Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Groundwater

R&D Technical Report P305

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This document provides a review of current knowledge on natural attenuation of two common organic pollutants in groundwater systems: petroleum hydrocarbons and chlorinated solvents. It also identifies future research needs in this topic area.

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1. INTRODUCTION AND BACKGROUND TO THE PROJECT

Historical and widespread industrial activity in the UK has left a legacy of contaminated or potentially contaminated sites, many of which pose a threat to groundwater. The anticipated implementation of Part IIA of the Environmental Protection Act 1990 later this year will introduce a new formal definition of ‘contaminated land’, and provide a new driver for the remediation of such sites.

The Government is committed to the redevelopment and remediation of land and groundwater affected by contamination within a risk based framework, taking into account the potential costs and benefits involved. The Environment Agency and Local Authorities have the responsibility for regulating this policy, and in this context there is a requirement for sufficient information on potential remedial technologies to enable selection of the most appropriate technique.

In response to this requirement, the Environment Agency have commissioned a comprehensive study of the theory and application of Monitored Natural Attenuation (MNA) as it relates to two widespread groups of contaminants; petroleum hydrocarbons and chlorinated solvents. This report presents the results of the study.

MNA is not currently common practice in the UK and there is comparatively little hard data available, although there is a great deal of published information on the natural attenuation of petroleum hydrocarbons/chlorinated solvents and other compounds in North America and parts of Europe. The study has been aimed at the application of this information to hydrogeological conditions in the UK.

There has been no attempt herein to consider the attenuation of petroleum hydrocarbons/chlorinated solvents in media other than groundwater (for example, the soil, the unsaturated zone, or non-dissolved phase/free product), nor has there been any consideration of compounds other than those stated. It is likely that such considerations will form part of future research projects. In addition, extensive study of the natural attenuation of petroleum hydrocarbons/chlorinated solvents has only been carried out fairly recently, and many apparent contradictions may be found in the literature as understanding within the scientific community develops. There has been a conscious attempt within this work to concentrate on those papers published since about 1995, but nevertheless, it is anticipated that many theories considered valid at this time may soon be proven to be false or incomplete. The micro-organisms involved may also be evolving rapidly!

Finally, although it was unavailable until the end of this project, the publication "Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface" (Wiedemeier et al., 1999) covers much of the work described herein (often in significantly more detail), and is recommended reading for those particularly interested in the subject.

1.1 Petroleum hydrocarbons in the environment

Crude oil is a complex mixture of thousands of chemical substances including gases, liquids and solids, the majority of which are hydrocarbons (substances made up only of carbon and hydrogen). Petroleum hydrocarbons produced from the refining of crude oil include methane, jet fuels/kerosene, petroleum hydrocarbons (primarily benzene, toluene, ethylbenzene and xylene, collectively referred to as BTEX), diesel, light fuel oils, heavy fuel oils (gas oils or residual fuel oils), motor and lubricating oils.

Petroleum hydrocarbons are a common contaminant in the soil-groundwater system, due in part to their widespread usage (consider the number of petrol filling stations in existence across the UK), and to their storage, transport and use typically in liquid form.

Certainly in terms of groundwater contamination, the liquid fractions have the greatest potential to reach the water table through leakage, spillage or deliberate disposal (a liquid can easily infiltrate permeable ground whereas a solid will not). The volume required to cause significant contamination may be small compared with the total amount stored, particularly where the accuracy of stock loss calculations may be as much as ±1%. In general, it is the more soluble and mobile compounds which are of most immediate concern, and particularly those which are, in addition, most toxic. The following refers to BTEX:

"Because of their toxicity and especially their environmental mobility, these chemicals are typically the constituents of concern at petroleum release sites. Other compounds (for example, oxygenated additives and naphthalene) may be of concern on a site specific basis depending on the age and nature of the petroleum release" (ASTM, 1995).

In limited circumstances jet fuels are also of major concern, and the proliferation of published material relating to these two groups of compounds (BTEX and jet fuels) reflects this.

