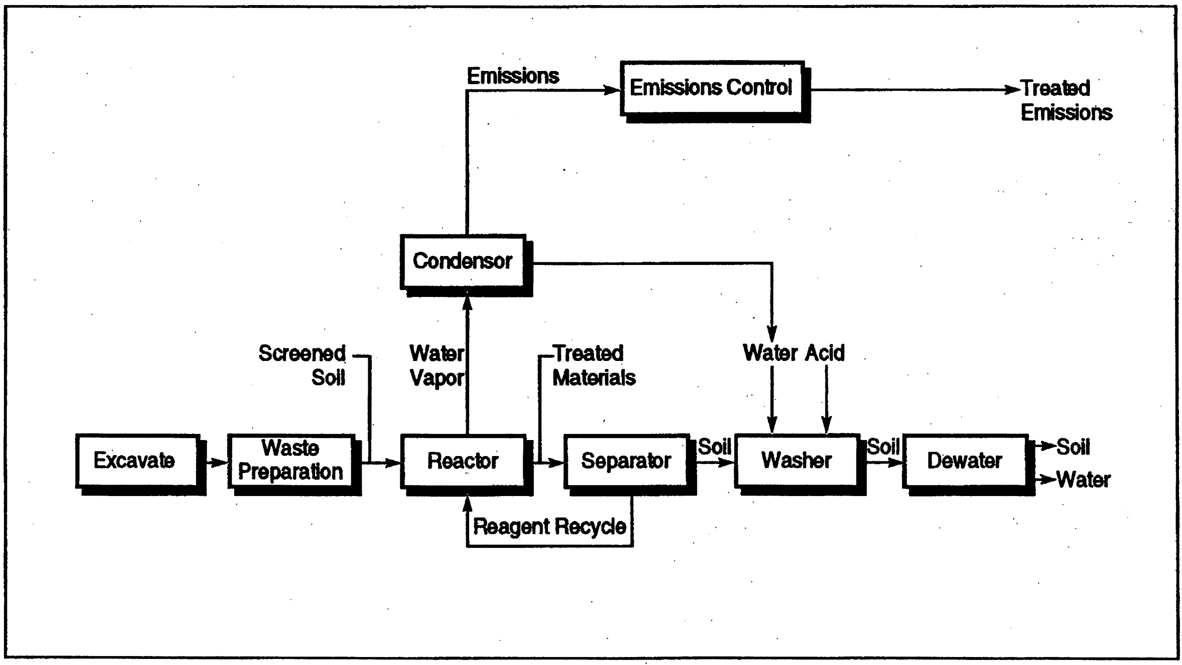

Figure 6.18:Dehalogenation (Glycolate) Process (USEPA, 1990).

Applicability: Dehalogenation (glycolate) is an ex situ treatment for contaminated soil only. The target groups for glycolate dehalogenation are halogenated SVOCs and pesticides. The technology can be used but may be less effective against selected halogenated VOCs and will generally be more expensive than alternative technologies.

Limitations: Factors that may limit the applicability and effectiveness of the process include:

- The technology is generally not cost effective for large waste volumes.
- Media water content above 20% requires excessive reagent volume.
- Concentrations of chlorinated organics greater than 5% require large volumes of reagent.

Data Needs: In addition to the soil and contaminant characteristics described in the introduction to this section, the following factors should be particularly considered: treatability tests should be conducted to identify parameters such as water, alkaline metals and humus content in the soils; the presence of multiple phases; pH; and total organic halides that could affect processing time and cost.

Performance Data: Bench and pilot scale testing has been successful for treating dioxins, PCB, chlorinated pesticides and PCPs. The technology has achieved removal efficiencies of up to 98% for chlorobenzene.

Costs: At present, the costs involved in this technology are high. As advances are made in the development of the technology, costs are expected to fall. Costs depend primarily on the amount of soil to be treated.

Case Study:

To date, no field scale studies using glycolate dehalogenation to treat DNAPLs have been conducted.

References:

Taylor, M.L., et al. (PEI Associates) (1989) *Comprehensive Report on the KEPG Process for Treating Chlorinated Wastes.* EPA Contract No. 68-03-3413. EPA RREL, Cincinnati, OH.

USEPA (1987) *Catalytic Dehydrohalogenation: A Chemical Destruction Method for Halogenated Organics, Project Summary.* EPA/600/52-86/113.

USEPA (1989) *Innovative Technology - Glycolate Dehalogenation.* EPA OSWER, Washington DC, Directive 9200 5-254FS.

USEPA (1990) *Chemical Dehalogenation Treatment: APEG Treatment, Engineering Bulletin.* EPA OERR and ORD, Washington DC, EPA/540/2-90/015.

USEPA (1990) *Treating Chlorinated Wastes with the KEPG Process, Project Summary.* EPA RREL, Cincinnati, OH, EPA/600/S2-90/026.

USEPA (1992) *A Citizens Guide to Glycolate Dehalogenation.* EPA, OSWER, Washington DC. EPA/542/F-92/005.

USEPA (1994) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, Oct 1994.

TECHNOLOGY 30 - ULTRAVIOLET OXIDATION

Description: Ultraviolet (UV) oxidation is a destruction process that oxidises organic constituents in wastewaters, by the addition of strong oxidisers and irradiation with UV light. Oxidation reactions are achieved through the synergistic action of UV light in combination with ozone (O_3) and/or hydrogen peroxide (H_2O_2). If complete mineralisation is achieved, the final products of oxidation are carbon dioxide, water and salts.

Hydrogen peroxide is added to contaminated groundwater and passed through a mixer into a reactor. Ozone may be added to the process either prior to the mixer or directly into the reactor. Reactor off gasses are treated by ozone decomposition, thermal destruction or carbon adsorption. The processes can be configured in batch or continuous flow modes depending on the throughput under consideration.

The process is a well established disinfection technology for drinking water and wastewater. The main advantage of UV oxidation is that it is a destruction process as opposed to air stripping or carbon adsorption whereby contaminants are extracted and concentrated in a separate phase.

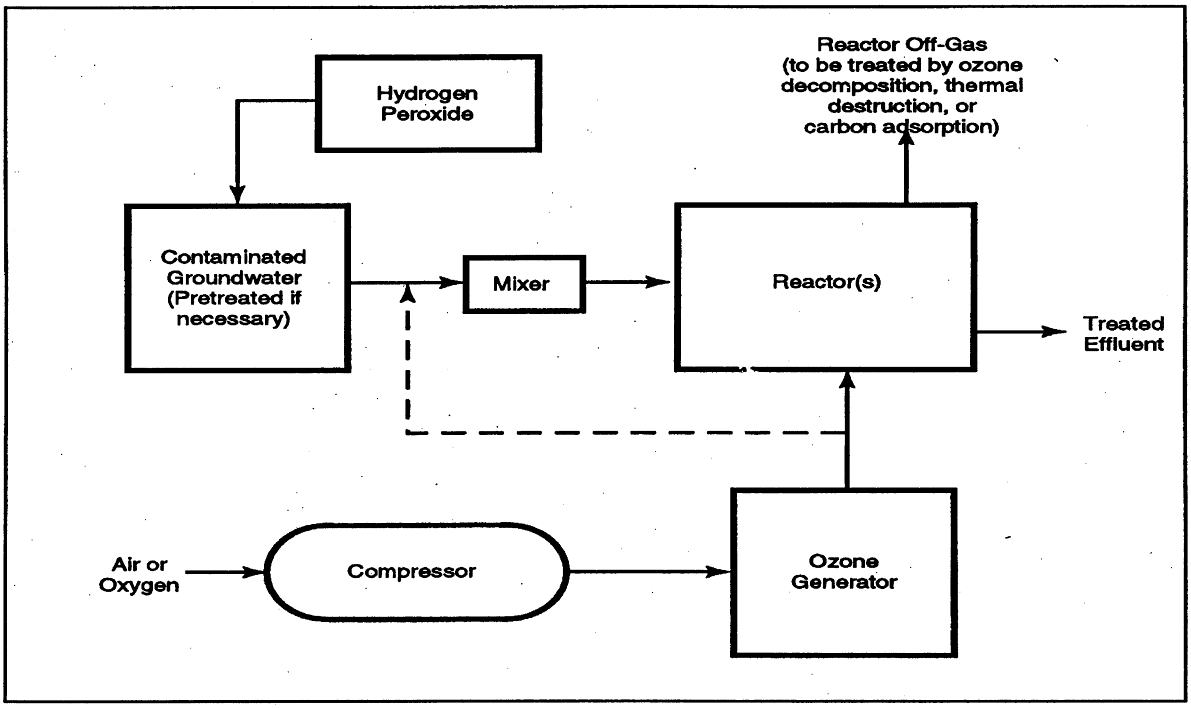

Figure 6.19: UV Oxidation Groundwater Treatment System (USEPA 1990a).

Applicability: UV Oxidation is a groundwater treatment technology only. A wide variety of organic contaminants are susceptible to destruction by UV oxidation including chlorinated solvents. Organic compounds with double carbon bonds (e.g. TCE, PCE and vinyl chloride) are rapidly destroyed in the UV oxidation process.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- The aqueous stream being treated must allow for good transmission of UV light (high turbidity causes interference). This factor maybe more critical for UV/H_2O_2 than UV/O_3. Turbidity does not affect direct chemical oxidation of the contaminant by H_2O_2 or O_3.

- Free radical scavengers can inhibit contaminant destruction efficiency. Excessive dosages of chemical additives may act as scavenges.

- When UV/O_3 is used on volatile organics such as TCA, the contaminants may be volatilised rather than destroyed. They would then have to be removed from the off gas by activated carbon adsorption or catalytic oxidation.

- Costs may be higher than competing technologies because of energy requirements.

- Pre-treatment of the aqueous stream may be required to minimise ongoing cleaning and maintenance of UV reactor and quartz sleeves.

Data Needs: Design and operational parameters include contact or retention time, oxidiser influent dosages, pH, temperature, UV light intensity and various catalysts.

Performance Data: UV oxidation has been successfully used to treat groundwater contaminated with chlorinated solvents. Contaminant clean up consistently meets required targets, and clean up of >99.95% has been achieved.

Costs: Factors that influence the cost of implementing UV Oxidation include: types and concentration of contaminants (they affect oxidiser selection and dosage), UV light intensity and treatment time, degree of contaminant destruction required, desired water flow rates and requirements for pre-treatment and/or post-treatment.

Case Studies:

- Kansas City Plant, Kansas City, Missouri (USEPA 1995) - *Pump and Treat System Utilising UV Oxidation to Treat Contaminated Groundwater.*

- Ultrox International, (USEPA 1990) - *UV Radiation and Oxidation Demonstration Test.*

References:

USEPA (1990) *Ultrox International - UV Ozone Treatment for Liquids.* Technology Evaluation. EPA/540/5-89/012, 1990.

USEPA (1994a) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, Oct 1994.

USEPA (1994b) *Superfund Innovative Technology Evaluation Program.* EPA/540/R-94/526, Nov 1994.

USEPA (1995) *Abstracts of Remediation Case Studies.* EPA/542/R-95/001, Mar 1995.

TECHNOLOGY 31 - HIGH TEMPERATURE THERMAL DESORPTION

Description: High temperature thermal desorption (HTTD) is a physical separation process in which wastes are heated to volatilise water and organic contaminants. A carrier gas or vacuum system transports volatilised water and organics to the gas treatment system.

HTTD is a full scale technology frequently used in combination with incineration depending on site specific conditions. The technology can produce a final contaminant concentration level below 5mg/kg for the target contaminants identified below.

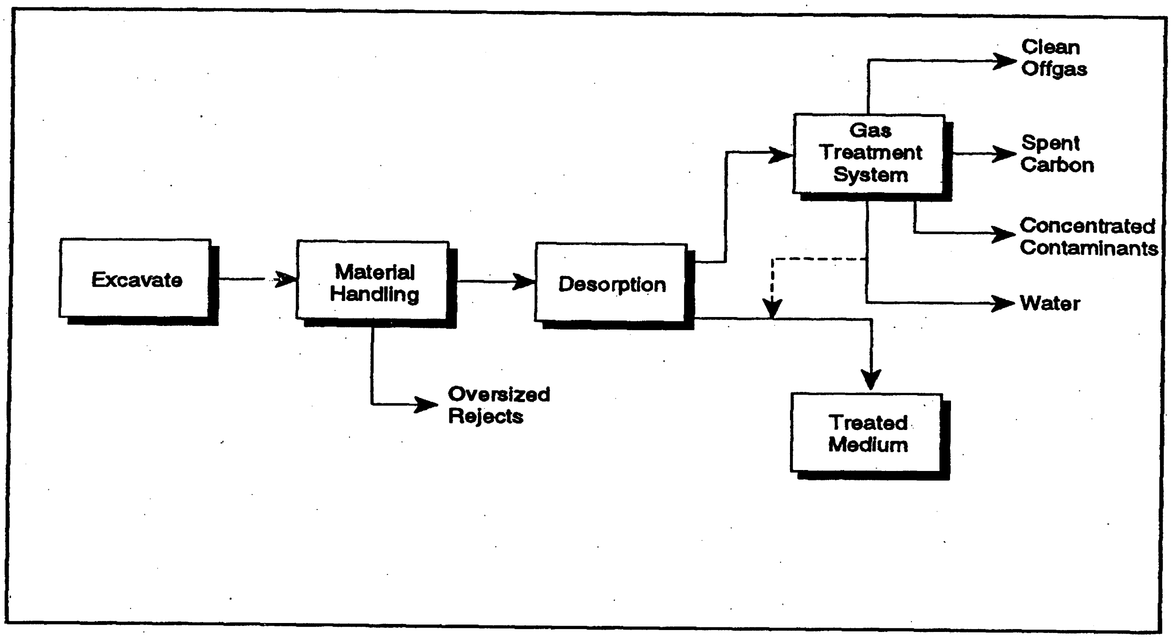

Figure 6.20: High Temperature Thermal Desorption Process (USEPA, 1994a).

Applicability: HTTD remediates contaminated soils and contaminants present in the dissolved, adsorbed and free phases. The target contaminants are SVOCs, PAHs, PCBs and pesticides. However, HTTD has effectively treated chlorinated hydrocarbons although the treatment may be less cost effective.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Feed particle size >5 cm can impact applicability or cost at specific sites.
- Dewatering may be necessary to reduce the amount of energy required to heat the soil.
- Highly abrasive feed can potentially damage the processor unit.

- Clay and silty soils and humic content soils increase reaction time as a result of the binding of contaminants.

Data Needs: In addition to identifying soil contaminants and their concentrations, information necessary for engineering thermal systems to specific applications includes; soil moisture content and classification, determination of relevant contaminant boiling points, and treatability tests to determine the removal efficiency of thermal desorption at various temperatures and residence times.

Performance Data: Bench and pilot scale tests have demonstrated that thermal desorption achieves treatment efficiencies of 99% for VOCs and SVOCs. HTTD has also been used to treat TCE contamination successfully (McKin Superfund Site).

Costs: Costs are both capital and operating intensive and depend on; the quantity of waste to be processed, the term of the remediation contract, moisture content, organic consistency of the contaminated medium and the clean up standards to be achieved.

Case Study:

- McKin Company Superfund Site, Gray, Maine USA, 1987 (USEPA, 1995) - 11,500 tonnes of soil with TCE levels of up to 3,310 mg/kg were excavated and treated. The treatment took 10 months to reduce TCE concentrations to 0.1mg/kg.

References:

Anderson, W.C. (1993) *Innovative Site Remediation Technology-Thermal Desorption.* American Academy of Environmental Engineers.

USEPA (1994a) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, Oct 1994.

USEPA (1994b) *Superfund Innovative Technology Evaluation Program.* EPA/540/R-94/526, Nov 1994.

USEPA (1994c) *Thermal Desorption Treatment. Engineering Bulletin.* EPA OERR and ORD, Washington DC, EPA/540/5-94/501.

USEPA (1995) *Abstracts of Remediation Case Studies.* EPA/542/R-95/001, Mar 1995.

TECHNOLOGY 32 - INCINERATION

Description: Incineration uses high temperatures (870 - 1,200°C) to volatilise and combust organic contaminants in soils.

The solid is passed through a rotary kiln in which a primary chamber operates between 540°C and 980°C. The unit evaporates moisture, volatilises and partially combusts the organic components. A second chamber in the kiln, operating between 870°C and 1,200°C, is used to ensure adequate destruction of the partially combusted gases. The operating conditions (temperature, residence time, etc.) vary depending on the contaminants and clean up regulations. Incinerator off-gas requires treatment by an air pollution control system to remove particulates and to neutralise and remove acid gases.

Incineration is the most regulated treatment technology and the process most frequently chosen for the destruction of organic contaminants.

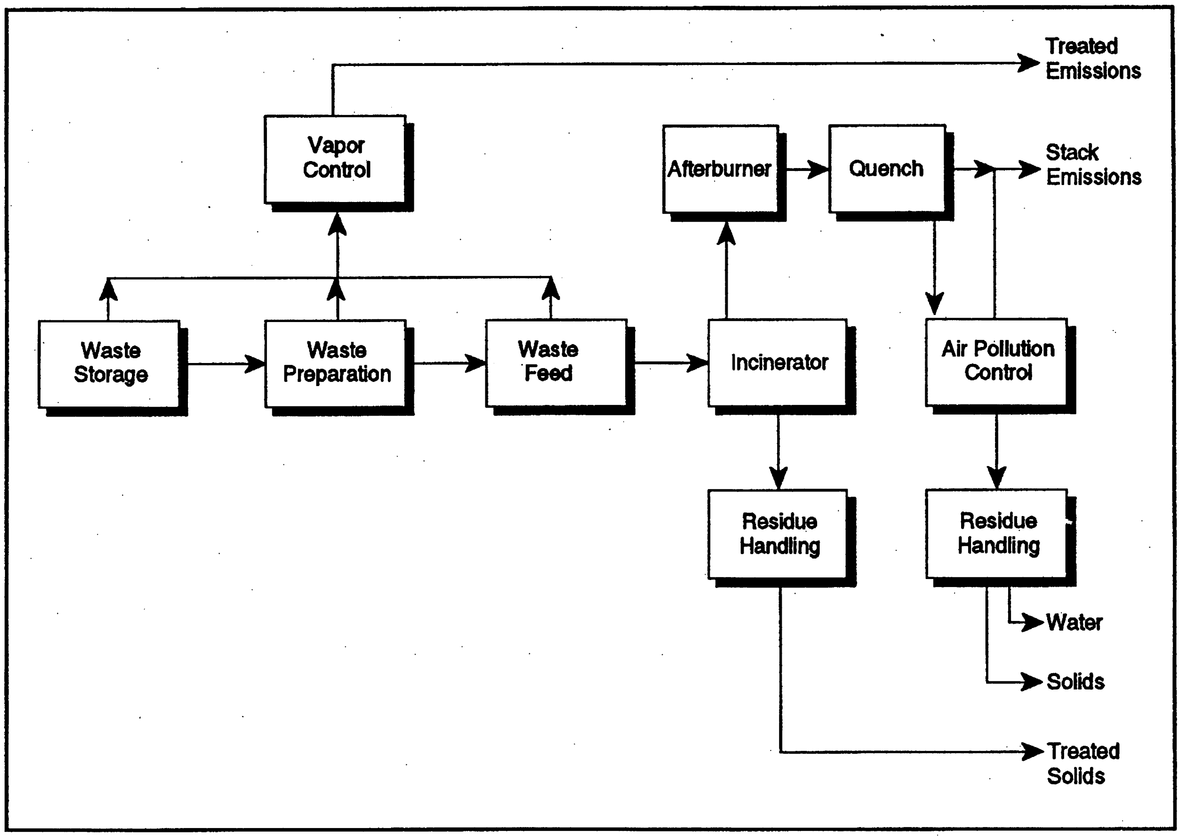

Figure 6.21: Mobile / Transportable Incineration Process (USEPA, 1994a).

Applicability: Incineration can be used to remediate soils contaminated with explosives and hazardous wastes, particularly chlorinated hydrocarbons, PCBs and dioxins.

Limitations: Major factors that limit the applicability and effectiveness of the process include:

- Specific feed size and materials' handling requirements that can impact applicability or cost.
- Heavy metals within the waste can produce a bottom ash that requires stabilisation.
- Metals can react with other elements in the feed stream (such as chlorine or sulphur) forming more volatile and toxic compounds than the original species. Such compounds are likely to be short-lived reaction intermediates that can be destroyed in a caustic quench.

Data Needs: In addition to identifying soil contaminants and their concentrations, information necessary for engineering thermal systems to specific applications includes: soil moisture content and classification, the soil fusion temperature and the soil heating value.

Performance Data: Incineration has been used effectively at numerous sites in the USA to achieve removal efficiencies of up to 99.99%.

Costs: Capital costs are relatively independent of site size and include site preparation, permits, mobilisation/demobilisation, trial burn and equipment costs. Operational costs vary significantly depending on the type of waste treated and site size, and include labour, utilities, fuel and maintenance costs.

Case Studies:

- Brio site, Friendswood, Texas, USA. (Shiro Infrared Systems, 1987) - Demonstration of an on-site incineration unit.
- McColl Superfund Site, Fullerton, California, USA. (USEPA, 1989) - Demonstration of an Ogden circulating bed combustor.

References:

Shiro Infrared Systems Portable Test Unit (1987) *Final Report : On Site Incineration Testing at Brio Site Friendswood, Texas*. n.p. Report No. 846-87-1.

USEPA (1987) *Incineration of Hazardous Waste, Fact sheet.* EPA, Office of Solid Waste, Washington DC. EPA/530/SW-88/018.

USEPA (1989) *SITE : Treatability Study Report - Results of Treating McColl Superfund Waste in Ogden's Circulating Bed Combustor Research Facility.* Risk Reduction Engineering Laboratory, Cincinnati, Ohio. EPA/600/X-89/342.

USEPA (1994a) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, Oct 1994.

USEPA (1994b) *Superfund Innovative Technology Evaluation Program.* EPA/540/R-94/526, Nov 1994

7. REMEDIAL SYSTEM FEASIBILITY STUDIES

7. REMEDIAL SYSTEM FEASIBILITY STUDIES

7.1 Introduction

The Feasibility Study (FS) is an evaluation process to evaluate and select the most suitable remedial technologies. This section provides guidance for conducting an FS.

An FS comprises the following major tasks:

- **Development and Screening of Remedial Alternatives** - Initial phase to review all remedial technologies and to develop a short list of the most promising remedial alternatives according to site specific conditions (contaminant type or mix, aquifer type, depth, etc.). The alternatives may include more than one technology and represent a complete remedial solution.

- **Detailed Analysis of Applicable Remedial Alternatives** - Detailed study involving a comparative analysis of all applicable remedial alternatives against set evaluation criteria. Ranking systems are commonly used for this task referring to advantages and limitations of each alternative in the light of site specific conditions and cost benefit analysis results.

- **Treatability Studies (Optional)** - Treatability studies represent an optional phase. The aim of the treatability study is to provide operational data for an individual or number of applicable remedial alternative(s), to aid the decision process and/or obtain important design and performance data.

Figure 7.1 illustrates the major tasks and their objectives in a flow chart.

At the conclusion of the FS, a remedial alternative is selected and the remedial action implementation process proceeds to the design phase.

7.2 Development and Screening of Remedial Alternatives

The main objectives of this task are described as follows:

- Identify potential treatment technologies and contaminant/disposal requirements for residuals and untreated waste.

- Assemble technologies into remedial alternatives (i.e. treatment trains).

- Screen alternatives to reduce number (subject to detailed analysis).

- Identify action-specific ARARs (Applicable or Relevant Appropriate Requirements).

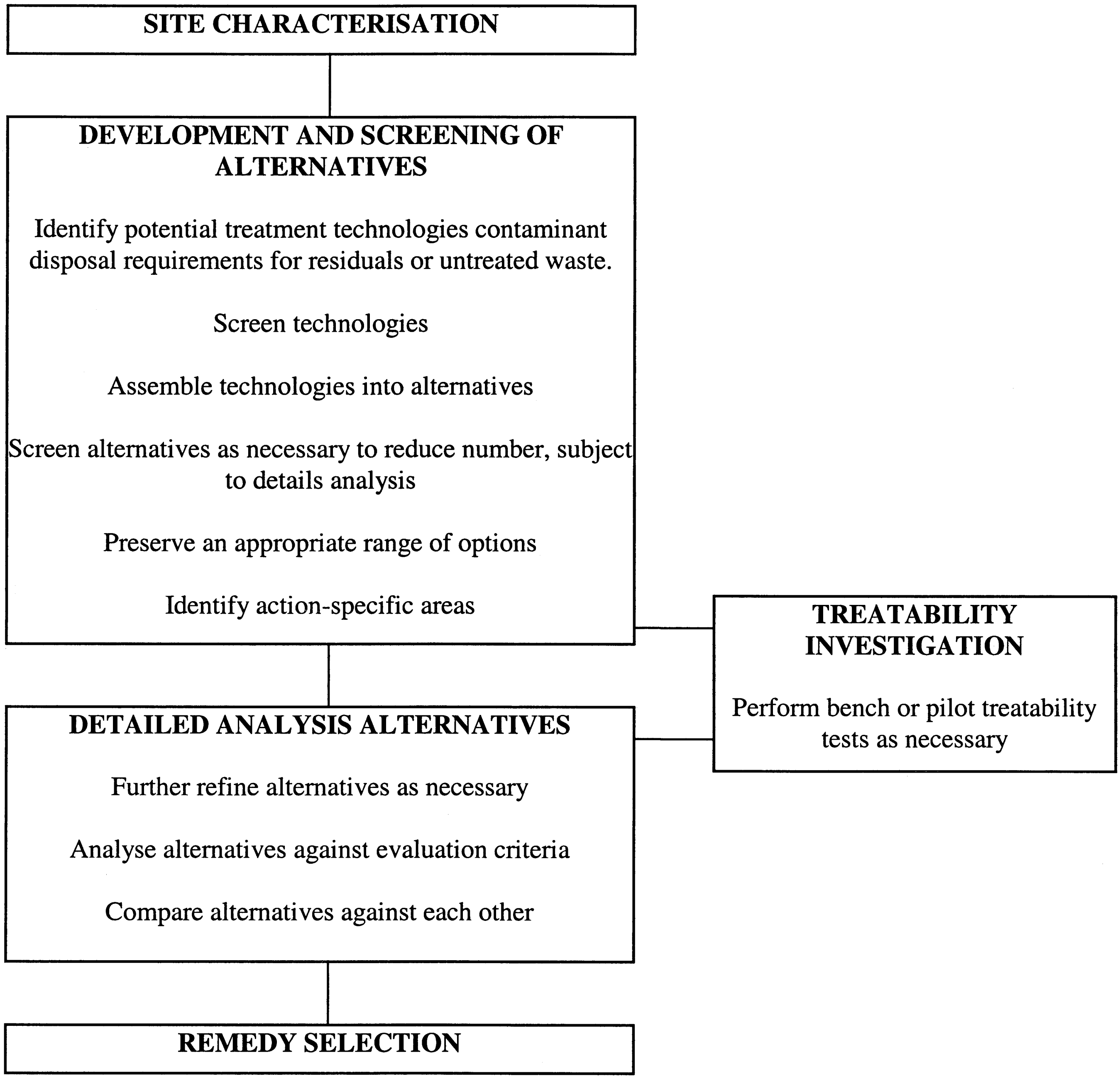

Figure 7.1: Feasibility Study Process

The USEPA recommend that the development and screening of remedial alternatives is a six stage evaluation process, these stages are described below:

1) **Develop Remedial Action Objectives** - Medium specific or operable unit specific goals for protecting human health and the environment.

2) **Develop General Response Actions** - General response actions which will satisfy the remedial action objectives include treatment, containment, excavation, extraction, disposal and institutional actions.

3) **Identify Volume or Areas of Media -** Volumes of areas of media to which general response actions are to be applied are identified, including consideration of acceptable exposure levels, potential exposure routes, site conditions, nature and extent of contamination.

4) **Identify and Screen Remedial Technologies -** Remedial technologies applicable to each general response action are screened. Process options and entire technology options are eliminated from further consideration on the basis of technical implementability. Screening matrices are useful tools in this decision process. An example of a technology screening matrix is presented as Table 7.1.

5) **Identify and Evaluate Technology Process Options -** A representative process for each technology type is selected and retained for consideration in respect to effectiveness, implementability and cost. Table 7.2 presents an example of the process option evaluation process. Cost benefit analysis methodologies may be implemented at this stage.

6) **Assemble the Selected Representative Technologies** - The technologies are selected into alternatives representing a range of treatment and containment combinations as appropriate.

Following assemblance, the selected remedial alternatives are screened to ensure the options protect human health and the environment from each potential pathway of concern. Alternatives with the most favourable composite evaluation of all factors should be retained for further consideration in the detailed analysis phase. Table 7.3 illustrates examples of remedial action objectives, general response actions, technology types and example process options.

7.3 Detailed Analysis of Applicable Remedial Alternatives

The detailed analysis task involves analysis and presentation of relevant information required for the selection of an alternative. The major objectives are as follows:

- Provide the decision maker with adequate information to compare remedial alternatives and make a selection.

- Demonstrate that the remedies satisfy the remedial objectives.

The task can be divided into three steps:

1) Further definition of each alternative if necessary.

2) Assessment and summary profile of each alternative against a set of evaluation criteria.

3) Comparative analysis of the remedial alternatives.