Generally, the petroleum hydrocarbons of concern are part of a group of compounds known as light non-aqueous phase liquids (LNAPLs) and in the environment they tend to float on the water table (Figure 1).

A number of compounds are, or have been, added to petrol to improve its performance. The additive currently featuring in most in the published literature is MTBE (methyl tertiary butyl ether), included as an oxygenate in about 40% of petrol blends in the UK (Turrell & Blackmore, 1998). MTBE is mobile in groundwater, and concerns have been expressed over the human health impact of long term exposure to the compound in drinking water (Hyman et al., 1998).

A more detailed discussion of the constituents of crude petroleum, their nature, occurrence and chemistry, is presented in ASTM E1739-95 “Standard Guide for Risk Based Protective Action Applied at Petroleum Release Sites”.

1.2 Chlorinated solvents in the environment

Chlorinated solvents were first produced in Germany in the nineteenth century, although their widespread use did not occur until World War II. In the following three decades production and use increased markedly (Pankow & Cherry, 1996). Unlike many other contaminants, chlorinated solvents are not always associated with heavy industry but are also found typically within lighter ‘cleaner’ industries, such as the dry cleaning, printing, aerospace and photographic industries, and the manufacture of electronic components. Solvents are commonly used for metal cleaning and degreasing.

Chlorinated solvents are generally transported, stored and used in liquid form, and this, along with their widespread use in what are often small local businesses, gives them immense potential for soil and groundwater contamination. The volume of leakage or spillage required to cause significant contamination may be small compared with the total volume of solvent stored, and leaks or spills may go unnoticed in situations where large unquantified losses are occurring through vapourisation.

Chlorinated solvents are one of a group of compounds known as dense non-aqueous phase liquids (DNAPLs), a group which also includes substances such as halogenated benzenes, polychlorinated biphenyls (PCBs), some pesticides, coal tars and creosotes. In the environment, DNAPLs present unique behaviour which makes them particularly difficult to locate and remediate.

Since they are more dense than water, DNAPLs do not float on the water table like petroleum hydrocarbons, but typically settle above layers or lenses of low permeability material. Subsequent movement may then be gravity controlled, determined by the elevation and topography of the surface of the low permeability layer rather than the direction of groundwater flow. The undissolved "free product" may therefore be remote from the initial spill (both horizontally and vertically), leading to difficulties in locating the source of the contaminant plume (Figure 2).

As the source DNAPL is difficult to detect, and equally difficult to remove, there is the potential for extremely large dissolved chlorinated solvent plumes. This is of particular concern since the drinking water limits and Environmental Quality Standards set for these contaminants are low compared to their solubilities (for example, TCE solubility is about 1000 mg/l compared with a UK drinking water standard of 0.03 mg/l). In addition, at low concentrations, chlorinated solvents are (unlike petroleum products), generally not noticed by taste or odour and until recently, analytical techniques have been insufficiently accurate for their detection.

For these reasons the serious nature of chlorinated solvent contamination of groundwater was not recognised until the 1970s. It is now, however, commonly accepted in many urban and industrial areas as a situation of major concern, particularly for the Water Companies since the cost of treatment can be significant. Chlorinated solvents are suspected human carcinogens, and are known to have systemic effects on, for example, the liver and kidney.

The more common chlorinated solvents tend to be covered by a number of names in common usage. Table 1 is based on that quoted in Pankow & Cherry (1996);

Table 1. Alternative names for chlorinated solvents.

Chemical Name	**Synonyms**
Tetrachloroethene	*PCE*, perchloroethene, TeCE, perchloroethylene, perchlor, tetrachloroethylene, ethylene tetrachloride, Nema, Tetracap, Tetropil, Perclene, Ankilostin, Didakene, PerSec, Perc.
Trichloroethene	*TCE*, trichloroethylene, ethinyl trichloride, Tri-Clene, Trielene, Trilene, Trichloran, Trichloren, Algylen, Trimar, Trline, Trethylene, Westrosol, Chlorylen, Gemalgene, Germalgene, Tric.
1,1,1-Trichloroethane	*TCA*, 1,1,1-TCA, methyl chloroform, Chlorothene, Solvent 111, TRI-ETHANE.
Tetrachloromethane	*CT*, CTET, carbon tetrachloride.
Trichloromethane	*TCM*, CF, chloroform.
Dichloromethane	*DCM*, methylene chloride, methylene dichloride, methylene bichloride.
Vinyl Chloride	*VC,* chloroethene.

(Abbreviations in italics are those used within this report)

The most common chlorinated solvents have also proven to be the most frequently identified in groundwater (Pankow & Cherry, 1996).

For a more detailed description of the nature, occurrence and chemistry of chlorinated solvents, the reader is referred to Pankow & Cherry (1996).

1.3 Natural attenuation - a definition

Natural attenuation, or the reduction of mass, toxicity, mobility, volume, flux or concentration of contaminants in soil or groundwater without human intervention, occurs through a number of physical, chemical and/or biological processes. In some instances, this attenuation may be sufficient to be considered as part of (or the sole) remedial strategy for the site. The US EPA define 'monitored natural attenuation' (MNA) as *"the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remedial objectives within a time frame that is reasonable compared to that offered by other more active methods"* (US EPA OSWER, 1997).

Implicit in this definition is the concept that human health and the ecosystem are protected.

Alternative terms associated with MNA encountered in the literature include intrinsic remediation, in situ bioremediation, passive remediation, intrinsic bioremediation and remediation by natural attenuation (RNA). Although often used synonymously with MNA, many of these terms have their own specific meanings and for the purposes of this report the terms natural attenuation or MNA will be used, as defined above.

1.4 The use of MNA as a remedial option

The United States Environmental Protection Agency (US EPA) recognise MNA as a remediation option for groundwater under the Superfund, RCRA Corrective Action and UST (underground storage tank) remediation programmes (Lovelace & Feldman, 1997). It has been successfully implemented at a number of sites across the US (Wiedemeier et al., 1995).

2. THE NATURAL ATTENUATION OF BTEX - AN OVERVIEW

The reduction in contaminant mass, concentration, volume, mobility or toxicity which has been identified as the basis of the natural attenuation of contaminants in groundwater can occur through a number of physical, chemical and microbiological processes, and each is described in detail in Appendix 1. The dominant attenuating process within a contaminant plume will depend on the interaction of the major contaminant with other co-existent contaminants and on given site conditions.

The term 'natural attenuation' is, however, commonly used interchangeably with the idea of biodegradation and the remediating effects of microbes. Although natural attenuation, can progress effectively without biodegradation (Wiedemeier & Pound, 1998), attenuation through dilution is unlikely to be accepted in the UK as a remedial option since the total mass of the contaminant is not reduced. Barker (1998) states that *"while dispersion and sorptive retardation contribute to contaminant attenuation, chemical or biological reaction is usually required to meet the stringent remedial objectives usual for organic contaminants".* For petroleum hydrocarbons, biodegradation is considered to be the primary mechanism by which the solute mass is removed (ASTM, 1998).

The biodegradation of petroleum hydrocarbons occurs through their use by micro-organisms as primary substrates (sources of carbon and energy). During the metabolism process, electrons are transferred from the hydrocarbon to facilitate the release of energy. The hydrocarbon is therefore termed an 'electron donor'. The process also requires an 'electron acceptor' for the transferred electrons, and nutrients such as nitrate or phosphate. Typical electron acceptors are oxygen, nitrate, iron III, sulphate, and carbon dioxide which are utilised strictly in that order. Under some circumstances, manganese IV or chlorinated solvents may also be used as electron acceptors. The degradation of petroleum hydrocarbons occurs most effectively under aerobic (oxygen reducing) conditions, and reaction efficiency reduces significantly down the scale of electron acceptors. The efficient biodegradation of petroleum hydrocarbons is therefore commonly considered not to occur under anaerobic (particularly sulphate reducing and methanogenic) conditions, although it is now becoming recognised that in terms of total mass removal, the slower but more prevalent anaerobic degradation processes may be significant. The degradation process is limited by the supply of electron acceptors, but since these are generally present in abundance in the natural environment, the biodegradation of petroleum hydrocarbons under aerobic conditions typically proceeds to complete degradation to non-toxic by-products.