Table 7.1 Treatment technologies screening matrix (adapted from USEPA, 1994)

	Development Status	Availability	Residuals Produced	VOCs	SVOCs	Fuels	Inorganic	Explosives	System reliability	Clean up time	Overall cost	O&M or Capital Intensive
GROUNDWATER, SURFACE WATER, AND LEACHATE												
In Situ Biological Treatment												
30 Co-Metabolic Treatment	Pilot	-	None	+	+	0	-	0	-	0	0	O&M
31 Nitrate Enhancement	Pilot	-	None	+	+	+	-	0	0	0	+	Neither
32 Oxygen Enhancement with Air Sparging	Full	+	None	+	+	+	-	0	+	0	+	Neither
33 Oxygen Enhancement with H_2O_2	Full	+	None	+	+	+	-	0	-	0	0	O&M
In Situ Physical/Chemical Treatment												
34 Air Sparging	Full	+	Vapour	+	-	+	-	-	+	+	+	Neither
35 Directional Wells Enhancement	Ful	-	NA	0	0	0	0	0	+	+	+	Neither
36 Dual Phase Recovery	Full	+	L+V	+	-	+	-	-	0	+	1	O&M
37 Free Product Recovery	Full	+	Liquid	-	+	+	-	-	0	+	+	Neither
38 Hot Water or Steam Flushing/Stripping	Pilot	0	L+V	0	+	+	-	-	-	+	0	CAP
39 Hydrofracturing (Enhancement)	Pilot	1	None	0	0	0	0	0	+	+	0	Neither
40 Passive Treatment Wells	Pilot	-	Soils	+	+	0	+	+	1	-	1	CAP
41 Slurry Walls (containment only)	Full	+	NA	0	0	0	0	0	+	+	+	CAP
42 Vaccum Vapour Extraction	Pilot	-	L+V	+	0	+	1	-	+	0	0	CAP
Ex Situ Biological Treatment (assuming pumping)												
43 Bioreactors	Full	+	Solid	+	+	+	-	0	0	NA	-	CAP
Ex Situ Physical/Chemical Treatment (assuming pumping)												
44 Air stripping	Full	+	L+V	+	0	0	-	-	+	NA	+	O&M
45 Filtration	Full	+	Solid	-	-	-	+	0	+	+	+	Neither
46 Ion Exchange	Full	+	Solid	-	-	-	+	-	+	0	+	Neither
47 Liquid Phase Carbon Adsorption	Full	+	Solid	+	+	0	0	+	+	NA	-	O&M
48 Precipitation	Full	+	Solid	-	-	-	+	1	+	0	+	Neither
49 UV Oxidation	Full	+	None	+	+	+	-	+	-	NA	0	Both
Other Treatment												
50 Natural Attendation	Full	+	None	+	+	+	-	-	+	-	+	Neither

Definition of symbols used in the treatment technologies screening matrix

FACTORS AND DEFINITIONS	WORSE	AVERAGE	BETTER
AVAILABILITY			
Number of vendors that can design construct and maintain the technology	Fewer than 2 vendors	2-4 vendors	More than 4 vendors
CONTAMINANTS TREATED	No expected effectiveness	or non target (e.g VOC treatment by thermally enhanced SVE)	This contaminant is treatment target of this technology
SYSTEM RELIABILITY/MAINTAINABILITY			
The degree of system reliability and level of maintenance requuired when using the technology	Low reliability and high maintenance	Average reliability and average maintenance	High reliability and low maintenance
CLEAN UP TIME			
Time required to clean up a standard site using the technology. The standard site is assumed to be 20,000 tonnes (18,200 metric tonnes) for soils and 1 million gallons (3,758,000 litres) for groundwater.	More than 10 years for water		Less than 3 years
OVERALL COST			
Design construction and (O&M) costs of the core process that defines each technology, exclusive of mobilisation, demobilisation and pre and post treatment. For ex situ soil, sediment and technologies, it is assumed that pumping costs average \$0.77/1,000 litres	More than \$2.64/1,000 litres for groundwater		Less than \$0.79/1,000 litres

Table 7.2 Evaluation of Process Options (copied from USEPA, 1988)

GROUNDWATER GENERAL RESPONSE ACTION	REMEDIAL TECHNOLOGY	PROCESS OPTIONS	EFFECTIVENESS	IMPLEMENTABILITY	COST
No Action	None	Not Applicable	Does not achieve remedial action objectives	Not acceptable to local/public government	None
Institutional Action	Access Restrictions	Deed Restrictions	Effectiveness depends on continued future implementation. Does not reduce contamination	Legal requirement and authority	Negligible cost
	Alternate water supply	City water supply	Effective in preventing use of contaminated groundwater. No contaminated reduction	Conventional construction, required local approvals	High capital, low O&M
		New community well	Effective in preventing use of contaminated groundwater. No contaminant reduction	Conventional construction, required local approvals	High capital, low O&M
		Groundwater monitoring	Useful for documenting conditions does not reduce risk by itself	Alone not acceptable to the public/local government	High capital, low O&M
Collection	Subsurface drains	Interceptor trenders	Effective for down gradient fracture flow interception	Very difficult to implement, requires deep trenching through rock	Very high capital, low O&M
Discharge	Onsite discharge	Local stream	Effective and reliable discharge method does not eliminate contamination	Discharge permits required	Low capital, very low O&M
	Off site	POTW	Effective and reliable discharge method does not eliminate contamination	Discharge permits required	High capital, low O&M
		Pipeline to river	Effective and reliable discharge method does not eliminate contamination	Discharge permits required	High capital, low O&M
Containment	Cap	Clay + Soil	Effective, susceptible to cracking but has self healing properties	Easily implemented, restrictions on future land use	Low capital, low maintenance
		Asphalt	Effective but susceptible to weathering and cracking	Easily implemented, restrictions on future land use	Low capital, high maintenance
		Concrete	Effective but susceptible to weathering and cracking	Easily implemented, restrictions on future land use	Moderate capital, high maintenance
		Multi media cap	Effective, least susceptible to cracking	Easily implemented, restrictions on future land use	Moderate capital, moderate maintenance
Collection	Subsurface drains	Interceptor drains	Effective for downgradient fracture flow interception	Very difficult to implement, requires deep trenching through rock	Very high capital, low O&M
Treatment	Physical/chemical treatment	Precipitation	Effective and reliable, conventional technology. Requires sludge disposal.	Readily implementable	High capital, moderate O&M.
		Ion exchange	Effective and reliable; proper pre-treatment required	Readily implementable	High capital, high O&M
Discharge	Off-site treatment	POTW	Effectiveness and reliability require pilot test to determine	Readily implementable	High capital, moderate O&M
		RCRA facility	Effective and reliable treatment, transportation required	Nearest RCRA facility 250 miles away	High transportation cost
	On-site discharge	Local Stream	Effective and reliable	Readiliy implementable permit required	Low capital, very low O&M
	Off-site discharge	POTW	Effective and reliable	Permit required	High capital, low O&M
		Pipeline to river	Effective and reliable	Permit required	High capital, low O&M

Table 7.3 Example of Remedial Action Objectives, General Response Actions, Technology Types, and Example Process Options for the Development and Screening of Technologies

Environmental Media	Remedial Action Objectives (from site characterisation)	General Response Actions (for all remedial action objectives)	Remedial Technology Types (for general response actions)	Process Options
Groundwater	*For Human Health:* Prevent ingestion of water having carcinogen(s) in excess of MCL(s) and a total excess cancer risk for all contaminants of greater than 10 to 10. Prevent ingestion of water having non-carcinogen(s) in excess of MCL(s) or reference dose(s)	*No Action/Institutional Actions:* No action Alternative residential water supply Monitoring	*No Action/Institutional Options:* Fencing Deed restrictions	
		Containment Actions: Containment	*Containment Technologies:* Capping Vertical barriers Horizontal barriers	Clay cap, synthetic membrane, multi-layer Slurry wall, sheet piling Liners, grout injection
	For Environmental Protection: Restore groundwater aquifer to concentration(s) for contaminant(s).	*Collection/Treatment Actions:* Collection/treatment discharge/ in situ groundwater treatment Individual home treatment units	*Extraction Technologies:* Groundwater collection/ pumping Enhanced removal	Wells, subsurface or leachate collection Solution mining, vapour extraction, enhanced oil recovery
			Treatment Technologies: Physical treatment Chemical treatment In situ treatment	Coagulation/flocculation, oil-water separation, air stripping, adsorption Neutralisation, precipitation, ion exchange Oxidation/reduction Subsurface bioreclamation
			Disposal Technologies: Discharge to POTW (after treatment) *Discharge to surface water* (after treatment)	

Table 7.3 Cont'd Example of Remedial Action Objectives, General Response Actions, Technology Types, and Example Process Options for the Development and Screening of Technologies

Environmental Media	Remedial Action Objectives (from site characterisation)	General Response Actions (for all remedial action objectives)	Remedial Technology Types (for general response actions)	Process Options
Soil	*For Human Health:* Prevent ingestion/direct contact with soil having non-carcinogen(s) in excess of reference dose(s).	*No Action/Institutional Actions:* No action Access restrictions	*No Action/Institutional Options:* Fencing Deed restrictions	
	Prevent direct contact/ ingestion With soil have 10 to 10 excess cancer risk from carcinogen(s). Prevent inhalation of carcinogen(s) posing excess cancer risk levels of 10 to 10	*Containment Actions:* Containment	*Containment Technologies:* Capping Vertical barriers Horizontal barriers Surface controls	Clay cap, synthetic membrane, multi-layer Slurry wall, sheet piling Liners, grout injection Diversion/collection, grading, soil stabilisation
	For Environmental Protection: Prevent migration of contaminants that would result in groundwater contamination in excess of concentration(s) for contaminant(s).	*Excavation/Treatment Actions:* Excavation/treatment/disposal In situ treatment Disposal excavation	*Sediment control barriers:* Dust controls	Coffer dams, curtain barriers Revegetation, capping
			Removal Technologies: Excavation	Solids excavation
			Treatment Technologies: Solidification, fixation, stabilisation, immobilisation Dewatering Physical treatment Chemical treatment Biological treatment In situ treatment Thermal treatment	Sorption, pozzolanic agents, encapsulation Belt filter press, dewatering, and drying beds Water/solvent leaching (with subsequent liquids treatment) Lime neutralisation Cultured micro-organisms Surface bioreclamation Incineration, pyrolysis
Surface Water	*For Human Health:* Prevent ingestion of water having carcinogen(s) in excess of MCL(s) and a total excess cancer risk of greater than 10 to 10	*No Action/Institutional Actions:* No action Access restrictions Monitoring	*No Action/Institutional Options:* Fencing Deed restrictions	Grading, diversion and collection Coagulation/flocculation, oil-water separation, filtration, adsorption
	Prevent ingestion of water having non-carcinogen(s) in excess of MCL(s) or reference dose(s)	*Collection/Treatment Actions:* Surface water run off interception/treatment/ discharge	*Collection Technologies:* Surface controls	Precipitation, ion exchange, neutralisation, freeze crystallisation biological treatment, Aerobic and anaerobic spray irrigation In situ precipitation, in situ bioreclamation

Table 7.3 Cont'd Example of Remedial Action Objectives, General Response Actions, Technology Types, and Example Process Options for the Development and Screening of Technologies

Environmental Media	Remedial Action Objectives (from site characterisation)	General Response Actions (for all remedial action objectives)	Remedial Technology Types (for general response actions)	Process Options
Surface Water Cont'd	*For Environmental Protection:* Restore surface water to ambient water quality criteria for contaminant(s)		*Treatment Technologies:* Physical treatment Chemical treatment Biological treatment (organics) In situ treatment *Disposal Technologies:* Discharge to POTW (after treatment)	
Sediment	*For Human Health:* Prevent direct contact with sediment having carcinogen(s) in excess of 10 to 10 excess cancer risk	*No Action/Institutional Actions:* No action Access restrictions to Monitoring	*No Action/Institutional Options:* Fencing Deed restrictions	
		Excavation Actions: Excavation	*Removal Technologies:* Excavation	Sediments excavation
	For Environmental Protection: Prevent releases of contaminant(s) from sediments that would result in surface water levels in excess of ambient water quality criteria	*Excavation/Treatment Actions:* Removal/disposal Removal/treatment/disposal	*Containment Technologies:* Capping Vertical barriers Horizontal barriers Sediment control barriers	Removal with clay cap, multi-layer, asphalt Slurry wall, sheet piling Liners, grout injection Coffer dams, curtain barriers, capping barriers
			Treatment Technologies: Solidification, fixation, stabilisation Dewatering Physical treatment Chemical treatment Biological treatment In situ treatment Thermal treatment	Sorption, pozzolanic agents, encapsulation Sedimentation, dewatering and drying beds Water/solids leaching (with subsequent treatment) Neutralisation, oxidation, electrochemical reduction Landfarming Surface bioreclamation Incineration, pyrolysis

Table 7.3 Cont'd Example of Remedial Action Objectives, General Response Actions, Technology Types, and Example Process Options for the Development and Screening of Technologies

Environmental Media	Remedial Action Objectives (from site characterisation)	General Response Actions (for all remedial action objectives)	Remedial Technology Types (for general response actions)	Process Options
Air	*For Human Health:* Prevent inhalation of carcinogen(s) in excess of 10 to 10 excess cancer risk	*No Action/Institutional Actions:* No action Access restrictions to Monitoring	*No Action/Institutional Options:* Fencing Deed restrictions	
		Collection Actions: Gas collection	*Removal Technologies:* Landfill gas collection	Passive vents, active gas collection systems
Structures	*For Human Health:* Prevent direct contact with carcinogen(s) in excess of 10 to 10 excess cancer risk	*No Action/Institutional Actions:* No action Access restrictions	*No Action/ Institutional Options:* Fencing Deed restrictions	
	Prevent migration of carcinogen(s) which would result in groundwater concentrations in excess of MCL(s) or 10 to 10 total excess cancer risk level	*Demolition/Treatment Actions:* Demolition/disposal Decontamination	*Removal Technologies:* Demolition Excavation	Demolition Excavation, debris removal
	Prevent migration of carcinogen(s) which would result in soil concentrations in excess of reference dose(s).		*Treatment Technologies:* Solids processing Solids treatment	Magnetic processes, crushing and grinding, screening Water leaching, solvent leaching, steam cleaning
	For Environmental Protection: Prevent migration of contaminant(s) that would result in groundwater concentrations in excess of concentrations(s)			
Solid Wastes	*For Human Health:* Prevent ingestion/direct contact with wastes having non-carcinogen(s) in excess of reference dose(s)	*No Action/Institutional Actions:* No action Access restrictions	*No Action/Institutional Options:* Fencing Deed restrictions	Clay cap, synthetic membranes, multi-layer Slurry wall, sheet piling Liners, grout injection Dust controls
	Prevent ingestion/direct contact with wastes having 10 to 10 excess cancer risk from carcinogen(s)	*Containment Actions:* Containment	*Containment Technologies:* Capping Vertical barriers Horizontal barriers	

Table 7.3 Cont'd Example of Remedial Action Objectives, General Response Actions, Technology Types, and Example Process Options for the Development and Screening of Technologies

Environmental Media	Remedial Action Objectives (from site characterisation)	General Response Actions (for all remedial action objectives)	Remedial Technology Types (for general response actions)	Process Options
Soild Wastes Cont'd	Prevent inhalation of carcinogen(s) posing excess cancer risk levels of 10 to 10 Prevent migration of carcinogen(s) which would result in groundwater concentrations in excess of MCL(s) or 10 to 10 total excess cancer risk levels *For Environmental Protection:* Prevent migration of contaminants that would result in groundwater contamination in excess of concentration(s) for contaminant(s)	*Excavation/Treatment Actions:* Removal/disposal Removal/treatment/disposal	*Removal Technologies:* Excavation Drum removal	Solids excavation Drum and debris removal
			Treatment Technologies: Physical treatment Chemical treatment Biological treatment Thermal treatment Solids processing	Water/solvent leaching (with subsequent liquids treatment) Neutralisation Cultured micro-organisms Incineration, pyrolysis, gaseous Incineration Crushing and grinding, screening, classification
Liquid Wastes	*For Human Health:* Prevent ingestion/direct contact with wastes having non-carcinogen(s) in excess of reference dose(s) Prevent ingestion/direct contact with wastes having 10 to 10 excess cancer risk from carcinogen(s) Prevent inhalation of carcinogens(s) posing excess cancer risk levels of 10 to 10 Prevent migration of carcinogen(s) which would result in groundwater concentrations in excess of 10 to 10 total excess cancer risk levels *For Environmental Protection:* Prevent migration of contaminants that would result in groundwater contamination in excess of concentration(s) for contaminant(s).	*No Action/Institutional Actions:* No action Access restrictions to (location)	*No Action/Institutional Options:* Fencing Deed restrictions	
		Containment Actions: Containment	*Containment Technologies:* Vertical barriers Horizontal barriers	Slurry wall Liners
		Removal/Treatment Actions: Removal/disposal Removal/treatment/disposal	*Removal Technologies:* Bulk liquid removal Drum removal	Bulk liquid removal Drum removal
			Treatment Technologies: Physical treatment Chemical treatment Biological treatment Thermal treatment (organics)	Coagulation/flocculation, adsorption, evaporation, distillation Neutralisation, oxidation, reduction, photolysis Aerobic/anaerobic biological treatment, biotechnologies incineration, pyrolysis, co-disposal
			Disposal Technologies: Produce reuse Discharge to POTW (after treatment)	

Table 7.3 Cont'd Example of Remedial Action Objectives, General Response Actions, Technology Types, and Example Process Options for the Development and Screening of Technologies

Environmental Media	Remedial Action Objectives (from site characterisation)	General Response Actions (for all remedial action objectives)	Remedial Technology Types (for general response actions)	Process Options
Sludges	*For Human Health:* Prevent direct contact with sludge having carcinogen(s) in excess of 10 to 10 excess cancer risk Prevent ingestion/contact with sludge having non-carcinogen(s) in excess of reference dose(s) Prevent migration of carcinogen(s) which would result in groundwater concentrations in excess of 10 to 10 excess cancer risk.	*No Action/Institutional Actions:* No action Access restrictions to (location)	*No Action/Institutional Options:* Fencing Deed restrictions	
		Containment Actions: Containment	*Containment Technologies:* Vertical barriers Horizontal barriers	Slurry wall, sheet piling Liners
		Removal/Treatment Actions: Removal/disposal	*Removal Technologies:* Bulk sludge removal Drum removal	Semi-solid excavation, pumping Drum removal
	<u>*For Environmental Protection:*</u> Prevent releases of contaminant(s) from sludge that would result in surface water levels in excess of ambient water quality criteria Prevent releases of contaminant(s) from sludge that would result in groundwater levels of contaminant(s) in excess of concentration(s).	*Removal/treatment/disposal*	*Treatment Technologies:* Solidification, fixation Physical treatment Chemical treatment Biological treatment Thermal treatment (organics) Dewatering	Sorption, pozzolanic agents, encapsulation Freeze crystallisation, neutralisation, oxidation, electrochemical reduction Oxidation, reduction, photolysis Aerobic/anaerobic treatment, land treatment new biotechnologies Incineration, pyrolysis, co-disposal Gravity thickening, belt filter press, vacuum filtration
			Disposal Technologies: Product reuse Landfilling (after treatment)	

Table 7.4 Long term effectiveness and permanence

Analysis Factor	Specific Factor Considerations
Magnitude of residual risks	• What is the magnitude of the remaining risks? • What remaining sources of risk can be identified? How much is due to treatment residuals, and how much is due to untreated residual contamination? • Will a five year review be required?
Adequacy and reliability of controls	• What is the likelihood that the technologies will meet required process efficiencies or performance specifications? • What type and degree of long term management is required? • What are the requirements for long term monitoring? • What operation and maintenance functions must be performed? • What difficulties and uncertainties may be associated with long term operation and maintenance? • What is the potential need for replacement of technical components? • What is the magnitude of the threats or risks if the remedial action needs replacement? • What is the degree of confidence that controls can adequately handle potential problems? • What are the uncertainties associated with land disposal of residuals and untreated wastes?

Evaluation Criteria

In the USA, the EPA has a standard practice for conducting FS studies under CERCLA (Comprehensive Environmental Response, Compensation and Liability Act of 1988). This legislation requires the following statutory requirements for any remedial action implemented at a superfund site:

- Be protective of human health and the environment.
- Attain ARARs (Applicable or Relevant Appropriate Requirements).
- Be cost effective.
- Utilise permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable.
- Satisfy the preference for treatment that reduces toxicity, mobility or volume as a principle element.

In addition, CERCLA places emphasis on evaluating long term effectiveness and related considerations of reduction of toxicity, mobility and persistence, implementability and costs.

The following nine evaluation criteria were developed by the USEPA to address these statutory requirements and associated considerations (see overleaf).

1) **Overall protection of human health and the environment**
Adverse environmental heath effects and the risks associated with these. For example, noise pollution, visual impact, release of airborne contaminants and the lowering of groundwater levels.

2) **Compliance with ARARs (Applicable or Relevant and Appropriate Requirements)**
Compliance with health, safety and environmental regulations and standards. Including consideration of required approvals, financial and environmental liabilities.

3) **Long term effectiveness and permanence**
The ability of remedial technologies to achieve the desired clean-up criteria i.e. evaluation in terms of the risks remaining at the site after the response objectives have been met. Time limiting factors and maintenancce requirements must also be considered. Analysis and specific factor considerations are presented in Table 7.4. An example of a detailed evaluation of a remedial technology (air sparging) is presented as Figure 7.3 (page 236).

4) **Reduction of toxicity, mobility or volume**
The ability of the alternative to effectively reduce the toxicity, mobility or volume of the hazardous substances. Analysis and specific factor considerations are presented in Table 7.5.

5) **Short term effectiveness**
Effects of the remedial alternatives during the construction and implementation phase; including consideration of protection of workers and community, environmental impacts and time scales. Analysis and specific factor considerations are presented in Table 7.6.

6) **Implementability**
Evaluation of site specific conditions as they affect implementation and time scales. Analysis and specific factor considerations are presented in Table 7.7.

7) **Cost**
Total capital and operational costs.

8) **Local government acceptance**
Technical and administrative issues.

9) **Community acceptance**
Factors such as noise, visual aesthetics and odour.

Table 7.5 Reduction of toxicity, mobility, or volume through treatment (USEPA, 1988)

Analysis Factor	Specific Factor Consideration
Treatment process and remedy	• Does the treatment process employed address the principle threats? • Are there any special requirements for the treatment process?
Amount of hazardous material destroyed or treated	• What portion (mass, volume) of contaminated material is destroyed? • What portion (mass, volume) of contaminated material is treated?
Reduction in toxicity, mobility, or volume	• To what extent is the total mass of toxic contaminants reduced? • To what extent is the mobility of toxic contaminants reduced? • To what extent is the volume of toxic contaminants reduced?
Irreversibility of the treatment	• To what extent are the effects of the treatment reversible?
Type and quantity of treatment residual	• What residuals remain? • What are their quantities and characteristics? • What risks to treatment residuals pose?
Statutory preference for treatment as a principle element	• Are principle threats within the scope of the action? • Is treatment used to reduce inherent hazards posed by principle threats at the site?

Table 7.6 Short term effectiveness (USEPA, 1988)

Analysis Factor	Basis For Evaluation During Detailed Analysis
Protection of community during remedial actions	• What are the risks to the community during remedial action that must be addressed? • How will the risks to the community be addressed and mitigated? • What risks remain to the community which cannot be readily controlled?
Protection of workers during remedial actions	• What are the risks to the workers that must be addressed? • What risks remain to the workers that cannot be readily controlled? • How will risks to the workers be addressed and mitigated?
Environmental impacts	• What environmental impacts are expected with the construction and implementation of the alternative? • What are the available mitigation measures to be used and what is their reliability to minimise potential impacts? • What are the impacts that cannot be avoided should the alternative be implemented?
Time until remedial response objectives are achieved	• How long until protection against the threats being addressed by the specific action achieved? • How long until any remaining site threats will be addressed? • How long until remedial response objectives are achieved?

Table 7.7 Implementability (USEPA, 1988)

Analysis Factor	Specific Factor Considerations
Technical Feasibility	
Ability to construct and operate technology	• What difficulties may be associated with construction? • What uncertainties are related to construction?
Reliability of technology	• What is the liklihood that technical problems will lead to schedule delays?
Ease of undertaking additional remedial action	• What likely future remedial actions may be anticipated?
Monitoring considerations	• Do migration or exposure pathways exist that cannot be monitored adequately? • What risks of exposure exist should monitoring be insufficient to detect failure?
Administrative Feasibility	
Coordination with other agencies	• What steps are required to coordinate with other agencies? • What steps are required to set up long term or future coordination among agencies? • Can permits for off site activity be obtained if required?
Availability of services and materials	
Availability of treatment, storage capacity and disposal services	• Are adequate treatment, storage capacity and disposal services available? • How much additional capacity is necessary? • Does the lack of capacity prevent implementation? • What additional provisions are required to ensure the needed additional capacity?
Availability of necessary equipment and specialists	• Are the necessary equipment and specialists available? • What additional equipment and specialists are required? • Does the lack of specialists and equipment prevent implementation? • What additional provisions are required to ensure the needed equipment and specialists?
Availability of prospective technologies	• Are technologies under consideration generally available and sufficiently demonstrated for the specific application? • Will technologies require further development before they can be applied full-scale to the type of waste at the site? • When should the technology be available for full scale use? • Will more than one vendor be available to provide a competative bid?

1. OVERALL PROTECTION OF HUMAN HEALTH AND THE ENVIRONMENT

- How alternatives provides human health and environmental protection
-

2. COMPLIANCE WITH ARARs

- Compliance with chemical specific ARARs
- Compliance with action specific ARARs
- Compliance with location specific ARARs
- Compliance with other criteria, advisories and guidances
-
- Compliance with chemical specific

3. LONG TERM EFFECTIVENESS AND PERMANENCE	4. REDUCTION OF TOXICITY, MOBILITY AND VOLUME THROUGH TREATMENT	5. SHORT TERM EFFECTIVENESS	6. IMPLEMENTABILITY	7. COST
• Magnitude of residual risk • Adequacy and reliability of controls	• Treatment process used and materials treated • Amount of hazardous materials destroyed and treated • Degree of expected reduction in toxicity, modility and volume • Degree to which treatment is irreversible • Type and quantity of residuals remaining after treatment	• Protection of community during remedial actions • Protection of workers during remedial actions • Environmental impacts • Time until remedial action objectives are achieved	• Ability to construct and operate the technology • Reliability of the technology • Ease of undertaking additional remedial actions if necessary • Ability to monitor effectiveness of remedy • Ability to obtain approvals from other agencies • Coordination with other agencies • Availability of off-site treatment, storage and disposal services and capacity • Availability of necessary equipment and specialists • Availability of prospective technologies	• Capital costs • Operating and maintenance costs • Present worth cost

8. STATE ACCEPTANCE

9. COMMUNITY ACCEPTANCE

Figure 7.2 Criteria for detailed analysis of alternatives (USEPA, 1988)

The criteria are summarised in Figure 7.2, for a full explanation of these criteria the reader is referred to USEPA, 1988. The first two are actual requirements that the selected remedy must comply with; (3) to (7) are used to compare technologies and identify trade-offs and the final two are modifying considerations that can only be evaluated once a proposed action plan has been completed. Important considerations for each criteria are also shown in Figure 7.2.

A similar set of evaluation criteria, recommended in the UK by the Institute of Petroleum (IP) Code of Practice (1992), are listed below:

1) Effectiveness
2) Reliability
3) Institutional Factors
4) Ease of Implementation and Timescale
5) Cost-Effectiveness
6) Public Acceptability
7) Associated Impacts

Comparative Analysis

A comparative analysis is conducted to evaluate the relative performance of each alternative in relation to each specific evaluation criteria. The purpose of the analysis is to identify advantages and disadvantages of each alternative in relation to one another. An example of a comparative analysis is presented in Table 7.8.

Ranking systems using evaluation criteria are commonly employed to aid the decision process whereby all technically feasible alternatives are ranked and compared.

7.4 Treatability Investigations

A treatability investigation is an optional phase of the feasibility study. The investigation may be implemented at a number of different points during the feasibility study, depending on site and project specific conditions. The USEPA recommend the treatability study is conducted prior to the detailed analysis stage to achieve the following aims (USEPA, 1988):

- Provide sufficient data to allow treatment alternatives to be fully developed and evaluated during the detailed analysis and to support the remedial design of a selected alternative.

- Reduce cost and performance uncertainties for treatment alternatives to acceptable levels so that a remedy can be selected.

An alternative stage (to conduct an investigation) is after the detailed analysis phase. At this point, the aim is to determine performance and operating conditions of the selected technology which aids the design process.