The process and the progression of redox conditions as electron acceptors become exhausted is summarised in diagrammatic form on Figures 3 and 4.

Wiedemeier et al. (1999) and the US AFCEE publications on the natural attenuation of petroleum hydrocarbons and chlorinated solvents (Wiedemeier 1995 and overview 1997) contain extensive sections providing further background information.

3. THE NATURAL ATTENUATION OF CHLORINATED HYDROCARBONS - AN OVERVIEW

The reduction in contaminant mass, concentration, volume, mobility or toxicity which has been identified as the basis of the natural attenuation of contaminants in groundwater can occur through a number of physical, chemical and microbiological processes, and each is described in detail in Appendix 1. The dominant attenuating process within a contaminant plume will depend on the interaction of the major contaminant with other co-existent contaminants and on given site conditions.

The term 'natural attenuation' is, however, commonly used interchangeably with the idea of degradation (biotic or abiotic) and the remediating effects of microbes. Although natural attenuation can progress effectively without biodegradation (Wiedemeier & Pound, 1998), attenuation through dilution is unlikely to be accepted in the UK as a remedial option since the total mass of the contaminant is not reduced. Barker (1998) states that *"while dispersion and sorptive retardation contribute to contaminant attenuation, chemical or biological reaction is usually required to meet the stringent remedial objectives usual for organic contaminants"*. Biodegradation is usually the predominant process of natural attenuation at chlorinated solvent sites (RTDF, 1997).

Micro-organisms obtain the carbon and energy that they require for survival, growth and reproduction through the transformation of organic molecules. The energy is released during the movement of electron(s) from the organic carbon source (electron donor) through a series of enzyme catalysed oxidation-reduction reactions to an electron acceptor. The biodegradation of chlorinated solvents can occur in three ways:

- where the chlorinated solvent acts as electron donor. Under aerobic and occasionally under ferric iron reducing conditions, this is the primary mechanism for the biodegradation of the less chlorinated solvents in the field but is not considered to be effective for the more highly chlorinated compounds such as PCE and TCE. The oxidation of vinyl chloride is the only known example of chlorinated solvents acting as an electron donor under anaerobic conditions (Wiedemeier et al., 1999);
- where the chlorinated solvent acts as electron acceptor. In this process, known as reductive dehalogenation, chlorine atoms are replaced sequentially with hydrogen atoms so that, for example, PCE degrades to TCE, which degrades further to

DCE. Reductive dehalogenation is the most important process for the natural biodegradation of the more highly chlorinated solvents (Wiedemeier et al., 1997), and occurs best under reducing conditions (sulphate reducing and methanogenic, and occasionally iron III or nitrate reducing conditions). Reductive dehalogenation can occur for the less chlorinated solvents, but it is less efficient and typically these compounds tend to accumulate in anaerobic groundwater. The reductive process is limited by the supply of electron donors (organic carbon) which is often inadequate in the natural environment so degradation ceases before non-toxic end products have been reached. Consequently, an additional source of organic carbon such as leaked BTEX is required to facilitate complete reductive dehalogenation; and

- where the chlorinated solvent is degraded fortuitously by an enzyme or co-factor produced during the microbial metabolism of another compound (co-metabolism). The co-metabolic process is described as slow and incomplete (Gossett & Zinder, 1997), and very limited under natural conditions (Wiedemeier et al., 1999), although vinyl chloride has been noted as readily and very efficiently co-metabolised by methane, phenol or toluene oxidisers (McCarty, 1997).

The significant processes and the development of redox zones as degradation progresses are summarised in diagrammatic form on Figure 5 to 10.

Wiedemeier et al. (1999) and the US AFCEE publications on the natural attenuation of petroleum hydrocarbons and chlorinated solvents (Wiedemeier 1995 and overview 1997) contain extensive sections providing further background information.

4. THE NATURAL ATTENUATION OF MTBE

Although initially considered to be a conservative species resistant to biodegradation (and hence not suitable for consideration within a MNA scheme), an increasing number of studies suggest that MTBE, an additive to petrol since the 1980s, can degrade under certain conditions.

For example, Hyman et al. (1998) have demonstrated the effective degradation of MTBE in laboratory microcosm studies, and a field investigation designed to delineate the extent of an apparently recalcitrant MTBE plume 8 years after a natural gradient tracer test showed that only 3% of the original mass remained (Schirmer & Barker, Spring 1998, Schirmer et al., May, 1998).

Although the attenuation of MTBE has not been covered in detail in this study, the interested reader is referred to published documents such as Hyman et al. (1998), Schirmer & Barker, Spring 1998, Schirmer et al. (May, 1998), Tyener et al. (1998), Eweis et al. (1998) and Turrell & Blackmore (1998).

5. NATURAL ATTENUATION AS A REMEDIAL OPTION

5.1 Why MNA?

The processes of contaminant attenuation are occurring, to some extent, all the time, and the challenge of using MNA as a remedial option is to exploit those processes to achieve site specific remedial targets. However, although it is a passive option, MNA must be actively selected as the optimal remedial technique on the same basis as any other technique.

Part IIA of the Environmental Protection Act 1990 refers to the 'best practical technique' to manage site specific risks to human health and the environment. This will include consideration of efficiency, effectiveness, durability, reasonableness and practicability.

In addition, in the National Oil and Hazardous Substances Pollution Contingency Plan, the US EPA (1990) sets out nine evaluation criteria for the objective assessment of the overall feasibility and acceptability of any remedial alternative:

- protection of human health and the environment;
- compliance with ARARs (applicable or relevant and appropriate requirements). These define the appropriate level of environmental and health protection to be achieved, such as Environmental Quality Standards;
- long term effectiveness and permanence;
- reduction of toxicity, mobility or volume through treatment;
- short term effectiveness;
- "implementability";
- cost;
- state acceptance;
- community acceptance.

Although specifically referring to treatment technologies, these criteria provide a base for the consistent and objective comparison of MNA with other strategies.

It therefore becomes apparent that although in many instances MNA may appear at the outset to be an attractive option financially, **it is essential** that good hydrogeological, geological and chemical characterisation and modelling are carried out to enable rigorous defensible predictions of the likely movement of the plume over time and the associated risk to identified receptors. In the end MNA may prove to be costly, may require a large body of time series data, and may take a significant time to complete.

The key to the successful implementation of MNA as a remediation technique is its use within the context of a risk based approach, ensuring that the goals of remediation and the effects on potential receptors are adequately assessed. The identification of remedial objectives (inherent within a risk assessment approach) is vital - is mass flux the crucial issue or contaminant concentration? Is the receptor at risk groundwater or surface water, or both? Protection of the receptor(s) must continue throughout the time during which the source is likely to be active, and this may involve the inclusion of contingency measures should conditions change, to ensure that exposure remains within acceptable limits.

The US EPA OSWER (1997) state that:

"Monitored natural attenuation is an appropriate remediation method only where its use will be protective of human health and the environment and it will be capable of achieving site-specific remediation objectives within a timeframe that is reasonable compared to other alternatives".

If contaminant concentrations in groundwater at the identified receptor are currently above protective concentration guidelines, then MNA alone should not be considered. (Wiedemeier et al., 1997).