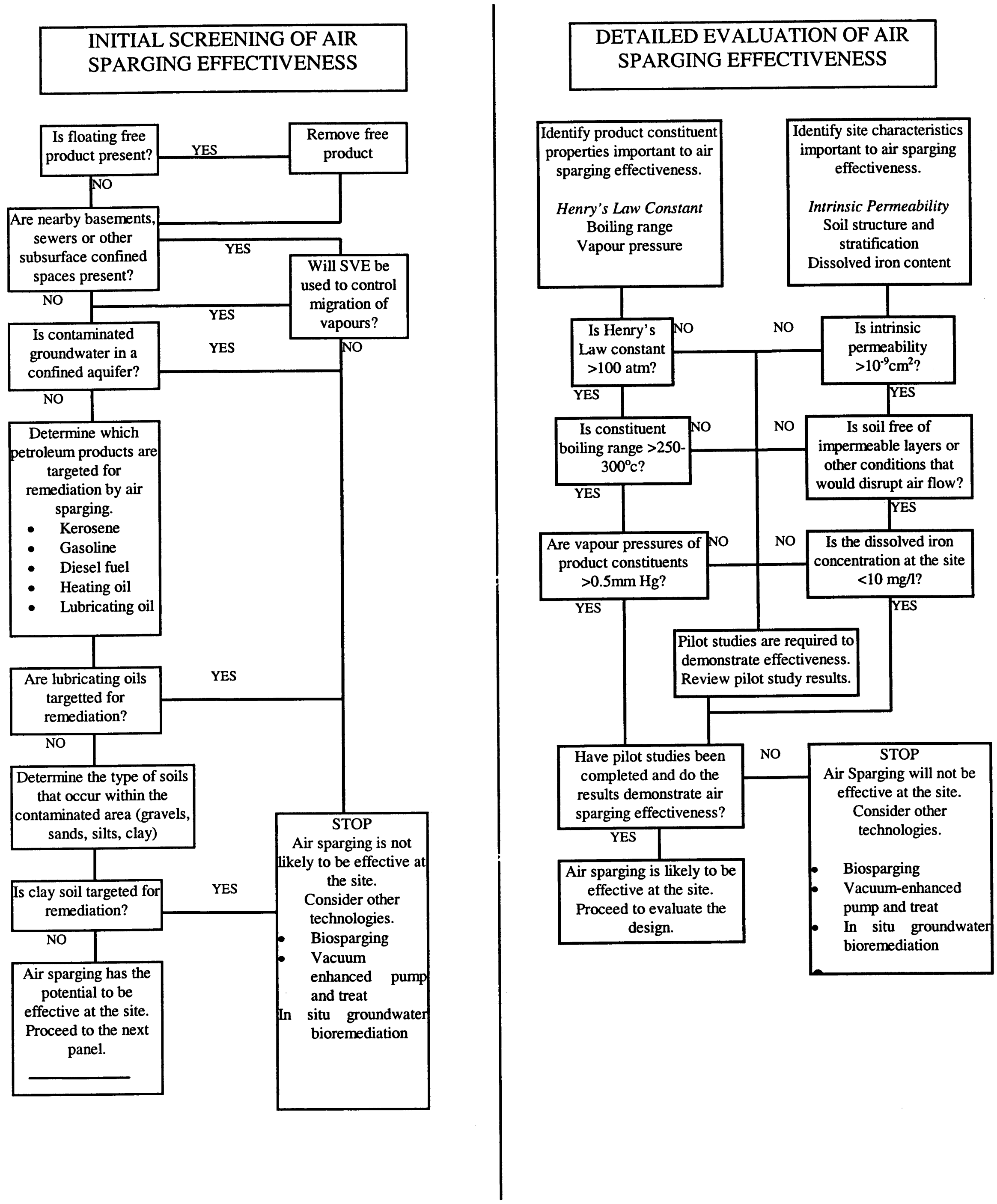

Figure 7.3 Example - Air sparging evaluation process flow chart

Table 7.8 Example - Individual evaluation of final alternatives

Criteria	Alternative 1: No Action	Alternative 2: Cap, Natural Attenuation	Alternative 3: In Situ Soil Vapour Extraction, Cap, Ground-Water Pump And Treat	Alternative 4: In Situ Soil Vapour Extraction, In Situ Soil Fixation, Cap, Ground-Water Pump And Treat	Alternative 5: In Situ Soil Fixation, Cap, Incineration, Groundwater Pump And Treat
OVERALL PROTECTIVENESS					
Human Health Protection					
- Direct Contact/Soil Ingestion	No significant reduction in risk. Some reduction in access to risk through fence	Cap reduces direct contact risk and soil ingestion risk to less than $1\text{x}10^{-6}$	Cap and vapour extraction reduce direct contact/ soil ingestion risk to less than $1\text{x}10^{-6}$	Cap, fixation, vapour extraction reduce direct contact/soil ingestion risk to less than $1\text{x}10^{-6}$	Cap, fixation, incineration reduce direct contact/soil ingestion risk to less than $1\text{x}10^{-6}$
- Groundwater Ingestion for Existing Users	No reduction in risk	Protects against existing risk by providing an alternate water supply	Reduces risk to less than $1\text{x}10^{-6}$ by pump and treat	See Alternative 3	See Alternative 3
- Groundwater Ingestion for Future Users	No reduction in risk	Institutional controls provide protection against risk from groundwater ingestion	Reduces risk to less than $1\text{x}10^{-6}$ by pump and treat	See Alternative 3	See Alternative 3
Environmental Protection	Allows continued contamination of the groundwater	Continued contamination is curtailed by use of cap. Continued migration of contaminated groundwater is allowed	Continued contamination is curtailed by soil vapour extraction and by cap. Migration of Contaminated groundwater is curtailed by pump and treat	Continued contamination is curtailed by soil vapour extraction, soil fixation, and cap. Migration of contaminated groundwater is curtailed by pump and treat	Continued contamination is curtailed by soil fixation and incineration. Migration of contaminated groundwater is curtailed by pump and treat
COMPLIANCE WITH ARARs					
Chemical-Specific ARARs	Does not meet groundwater standards past the site boundary	Would meet MCls at the waste boundary in over 50 years	Would meet MCls at the waste boundary in 25-40 years	See Alternative 3	See Alternative 3

Table 7.8 Cont Example - Individual evaluation of final alternatives

Criteria	Alternative 1: No Action	Alternative 2: Cap, Natural Attenuation	Alternative 3: In Situ Soil Vapour Extraction, Cap, Ground-Water Pump And Treat	Alternative 4: In Situ Soil Vapour Extraction, In Situ Soil Fixation, Cap, Ground-Water Pump And Treat	Alternative 5: In Situ Soil Fixation, Cap, Incineration, Groundwater Pump And Treat
Location-Specific ARARs	Not relevant. There are no location-specific ARARs	See Alternative 1	See Alternative 1	See Alternative 1	See Alternative 1
Action-Specific ARARs	Would not meet any ARARs since there will be no action	Would meet RCRA landfill closure requirements	Would meet RCRA landfill closure requirements. Would also meet air release standards from the vapour extraction system. Would meet NPDES requirements	Would meet air release Standards from air strippers and vapour extraction system. Would meet NPDES requirements. Would meet RCRA landfill closure requirements	Would meet regulations concerning incineration and air stripping. Would meet NPDES requirements. Would meet RCRA landfill closure requirements
Other Criteria and Guidance	Would allow ingestion of groundwater exceeding $1x10^{-6}$. Would not protect against Pb levels above 200mg/kg in soil	Protects against soil ingestion to $1x10^{-6}$ level and groundwater ingestion at $1x10^{-6}$ level. Covers soil with Pb above 200mg/kg	See Alternative 3	See Alternative 3	See Alternative 3
<u>LONG-TERM EFFECTIVENESS AND PERMANENCE</u>					
Magnitude of Residual Risk					
- Direct Contact/Soil Ingestion	Source has not been removed. Existing risk will remain	Risk eliminated as long as cap is maintained. Because source is only contained, inherent hazard of waste remains	Risk eliminated through vapour extraction and cap. Some inherent hazard remains in the lead material under the cap. Risk from lead would only occur if the cap were destroyed	Slight chance of future risk from fixed lead-contaminated soil	See Alternative 4

Table 7.8 Cont Example - Individual evaluation of final alternatives

Criteria	Alternative 1: No Action	Alternative 2: Cap, Natural Attenuation	Alternative 3: In Situ Soil Vapour Extraction, Cap, Ground-Water Pump And Treat	Alternative 4: In Situ Soil Vapour-Extraction, In Situ Soil Fixation, Cap, Ground-Water Pump And Treat	Alternative 5: In Situ Soil Fixation, Cap, Incineration, Groundwater Pump And Treat
- Groundwater Ingestion for Existing Users	Future risk greater as plume migrates to residents. Eventually natural attenuation and dilution may decrease risk. Risk significant for about 100 years	Risk eliminated by providing alternate water supply. Some risk would remain for over 100 years if the groundwater is used	Risk eliminated by extracting groundwater exceeding 10^{-6} cancer risk levels. Safe drinking water achieved in 25-40 years with source control	See Alternative 3	See Alternative 3
- Groundwater Ingestion for Future Users	Risk greater as area of contamination increases. Eventually natural attenuation and dilution may decrease risk. Risk significant for about 100 years	Institutional controls used To control use of contaminated groundwater. Unauthorised use of groundwater would result in increased risk	Risk eliminated by extracting groundwater exceeding 10^{-6} cancer risk levels. Safe drinking water achieved in 25-40 years with source control	See Alternative 3	See Alternative 3
Adequacy and Reliability of Controls	No controls over remaining contamination. No reliability	Risk to groundwater controlled by alternate water supply and institutional controls. Soil/ clay cap controls contaminated soil. Cap effective for Area 2 even if metals are present. Institutional controls are limited in effectiveness	Soil/clay cap controls remaining contaminated soil in Area 1. Would need additional controls for Area 2. If metals are present since soil vapour extraction would not remove metals. Groundwater extraction controls contaminated groundwater. Both are adequate	See Alternative 3	Similar to Alternative 3. Incinerator ash disposed in municipal landfill. If metals are present in Area 2, incinerator ash would be disposed in RCRA landfill

Table 7.8 Cont Example - Individual evaluation of final alternatives

Criteria	Alternative 1: No Action	Alternative 2: Cap, Natural Attenuation	Alternative 3: In Situ Soil Vapour Extraction, Cap, Ground-Water Pump And Treat	Alternative 4: In Situ Soil Vapour Extraction, In Situ Soil Fixation, Cap, Ground-Water Pump And Treat	Alternative 5: In Situ Soil Fixation, Cap, Incineration, Groundwater Pump And Treat
		Reliability of cap can by high if maintained. Institutional controls to control use of groundwater not very reliable	Reliability of vapour extraction high because no long-term O&M is required. Cap reliable if maintained. Groundwater pump and treat is reliable.	Reliability of fixation with cap high, as are vapour extraction and groundwater pump and treat	Incineration very reliable because material is destroyed. Fixation with cap and groundwater pump and treat are reliable
Need for 5-Year Review	Review would be required to ensure adequate protection of human health and the environment is maintained	See Alternative 1. TCE and lead soil would remain on site	See Alternative 1. Lead contaminated soil would remain on site	See Alternative 1. Fixed lead residuals would remain on site	See Alternative 1. Fixed lead residuals would remain on site
REDUCTION OF TOXICITY, MOBILITY, OR VOLUME THROUGH TREATMENT					
Treatment Process Used	None	None	Vapour extraction of soil and groundwater air stripping	Vapour extraction, soil fixation, and groundwater air stripping	Incineration, soil fixation and groundwater air stripping
Amount Destroyed or Treated	None	None	99.9% of volatiles in soil and 96% volatiles in groundwater removed and destroyed by carbon regeneration	Same as Alternative 3 plus 25,000 cy of contaminated soil is fixed	99.8% of volatiles in 20,000 cy of soil destroyed and 25,000 cy of contaminated soil is fixed
Introduction of Toxicity, Mobility, or Volume	None	None	Reduced volume and toxicity of contaminated groundwater. Toxicity of soil contamination reduced	Reduced volume and toxicity of contaminated groundwater. Toxicity of soil contamination in Area 2 reduced 97%. Mobility of contaminants	Incineration reduces volume of contaminated soil by 20,000 cy and reduces toxicity. Mobility of contaminants in Area 1 is reduced. Volume

Table 7.8 Cont Example - Individual evaluation of final alternatives

Criteria	Alternative 1: No Action	Alternative 2: Cap, Natural Attenuation	Alternative 3: In Situ Soil Vapour Extraction, Cap, Groundwater Pump And Treat	Alternative 4: In Situ Soil Vapour Extraction, In Situ Soil Fixation, Cap, Groundwater Pump And Treat	Alternative 5: In Situ Soil Fixation, Cap, Incineration, Groundwater Pump And Treat
				in Area 1 reduced 10% while volume increased 20%	and toxicity of contaminated groundwater is reduced
Irreversible Treatment	None	None	Vapour extraction and air stripping are irreversible with regeneration of carbon used for air stream treatment	See Alternative 3	Incineration is irreversible
Type and Quantity of Residuals Remaining after Treatment	No residuals remain	None	No detectable residuals in Area 2 remain. Carbon from gaseous treatment requires regeneration	No detectable residuals in Area 2 remain. 30,000 cy of fixed soils remain in Area 1	Incinerated soil (18,000 cy) and fixed soils (30,000 cy) remain. Incinerated soil expected to be non-harzardous. Carbon from gaseous treatment remains, re-quiring regeneration
Statutory Preference for Treatment	Does not satisfy	Does not satisfy	Satisfies	Satisfies	Satisfies
SHORT TERM EFFECTIVENESS					
Community Protection	Risk to community not increased by remedy implementation, but contaminated water may reach the residents within one to three years	Temporary increase in dust production through cap installation. Contaminated soils remain undisturbed	Soil would remain uncovered during vapour extraction for three to five years. Temporary increase in dust production during cap installation	Similar to Alternative 3. Fixation may result in dust and odor increase	Soil would remain uncovered during incineration (about 1 year). Excavation and fixation would release dust and odours to the atmosphere

Table 7.8 Cont Example - Individual evaluation of final alternatives

Criteria	Alternative 1: No Action	Alternative 2: Cap, Natural Attenuation	Alternative 3: In Situ Soil Vapour Extraction, Cap, Ground-Water Pump And Treat	Alternative 4: In Situ Soil Vapour Extraction, In Situ Soil Fixation, Cap, Ground-Water Pump And Treat	Alternative 5: In Situ Soil Fixation, Cap, Incineration, Groundwater Pump And Treat
Worker Protection	No significant risk to workers	Protection required against dermal contact and inhalation of contaminated dust during cap construction	Protection required against dermal contact, vapour or dust inhalation during construction and operation of vapour extraction system and air stripper	Protection required against dermal contact, vapour or dust inhalation during construction and operation of vapour extraction system, fixation, and air stripper	Protection required against dermal contact and inhalation of volatiles and particulates as a result of excavation, fixing and incinerating TCE soil
Environmental Impacts	Continued impact from existing conditions	Would be some migration of contaminant plume as part of attenuation process	Vapour extraction may impact air quality and odours although it will meet emission standards. Would be aquifer drawdown during groundwater extraction	See Alternative 3. Fixation may also affect air quality and produce odours	Incineration may impact air quality, produce odours, although it will meet emission standards
Time Until Action is Complete	Not applicable	Cap installed in six months. Risk from groundwater reduced within three months due to alternate water supply and institutional controls	Soil vapour extraction complete in three to five years. Capping complete in six months. Groundwater remedial action complete in 25-40 years	Fixation and capping completed in nine months. Soil vapour extraction complete in three to five years.Groundwater action complete in 25-40 years	Incineration complete in two years from design completion. Fixation and capping complete in nine months. Groundwater action complete in 25-40 years

Table 7.8 Cont Example - Individual evaluation of final alternatives

Criteria	Alternative 1: No Action	Alternative 2: Cap, Natural Attenuation	Alternative 3: In Situ Soil Vapour Extraction, Cap, Ground-Water Pump And Treat	Alternative 4: In Situ Soil Vapour Extraction, In Situ Soil Fixation, Cap, Ground-Water Pump And Treat	Alternative 5: In Situ Soil Fixation, Cap, Incineration, Groundwater Pump And Treat
IMPLEMENTABILITY					
Ability to Construct and Operate	No construction or operation	Simple to operate and construct. Would require materials handlong of about 50,000 cy of soil and clay	Vapour extraction requires some operation. Fairly straightforward to construct. Cap construction would require materials handling of 25,000 cy of soil and clay. On site groundwater treatment requires operation	Fixation with cap somewhat difficult to construct. Otherwise similarly to Alternative 3	Incineration is difficult to operate. Fixation with cap is somewhat difficult to construct. Similar to Alternative 3 with respect to groundwater
Ease of Doing More Action if Needed	If monitoring indicates more action is necessary, may need to go through the FS/ROD process again	Simple to extend extraction system and cap. Cap would be sufficient if metals were significant in Area 2. Could implement groundwater treatment if necessary	Simple to extend groundwater extraction system, vapour extraction system, and cap. However, if significant metal concentrations are present in Area 2, may need additional soil treatment or would need to extend cap	Fairly complete alternative. Can increase volume of or modify all technologies. If significant metal concentrations are present in Area 2, could use fixation	Complete alternative. Can handle varying volumes or concentrations
Ability to Monitor Effectiveness	No monitoring. Failure to detect contamination means ingestion of contaminated groundwater	Proposed monitoring will give notice of failure before significant exposure occurs	See Alternative 3	See Alternative 3	See Alternative 3

Table 7.8 Cont Example - Individual evaluation of final alternatives

Criteria	Alternative 1: No Action	Alternative 2: Cap, Natural Attenuation	Alternative 3: In Situ Soil Vapour Extraction, Cap, Ground-Water Pump And Treat	Alternative 4: In Situ Soil Vapour Extraction, In Situ Soil Fixation, Cap, Ground-Water Pump And Treat	Alternative 5: In Situ Soil Fixation, Cap, Incineration, Groundwater Pump And Treat
Ability to Obtain Approvals and Coordinate with Other Agencies	No approval necessary	See Alternative 1	Need an NPDES permit. Should be easy to obtain	See Alternative 3	Need to demonstrate technical intent of incinerator permit. Need an NPDES permit
Availability of Services and Capacities	No services or capacities required	See Alternative 1	See Alternative 1	Need fixation services	Need fixation and incineration services
Availability of Equipment, Specialists, and Materials	None required	No special equipment, material or specialists required. Cap materials available within 20 miles	Needs readily available specialists to install and monitor vapour extraction system. Need treatment plant operators. Cap materials available within 20 miles	See Alternative 3	Need a mobile incinerator and trained operators. Need treatment plant operators. Closest source of incinerator is 500 miles from site
Availability of Technologies	None required	Cap technology readily available	Vapour extraction well developed. Will require pilot testing	Vapour extraction and fixation well developed. Will require pilot testing	Incineration and fixation well developed. Will required pilot testing
COST (US$)					
Capital Cost ($)	0	4,200,000	3,300,000	6,200,000	13,000,000
First Year Annual O&M Cost ($)	0	60,000	440,000	480,000	1,200,000
Present Worth Cost ($)	0	4,800,000	7,300,000	10,200,000	16,000,000

The decision to conduct a treatability test must be made by weighing the cost and time required to complete the investigation against the potential value of the information in resolving uncertainties associated with the selection of a remedial action or design of a remedial system.

Treatability investigations may not be required if:

- The developed technology is well proven on similar applications.
- Substantial experience exists with a technology employing treatment of well documented waste materials.
- Relatively low removal efficiencies are required and data is already available.

7.4.1 Guidelines on Conducting Treatability Studies

Treatability testing can be performed using bench or pilot scale testing. In general the following steps are followed:

- Determination of data requirements
- Preparing a work plan (or modifying existing work plan) for the bench or pilot studies
- Performing field sampling, and/or bench testing, and/or pilot testing
- Evaluating data from field studies, and/or bench testing, and/or pilot testing
- Reporting results

Data Requirements

The data required to evaluate the feasibility of remedial technologies should, as far as possible, be collected during the site investigation stage. However, data requirements change depending on specific treatment processes. The need for detailed data may not become apparent until the completion of the initial technology screening phase. If the data is not adequate for the feasibility assessment, a treatability study must be conducted. Table 7.9 indicates typical data requirements for a few examples, and the *Technology Screening Guide for Treatment of CERCLA Soils and Sludges (USEPA, September 1988)* summarises data needed for a larger number of available and innovative technologies.

Bench Scale Tests

Bench scale tests are usually performed in the laboratory and are used to test comparatively small volumes of waste for specific treatment technology parameters. Bench scale testing should be performed, as appropriate, to determine the following:

Table 7.9: Typical data requirements for remediation technologies

Technology	Waste Matrix	Example Data Required
Thermal Destruction	Soils	Moisture content Heat value Chlorine content Destruction efficiency
	Liquids	Heat value Concentration of metals Destruction efficiency
Air Stripping	Groundwater	Concentration of volatile contaminants. Concentration of non-volatile contaminants Contaminant removal efficiencies (obtainable from mathematical models)
Metal Hydroxide Precipitation	Groundwater	Metals concentration Contaminant removal efficiency Sludge generation rate and composition
In situ Soil Vapour Extraction	Soils	Soil type Particle size distribution. Concentration of volatile compounds Presence of non-volatile contaminants Contaminant removal efficiencies (usually requires bench or pilot scale work)

- Effectiveness of the treatment alternative on the waste
- Differences in performance between competing manufacturers
- Differences in performance between alternative chemicals
- Sizing requirements for pilot scale studies
- Screening technologies to be pilot tested
- Sizing of those treatment units that would sufficiently affect the cost of implementing the technology
- Compatibility of materials with the waste

Examples of bench scale study parameters are presented in Table 7.10.

Table 7.10: Bench and pilot scale parameters

Parameter	Bench	Pilot
Purpose	Define process kinetics, material compatibility, impact of environmental factors, types of doses of chemicals, active mechanisms, etc.	Define design and operation criteria, materials of construction, ease of material handling and constructon, etc.
Size	Laboratory or bench top	1-100% of full scale
Quantity of waste and materials required	Small to moderate amounts	Relatively large amounts
Number of variables that can be considered	Many	Few (greater site specificity)
Time requirements	Days to weeks	Weeks to months
Typical cost range	0.5-2% of capital costs of remedial action	2-5% of capital costs of remedial action[1]
Most freqeunt location	Laboratory	On site
Limiting considerations	Wall boundary and mixing effects, volume effects, solids processing difficult to simulate, transportation of sufficient waste volume	Limited number of variables, large waste volume required, safety, health, and other risks, disposal of process waste material

[1] Actual percentage cost of pilot testing will depend significantly on the local cost of the remedial action.

Specific steps to be performed in carrying out a bench scale test include:

Experimental procedures - Specification of volume to be tested, materials required, accuracy of measurements, containers and preservatives to be used and a description of the reactor to be employed.

Treatability test - Test conducted under variable conditions and parameters measured if they vary under different test conditions.

Analytical methods - The most appropriate analytical method should be selected according to test objectives, technologies, waste and site conditions. The level of accuracy is specified and reference to standard procedures given. Initial testing is performed to determine optimal operating conditions. After achieving the best treatment, more complete and accurate testing is performed to confirm earlier results.

Data analysis and interpretation - The most useful form of data analysis is presentation of graphical results based on known physical and chemical phenomena or common practice.

Pilot Scale Testing

Pilot scale studies are designed to simulate the physical as well as chemical conditions of a full scale process. The equipment and test procedure is designed to minimise physical and geometric effects on treatment performance, however time and budget constraints often limit the size and extent of the test.

The specific steps of a pilot scale test are as follows:

1) Definition of pilot plant operation and maintenance procedures - Specific conditions under which the pilot test is conducted.

2) List parameters tested - Operating conditions and variations in control parameters that are evaluated.

3) Sampling plan - Report locations and schedules for sample collection to evaluate performance of the pilot scale operation.

4) Health and safety plan - Ensure equipment design and construction complies with applicable code requirements.

Data Analysis and Interpretation

Data should be analysed with respect to effectiveness, implementability and cost, allowing comparisons between anticipated and actual results. The level of reliability of the test results is usually based on the accuracy of the analytical methods employed.

Major differences between anticipated and actual results may necessitate modification of the work plan and re-testing of the technology. Contaminant removal rates, by-products and emissions are evaluated to predict the ability of a full scale unit to meet the performance specifications.

The results of the bench and pilot scale field studies can be used to ensure that conventional and innovative treatments can be evaluated with non-treatment options during the detailed analysis phase of the feasibility study.

The treatability study provides information for design of the selected remedial technology and measurements of the residual and effluent concentrations. This can be used to predict effects on disposal and/or emission requirements during full-scale operations.

Modification of Results for Full Scale Application

The treatability investigation results need to be evaluated for application of the technology at full scale, compensating for bench and pilot scale tests. Scaling up results can be done on the

Table 7.11: Examples of bench- and pilot-scale testing programmes

Remedial Technology	Example Testing Programmes
A. AIR POLLUTION AND GAS MIGRATION CONTROL 1. Capping 2. Dust control 3. Vapour collection and treatment (carbon adsorption, air stripping, etc.)	Bench: Soil density and bearing capacity vs. moisture content curves for proposed capping materials Pilot: In-place soil densities; determination of gas withdrawal rates to control releases
B. SURFACE WATER CONTROLS 1. Capping 2. Grading 3. Revegetation 4. Diversion and Collection	Bench: Column testing of capping material compatibility with wastes present Pilot: In-place testing of geotextiles for control of erosion in grass diversion ditches
C. LEACHATE AND GROUNDWATER CONTROLS 1. Containment barriers (slurry walls, grout curtains, etc.) 2. Groundwater pumping (well points, suction wells, etc.) 3. Subsurface collection drains 4. Permeable treatment beds (limestone, activated carbon, etc.) 5. Capping	Bench:Determination of basicity and head loss vs. grain size of limestone materials for a treatment bed; determination of chemical compatibility of compacted clay with a leachate stream Pilot: In-place testing of a soil type and grain size specification and tile drain configuration for a subsurface collection drain
D. DIRECT WASTE CONTROL 1. Thermal treatment 2. Solidification/stabilisation 3. Biological treatment • Activated sludge • Facultative lagoons • Trickling filters 4. Chemical treatment • Oxidation/reduction • Precipitation • Neutralisation • Ion exchange resins 5. Physical treatment • Carbon adsorption • Flocculation • Sedimentation • Membrane processes • Dissolved air flotation • Air stripping • Wet air oxidation 6. In-situ treatment • Vapour extraction • Soil flushing • Microbial degradation • Neutralisation/detoxification • Precipitation • Nitrification 7. Land disposal (landfill, land application)	Bench: Characterisation of chemical and heat content of hazardous waste mixes; chemical, physical and biological treatability studies to define rate constants, minimal-maximal loading rates and retention times, optimal pH and temperature, sludge generation rates and characteristics and oxygen transfer characteristics; chemical type and dose rates;solids flux rate vs. solids concentration in sludge thickening systems; air/volume ratios for stripping towers Pilot: Test burns to determine retention times, combustion chamber and afterburner temperatures, destruction and removal efficiency, and fuel requirements for the incineration of wastes; endurance performance test on membranes in reverse-osmosis units for groundwater treatment; in situ microbial degradation testing of nutrient dose and aeration to support in-place degradation of underground leak; evaluation of inplace mixing procedures for the solidification of sludge in a lagoon
E. SOIL AND SEDIMENT CONTAINMENT AND REMOVAL 1. Excavation 2. Dredging 3. Grading 4. Capping 5. Revegetation	Bench:Determination of soil adsorptive (cation exchage capacity) properties and chemical composition Pilot: Small scale dredging to assess sediment resuspension or production rates

basis of previous experience with the remedial equipment or by established rules of similitude (used to relate physical laws to variations in scale) and mathematical models. This evaluation may include sensitivity analysis to identify key parameters and unknowns.

7.5 References

Institute of Petroleum (IP) (1992) *Code of Practice for the Investigation and Mitigation of Possible Petroleum-Based Land Contamination.*

USEPA (1988) *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA* EPA/540/G-89/004, October 1988.

USEPA (1988) *Guidance on Remedial Actions for Contaminated Groundwater at Superfund Sites.* EPA/540/G-88/003, Dec 1988.

USEPA (1992) *Methodologies for Evaluating In Situ Bioremediation of Chlorinated Solvents.* EPA/600/R-92/042, March 1992.

USEPA (1994) *Remediation Technologies Screening Matrix and Reference Guide.* EPA/542/B-94/013, October, 1994.

8. CASE STUDIES

Introduction

This section describes eleven different case studies where remedial actions have been taken on sites where soil and/or groundwater has been contaminated by organic solvent contaminants. The case studies were chosen to represent a range of different site conditions and remedial technologies. Table 8.1 summarises the site and contamination types.

Of the eleven case studies, three are in the UK, one in Germany and seven are from the United States. There are many more sites within the UK which comply with the criteria however the site details are confidential and could not be presented here. However, an indication of the extent of groundwater pollution by organic solvent compounds in the UK is available through the following two separate Environment Agency studies:

- Environment Agency (1995). Effects of old landfill sites on Groundwater Quality - Phase I. R&D Note 415 (Report for internal circulation only).

- Environment Agency (1997). Groundwater Pollution: Evaluation of the extent and character of groundwater pollution from point sources in England and Wales.

Table 8.1 Case Study Summary Table

	Case Study Name & Location	Main Contaminants	Geology	Remedial Technology
1	Eastern Counties Leather, Sawston, Cambridgeshire	PCE	Sand and gravel drift over chalk	‘Hydraulic containment’, i.e. abstraction from well in source area, no treatment
2	Knitwear Manufacturer, Northumberland	PCE	Sand and gravel drift with thin boulder clay over interbedded sandstone and mudstone bedrock	Ex situ air stripping of groundwater from impacted abstraction well SVE
3	IBM-Dayton, New Jersey, USA	1,1,1-TCA , PCE	Shallow sand over clay over sandstone bedrock	Hydraulic containment using strategically placed abstraction wells
4	Harwell Laboratory, Oxfordshire	TCE, TCM, TeCM	Chalk	Hydraulic containment by abstraction from strategically located wells and treatment of abstracted groundwater by ex situ air stripping and activated carbon adsorption
5	Portsmouth Uranium Enrichment Plant, Ohio, USA	TCE	Clay, silt and sand drift over shale and sandstone bedrock	DNAPL recovery followed by installation of interception trench and ex situ air stripping of groundwater pumped from trench
6	Niagara Falls Landfills, New York, USA (Love Canal & Hyde Park Landfill)	Various VOCs	Silty clay and glacial till over fractured dolomite	Hydraulic containment using a perimeter drain at Love Canal and hydraulic containment using strategically located abstraction and injection wells at Hyde Park Landfill
7	Pintsch Waste Oil Refinery, Hanau, Germany	LNAPL BTEX with entrained TCE, PCE and 1,1,1-TCA	Loamy and sand and gravel alluvium over clay	LNAPL recovery, unsaturated zone excavation and ex situ bioremediation, enhanced anaerobic-aerobic biodegradation
8	AT&T Merrimack, Massachusetts, USA	PCE, TCE, 1,1,1-TCA	Alluvial sand and clay over fractured sandstone and siltstone bedrock	Hydraulic containment using strategically located abstraction wells and ex situ air stripping
9	Tyson’s Dump, King of Prussia, Pennsylvania, USA	1,2,3-trichloropropane, xylene, ethyl benzene	Predominantly sand and gravel drift over sandstone and siltstone bedrock	SVE and hydraulic containment using strategically placed abstraction wells and ex situ air stripping and carbon adsorption unit
10	Textile Factory, Hawkesbury, Ontario	PCE, TCE, DCM, 1,1,1-TCA	Fill and silty sand drift over glacial till	Natural biodegradation
11	Chemical Manufacturing Facility, New Jersey, USA	PCE, TCE, 1,2-DCE, VC, chlorobenzene	Glacial sand and clay drift over sandstone, shale and basalt bedrock	SVE and dual phase vapour extraction with density separation of DNAPL from abstracted groundwater, air stripping and carbon sorption

8.1 Case Study 1 - Eastern Counties Leather, Sawston, Cambridgeshire

8.1.1 Brief History

Background Information

Up until 1983, Cambridge Water Company Limited operated a public water supply borehole, Sawston Mill PWS (SMPWS), located in the River Cam valley about 2km north of Sawston (Figure 8.1). The pumping station was licenced to abstract up to 1.5 million gallons per day from the Chalk aquifer.

Groundwater quality monitoring at SMPWS identified water entering the distribution system containing between 50μg/l and 130μg/l tetrachloroethene (PCE). The PWS was taken out of production in October 1983 upon the discovery of the PCE.

Initial investigations identified two local tanneries as potential PCE sources, Eastern Counties Leather (ECL) was later determined to be the most probable source area of PCE contamination. Detailed subsurface investigations at the ECL site have been ongoing since 1984, largely to provide evidence for a lawsuit between Cambridge Water Company and ECL. It eventually ended in ECL's favour in the House of Lords Ruling of December 1993. The ECL site has commanded a great deal of attention and subsequently become an important legal as well as technical test case.

Environmental Setting

The Middle and Lower Chalk comprises a major aquifer in the area and is overlain by a minor drift aquifer. The two aquifers are in hydraulic continuity and the water table beneath the site is between 1m and 2m below ground level (bgl). The Chalk Marl horizon at the base of the Lower Chalk (about 50m bgl) is considered to form the base of the aquifer.