The following advantages of MNA over other conventional remediation technologies are recognised (e.g. Wiedemeier et al., 1995 and 1998, ASTM, 1998):

- contaminants may ultimately be transformed to innocuous by-products (such as carbon dioxide and water) rather than simply being transferred to another phase or location;
- it is minimally intrusive, and continuing use of infrastructure is possible during remediation;
- other engineered remedial technologies which transfer contaminants to the atmosphere may pose a greater risk (or additional risks) to ultimate receptors;
- it can be less costly than currently available technologies, such as conventional pump and treat systems;
- it is not subject to the limitations of mechanised equipment (there is no down time);

- compounds which are most mobile and toxic (such as benzene) can be the most susceptible to biodegradation.

In cases where active remediation of NAPL phase contaminant has reduced groundwater concentrations to asymptotic conditions which are above groundwater quality targets (diffusion controlled release), or where heterogeneity of the environment makes accurate characterisation of the hydrogeological regime too difficult to effectively design engineered remediation strategies, the remediation of the remaining contaminant plume through MNA is often the only feasible option. (Zhang et al., 1998, referencing US NRC Report).

5.2. MNA - the argument against

Despite its obvious attractions, MNA will not provide the optimum remediation technique for all contaminant plumes. In comparison with more conventional clean-up technologies, the timescale required for groundwater remediation through MNA may be unacceptably long (ASTM, 1998), or the extensive monitoring (both spatially and temporally) and modelling required for confirmation that MNA will be protective of the identified receptor may result in MNA being less cost effective than other techniques.

The issue of plume complexity and site characterisation is important. In contrast to the diagrams found in many texts, contaminant plumes do not tend to form smooth ellipses in the field - there is widespread evidence that ‘fingering’ is common where there are variations in, for example, permeability (even minor variations), reaction rate (particularly where there is inadequate mixing with nutrients, electron donors or electron acceptors), or the strength number and position of the source(s). The high-concentration plume core may form only a small proportion of the total plume volume (Cherry, 1999). The position and strength of the plume may also vary temporally due to changes in groundwater flow or recharge. This plume heterogeneity or the existence of multiple contaminant plumes may make adequate site characterisation and proof of MNA complex (and therefore costly), or even impossible, particularly where it may not be possible to position monitoring points in optimum locations.

Quite apart from the above, microbial activity, which in many cases is the key to the destruction of contaminants, is highly dependent on local conditions and is susceptible to natural or anthropogenic changes. It may reduce or cease entirely for any one of the following reasons: contaminant concentrations may change, co-contaminant or degradation products may be high enough to be toxic to bacteria, the number and/or type of micro-organism may be inadequate for biodegradation, conditions may be too acid or alkaline, nutrients or required enzymes may be lacking, or the site may be too wet or dry (Cauwenberghe & Roote, 1998). Environmental conditions are not likely to be conducive to contaminant biodegradation at every site (ASTM, 1998).

In addition, the intermediate by-products of contaminant degradation may be more toxic and/or mobile than the original contaminant, resulting in an increase in the risk posed to the receptors. Institutional controls may need to be implemented to prevent inappropriate groundwater use before remediation is effectively complete. Other remedial technologies in use may hinder or prevent the natural attenuation processes.

Until the use of MNA as a remedial technique has become more widespread and understanding has increased, it may be necessary to spend greater time and resources convincing the stakeholders that MNA is the most appropriate cost effective risk management technique for a given site.

5.3 The feasibility of MNA in groundwater remediation

Much of the published information for MNA relates to studies undertaken in the US in shallow unconfined relatively homogeneous aquifers (CIRIA, 1999). The key circumstances favouring MNA of organic contaminants under these circumstances include:

- consistent groundwater flow (speed and direction) throughout the seasons;
- seasonal variation in depth to groundwater of less than 1m;
- seasonal variation in regional flow trajectory of less than 25 degrees;
- presence of carbonate minerals (limestone, dolomite, shell material) to buffer pH;
- presence of elemental nutrients (especially nitrogen and phosphorous);
- high concentration of electron acceptors such as oxygen, nitrate, ferric iron or sulphate (for petroleum hydrocarbons).