Bedding plane fissures frequently control groundwater flow, and fissured hardgrounds such as the Melbourn Rock and Totternhoe Stone have been identified in the study area as preferential flow horizons due to high secondary permeabilities. Both the Melbourn Rock and the Totternhoe Stone are underlain by low permeability horizons; the Plenus Marls and the Chalk Marl respectively.

The regional groundwater flow direction is northwards but local abstraction and upward discharge to surface water have a localised influence, producing a modified north-easterly flow direction at Sawston.

8.1.2 Site Characterisation

The site characterisation exercise to define the extent of the contaminant plume has been undertaken progressively over the ten year period since groundwater contamination was initially identified. Several remedial strategies have been implemented during this period as the site conceptual model was progressively developed. The site characterisation works undertaken are described chronologically below:

In 1984, 21 investigation boreholes were drilled into the Chalk aquifer at 12 locations between the two potential PCE sources and the SMPWS borehole by Anglian Water Authority (AWA). Four of the boreholes extend to the base of the Chalk, eight to a depth of approximately 15m in the Chalk, and nine to the base of the drift (which varies between 4m and 7m deep). These boreholes are referred to as 'AWA boreholes' to distinguish them from subsequent boreholes, and are shown in Figure 8.1. The boreholes provided geological information and an initial understanding of the distribution of contaminants with depth. Three gauging stations were also installed on the surface water courses. PCE concentrations were discovered in the River Cam which were traced to the Sawston streams.

The results from this study confirmed local contamination of the Chalk aquifer and indicated that the ECL tannery was the most probable source. The areal extent of the impacted aquifer area however, was not adequately characterised (Tester, Carey, Elder and Price, 1984).

A pumping test was conducted in the SMPWS well to assess the effects of groundwater abstraction on the Chalk and drift aquifers and surface water (Tester and Carey, 1985). Pumping test results were evaluated and a radial flow model used to simulate groundwater flow during the pumping test.

Geotechnical investigations using a flow meter and dye tracers were conducted at borehole AWA11, located 50m from the SMPWS well. Two geological horizons of relatively higher hydraulic conductivity were identified (Anglian Water Authority, 1985 Report No 3).

A geophysical borehole logging investigation was conducted in the SMPWS well and the AWA investigation boreholes in the Chalk (AWA 1, 8, 10 and 11) by the British Geological Survey (BGS). Logs for fluid temperature, fluid conductivity, borehole diameter, natural gamma, electrical resistivity, density and porosity (neutron) were produced (Buckley and Perkins, 1987).

A second series of investigation boreholes were drilled by the BGS on, and immediately adjacent to, the ECL site. The boreholes were numbered SC01, 02, 4a, 4b, 05, 06, 07 and extended to various depths within the Chalk (Figure 8.2). Geophysical logging identified some major flow horizons within the Chalk which correlated between boreholes on the ECL site (Buckley, Cripps and Shedlock, 1989). Depth sampling and porewater analysis was conducted in most of the boreholes and identified vertical variation in contamination relating to geological horizons in the Chalk.

Cores from SC01 were collected and analysed in the laboratory for permeability, porosity and density parameters. The results confirmed the findings of geophysical logging and helped characterisation of geology at the site (Bird, 1987).

In 1988, a report was produced describing the development of the sites conceptual model to date. The report is largely conceptual and recommended the drilling of more investigation boreholes to confirm the existing site conceptual model (Lawrence and Chilton, 1988).

In 1989, a preliminary soil gas survey around the ECL industrial site was conducted using a 5m grid spacing along four straight traverses. The survey results detected the presence of a shallow VOC vapour plume. It is assumed that the concentration of volatile contaminants in the soil gas reflected the dissolved concentration at the water table (Lawrence and Stuart, 1989).

Subsequent to the preliminary soil gas survey (Lawrence and Stuart, 1990), a second more extensive soil vapour survey was conducted. This involved measuring soil gas concentrations for PCE and carbon dioxide on a 30m grid spacing over the area to the north and west of the ECL factory. Twenty two shallow piezometers were also drilled to confirm the geology and collect shallow groundwater samples. The presence of two separate dissolved plumes was inferred; one broad plume in the shallow subsurface at the interface between the drift and the Chalk aquifer and one elongate narrow plume at a depth of 50m in the Chalk. The source of contamination in the shallow plume was indicated as the area of disused effluent settlement pits collecting the discharge from the ECL factory. The area is now waste ground situated approximately 50m to the west of the factory (Stuart, Cheney and Boyes, 1990).

A 45m deep borehole (SC08) was drilled to confirm the presence of the deep plume, indicated in the soil vapour surveys. Porewater analysis from SC08 contained relatively high concentrations of PCE beyond a depth of 45m. This suggests preferential migration of the dissolved contaminant near the base of the Chalk aquifer. Four existing boreholes (SC02, SC04B, SC07 and AWA1) were also sampled during this period of field work and the results confirmed the presence of two contaminant plumes (Stuart and Lawrence, 1990).

A shallow subsurface site investigation was conducted on the area of waste land to the west of the ECL site. The purpose of the investigation was to identify contamination in the upper 2m soil profile that may restrict proposed future developments of the site. Widespread solvent concentrations were discovered beneath the site, with the highest concentrations around the area of the old settlement pits. Recommendations for soil remediation prior to redevelopment of this area were presented (Berridge Environmental Laboratories Ltd, 1990).

In 1993, an evaluation of data on the ECL contaminant problem was performed and an updated site conceptual model was formed (Figure 8.1). The mass of phase-separated PCE in the Chalk and drift at the ECL site was estimated from results of previous field work. The total PCE mass in the subsurface was calculated as 140 tonnes, and preliminary estimates of rates of dissolution and transport from the site were suggested. The feasibility and costs of five remedial options for the Chalk aquifer were presented. Recommendations for further investigations to characterise contamination in more detail, and increase confidence in the conceptual model were presented. It was suggested that these investigations should be undertaken before selection of a remedial strategy (Dames and Moore International, 1993).

Further hydrogeological investigations at the ECL site were conducted in 1994 when an industrial water supply well for the ECL factory (Borehole B) was designed, installed and tested. Although elevated dissolved PCE (and degradation compounds) was identified throughout the entire chalk aquifer section, the well screen extended from 40m to 50m bgl, which was identified as the horizon containing the highest concentrations of dissolved PCE. This was performed in part, to contain the "deep" PCE plume from migrating off site. Replacement groundwater monitoring wells were also drilled as three of the SC series of investigation boreholes on the ECL site (SC05, 06, 07) were destroyed between 1987 and 1994. Two further boreholes (boreholes A and C) were sunk to the base of the Lower Chalk at 50m. Several horizons of elevated dissolved PCE were recorded in groundwater from boreholes A and C and from discrete depth samples.

The site investigation included a five stage step test, a five day constant rate pump test and discrete depth sampling using packers during drilling. These investigations produced hydraulic parameter estimates and provided an indication of the variation of contamination with depth, including identification of degradation products (Geraghty & Miller International, 1994).

8.1.3 Remedial Strategy

Three phases of remedial works have been undertaken in attempts to contain and reduce further migration of solvent at the ECL site:

Pumping from Sawston Mill PWS Borehole

Elevated concentrations of PCE were identified in Sawston Mill PWS borehole in 1983 and the borehole was taken out of production. Since 1983, the borehole has been intermittently pumped under the direction of the regulating authority (Anglian Water until 1989 and the National Rivers Authority since 1989). SMPWS is approximately 1km from the identified source of contamination, Eastern Counties Leather, Sawston.

Groundwater abstraction between July 1985 and September 1987 removed an estimated volume of 350 litres of PCE from the aquifer (Lawrence and Chilton, 1988). It is considered that pumping from SMPWS, which is over 1km from the source of contamination, has probably had a considerable impact by distributing the dissolved PCE further through the aquifer.

Pumping from AWA 3 at ECL

Borehole AWA 3 was drilled at the ECL site in 1984 as part of the initial investigation into groundwater contamination. The well extends to 15m below ground level and is screened throughout the saturated thickness. Analyses have shown concentrations of PCE in the groundwater as high as 40,000 μg/l (Tester, Carey, Elder and Price, 1984).

Between July 1985 to September 1987, groundwater abstraction at a rate of 2 l/s removed an approximate volume of 2630 litres of PCE from the aquifer. This borehole has been backfilled in the period since 1987 (Lawrence and Chilton, 1988).

Pumping from Borehole B at ECL

A preliminary feasibility study on potential remedial techniques applicable to the contaminated Chalk aquifer at ECL was commissioned by the NRA (Dames & Moore International, 1992). However, uncertainty in the conceptual model particularly with regard to volumes of free phase DNAPL that remain in the aquifer have restricted further action on this subject.

Abstraction from Borehole B at the ECL site is the favoured interim remedial strategy. Borehole B is screened across the most highly contaminated Chalk horizons, 40m to 50m bgl. The abstraction licence for this source limits the amount of water pumped to a maximum of 50,000 gal/hr or 80,000 gal/day. However, the borehole pump is controlled by a demand switch and therefore pumping is irregular and pumping periods are not recorded. The water is used in the factory operations and subsequently discharged to the main sewerage system via a collection tank where the water is aerated and the pH routinely monitored.

Abstraction from Borehole B at ECL is reducing the quantity of PCE in the aquifer close to the contaminant source and therefore reducing the potential for contaminant migration off site. Concentrations of PCE observed in groundwater samples indicate that residual DNAPL is probably still present in the Chalk aquifer beneath the ECL site.

Remedial techniques implemented at ECL are not ideal and are not considered to be the most efficient or cost effective means of aquifer clean up. The remedial investigation is on-going and selection of a suitable remedial alternative is planned.

8.1.4 References for Case Study 1

Anon (1985) *Tetrachloroethene Pollution at Cambridge Water Company Source at Sawston Mill.* Report no.3 - Testing Pumping at Sawston Mill, Anglian Water Authority.

Berridges Environmental Laboratories Ltd. (1990) *A Summary Report of a Site Investigation Carried out for Eastern Counties Leather Plc.*

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Tester D J and Carey M (1985) *Tetrachloroethene Pollution at Cambridge Water Company Source at Sawston Mill.* Report no. 2 - Situation report, Anglian Water Authority

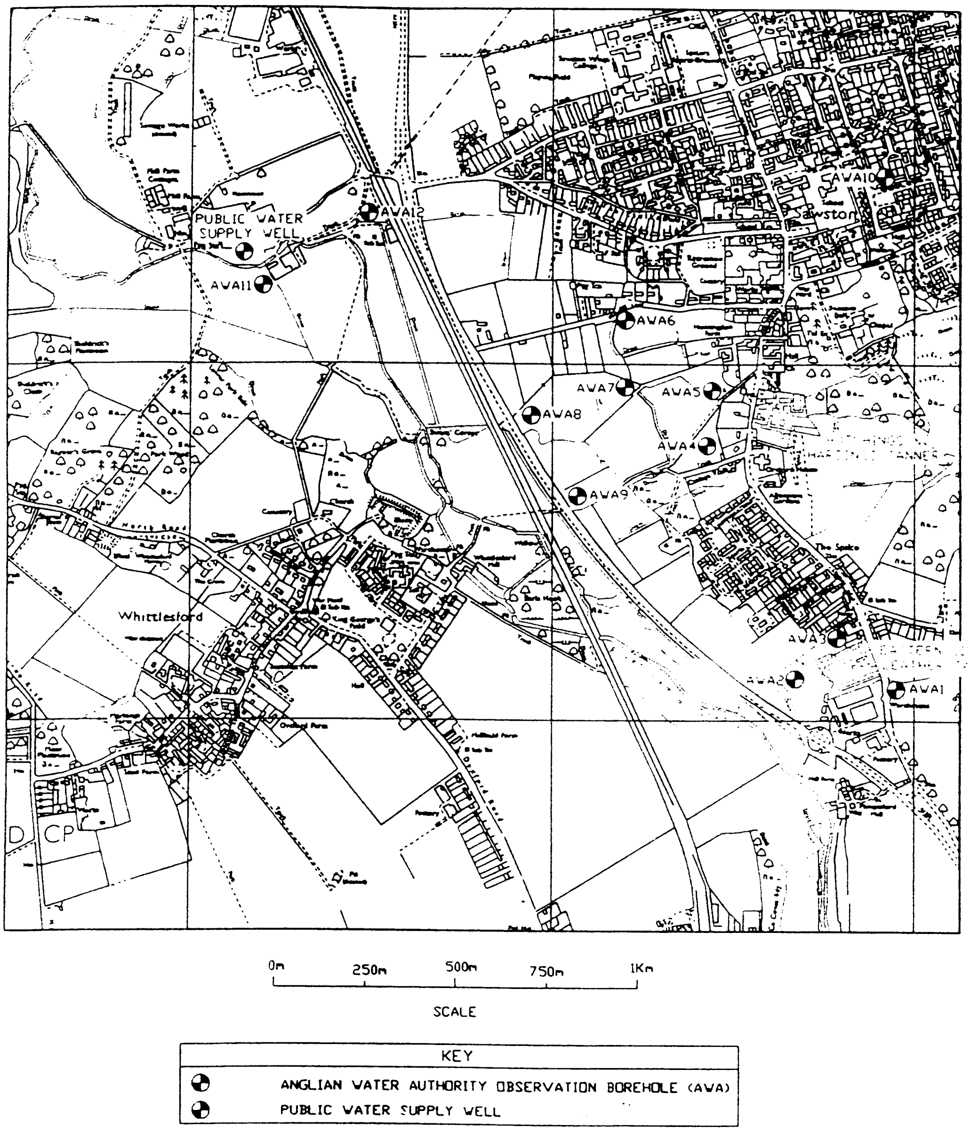


Figure 8.1 **Eastern Counties Leather and Sawston Mill PWS location map (from Geraghty & Miller, 1994)**

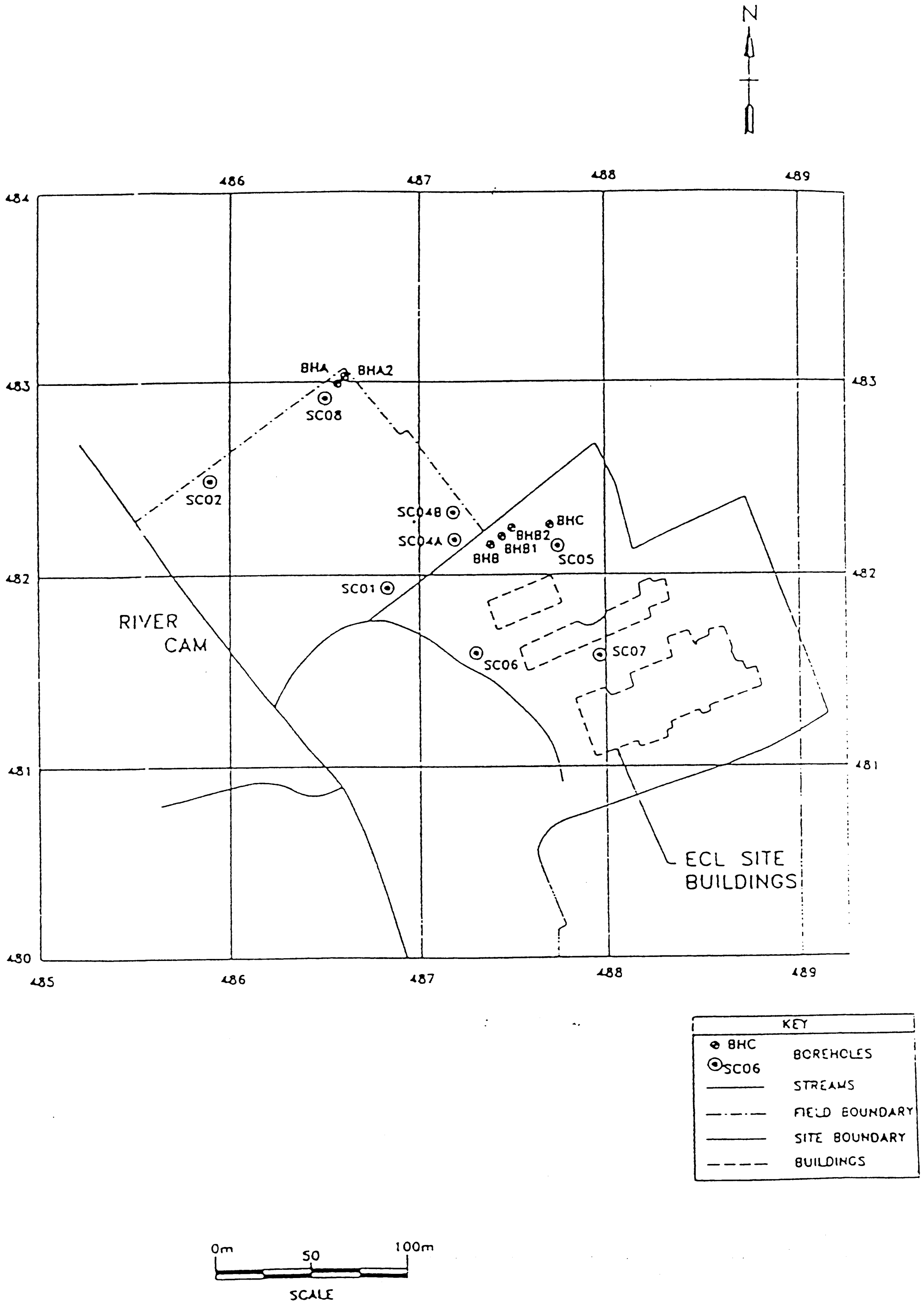
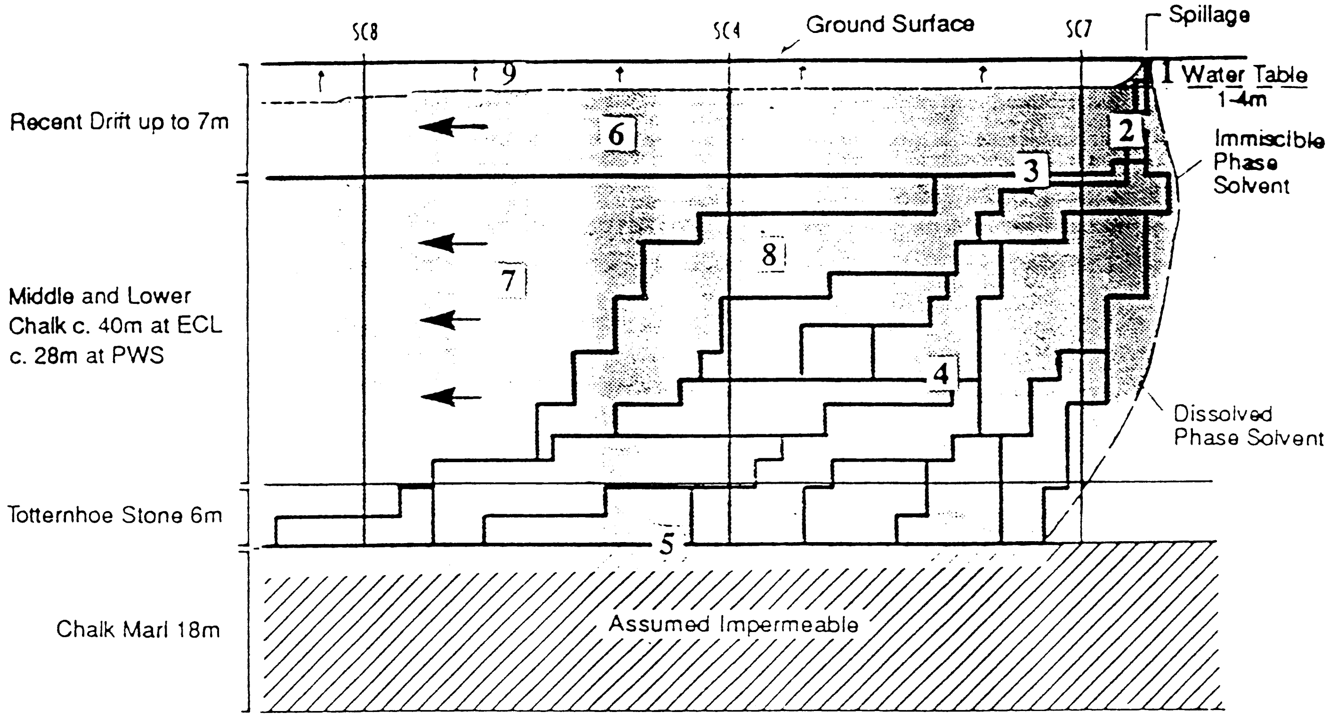


Figure 8.2 ECL site plan showing existing borehole locations, 1995



1 Residual NAPL PCE and dissolved PCE above the water table
2 Residual NAPL PCE below the water table in the Drift
3 Pools of NAPL PCE at the base of the Drift and/or perched on less permeable horizons within the Chalk
4 Residual NAPL PCE on fissure surfaces in the Chalk
5 Pool of NAPL PCE at the base of the Totternhoe Stone
6 Dissolved and sorbed PCE migrating in the Drift
7 Dissolved and sorbed PCE migrating in fissures in the Chalk
8 Dissolved PCE in the relatively immobile Chalk porewaters
9 PCE vapour in the unsaturated zone

Figure 8.3 **Conceptual model in cross section at ECL site (from Dames & Moore, 1993)**

8.2 Case Study 2 - Knitwear Manufacturer, Northumberland

8.2.1 Brief History

Background Information

In October 1991, a substantial spillage of the organic solvent tetrachloroethene or PCE was reported to the National Rivers Authority (NRA) at a knitwear factory in Berwick-upon-Tweed. The spillage had occurred during a bulk delivery of solvent. Subsequent investigations into solvent handling at the site discovered that discharge of solvent-contaminated process water had been occurring via a soakaway without the required consent to discharge.

Water discharging to the soakaway was effluent produced by separating a water-PCE mixture in a condensing separator used in industrial dry cleaning of garments at the factory. The discharged water had a concentration of PCE thought to exceed 150,000 μg/l.

Environmental Setting

The site is located on the Fell Sandstone Group, a sequence of sandstone lithologies separated by laterally persistent mudstone units. Individual sandstone units have not been mapped in the Berwick-upon-Tweed area, however, they commonly have a lens shaped geometry and rarely exceed 30m in thickness.

The Fell Sandstone Group is a locally important aquifer with four large public water supply boreholes in the Berwick area. Supply boreholes generally penetrate several sandstone units and achieve average yields of 2500m^3/d. The mudstone horizons separate the sandstones into hydraulically distinct units. The lower sandstones are generally artesian. Water quality in the Fell Sandstone Group aquifer units is generally good although there is potential for saline intrusion.

Thin superficial deposits overlie the Fell Sandstone Group in the vicinity of the knitwear factory in Berwick-upon-Tweed. Two production boreholes on a grain malting site are located approximately 100m down geological dip from the knitwear factory soakaway. The boreholes are licensed to produce 1500m^3/d, and are 107m and 95m deep. Approximately 75% of supply is provided by the shallower borehole.

8.2.2 Site Characterisation

Following the discovery of the soakaway at the knitwear factory the NRA undertook a series of investigations. Sampling of the maltings boreholes identified PCE contaminated groundwater in the deeper borehole with PCE concentrations of up to 60μg/l, PCE concentrations are generally <1μg/l in the shallower borehole.

A survey of all local industry was undertaken to identify any other potential sources of PCE.

Three monitoring boreholes were installed by the NRA to characterise the nature of the drift deposits overlying the Fell Sandstone. Geophysical borehole logging was undertaken, the borehole locations and natural gamma logs are shown in Figure 8.4 and Figure 8.5.

PCE contaminated groundwater was identified in the drift deposits near the soakaway and in observation well no.2 (2,150m south of the soakaway). No PCE was identified in observation well no.1 (1,400m southwest of the soakaway).

A conceptual model of the subsurface and potential migration pathways of solvent was developed and is illustrated in Figure 8.6. In both observation borehole no.2 and at the soakaway, the drift comprises mainly sands and gravels. A thin boulder clay layer overlies the Fell Sandstone Group and perched groundwater with a hydraulic gradient to the northeast, away from the production boreholes, is contained within the shallow sands and gravels. The sand and gravel deposits do not extend to the south and are absent in both production boreholes.

It is probable that contaminated groundwater flowed northeast in the sand and gravel aquifer until the boulder clay thinned. The impacted water then permeated into the underlying sandstone unit and migrated down gradient towards the south. The shallower sandstone units penetrated by observation borehole no.2 are protected by overlying boulder clay.

8.2.3 Remedial Strategy

A groundwater treatment plant has been installed at the malting factory. Abstracted groundwater is passed through a carbon filter treatment plant to bring it to within the maximum admissible drinking water concentration of 10µg/l for PCE.

The knitwear company has appointed consultants to investigate the options for aquifer remediation.

8.2.4 References for Case Study 2

Anon. (1992) *Knitwear Firm in NRA's First Major Aquifer Pollution Case* ENDS Report, August 1992, 211, p37.

Kershaw, M. and J.E. Clews (1993) *Investigation of a Solvent Problem Incident in Northeast England.* In Groundwater Pollution, proceedings from IBC Groundwater Pollution Conference, March 1993.

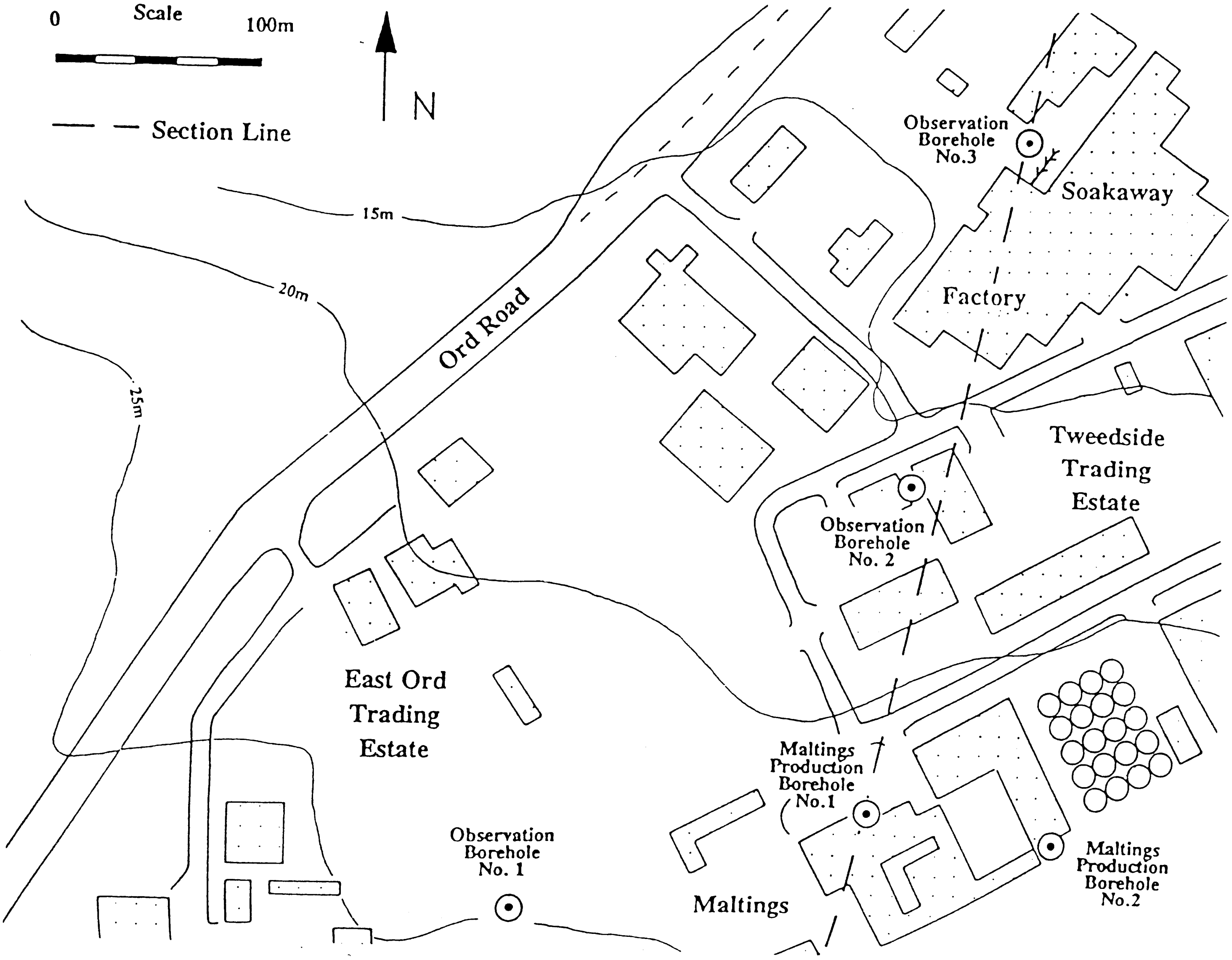


Figure 8.4 Knitwear Factory location plan (from Kershaw and Clews, 1993)

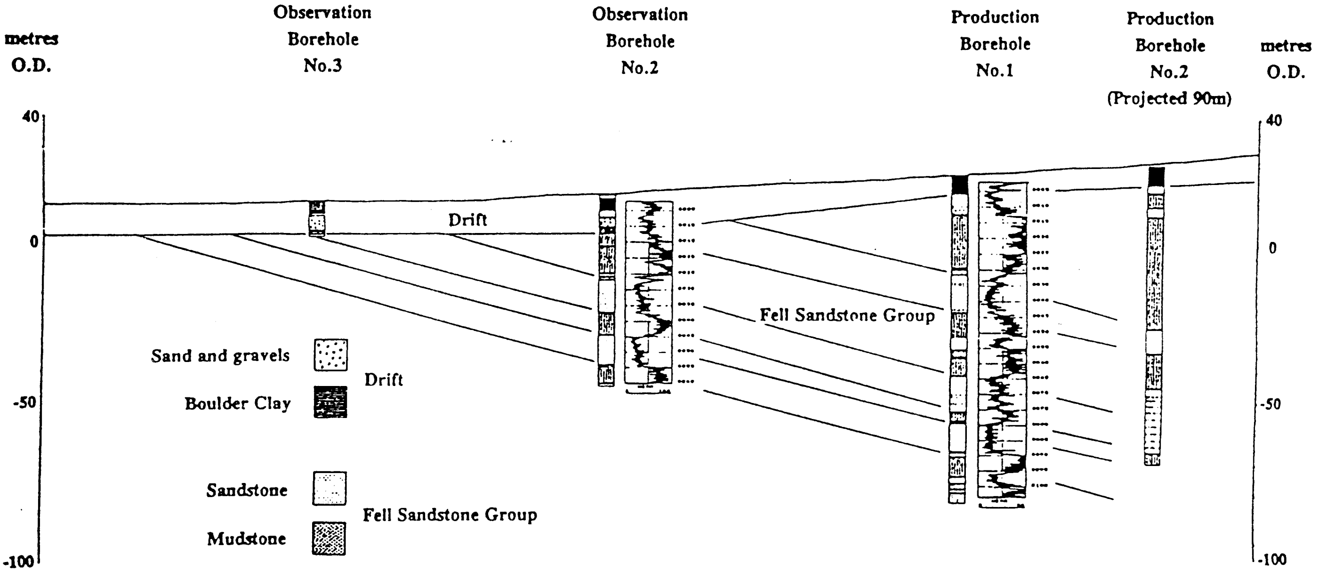


Figure 8.5 Geological cross section, line of section marked in Figure 8.2.1 (from Kershaw and Clews, 1993)

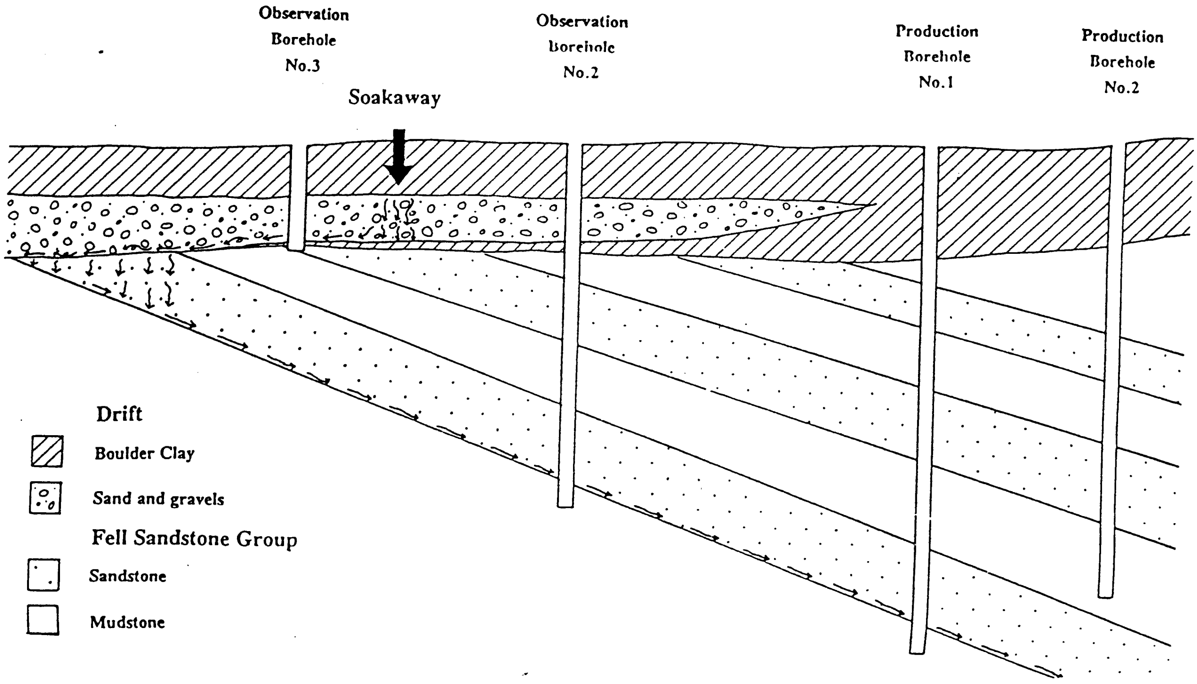


Figure 8.6 Conceptual cross section showing contaminant migration pathways (from Kershaw and Clews, 1993)

8.3 Case Study 3 - IBM-Dayton, South Brunswick, New Jersey, USA

8.3.1 Brief History

Background Information

The IBM-Dayton site is situated in South Brunswick, New Jersey. In December 1977, contamination of a public supply well, SB11, with organic solvents (primarily 1,1,1-TCA and PCE) was discovered. Subsequent investigations identified three potential industrial sources of the contamination and Figure 8.7 shows the TCA plumes defined from these investigations. It was determined from the preliminary investigations that IBM was the primary contributor to contamination at SB11.

Environmental Setting

The site is underlain by 35m of unconsolidated Pleistocene deposits, mainly silty sand, sand and gravel or clay, known as the Pensauken Formation. It overlies the Cretaceous silty sand of the Old Bridge Sand member of the Magothy Formation. The two units comprise the unconfined shallow aquifer beneath the site.

The Cretaceous Woodbridge Clay of the Raritan Formation forms an aquiclude beneath the upper unconfined aquifer, although it is locally absent notably in the area of SB11. A locally productive aquifer, the Cretaceous Farrington Sand, underlies the Woodbridge Clay, and is in turn underlain by a thick shale unit.

Groundwater flow in both the deep and shallow aquifers is dominated by the SB11 public supply well, and flow direction is to the northeast at the site.

8.3.2 Site Characterisation

The site characterisation investigations were designed to 1) define subsurface lithology, 2) determine directions and rates of groundwater movement, and 3) define the extent of contaminant plumes.

By 1984, 104 monitoring wells had been installed in the shallow aquifer and 44 in the Farrington Sand. Over 25,000 groundwater samples had been analysed. Lithologic logs defined the 'window' through the Woodbridge Clay in the vicinity of SB11 and identified the migration pathway for large volumes of recharge from the shallow aquifer to enter the Farrington Sand.

Although DNAPL was never directly observed, concentrations in the shallow aquifer up to 12,000μg/l TCA and 8,050μg/l PCE, that is 0.8% and 5.37% of their aqueous solubilities, suggested the probable presence of DNAPL. Contamination in the Farrington Sand generally involved the same contaminants at lower concentrations.

8.3.3 Remedial Strategy

The remedial objective (defined in 1978) was to restore groundwater quality in both the shallow aquifer and Farrington Sand aquifer to levels that would be suitable for municipal drinking water supply.

The suspected source of contamination at the IBM-Dayton site, several underground chemical storage tanks, was removed in 1978.

A groundwater abstraction system aimed at hydraulic containment of the contaminant plume was initiated in 1978. By 1984, the remediation system comprised 13 on-site abstraction wells in the shallow aquifer and one on-site abstraction well in the deep aquifer, operating intermittently in conjunction with the impacted public supply well SB11. Groundwater abstracted from the on-site wells was treated by air stripping and then used for spray irrigation to a local field. In 1982, an additional off site abstraction system was added between the IBM site and SB11, comprising seven abstraction wells and, for a short period in 1982, reinjection of the water from the off site wells to wells along the northern site boundary was undertaken. The use of injection wells was eventually stopped due to a deterioration in injection capacities of the injection wells.

Extensive groundwater sampling from over 100 monitoring wells indicated considerable reductions in TCA and PCE concentrations, although TCA was removed more readily due to its higher solubility and lower sorbing onto soil. By 1984 it was considered that continued pumping would not further reduce the TCA and PCE concentrations in groundwater and so the remedial operations were halted. It was assumed that natural attenuation would complete restoration of the aquifers.

Groundwater monitoring continued after 1984 and it soon became apparent that VOC concentrations were increasing, shown in Figure 8.8. By 1987, VOC concentration in the re-emergent plume was approximately 40% of the maximum 1978 concentration. The new plume was narrower and more readily defined than the original plume, and appeared to be influenced by the hydraulics of well SB11. Hydrogeologic assessments undertaken during 1987 and 1988 suggest the resurgence of VOC contamination is related to the presence of residual DNAPL in the shallow aquifer.

The inferred presence of DNAPL led to the abandonment of aquifer restoration objectives and led to a more pragmatic approach of long term hydraulic containment. The hydraulic containment operations were begun in October 1990 using existing abstraction wells and the existing ex situ air stripping unit.

8.3.4 References for Case Study 3

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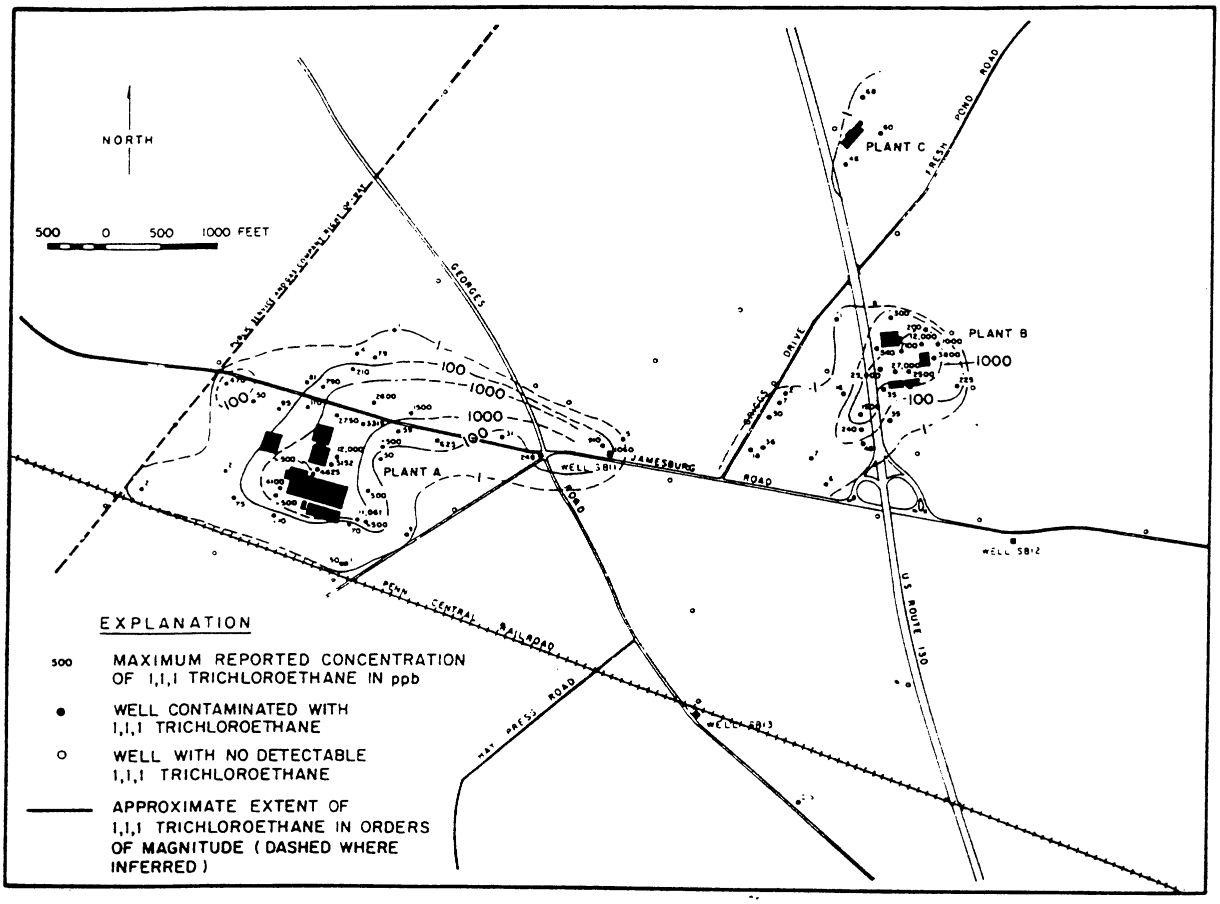

Figure 8.7 TCA distribution in Old Bridge Sand aquifer in 1978-1979 associated with three sites near SB11 (from USEPA, 1992)

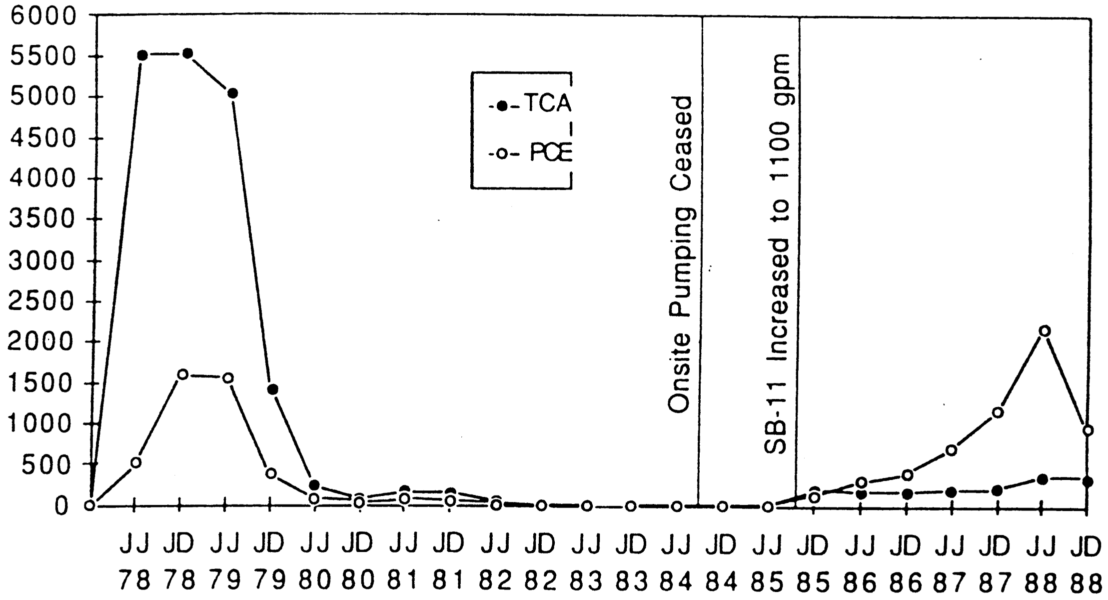

Figure 8.8 **History of TCA and PCE concentration in abstraction well GW168B, six month average concentrations shown (from USEPA, 1989)**

8.4 Case Study 4 - Harwell Laboratory, Oxfordshire

8.4.1 Brief History

Background Information

Contamination of the Thames Water public supply boreholes at Blewbury and Upton in Oxfordshire by the halogenated solvents TCE, TCM and TeCM was first reported to the NRA in 1990. Concentrations of these solvents were observed above background levels, generally between 1-2μg/l. The NRA undertook extensive groundwater sampling in the area, and the observed contaminant distribution suggested that the probable source was the Harwell Laboratory site.

Harwell Laboratory is situated on the site of a former RAF station in southern Oxfordshire. In 1946, the site was taken over by the UK Atomic Energy Authority (AEA). Between 1946 and 1977, limited quantities of various organic chemicals and organic solvents were disposed of at two locations at the Harwell Laboratory site, (Western and Southern Storage Areas shown on Figure 8.9). The Southern Storage Area was used to deposit wastes produced by the laboratory until 1970, including TCM, TeCM, 1,1,1-TCA, TCE, PCE, and BTEX compounds. The Western Storage Area was used after 1970 and ceased operating as a waste disposal site in 1977. The Western Storage Area was also licensed to accept wastes from outside sources and, in addition to those compounds listed above, received various other organics including trimethyl-benzene, styrene, naphthalene, chlorobenzenes, chlorotoluenes, PCBs and pesticides.

Environmental Setting

The Harwell Laboratory site is underlain by the Lower Chalk which extends to an approximate depth of 65m and dips gently southwards. The Lower Chalk overlies the Upper Greensand, which is underlain by the Gault Clay aquiclude. The Lower Chalk consists of a series of hard chalk horizons and soft marl bands. Two hard chalk horizons have been identified beneath the Harwell site (H1 and H2). These have been interpreted as more permeable zones separated by low permeability porous limestones and marls. The basal bed of the Lower Chalk is the Glauconitic Marl, a regional aquitard approximately 10m thick at Harwell.

8.4.2 Site Characterisation

Site characterisation at Harwell commenced in 1990 and comprised the following:

- A Phase I study included an examination of waste disposal records and investigation into possible contamination sources from RAF Harwell, including maintenance areas, fuel storage and motor transport areas.

- Phase II site investigations included monitor well installations, groundwater sampling from all boreholes at and around the site, and a soil vapour survey. Multi-level sampling, geophysical logging and flow logging were conducted to identify preferential flow horizons within the Chalk and contaminant depth profiles. Investigations by the NRA detected concentrations of up to 20,000μg/l of TCM and significant levels of other halogenated solvents in boreholes close to the Western Storage Area at Harwell (Figure 8.10). A subsequent investigation conducted by the AEA identified a second distinct contaminant plume in the Chalk related to the Southern Storage Area (Figure 8.11).

- Following these investigations a monitoring programme comprising monthly water level measurements and quarterly water sampling events was instigated. The field data was interpreted and extrapolated by the use of computer modelling techniques.

- The investigations have demonstrated that groundwater flow direction on the western site fluctuates seasonally; east during the winter and south east during the summer. On the southern site, the flow is predominantly towards the east south-east.

- Groundwater beneath the western site is contaminated by herbicides and a degraded mineral oil. The mineral oil is present as separate phase LNAPL in a layer 1-2cm thick. Chlorinated solvents, PCBs and BTEX compounds are present in the dissolved phase in both the mineral oil and the groundwater. The highest levels of contaminants were detected in the higher permeability horizons in the Lower Chalk.

- At the southern site atrazine, BTEX compounds and chlorinated solvents are present at concentrations approximately two orders of magnitude lower than those detected at the western site. Porewater analysis of drill core indicated an impacted zone between 10m and 15m below ground level, where TCE, TeCM, TCA, TCM and PCE were all detected in the dissolved phase. The dissolved phase contamination is spread over an elliptical area of approximately 50 x 30m.

8.4.3 Remedial Strategy

Initially, a hydraulic containment system was installed. Strategic groundwater abstraction wells were located to capture the contaminant plumes approximately 100m hydraulically down gradient from both storage areas. Air stripping and activated carbon adsorption were used to treat the abstracted groundwater.

The system was designed using a computer model to predict the number and location of abstraction and reinjection wells required. Hydraulic and contaminant transport parameters were estimated using tracer tests.

No decision on a long term remedial solution for the groundwater contamination at the Harwell Laboratory site has been made to date. Options examined for the western site (where the range of contaminants is much greater) include:

1. Bioremediation and soil vapour extraction combined with the existing pump and treat system.
2. LNAPL recovery and continued pump and treat .
3. Steam stripping with oil-water separation and off site incineration of contaminated soil.
4. Deep excavation and disposal of impacted soils.

Physical containment was rejected due to anticipated problems with producing an effective, grouted seal in fractured rocks.

At the southern site it has been proposed to excavate the source material and dispose of it into a landfill or incinerator and install an in situ soil venting system to treat the impacted unsaturated zone.

A trial soil vapour extraction system was operated from September 1994 to January 1995. Five vapour extraction wells were linked to a soil venting plant with two gas phase carbon beds. The test comprised 31 days of continuous vapour extraction from all the wells. A total of 18kg of chlorinated hydrocarbons were removed during this period. As anticipated the concentrations in the off gas stream decreased with time. The system was subsequently numerically modelled and a reasonable fit to the experimental data achieved. Predictions on the performance and feasibility of a full scale system have been made.

8.4.4 References for Case Study 4

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Fellingham, L.R., Ateyo, P.Y. and N.L. Jefferies (1993) *The Investigation and Remediation of the Groundwater Pollution at Harwell Laboratory,* in Groundwater Pollution, proceedings of the groundwater pollution conference, London, March 1993 (IBC Technical Services, London)

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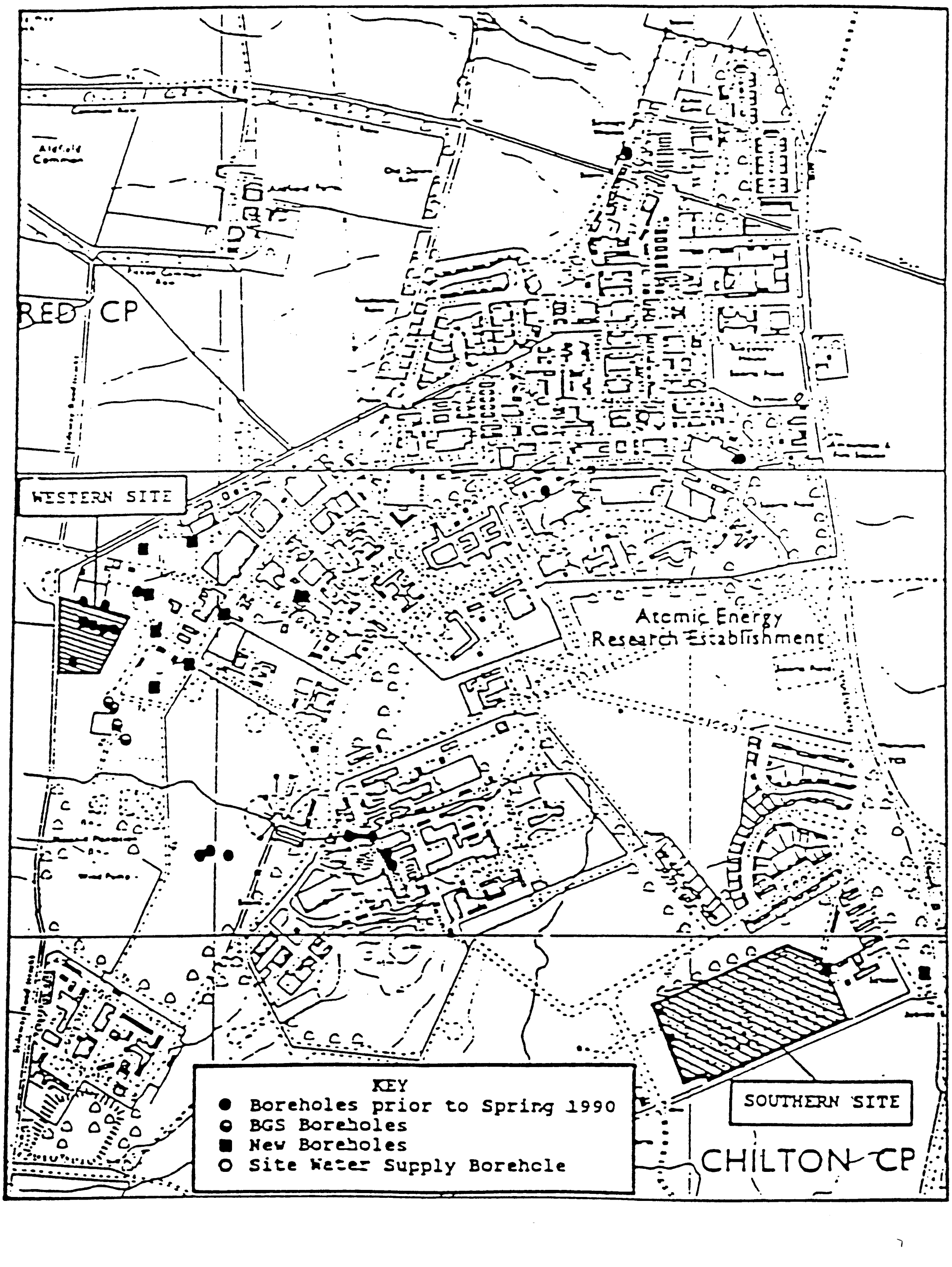


Figure 8.9 Harwell Laboratory site plan (from Fellingham et al., 1993)

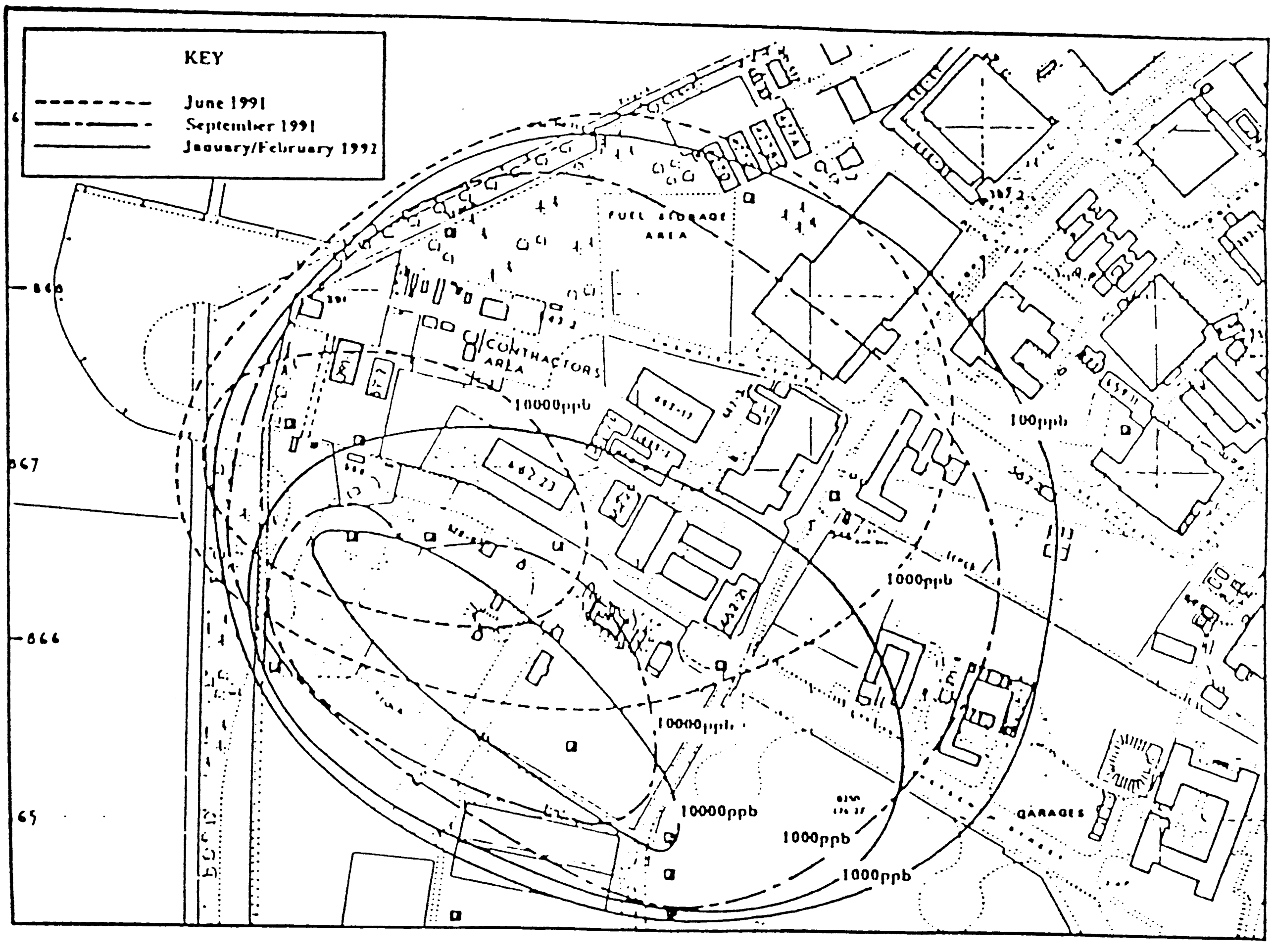


Figure 8.10 Total chlorinated solvent concentration distribution at the Western Storage Area (from Fellingham et al., 1993)

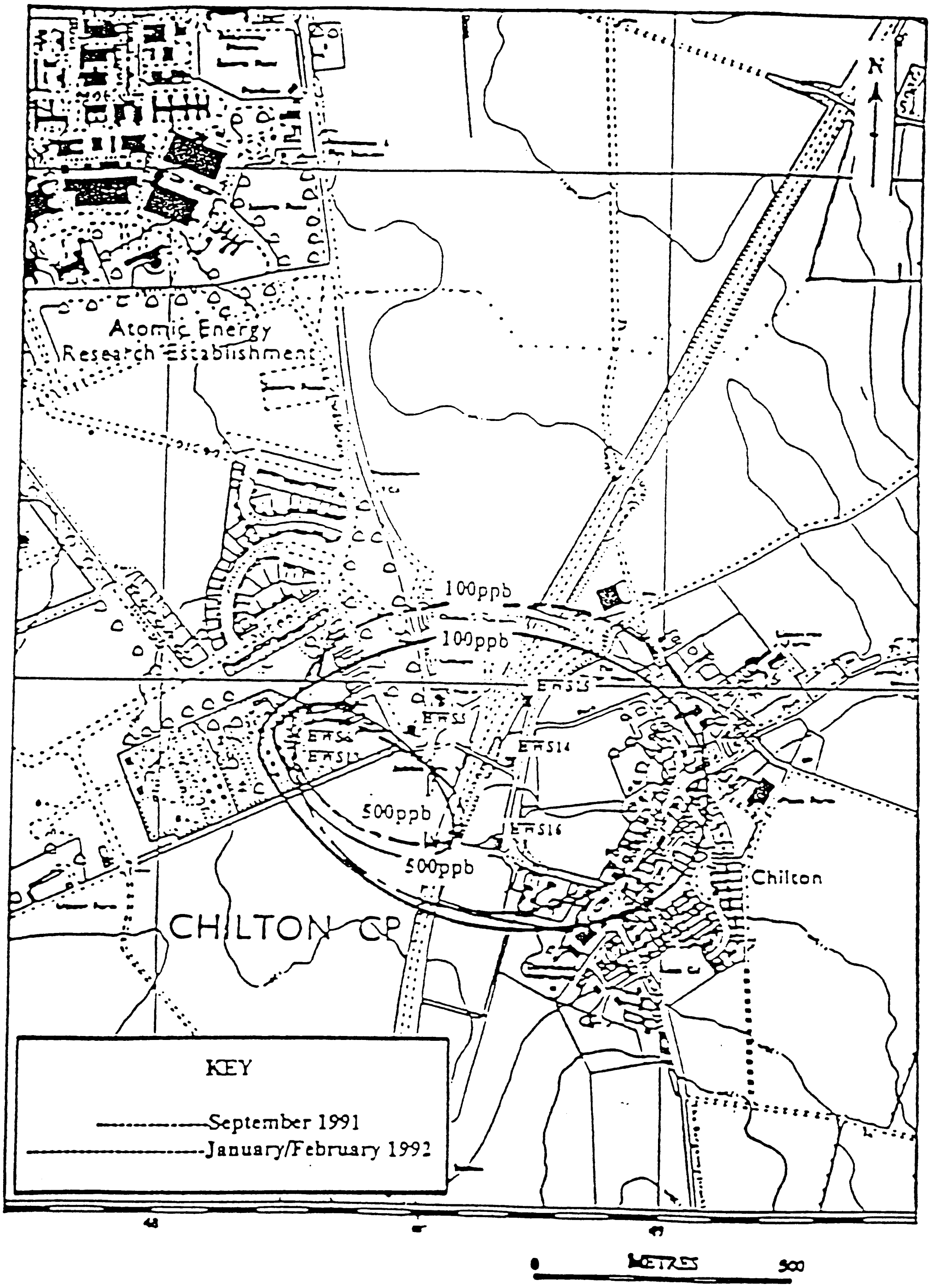


Figure 8.11 **Total chlorinated solvent concentration distribution at the Southern Storage Area (from Fellingham et al., 1993)**

8.5 Case Study 5 - Portsmouth Uranium Enrichment Plant, Ohio, USA

8.5.1 Brief History

Background Information

The Portsmouth Uranium Enrichment Plant, owned by the US Department of Energy, enriches uranium by means of gaseous diffusion for use in nuclear reactors. The 1600 hectare facility has over 100 Solid Waste Management Units (SWMUs), which are potential sources of solvent contamination, and has been designated a RCRA (covered under the Resources Conservation and Recovery Act (USA)) site by USEPA.