(CIRIA, 1999).

A relatively high proportion of natural organic matter in the soil or aquifer is also important, particularly in terms of sorption/retardation and/or the biodegradation of chlorinated solvents.

In general terms, the applicability of MNA to petroleum hydrocarbons and chlorinated solvent plumes in groundwater can be summarised as follows:

- within a risk management framework;
- for dilute contaminant plumes;
- with a controlled or controllable contaminant source;
- in combination with other remediation techniques;
- where an equilibrium concentration has been reached through other methods;
- where there is low current or future groundwater use, or the existence of an alternative supply;
- in situations with low receptor sensitivity;
- within a timeframe comparable with that for other techniques;
- with public acceptability/confidence.

(Lovelace & Feldman, 1997)

Petroleum hydrocarbon constituents are generally biodegradable, regardless of their molecular weight, as long as indigenous micro-organisms have an adequate supply of nutrients, and biological activity is not inhibited by toxic substances (US EPA Office of Underground Storage Tanks, Internet page on Natural Attenuation).

It has been *estimated* that MNA could provide the sole remediation technique at approximately 20% of all chlorinated solvent contaminated sites in the US, and a proportion of the remedy at an additional 50% of sites (RTDF, 1997). However, other sources express reservations, for instance the US EPA OSWER (1997) state that because of the nature and distribution of these compounds, MNA may not be effective as a remedial option, and the use of MNA as a remedial technique is likely to be the most appropriate when used in conjunction with other remedial technologies, or as a follow up to active remediation measures.

J T Wilson et al. (1997) sum up the time aspect:

"The rates of attenuation of chlorinated solvents and their less chlorinated daughter products in groundwater are slow as humans experience time. If concentrations of chlorinated organic compounds near the source are in the range of 10 000 to 100 000 micrograms per litre, then a residence time in the plume on the order of a decade or more will be required to bring initial concentrations to current maximum contaminant levels for drinking water [in the US]. *Biodegradation as a component of natural attenuation can be protective of groundwater quality in those circumstances only where the travel time of a plume to a receptor is long. In many cases, it will be necessary to supplement the benefit of natural attenuation with some sort of source control or plume management".*

More specifically a number of issues affect whether or not MNA is likely to be a cost effective and protective remedy at any given site. The following (Sections 5.3.1 to 5.3.13) is based on a review of available literature and an extensive study of case histories, both where MNA has been successful and where it has not worked or has not been proven:

5.3.1 Nutrient/substrate availability

One of the major factors influencing the effectiveness of MNA through biodegradation as a remedial technique is the availability of micro-organism nutrients.

For chlorinated solvents, it is the presence of an electron donor that is important, and in many pristine (otherwise uncontaminated aquifers) the supply of natural organic carbon is inadequate to maintain degradation rates sufficiently long to completely remediate the contaminant plume. Co-contamination with an anthropogenic source of organic carbon (such as BTEX) has been documented many times, allowing the progression of reductive dehalogenation, although it has been noted that benzene remains in the plume and is therefore probably not a good carbon substrate (Otten et al., 1998).

Where groundwater is contaminated by petroleum hydrocarbons it is the availability of electron acceptors which is the limiting factor. Once dissolved oxygen and nitrate have been exhausted, the plume quickly moves to an anaerobic state in which the degradation of petroleum hydrocarbons is slow (and possibly impractical as a remedial option).

The addition of substrates and/or nutrients to enhance contaminant attenuation is described further in Section 5.3.13.

5.3.2 Redox conditions

Over and over again in the literature, it is the redox conditions in the groundwater which determine whether or not MNA through biodegradation is a viable remedial option (see Sections 2 and 3 and Appendix 1 for general comments on optimum conditions). For example, Jackson (1998) describes long chlorinated solvent plumes in geochemically oxic conditions for which it is unlikely that MNA will be effective. It should be reiterated that it is not simply the occurrence of degradation which is important, but the rate or efficiency of the reaction.