Environmental Setting

The plant is located within the partially buried pre-glacial Portsmouth River Valley, comprising Mississippi shales and sandstones overlain by sand, gravel and clay. The stratigraphy and average hydraulic conductivity values of the geological units at the site are shown in Figure 8.12. At the uppermost unit the Minford lacustrine clay has an average thickness of 7.5m. Beneath the Minford formation lies the Gallia sand and gravel which varies in thickness from 0-3.5m, relating to bedrock topography.

Underlying the Gallia sands and gravels lies the bedrock surface of Sunbury Shale and Berea Sandstone which dips gently to the southeast. The Sunbury Shale comprises a black shale and overlies the Berea Sandstone, a fine grained calcite cemented sandstone. The Sunbury Shale thickness ranges from 0m in the western part of the site to 7.5m. The Berea Sandstone is approximately 10m thick and underlain by a thick shale unit. A schematic geological cross section is shown in Figure 8.13.

The Gallia alluvium forms a shallow aquifer of limited extent beneath the site. Groundwater is semi-confined by the Minford formation and flow direction is radial away from the site, with a dominant northward direction along the river valley. Gallia groundwater discharges to the small streams which surround the site.

The Berea Sandstone forms a deeper secondary aquifer. Groundwater flow is regionally to the southeast, following the structural dip. Locally, groundwater flow is influenced by streams which cut into the formation. On the eastern part of the site, the Sunbury Shale hydraulically separates the Gallia and Berea aquifers. However, to the west the Sunbury formation thins and the Gallia and Berea aquifers are in hydraulic continuity.

TCE contamination of the Gallia aquifer was identified during a routine quarterly groundwater monitoring event. A 0.5m thick layer of separated phase DNAPL TCE was identified in the base of a monitor well screened in the Gallia aquifer.

8.5.2 Site Characterisation

The environmental setting of the Portsmouth Gaseous Diffusion Plant was comprehensively known prior to discovery of separate phase TCE. Therefore, a focused site characterisation was undertaken to identify specific data required for the implementation of remedial action.

The initial desk study revealed the most likely source of TCE to be a holding pond on the northeast part of the site, used to hold acidic waste water containing metals, solvents and low level radioactive waste. The pond was used between the 1950s and 1988, therefore leakage could have been on going for over 30 years. The field investigations were focused in this area of the site.

Four monitor wells were installed within 12m of the contaminated well, and numerous monitor wells were installed hydraulically down gradient of the contaminated well. All wells were screened to the base of the Gallia formation. No further free phase DNAPL was discovered but several wells contained groundwater with TCE concentrations exceeding 100mg/l. A conceptual model of DNAPL in the Gallia aquifer is shown in Figure 8.14.

Sampling of surface water courses to which Gallia groundwater discharges was conducted. The results helped delineate the extent dissolved TCE plume. Figure 8.15 shows the extent and concentrations of the TCE plume identified during site characterisation.

Seven groundwater monitor wells were installed in the Berea Sandstone in the area of the shallow dissolved plume. However groundwater from these wells did not contain TCE indicating the Sunbury Shale acts as an effective hydraulic barrier.

Hydraulic testing of some monitor wells was undertaken to assess the hydraulic characteristics of the Gallia and Berea aquifers. Figure 8.12 indicates calculated hydraulic parameters.

A numerical groundwater flow model of the site was constructed using USGS MODFLOW (three dimensional finite difference groundwater flow model), and a particle tracking application (USGS MODPATH) was used to compute travel times and migration pathways of contaminants within the aquifer. The model covered the entire river valley and extended to the boundaries of the Gallia aquifer. The site wide model was refined using the ‘telescopic mesh refinement’ facility to produce a refined steady state groundwater flow model of the aquifer in the vicinity of the holding lagoon and the contaminant plume. The computer model was used as a tool to assist in the selection of a remedial alternative.

8.5.3 Remedial Strategy

The first priority of the remedial strategy was to remove the DNAPL pool at the base of the Gallia formation as this was acting as a source for dissolved TCE in the aquifer. A bladder pump was installed at the base of the well containing the separate phase DNAPL, and was pumped at less than 4 l/min until the DNAPL-water interface dropped below the pump intake. The pump operated intermittently to allow the DNAPL level to recover. As DNAPL recovery progressed the water breakthrough occurred faster and the DNAPL took longer to recover. Within a month, pumping only took place every few days and within three months pumping was only required every few weeks. After one year the pump was removed. At the cessation of pumping, DNAPL was present as a film <3mm thick within the well, and a total of 450 litres of DNAPL had been recovered.

The numerical groundwater flow model was used to assess two options for remediating the dissolved phase plume:

1) Groundwater abstraction/capture wells - The model was used to simulate the effect of varying locations and abstraction rates of the proposed wells on the flow regime. The capture zones of these wells were defined by particle tracking. The model showed that the number of wells required to capture the plume would be large as the saturated thickness of the Gallia aquifer limits the maximum radius of influence of the wells.

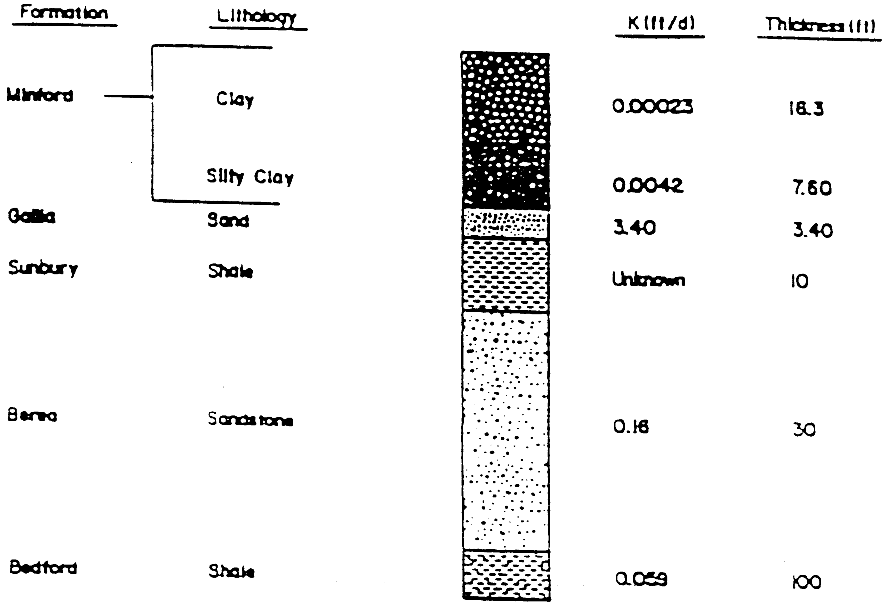
2) Interception drainage ditch - The drainage ditch would be designed to capture the plume and halt further migration. The disadvantages of this option are that it produces a large volume of contaminated soil and is a more expensive system to install than the capture wells. However, several drain geometrys were considered, including interception drain and slurry wall configurations, all of which were simulated by the numerical model.

Based on the results of the computer simulations, a 200m long interception drain penetrating the entire thickness of Minford and Gallia formations was constructed. The drain was located parallel to the north-south flowing water course and intercepted the entire dissolved plume. An existing site drain was incorporated into the 200m drain to reduce the volume of excavated material.

The model was used to determine the optimum hydraulic head in the drain to effectively capture the plume and the required discharge rate from the drain was calculated as 35 l/min. An ex situ air stripper and activated carbon adsorption unit was used to treat the abstracted groundwater.

8.5.4 References for Case Study 5

Matters, S. and J.O. Rumbaugh (1990) *Remediation of a DNAPL Pool and Associated Groundwater Contaminant Plume by Means of an Interceptor Drain.* Geraghty and Miller Inc., Dublin, Ohio.



Formation	Lithology	K (ft/d)	Thickness (ft)
Minford	Clay	0.00023	18.3
	Silty Clay	0.0042	7.60
Gallia	Sand	3.40	3.40
Sunbury	Shale	Unknown	10
Berea	Sandstone	0.16	30
Bedford	Shale	0.059	100

Figure 8.12 Stratigraphy at the Portsmouth site (from Matters and Rumbaugh, 1990)

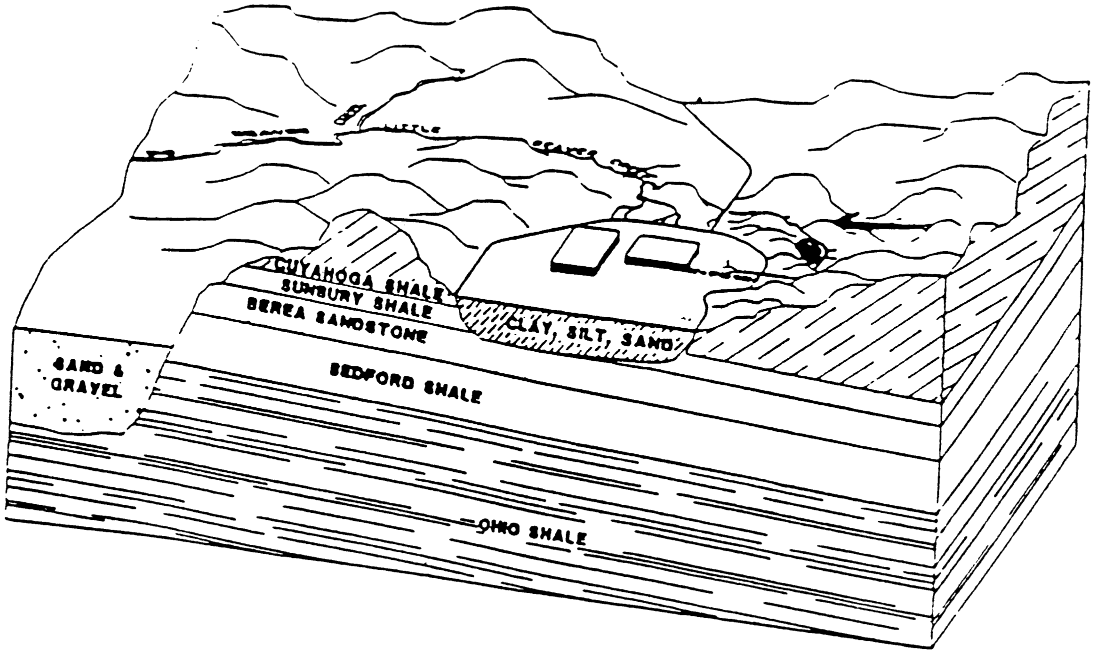


Figure 8.13 Schematic geological cross section (from Matters and Rumbaugh, 1990)

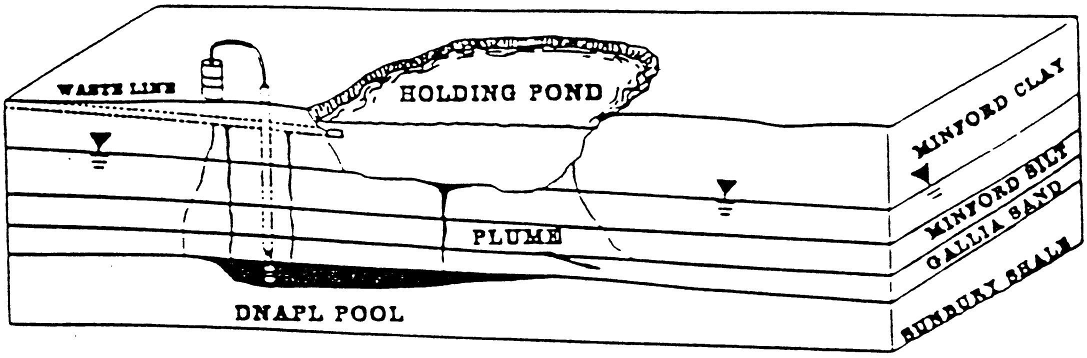


Figure 8.14 Conceptual model of DNAPL migration beneath the Portsmouth site (from Matters and Rumbaugh, 1990)

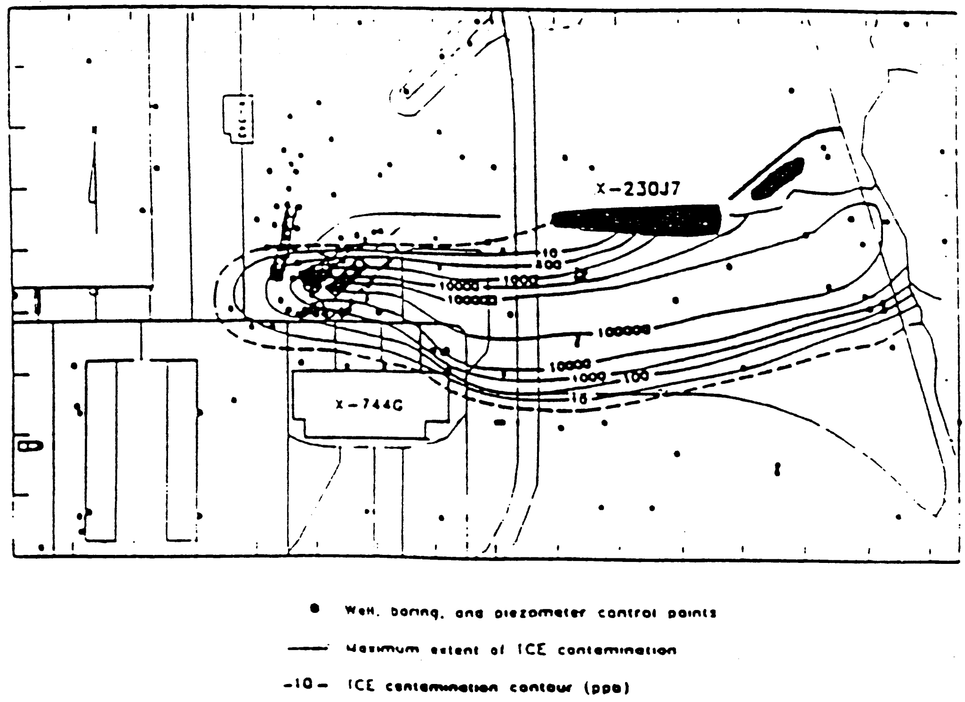


Figure 8.15 Plume of dissolved TCE in Gallia aquifer (from Matters and Rumbaugh, 1990)

8.6 Case Study 6 - Niagara Falls Landfills, New York, USA

8.6.1 Brief History

Background Information

Hooker Chemicals & Plastics Corporation, now known as Occidental Chemical Corporation (OCC), buried chemical wastes at the Love Canal, 102nd Street, S-Area and Hyde Park landfills in Niagara Falls between 1942 and 1975. A map showing the landfill locations in Niagara Falls is shown on Figure 8.16.

Love Canal

Love Canal was excavated in the 1890s to enable hydroelectric power generation to be developed in the area. However, this particular scheme failed in 1896. The resulting void (dimensions 920m long, 12-30m wide and 2.5-4.6m deep) was used for waste disposal of 22,000 tonnes of mainly drummed liquid and solid chemical waste from 1942 to 1953.

The Love Canal was first recognised as a site of serious environmental impact in 1976 when heavy precipitation exacerbated the situation and caused the following problems:

- subsidence of landfill surface and exposure of drummed waste
- ponding of contaminated surface water on adjacent properties
- unpleasant chemical odours cited by the local population as the cause of illness
- leachate migration into basements of nearby properties and through the local sewer system.

As a result, several health emergencies were announced by the New York State Health Commissioner and a State of Emergency at Love Canal was declared by President Carter in 1978 and again in 1980. The Love Canal incidents since 1976 have prompted further investigations at the other Niagara Falls chemical landfill sites mentioned above.

Hyde Park Landfill

The Hyde Park Landfill is 600m east of a deep gorge formed by the Niagara River, downstream of Niagara Falls. OCC started using Hyde Park landfill in 1953 for chemical wastes previously buried at Love Canal. Up until 1975, OCC dumped approximately 80,000 tonnes of liquid and solid chemical wastes into pits and trenches at the Hyde Park site.

Environmental Setting

Love Canal

A schematic cross section showing stratigraphy at the Love Canal landfill is shown in Figure 8.17. In Spring 1978, groundwater elevation monitoring at the site, identified the groundwater table immediately below or at the ground surface in the southern part of the landfill, and led to the development of overland flow and leachate ponds in low lying areas. A groundwater mound had developed at the site, resulting in radial groundwater flow away from the landfill.

The shallow aquifer comprises fill, silty sand and sandy silt overlying fractured hard silty clay. This shallow aquifer is hydraulically separated from the Lockport Dolomite aquifer by a soft silty clay horizon and glacial till. The Lockport Dolomite is an aquifer of regional resource importance. The Rochester Shale, an aquitard, underlies the Lockport Dolomite.

Hyde Park Landfill

At the Hyde Park landfill (approximately 8.5km northwest of Love Canal) the overburden is considerably thinner and comprises silty clay with no glacial till. The waste body is emplaced in a void excavated through the overburden to the upper surface of the Lockport Dolomite. A schematic diagram showing the geological formations and topographic features in the vicinity of the Hyde Park landfill are shown in Figure 8.18.

8.6.2 Site Characterisation

Love Canal

Extensive remedial investigations have been undertaken at Love Canal funded by city, state and federal governments. During the first major drilling programme in 1978, off site boreholes were augered at a spacing of approximately 3m along the line of a proposed hydraulic cut off drain. This investigation identified an oily film in the fractures of the hard silty clay, representing free phase DNAPL. This caused the cut off drain design to be altered so the hydraulic cut off was keyed into the soft silty clay, deeper than the hard silty clay.

A further detailed study of chemical conditions at Love Canal was undertaken in 1980 where continuous split spoon samples were taken at 64 locations immediately surrounding the landfill. This study documented the extent of the DNAPL in the subsurface and identified that the DNAPL was resting on the soft silty clay, comprising a capillary boundary.

In 1986, the installation of a further 21 borings allowed the upper surface of the DNAPL pool to be defined. DNAPL pumping experiments were performed during 1988 and 1990 to characterise the DNAPL migration further. DNAPL flow occurred mainly through the fractured silty clay and transmitted DNAPL into basements and drains. A dissolved phase plume and soil gas plume were identified associated with the migrating DNAPL plume.

Hyde Park Landfill

Groundwater investigations were initiated at Hyde Park in 1978 when OCC installed a shallow tile drain and clay cover at the site in order to reduce leachate generation and prevent contaminant migration to a surface water course (known as Bloody Creek) close to the landfill. Monitoring wells were also installed as part of this investigation.

In April 1982, OCC agreed to undertake further investigations following negotiations relating to an EPA enforcement action at the site. The agreement required OCC to: a) determine the extent of contamination, b) cap contaminated soils, c) collect and treat contaminated groundwater, and d) remediate contamination in Bloody Run stream.

OCC performed the required remedial investigations between 1982 and 1984. A major part of the investigation involved drilling to the top of the Rochester Shale along several lines of section in the vicinity of the site in order to determine the extent of contamination. The drilling programme was designed to avoid vertical cross contamination of the aquifer, and identify the extent of aquifer contamination. Drilling and hydraulic testing was undertaken in 5m sections to prevent any vertical migration of DNAPL or groundwater, as described in Section 4.0 of this report. If contamination was observed at levels exceeding specified levels, the hole was abandoned and grouted and a new hole drilled 250m further from the landfill along the line of section.

Hydrogeology in the Hyde Park area is controlled by the Niagara Gorge, man-made buried conduits and a canal constructed to provide water to a hydro-electric power station, all of which are groundwater discharge zones (shown in Figure 8.18). The overburden and Lockport Dolomite bedrock are generally in hydraulic continuity.

Analyses of the groundwater samples collected during the drilling exercise identified that contamination had migrated considerably further than previously thought. Contaminated groundwater was identified emanating from seeps in the Niagara Gorge in July 1984.

Figure 8.19 indicates the extent of the NAPL and dissolved phase plumes. It is considered that groundwater flow beneath the site has occurred in several directions since the 1950s due to the construction of the canal and buried conduits, and therefore the contaminant plumes identified during site investigation were more extensive than anticipated.

8.6.3 Remedial Strategy

Remedial actions at hazardous waste sites where groundwater has been contaminated, such as the Niagara Falls landfills, can generally be divided into three categories a) excavation of wastes and contaminated soils for burial at another landfill or incineration, b) hydraulic containment of subsurface chemicals, and c) no action or limited action, such as adding a clay cap to the landfill.

Feasibility studies have indicated that option a) would cost $237-560 per cubic yard to excavate and re-landfill, and $900-3300 to excavate and incinerate. Therefore, total cost of remediation of any of the Niagara Falls landfills by option a) would be between $100 million and $4 billion. Also the limited space available at hazardous waste landfills, and the exposure risks of excavation of the hazardous wastes are further impediments to remedial option a). As a result of these considerations, excavation of wastes at the Niagara Falls landfills has not been judged to be cost effective. Hydraulic containment has been selected as the preferred option at the Niagara Falls landfills.

Love Canal

Remediation at Love Canal has proceeded in stages since 1978. The main objectives have been to contain chemical migration, clean up contaminated areas and limit chemical exposure.

Following President Carter's Emergency Declaration of August 1978, Phase 1 of site remediation efforts was focused in the southern Love Canal section. This comprised construction of a leachate collection system of barrier drains parallel to the sides of the southern part of the Love Canal. Vitrified clay pipe was placed in trenches 3.7-4.6m deep and 1.2m wide. The trench was backfilled with crushed stone and sand to ground level. Leachate entering the drains passes by gravity to sumps and is then pumped to an on site treatment plant. In January 1979, eight lateral french drains were installed to increase rate of leachate head reduction prior to placement of clay cover.

In May 1979, the second phase of the remediation programme began as the leachate collection drain and lateral french drain system was extended around the central and northern sections of the Love Canal. In December 1979, construction of a permanent activated carbon treatment plant was completed, the effluent of which was discharged to a sanitary sewer.

In May 1980, the Emergency Declaration allowed residents in the Emergency Declaration Area (EDA) to be relocated at Government expense, and by May 1982, 570 households had been relocated. Also, in 1980, sewers considered to be acting as conduits for chemical migration off site were plugged. Additional remedial work to improve site containment was undertaken between 1982 and 1984, including:

a) Construction of a HDPE synthetic membrane cover over the entire site and the immediately surrounding area.
b) Installation of drainage on the HDPE cover to divert surface runoff.
c) Inspection, cleaning and repair of perimeter drains.
d) Placement of several strategic concrete cutoff walls,
e) demolition of many homes and a school.

A feasibility study into a concrete cutoff wall surrounding the entire site was undertaken, including numerical groundwater modelling to indicate hydraulic implications of the cutoff. The concrete cutoff was considered to be of limited benefit and the plans were shelved. In 1986, a major clean up of storm and sanitary sewers and surrounding surface water courses was undertaken, including pumping and dredging of contaminated sediments.

The hydraulic containment system has been operational since 1979 and monitoring data have shown that the average annual flow to the collection system has declined with time, indicating significant dewatering of the landfill.

Hyde Park

Subsequent to the extensive site characterisation at Hyde Park, OCC submitted a proposed remedial action plan. Negotiations with the Government continued until 1985 and resulted in a USEPA ‘Stipulation on Requisite Remedial Technology’. Additional investigations required by the Stipulation included drilling to determine the depth of chemical migration in bedrock and extensive groundwater monitoring. Remedial measures required by the Stipulation focus on source control, overburden remediation, bedrock remediation and control of seepage at the Niagara Gorge.

Two and three dimensional numerical groundwater flow and solute transport models were implemented to aid design of the containment system. The complexity of the geologic setting and uncertainty about the performance of certain innovative remedial technologies necessitated a phased approach that involved prototype systems and pilot studies. It is worth noting the extensive on-going monitoring programme at Hyde Park is an integral part of the remedial operations.

The source control programme includes dewatering of the waste and covering the waste body with a synthetic cover. A pilot study, where one large diameter sump for collection of liquid wastes was installed, was undertaken to test the efficiency of the dewatering system. Following which, a full scale dewatering scheme was implemented.

The overburden remedial programme is designed to achieve the lateral hydraulic containment of dissolved chemicals and NAPL. A tile drain around the perimeter of the dissolved phase plume in the overburden and abstraction wells designed to control hydraulic gradient and therefore halt further outward migration were installed.

The Lockport Dolomite fractured aquifer remedial system comprises a hydraulic containment system. Figure 8.20 shows the injection-abstraction well system designed to remove DNAPL from the aquifer. This system avoids dewatering the upper part of the Lockport Dolomite that is contaminated and forces the circulation of groundwater to aid aquifer clean up. A line of interceptor wells was installed within the dissolved phase plume west of the site close to the Niagara Gorge to stop the discharge of contaminated groundwater to the Niagara River via seepages in the gorge.

8.6.4 References for Case Study 6

Cohen, R.M., R.R. Rabold, C.R. Faust, J.O. Rumbaugh and J.R. Bridge (1987) *Investigation of Hydraulic Containment of Chemical Migration: Four Landfills in Niagara Falls.* Civil Engineering Practice, Journal of the Boston Society of Civil Engineers 2(1):33-58.

Cohen R.M. and J.W. Mercer (1993). *DNAPL Site Evaluation, Robert S Kerr Environmental Research Laboratory, Oklahoma.* USEPA Publication EPA/600/R-93/022, February 1993.

Koszalka, E.J. J.E. Paschal, T.S. Miller and P.B. Duran (1985) *Preliminary Evaluation of Chemical Migration to Groundwater and the Niagara River from Selected Waste Disposal Sites.* USEPA 905/4-85-001, March 1985.

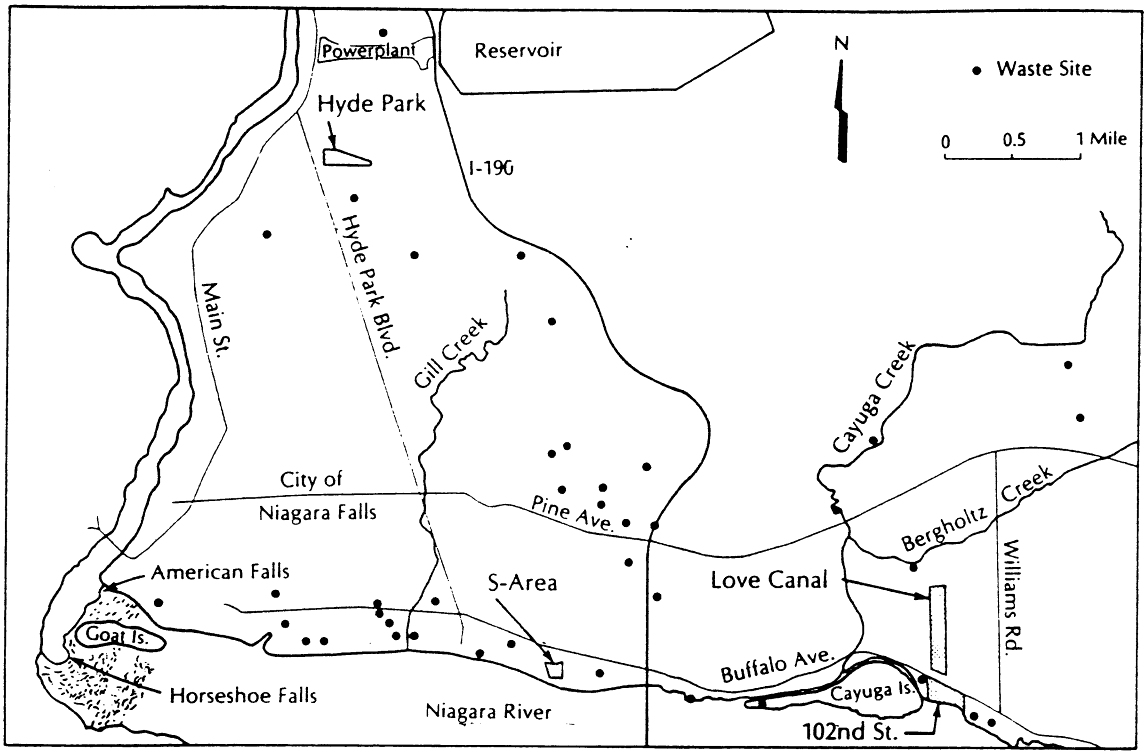


Figure 8.16 **Locations of waste disposal sites in Niagara Falls (from Cohen et al., 1987)**

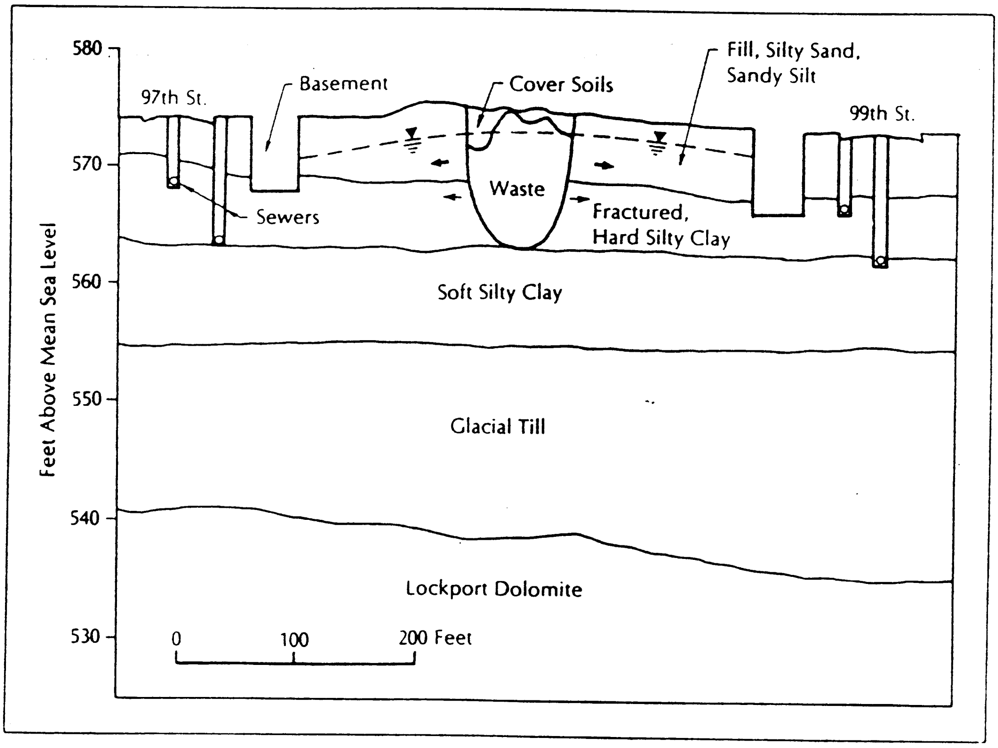


Figure 8.17 **Schematic geological cross section through Love Canal landfill (from Cohen at al., 1987)**

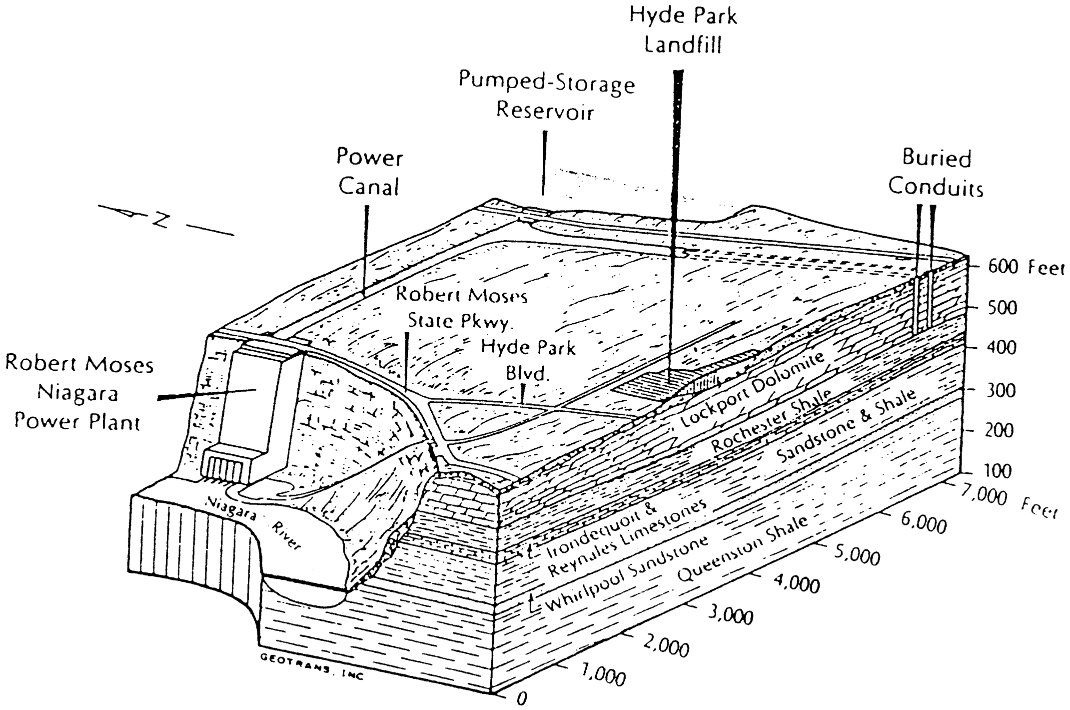


Figure 8.18 Schematic geological cross section showing Hyde Park landfill (from Cohen et al., 1987)

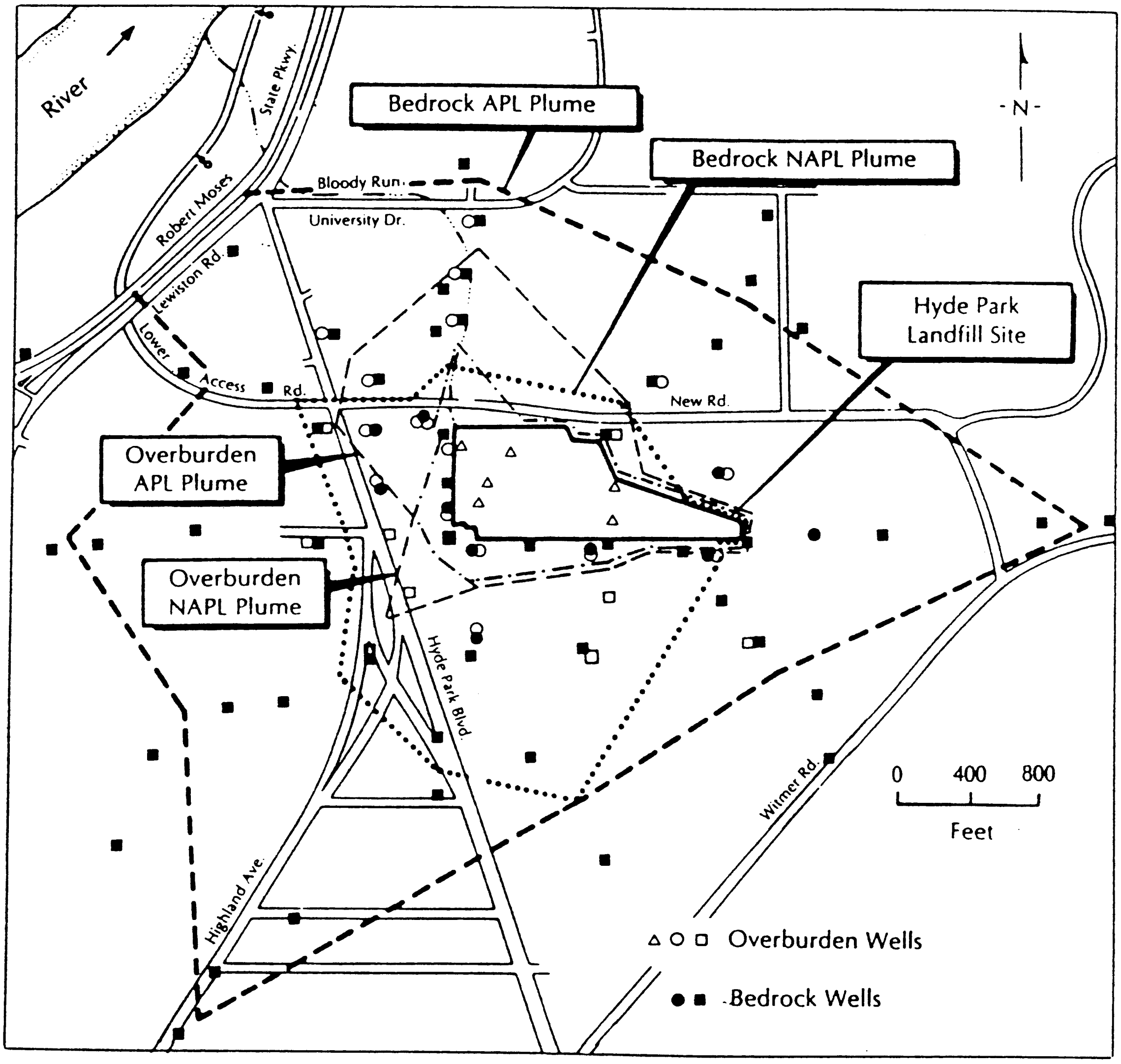


Figure 8.19 Boundaries of dissolved and NAPL contaminant plumes in drift and Lockport Dolomite at Hyde Park landfill (from Cohen et al., 1987)

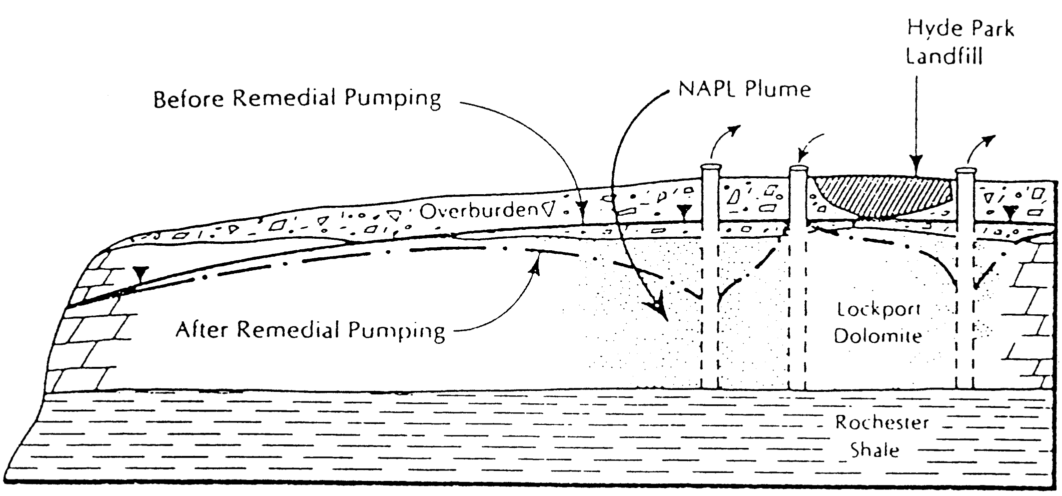


Figure 8.20 Conceptual cross section showing remedial system at Hyde Park landfill (from Cohen et al., 1987)

8.7 Case Study 7 - Pintsch Waste Oil Refinery, Hanau, Germany

8.7.1 Brief History

The Pintsch site is a former waste oil refinery located in Hanau near Frankfurt, Germany, and covers an area of 2.4 hectares. It had been operative for at least 40 years when an initial investigation identified gross contamination of the unsaturated and saturated zones with BTEX compounds and organic solvents.

The site is located in the valley of the River Main, a tributary of the Rhine, and is underlain by thin fill and thick alluvial deposits.

8.7.2 Site Characterisation

The site characterisation exercise involved installation of seven groundwater monitoring boreholes across the site, and 40 drive-tube (window) sampling holes to a depth of 2m. A site wide soil vapour survey confirmed large scale unsaturated zone contamination.

The geology at the site comprises a thin fill layer 1-2m thick overlying thick alluvium. The alluvial material comprises approximately 1.5m of loamy alluvial deposits representing a palaeo-soil horizon, underlain by 6-7m of alluvial sands and gravels, underlain in turn by a thick clay horizon. The unconfined water table is located in the upper part of the sand and gravel horizon.

Significant contamination of soils and groundwater was identified. A floating LNAPL phase of BTEX hydrocarbons was observed containing dissolved solvents, mainly TCE, PCE and 1,1,1-TCA. The unsaturated zone contained residual solvent and BTEX contamination throughout the site area. Groundwater contained dissolved BTEX and solvent contamination and significant concentrations of several solvent degradation products including vinyl chloride and cis-1,2-dichloroethene.

8.7.3 Remedial Strategy

Remediation of the site was undertaken in three phases according to the contaminant location; in the unsaturated zone, LNAPL phase, and dissolved in the groundwater.

The upper unsaturated zone, comprising fill and loamy alluvium, was excavated and treated by ex situ bioremediation on the former refinery site. The unsaturated sand and gravel was also excavated and treated by soil washing. The waste air stream from these remedial processes was treated by a three tier process of biofiltration, catalytic incineration and activated carbon adsorption.

The contaminated saturated zone, comprising 90,000m^3 of aquifer was treated using an innovative in situ biodegradation technique, designed to degrade the BTEX compounds and solvents. The whole refinery site was surrounded by a slurry wall keyed into the thick clay horizon, hydraulically isolating the contaminated sand and gravel aquifer.

A laboratory based research and development project had developed a technique involving sequential anaerobic-aerobic in situ enhanced biodegradation where an anaerobic-aerobic and vice versa switch was induced periodically. Five pilot tests were undertaken in 5-10m areas sealed from the rest of the sand and gravel aquifer by slurry walls installed keyed into the thick clay alluvium horizon and sealing the pilot test volumes from the rest of the contaminated aquifer.

The remediation technique involves addition of water to the aquifer supplemented with nutrients in the form of molasses, an easily degradable carbon source, via injection wells. An anaerobic microbiotic community is developed and consequently anaerobic biotransformation of more highly chlorinated compounds resulted in the accumulation of lower chlorinated metabolites, such as vinyl chloride.

The second part of the remediation cycle involves the addition of hydrogen peroxide (H_2O_2) to propagate aerobic conditions in the aquifer. During the aerobic phase the lower chlorinated metabolites, often as toxic as the parent solvents, are mineralised (oxidised).

The system works by abstraction and reinjection of groundwater from wells on the site to produce circulation of alternating aerobic and anaerobic groundwater in the hydraulically isolated zone within the perimeter slurry wall. The aerobic-anaerobic state of the injected water is switched every six to eight weeks, however micro-zones persist within the aquifer and an immediate switch does not necessarily occur. It is anticipated that the required operational period will be several years and the total costs for the in-situ groundwater remediation will amount to DM 24 million.

8.7.4 References for Case Study 7

Trischler und Partner GmbH (1995) *Remediation of the Pintsch Site, Contaminated with Volatile Chlorinated Solvents, BTEX Hydrocarbon Compounds and Other Contaminants.* Unpublished consultants report.

8.8 Case Study 8 - AT&T Merrimack Valley Works, Massachusetts, USA

8.8.1 Brief History

Background Information

The AT&T Merrimack Valley Works has been manufacturing vehicle transmission equipment on a 65 hectare site in North Andover, Massachusetts, since 1956. Various degreasing solvents and other industrial chemicals have been used and stored at the plant for the last 30 years, mainly in underground tanks and barrels.

The works has its own groundwater supply from three boreholes on site. Contamination of abstracted groundwater with low levels of volatile organic compounds, mainly TCE and 1,1,1-TCA, was first detected by AT&T in the supply water feeding into the site de-ionisation plant. State regulatory authorities were informed immediately and a consultant was engaged to investigate the contamination.

Environmental Setting

The AT&T Merrimack site is located close to the Merrimack River and three aquifers are present beneath the site. A shallow sand aquifer up to 15m thick is separated from a deeper localised sand and gravel channel aquifer (10m by 15 to 60m wide) by a silt and clay till of variable permeability. Fractured siltstone and sandstone bedrock form the base of the system.

Groundwater flow is predominately towards the Merrimack River. The three aquifer units are in partial hydraulic continuity except in areas where the middle channel aquifer is not present. Strong vertical gradients between the aquifers have been identified, but these vary in magnitude and direction across the site and are probably strongly influenced by the continuous pumping of the on site supply boreholes, screened in the buried channel aquifer. The aquifer system is recharged from Lake Cochichewick and infiltrating rainfall, and discharges to the River Merrimack.

8.8.2 Site Characterisation

The site characterisation was phased to allow remediation to begin as soon as a basic understanding of the site had been achieved.

The first phase of site characterisation comprised a historical and facility desk study and a review of the hydrogeology, geology and magnitude and extent of known aquifer contamination. Fourteen boreholes were drilled and monitoring wells installed in pairs. Low levels of VOCs were detected in the shallow and bedrock aquifers and no contamination was detected in the river or in the river sediments. This implied that the contamination had not caused a major impact off site. The results of this investigation stage were used to produce a conceptual model of the site, shown in Figure 8.21.

The second phase of site characterisation involved the installation of seven additional monitoring wells, groundwater sampling and a series of hydraulic parameter tests. A three dimensional numerical groundwater flow model using a finite element method and particle tracking model including advection, dispersion and decay processes was produced. The model simulated solvent transport from several potential on site sources over a 25 year period.

The additional boreholes constrained the extent of the buried channel and showed that the channel crossed site in a north-south direction. A seven day pump test using wells in the buried channel showed that flow along the buried channel is in a north-south direction. Leakage between the aquifers was also demonstrated by the aquifer testing programme.

Dissolved solvent concentrations varied considerably across the site. Particularly high concentrations were detected around the tank farms, in the range 200-300 mg/l total VOCs. Concentrations of between 10-100 μg/l total VOCs were found in the shallow aquifer, the buried channel and the bedrock, indicating the hydraulic continuity between the aquifers.

It was not possible to relate the dissolved solvent concentrations in the groundwater to contamination from specific sources as all of the detected compounds could have been produced from a number of on site sources. The degradation of solvents in the subsurface had produced daughter transformation compounds with concentrations of up to 800 μg/l in one well. These daughter compounds included DCE isomers, DCA, VC and chloroethane (CA). The ratio of daughter concentration to total VOC concentration of 0.89μg/l at one well implied that VOCs had been in the ground for many years and considerable natural biodegradation had occurred.

8.8.3 Remedial Strategy

After phase I of the site characterisation, 11 tanks from the four source areas were removed and one tank was permanently closed. On excavating the tanks (300m^3 of contaminated soil and 190,000 litres of contaminated groundwater) were removed and disposed of to landfill. This effectively removed the contamination source.

The computer models were used to define the optimum configuration of a hydraulic containment system comprising numerous groundwater abstraction wells. The final groundwater remediation system included two deep abstraction wells screened in the buried channel aquifer to remove contamination from the buried channel aquifer up gradient of the production well and to pull contamination down from the shallow aquifer. Abstracted water was treated with an air stripping plant and then used for works supply. The gas stream was treated by activated carbon absorption.

The clean up criteria was set as total VOC concentration of less than 100 μg/l in two consecutive groundwater samples from the hydraulic containment abstraction wells.

At the commencement of remediation in November 1990, the baseline groundwater quality was monitored and sampling continued monthly throughout remediation. Initially, concentrations of total VOCs in the extracted water rose as more contaminated shallow groundwater was drawn down from the shallow aquifer. In February 1991, the system was forced to shut down due to operational problems and was restarted in October 1991. The concentrations of VOCs in the pumped water increased as pumping restarted and has since been variable. The concentrations of total VOCs and TCE in the pumped water are shown in Figure 8.22, for the period from start up to December 1993.

8.8.4 References for Case Study 8

Muldoon, D., P. Connolly and A. Makovitch, (1994) *Groundwater Remediation of Chlorinated hydrocarbons at an Electronics Manufacturing Facility in the Northeastern United States,* from Groundwater Pollution Conference (IBC) March 1994.

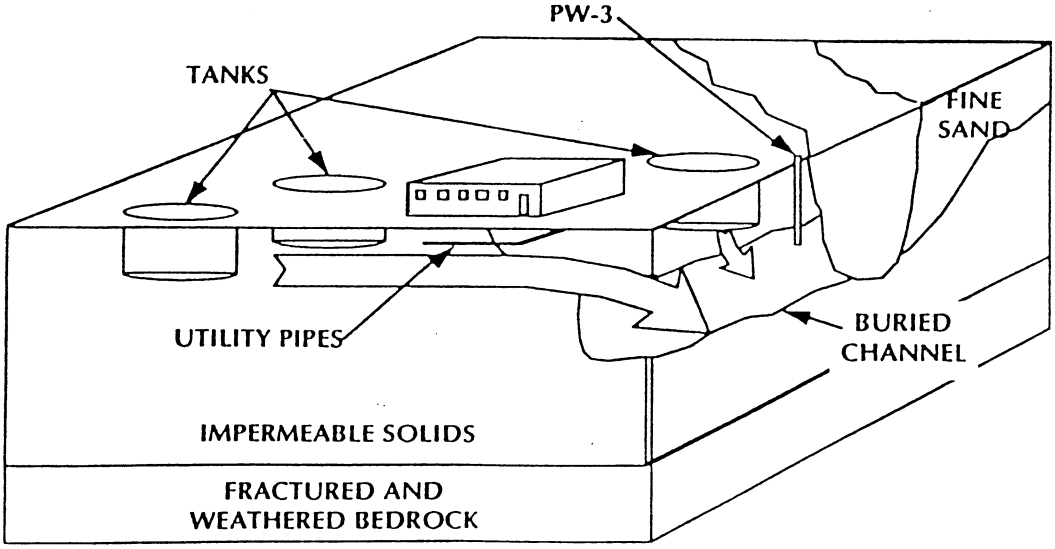


Figure 8.21 Conceptual model of AT&T site (from Muldoon et al., 1994)

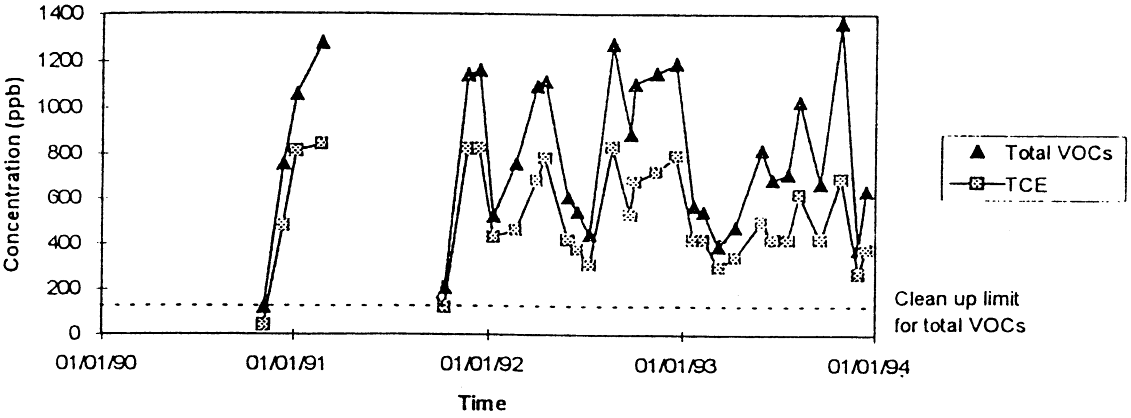


Figure 8.22 Concentration of total VOCs and TCE in groundwater from remedial hydraulic containment system (from Muldoon et al., 1994)

8.9 Case Study 9 - Tyson's Dump, King of Prussia, Pennsylvania, USA

8.9.1 Brief History

Background Information

Tyson's Dump is located in an abandoned sandstone quarry in King of Prussia, eastern Pennsylvania. The site is bounded to the north by a railway beyond which is the Schuylkill River, to the east and west by streams and to the south by the steep quarry face. The site layout is shown in Figure 8.23.

The site was operated as a series of waste disposal lagoons between 1960 and 1970 and during this time various septic and chemical wastes were brought on site in tankers and disposed of in unlined lagoons. As each lagoon filled with waste it was covered and a new lagoon was begun.

In 1973, the Pennsylvania Department of Environmental Resources (PADER) ordered the closure of the site. By this time most of the 1.6 hectare site south of the railway contained lagoons and the whole site was contaminated as a result of spills and overflows during operations. The site closure order required the owners of the site to empty the lagoons of liquid waste, backfill the voids with clean soil and revegetate the area.

Ten years later, in 1983, a complaint from a member of the public about ground conditions and odours at the site initiated USEPA investigations.

Environmental Setting

Tyson's Dump is located in a sandstone quarry in the Triassic lowlands of Pennsylvania. The bedrock comprises northward dipping sandstone and siltstone units of the Stockton Formation. The area north of the railway line is underlain by a relatively thin veneer of colluvium, fill and floodplain deposits that overlie the bedrock.

Groundwater occurs in both the unconsolidated deposits and in the fractured bedrock aquifer. Groundwater flow direction is northwards towards the River Schuylkill in both unconsolidated and bedrock aquifers, and a groundwater mound has been observed beneath the Tyson's Dump site due to enhanced recharge from liquid waste lagoons. Shallow groundwater is considered to discharge to the river but some deeper groundwater is considered to flow northwards underneath the river.

8.9.2 Site Characterisation and Remedial Strategy

Due to the integrated nature of site characterisation and remediation at the Tyson's Dump site, the works undertaken are described below in chronological order:

The investigations at Tyson's Dump began in January 1983 when soil, air and groundwater sampling identified high levels of environmental contamination, particularly with VOCs. The USEPA decided that immediate action was required to limit public exposure to uncontrolled chemical odours at the site.

Several initial emergency remedial measures were implemented in March 1983 including:

1) Construction of a soil cap over suspected lagoon areas and regrading to reduce infiltration of precipitation.
2) Construction of a leachate collection system and an air stripper with activated carbon leachate treatment system.
3) Construction of a security fence to limit unauthorised access to the site.

Between December 1983 and March 1984 an intensive field investigation of the Tyson's Dump lagoon area was undertaken by the USEPA. The investigation focused mainly on unsaturated zone and shallow groundwater contamination. The following recommendations arose from the investigative work:

1) Excavation and off site disposal of contaminated soil at a permitted landfill.
2) Upgrading the existing air stripping facility to treat leachate, shallow groundwater and surface runoff from excavation operations.
3) Excavation and off site disposal of contaminated sediments in the gully west of the treatment plant that receives effluent from the existing air stripper.

Between January and August 1985, further monitoring wells were installed and a geophysical magnetometer survey was undertaken to produce a detailed map of depth to bedrock, extent of waste materials, volume of contaminated soil and presence of metallic debris such as drummed waste.

Additional investigations north of the railway and off site were undertaken in 1986 and revealed the following:

1) DNAPL was present and significant quantities had passed through the soil zone, entered the bedrock aquifer and migrated to beneath the Barbados Island in the Schuylkill River channel.
2) Approximately 97% of aqueous phase contamination in bedrock was due to DNAPL dissolution.
3) Contaminated groundwater was discharging to the Schuylkill River.
4) Main contaminants are 1,2,3-trichloropropane (TCP), xylenes, ethyl benzene and toluene.

In November 1986, due to technology improvements and increased knowledge of site characteristics, it was proposed that in situ soil vapour extraction at the lagoon site, rather than excavation of contaminated material, would be the most cost effective long term solution for clean up of contaminated soils. A pilot scale SVE plant was installed which indicated that SVE was a suitable technology. The full scale SVE system in the lagoon area began operating in November 1988.

Site characterisation between 1989 and 1991 focused on defining the extent of DNAPL in the bedrock aquifer and the migration of contamination northwards beneath the Schuylkill River. A simplified conceptual model for the Tyson's Dump site is shown in Figure 8.24. DNAPL was identified beneath the site and is considered to have migrated a considerable distance northwards by gravity flow along bedding plane fractures.

The recovery of DNAPL from the bedrock aquifer was considered impossible and the DNAPL would continue to source aqueous phase contamination. The restoration of the aquifer was deemed unattainable because of the perceived volumes and extent of DNAPL in the fractured bedrock.

Two phases of hydraulic containment, one interim and one final, were proposed to intercept contaminated groundwater by strategic location of abstraction wells south of the river. The interim hydraulic containment system was proposed as it could be installed rapidly and would intercept most contaminated groundwater. A three dimensional numerical groundwater flow and particle tracking model was produced to aid design of the remedial system.

The interim system comprised four 15m abstraction boreholes and three 55m deep abstraction boreholes and initiated operation in November 1988. The second phase of hydraulic containment comprised an additional thirteen 55m deep abstraction boreholes and was installed in June 1991. Contaminated groundwater was treated by ex situ steam stripping and carbon adsorption.

8.9.3 References for Case Study 9

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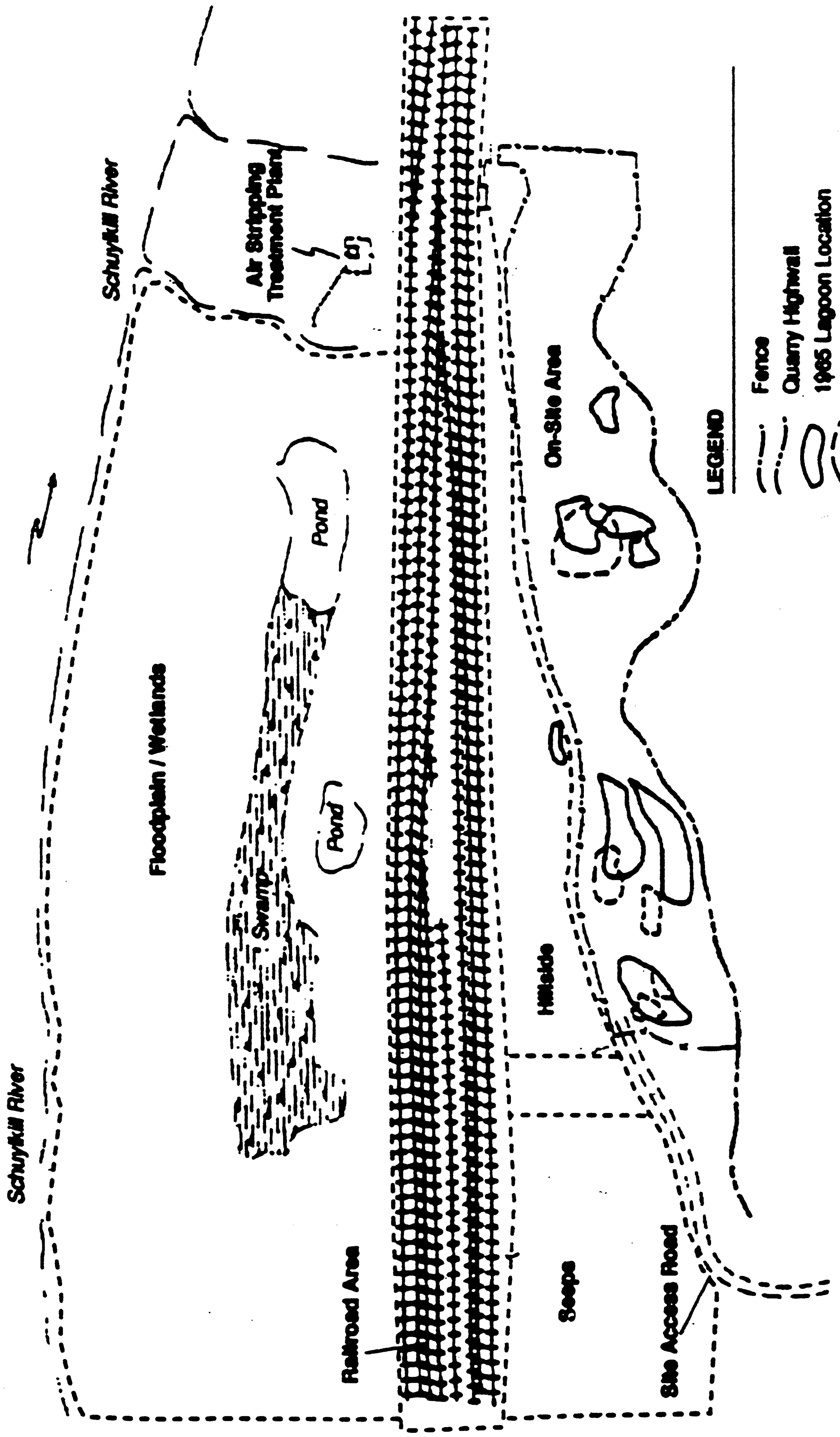

Figure 8.23 Site plan of Tyson's Dump site (from USEPA, 1992)

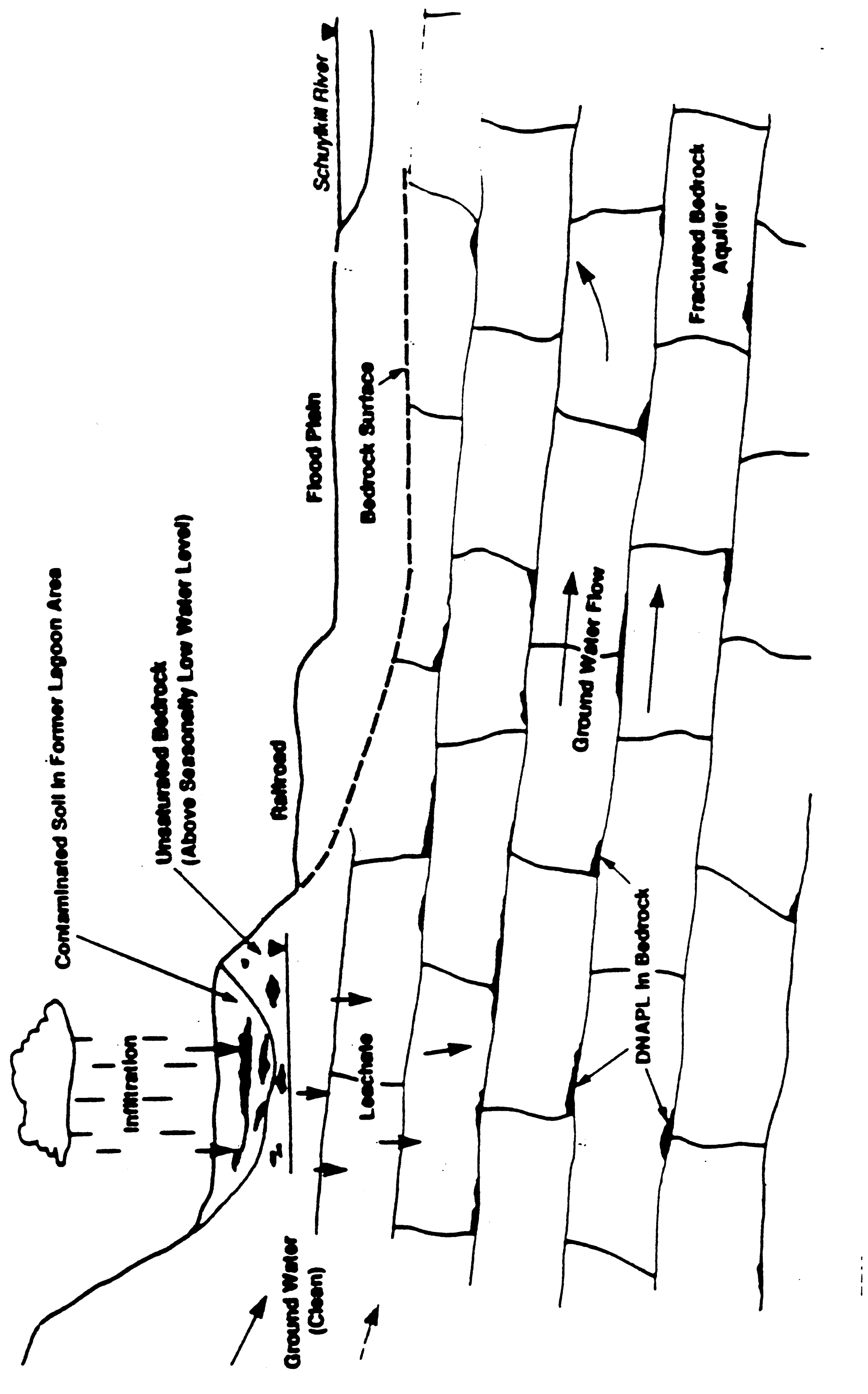

Figure 8.24 Simplified conceptual model of contaminant migration at Tyson's Dump (from USEPA, 1992)

8.10 Case Study 10 - Textile Factory, Hawkesbury, Ontario, Canada

8.10.1 Brief History

Background Information

The site of interest in this case study is a factory producing yarns, mainly for the production of carpet backing and other synthetic fabrics. The site is located approximately 2km south of the Ottawa River in the town of Hawkesbury, Ontario, Canada.

In the early 1970s waste material from the plant comprising PCE, TCE, DCM, 1,1,1-TCA, naphtha and latex was deposited in lagoons in the eastern part of the site. The lagoons were periodically pumped to a surplus yarn storage area in the north northeast part of the site, shown on Figure 8.25. The lagoons were excavated in 1991 as a response to regulatory pressure.

Environmental Setting

The site is underlain by fill material of reworked till, sands and silts which overlies weathered glacial silty sand till 1.2-3.1m thick. In the yarn waste area and lagoon area, the weathered till overlies unweathered sandy silt till with a maximum thickness of 4.9m, which in turn overlies fractured limestone shale bedrock.

Groundwater in the fill material discharges to surface drainage ditches east and southeast of the plant. The unweathered till above the bedrock acts as a confining layer in the site area, but off site, where unweathered till is not present, the bedrock aquifer is unconfined. Groundwater flow in the bedrock aquifer is to the northeast.

8.10.2 Site Characterisation

The conceptual model of subsurface contamination at the site was developed over several years of site characterisation studies. An initial site assessment identified solvent contamination of groundwater across most of the eastern part of the site. As a result of the initial site investigation, an extensive site characterisation programme was undertaken including installation of many monitoring wells.

A high permeability preferential flow horizon, developed by dissolution at the unweathered till-bedrock interface, exists beneath the site. Regional groundwater flow in this thin permeable zone is to the northeast and the hydraulic gradient averages 0.012. Hydraulic conductivity was determined by slug tests as $4.24\times10^{-6}ms^{-1}$ in the lagoon area and $7.14\times10^{-6}ms^{-1}$ in the yarn waste area. Effective porosity of the bedrock-till interface zone is approximately 0.1 and the average organic carbon content is 0.07%.

Monitoring wells were installed in the till-bedrock interface zone, the shallow bedrock and the fill-weathered till zone. Groundwater samples have been collected biannually since April 1991, using manually operated Waterra pumps and stored in laboratory supplied containers. Groundwater samples for VOC analysis were collected without headspace in glass vials and preserved with HCl. Sampling QA/QC called for the submittal of five matrix spikes, five replicate samples by sample splitting, five duplicate blind samples, four field blanks and four travel blanks.

Groundwater was analysed for VOCs with USEPA Method 8260 (USEPA, 1990). Methanol and ethanol, and the dissolved gases ethane and ethene were analysed with gas chromatography and flame ionisation detector (GC/FID).

One of the main primary contaminants at the site is DCM, a solvent with high solubility and low retardation factor. A plot of the 0.1mg/l plumes of DCM (April 1992) is shown in Figure 8.25 and indicates that the two DCM plumes, associated with the lagoon area and the waste yarn area, are limited in extent and confined to the site area. The 0.1mg/l plume of 1,1,1-TCA, also shown in Figure 8.25, indicates a plume of greater extent than the DCM plume which extends off site, probably along major bedrock fractures. Other known primary contaminants at the site that were present in the lagoons and the waste yarn area are PCE and TCE.

The groundwater sampling also identified the presence of many compounds that had never been used at the site, including 1,1-DCE, cis- and trans-1,2-dichloroethene (cis-1,2-DCE and trans-1,2-DCE), 1,1-DCA and VC. Figure 8.26 shows the plumes delineated for the degradation products cis-1,2-DCE and VC. Conversion to VC appears to have occurred rapidly in the lagoon area but considerably more slowly in the waste yarn area. Further sample analysis indicated that methane fermentation is a significant process and methane, ethene and trace ethane were found in the plume areas.

8.10.3 Natural Attenuation of Contamination

Reductive dechlorination of PCE and TCE can produce intermediates, such as dichloroethene isomers and vinyl chloride, with more serious health effects than the primary contaminant (Vogel and McCarty, 1985; Molton et al., 1987). Recent research has identified that the provision of requisite reducing power, using compounds such as methanol, hydrogen, acetate, formate, and glucose, can yield ethene, an intermediate of PCE reductive dechlorination. In another study, ethane, the end product of reductive dechlorination of PCE, was formed where lactate was the electron donor (de Bruin et al, 1992; Freedman and Gossett, 1989). The production of ethene has also been observed at sites contaminated by PCE and TCE. Trichloroethane (1,1,1-TCA) can be degraded through biological reductive dechlorination to produce 1,1-DCA and chloroethane (CA) or abiotically either by hydrolysis to produce acetic acid, or by elimination to yield 1,1-DCE. Continued reductive dechlorination of these intermediates would eventually also produce VC, ethane, and ethene.

Dichloromethane (DCM) is known to degrade under both aerobic and anaerobic conditions (Kohler-Staub et al, 1986; Freedman and Gossett, 1991). The initial degradation at the site may have been aerobic, causing dissolved oxygen depletion and leading to reduced conditions. One potential source of the observed methane in the contaminant source areas at the site is anaerobic degradation of DCM which produces methane and carbon dioxide.

The transformation products observed at the site are those associated with anaerobic reductive dechlorination, although abiotic mechanisms could also yield some of the transformation products. For example, the methanol observed could be the result of hydrolysis of DCM; the 1,1,-DCE could be the result of abiotic decomposition of 1,1,1-TCA; high concentrations of

1,1-DCA compared to 1,1-DCE and the presence of CA suggest reductive dechlorination is a major process.

The noted differences in size of the primary contaminant plumes suggest that degradation has played a key role in limiting off site migration. The DCM, PCE and TCE plumes are restricted to the site area whereas the 1,1,1-TCA plume extends off site. If dispersion and retardation alone had affected plume size, the DCM plume would be expected to be most extensive. However its restricted size suggests that significant degradation of DCM has occurred.

To conclude, 'natural' degradation by indigenous microorganisms at a site contaminated with PCE, TCE, 1,1,1-TCA, DCM and naphtha has produced metabolic intermediates and end products indicative of reductive dechlorination. The migration of the dissolved plumes of these contaminants has been significantly restricted by the degradation transformations.

However, it must be considered that an end product of anaerobic biotransformation is vinyl chloride, a compound equally as toxic as the primary solvent contaminants. For further degradation of vinyl chloride to a less or non-contaminating species requires aerobic biotransformation to occur.

8.10.4 References for Case Study 10

DeBruin, W.P.D., M.A. Kotterman, M.A. Posthumus, G. Schraa and A.J.B. Zehnder (1992) *Complete Biological Reductive Transformation of Tetrachloroethene to Ethane.* Appl. Env. Microbiol. 58(6):1996-2000.

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Molton, P.M., R.T. Hallen and J.W. Pyne (1987) *Study of Vinyl Chloride Formation at Landfill Sites in California.* BNWL-2311206978, Battelle Pacific Northwest Laboratories, WA.

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Vogel, T.M. and P.L. McCarty (1985) *Biotransformation of Tetrachloroethylene to Trichloroethylene, Dichloroethylene, Vinyl Chloride, and Carbon Dioxide Under Methanogenic Conditions.* Appl. Env. Microbiol. 49(5):1080-1083.

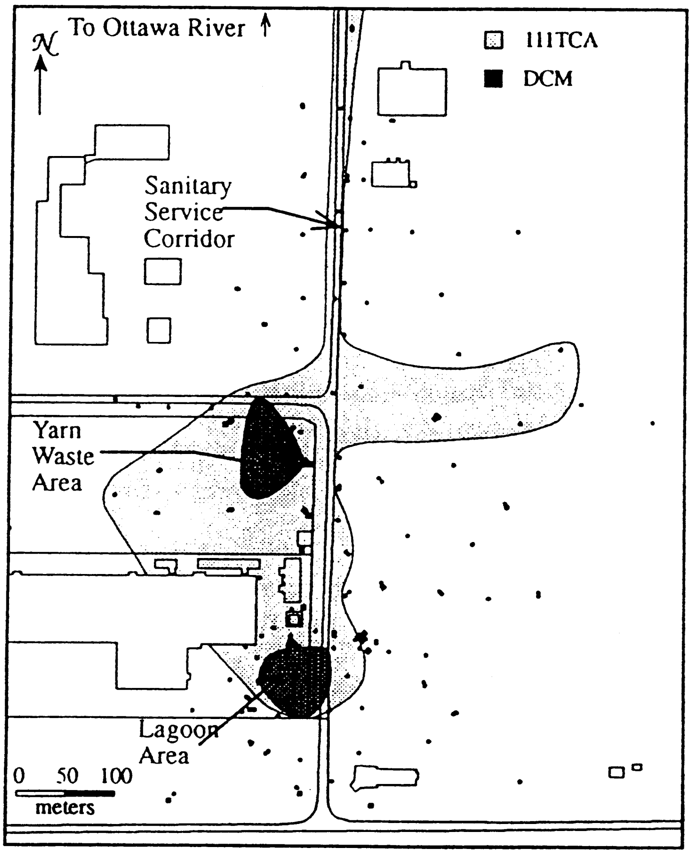

Figure 8.25 **Contours of 0.1mg/l DCM and 1,1,1-TCA in groundwater at textile factory, Hawkesbury (from Hinchee et al., 1994)**

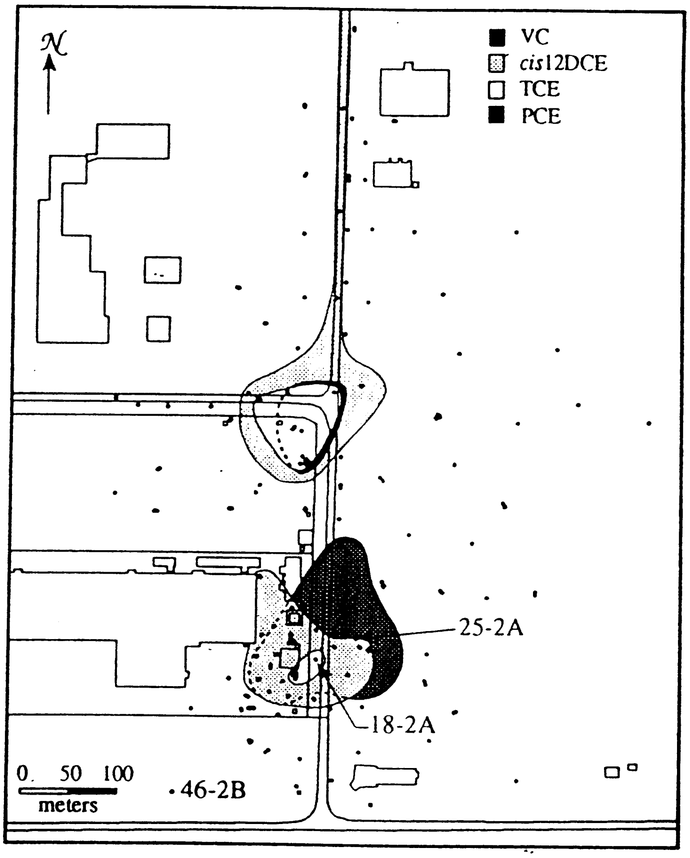

Figure 8.26 Contours of 0.1mg/l PCE, TCE, cis-1,2-DCE and VC in groundwater at textile factory, Hawkesbury (from Hinchee et al., 1994)

8.11 Case Study 11 - Chemical Manufacturing Facility, New Jersey, USA

8.11.1 Brief History

Background Information

The site has been used for chemical manufacturing and other industry since the 1830s. Since 1936 various organic pigments, mainly for the automotive industry, have been produced at the site. To the north of the site is the Oldham Pond and the majority of land surrounding the site is residential. The site is bounded to the east by Molly Ann Brook and to the south, north and west by tributaries to Molly Ann Brook.

Unlined lagoons were used for settling of process waters until 1977 and a large area in the northern part of the site was used for disposal of lime sludge and various process wastes. Operations at the plant ceased in 1988 and, under US environmental law, an environmental investigation was required by the New Jersey Department of Environmental Protection and Energy. A plan of the site is shown in Figure 8.27.

Groundwater sampling identified the presence of PCE, TCE and the degradation products 1,1-DCE and VC in the shallow groundwater at the site with concentrations of PCE up to 67,000μg/l. Dichloroethenes, chlorobenzenes, metals and volatile aromatics have also been identified at significantly elevated concentrations in shallow groundwater.

Environmental Setting

The site is located in the Ramapo River Basin in the Watchung Mountains area of New Jersey. A sequence of 6-24m of Pleistocene glacial deposits of poorly sorted sand, clay and cobbles overlies the bedrock. The bedrock is Triassic Brunswick Formation comprising interbedded fractured sandstone, shale and basalt. In the western site area the sandstone and shale unit is 1-12 m thick, whereas in the eastern site area these beds are absent. The basalts range in thickness from 66-104m.

Four aquifer units can be distinguished; the unconsolidated deposits, the shallow basalt zone, the deep basalt zone and the deep shale and sandstone aquifer. The basalt units comprise two basalt flows separated by a 1.5-6m low permeability interval. Shallow groundwater discharges to Molly Ann Brook and groundwater flow in the deeper aquifers is to the south-east and south-west. Significant downward vertical gradients exist between the four aquifer units.

8.11.2 Site Characterisation

Phase I

The initial site investigations, carried out by International Technology Corporation (IT) in 1990 and 1992, produced a characterisation of the contaminant distribution in the soil, air, groundwater and surface waters. Groundwater was sampled in 12 newly installed wells, and 13 existing wells. Groundwater flow in the shallow unconsolidated sediments was identified as being eastwards towards a local brook. In the unconsolidated deposits, VOC concentrations were strongly associated with the locations of 12 potential solvent source areas at the plant, identified in the desk study.

These remedial investigations indicated that the main areas of concern were the production area of the plant, the lime sludge area and the unconsolidated sediments and shallow bedrock groundwater. The North Yard lime sludge pit was estimated to cover an area of 2 hectares, with a thickness of 3-8 m. The compounds PCE, TCE, DCE, VC, DCM, xylenes and chlorobenzenes were found in the soils and unconsolidated aquifer groundwater at concentrations which exceeded the New Jersey Department of Environmental Protection and Energy (NJDEPE) clean up limits. No remediation was deemed to be necessary for surface water or stream sediments.

Phase II

The main objectives for the Phase II site characterisation undertaken by Geraghty and Miller were to determine the horizontal extent (i.e. off site) and the vertical extent of groundwater contamination. The Phase II investigation involved:

- Using fracture trace analysis to enable off site boreholes to be sited on fracture zones.
- The drilling and installation of five new boreholes on site and four off site.
- Multi-level sampling of the new boreholes to determine the water quality variation with depth and hydraulic conductivity of discrete intervals.
- Geophysical (gamma, SP and single point resistance, temperature) and video logging to identify fractures.
- Aquifer testing using interference techniques to establish the connection between the unconsolidated sediments and the bedrock and therefore to determine the applicability of a well screened in the basalt for remediation.

The piezometric surface in the unconsolidated aquifer is shown in Figure 8.28 and indicates groundwater flow generally eastwards, discharging to Molly Ann Brook. Vertical groundwater flow is either up or down to the upper basalt aquifer depending on the location. Groundwater in the shallow basalt flows towards the south-east under the regional flow regime. In the deeper basalt, flow is towards the south-west.

Volatile organic compounds, particularly PCE and TCE, are the major site contaminants. The observed concentrations of total VOCs in deep basalt were in the range of 100-1000mg/l. In the shallow basalt and unconsolidated sediments, total VOC concentrations in the range 10-100mg/l are present, with concentrations increasing towards the east. Some contamination was also detected in the deep sandstones. Free phase DNAPL was considered probable as PCE concentrations were >25% of PCE solubility at three wells at the site, and after aquifer hydraulic testing a black non-aqueous phase liquid was observed on the pump filter at one of the tested wells.

Off site contamination seems to be rather limited, probably because abstraction from the production well from the 1940s until 1977 prevented groundwater flowing off site. This pumping could also have been responsible for drawing the contamination down into the deeper basalt.

8.11.3 Remedial Strategy

Four alternative remedial strategies were designed and evaluated by Geraghty & Miller (G&M) and are discussed below. Capping alone was not considered to meet clean up goals for the soils or groundwater, or to reduce toxicity, mobility or volume of hazardous material on site. The excavation and removal of soils for off site disposal in a landfill was considered to result in greater short term impacts on the community, as well as being more costly than an in-situ alternative. This evaluation led to the production of three site wide alternatives:

I DPVE and SVE for soils with groundwater treatment:
- Dual phase vapour extraction (DPVE) with capping of the sludge pit.
- Soil vapour extraction (SVE) with capping of the plant production area.
- Ten year groundwater treatment and monitoring programme.
- Potential SVE and treatment of overburden groundwater east of the brook.

II In situ stabilisation with groundwater treatment:
- In situ chemical stabilisation and capping of the sludge pit.
- In situ soil chemical stabilisation and capping of the plant production area.
- Ten year groundwater treatment and 30 year monitoring programme.
- Potential SVE and treatment of overburden groundwater east of the brook.

III On site containment area with groundwater treatment
- On site containment for the sludge pit and plant production area using grout curtain.
- Ten year groundwater treatment programme and 30 year groundwater monitoring programme.
- Potential SVE and treatment of overburden groundwater east of the brook.

Of these possibilities, alternative I was the considered the most cost effective remedy for the site. G&M designed and implemented a remedial action design that consisted of site capping, abstraction and treatment of groundwater, a dual phase vacuum enhanced extraction system and an SVE system. The remedial system operation was initiated in May 1995.

Prior to full scale remedial system, implementation two DPVE pilot studies were undertaken. In the sludge pit area at North Yard, groundwater was recovered at a rate of 0.02 l/s. The radius of influence of the vacuum extraction was 15m. The pilot test in the plant production area had high air flow rates at low vacuums suggesting that SVE would be effective.

The full scale DPVE system consists of 40 wells placed at 15m intervals. The wells are paired so that air sparging and vapour extraction wells are next to each other, these roles are reversed periodically. A peristaltic pumping system was designed for the liquid extraction from DPVE wells to avoid installations of pumps and electricity supplies to all of the wells. The SVE system consists of 20 extraction wells which are evenly spaced across the plant production area.

Groundwater is pumped from two wells within the bedrock and from nine wells in the unconsolidated sediments. The water is treated firstly by density separation to remove free phase DNAPLs, and then by aeration, filtration, air stripping and granular activated carbon absorption to remove VOCs.

A capping layer has been placed over the 4.9 hectare area of the sludge pit area and the plant production area to minimise the infiltration of precipitation into the underlying impacted soil. The cap material consists of regraded sub-base, a low density membrane, synthetic drainage material, a geotextile, and finally soil cover.

8.11.4 References for Case Study 11

Geraghty & Miller, Inc. (1993) *Remedial Alternatives Analysis Report (Confidential Site).* Plainview, New York.

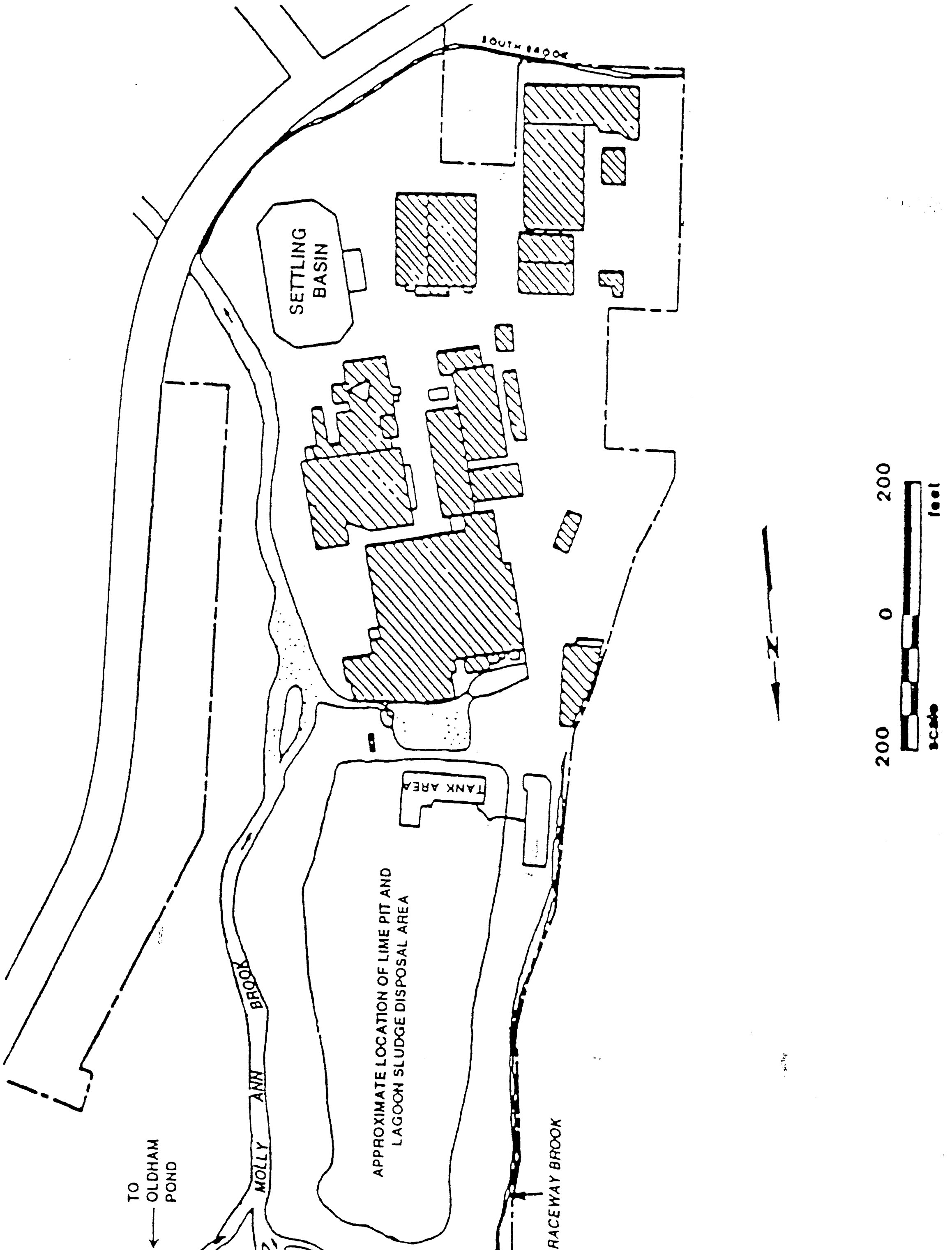

Figure 3.27 **Site plan of chemical manufacturing facility, New Jersey (from Geraghty & Miller, 1993)**

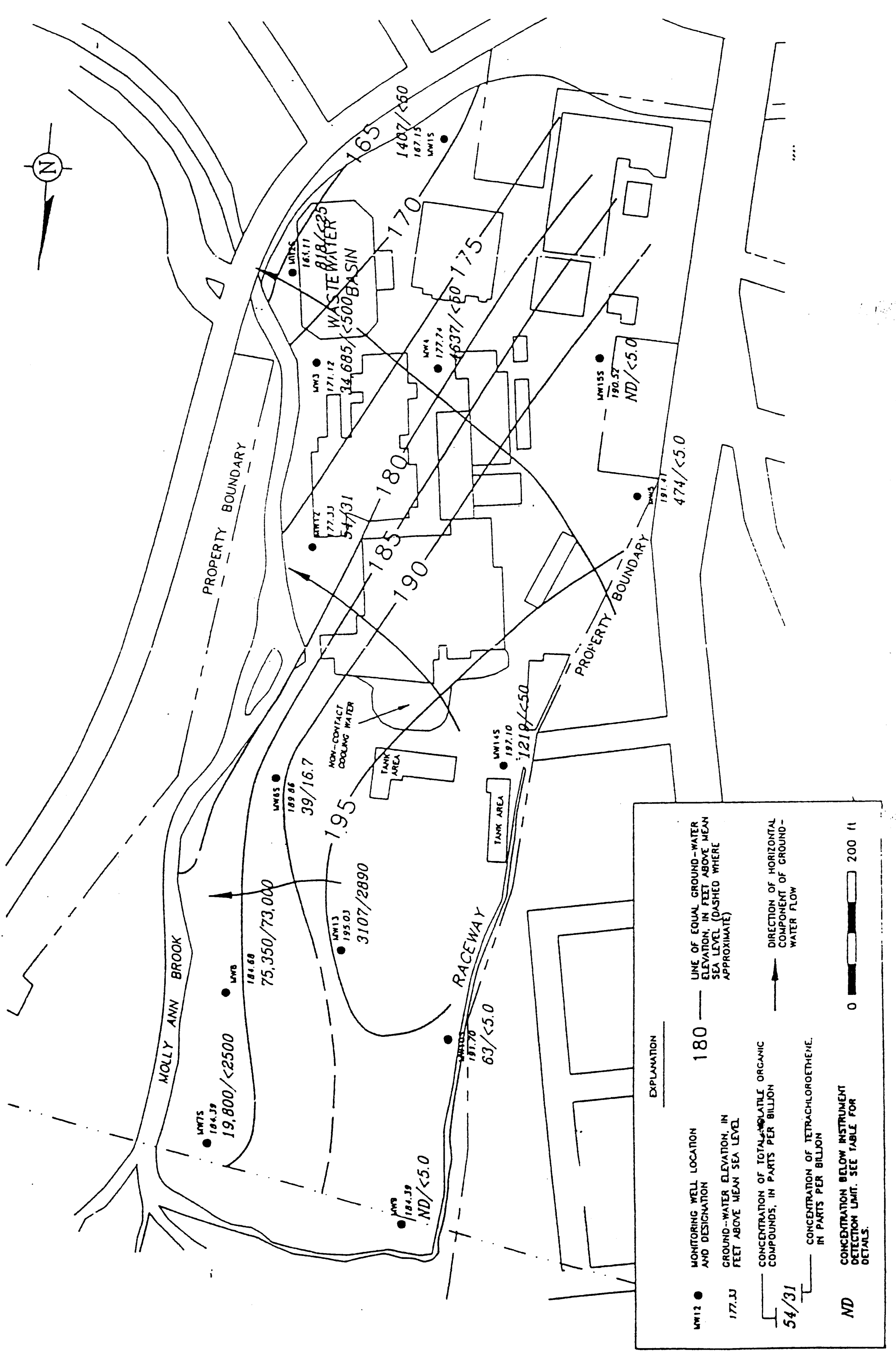

Figure 8.28 **Piezometric surface and groundwater quality in unconsolidated deposits at chemical manufacturing facility, New Jersey (from Geraghty & Miller, 1993)**