The various intermediaries (such as TCE, cis-DCE and VC) in chlorinated solvent degradation do not all efficiently degrade under the same conditions. Under the methanogenic and high organic carbon conditions favourable for the breakdown of the more highly chlorinated solvents, the rate of degradation of the less chlorinated compounds is much reduced, and therefore VC (and to some extent, DCE) tends to accumulate. Consistent redox conditions are not, therefore, necessarily the most favourable for complete degradation of chlorinated solvents to non-toxic products. In fact, the:

"natural attenuation [of chlorinated solvents] *is most efficient when contaminants are exposed to sequential reducing/oxidising conditions. The key to assessing the efficiency of chlorinated solvent natural attenuation is to accurately delineate the distribution and succession of redox conditions in groundwater systems"* (Chapelle, 1998).

Sequential redox conditions are not uncommon. In naturally oxic groundwater, the leading edges of a chlorinated solvent plume frequently exhibit aerobic conditions and vinyl chloride may be oxidised either aerobically or through iron III reduction. In these cases DCE and VC typically do not accumulate. Reductive dehalogenation of the more highly chlorinated solvents followed by the oxidation of VC, often at the plume fringes (McCarty, 1997 & Wiedemeier et al., 1997) is generally the most important in the natural system.

Conversely, if an attenuating plume intercepts adverse redox conditions, there may be incomplete degradation, for example, where the leading edge of a plume (requiring aerobic conditions) reaches a surface water body or marshy area associated with increased organic carbon and more reducing conditions (example given by Chapelle, March 1998).

In addition, *"the existence of anoxic conditions is not a sufficient condition for reductive dehalogenation, because inhibition of the microbial catalysis of reductive dehalogenation may occur due to high concentrations of dissolved chlorinated hydrocarbons affecting the functioning of anaerobic microbes (10-100 mg/l: Bouwer, 1994)"* (Jackson, 1998).

The sequential use of electron acceptors in petroleum hydrocarbon degradation results in a large anoxic core area of the plume in which electron acceptors early in the series have become exhausted and biodegradation is occurring slowly, surrounded by aerobic fringes within which aerobic respiration is degrading contaminants more quickly. The development of an anaerobic plume core in an otherwise aerobic aquifer has been documented a number of times, for example, Stauffer et al (1998).

Almost all types of fuel hydrocarbons can be biodegraded under aerobic conditions (Borden et al, quoted by Wiedemeier, 1995). Certainly in the shallow sandy aquifers of California in the US, benzene rarely impacts water supply wells because plumes become stable at short distances from the source, and there are restrictions on the use of shallow groundwater for drinking.

However, there are exceptions. Prommer et al. (September, 1998) describe a BTEX plume in a shallow sandy aquifer in Perth, Western Australia which biodegrades intrinsically in anaerobic conditions. The aquifer is sulphate rich and no degradation rate is quoted, although there are further references.

5.3.3 Aquifer materials

Geological heterogeneity and complex geological and hydrogeological regimes typically lead to difficulties in identifying the contaminant plume. This is particularly true for chlorinated solvents where the location of the free phase DNAPL in the subsurface is more often controlled by the presence and topography of low permeability layers or lenses than by the direction of groundwater flow. Sparse monitoring data therefore more frequently reflect the lower concentration fringes of plumes and *"conventional* [monitoring] *networks only rarely establish the existence of cores, except perhaps close to the source zone"* (Cherry, 1997).

The vast majority of published information on proven natural attenuation relates to shallow sandy aquifers with fairly uniform flow regimes. This is understandable, since these types of aquifer are the easiest to model and investigate, and many of the more studied test sites (such as Borden in Canada, and the St Joseph Superfund site, Michigan, US) are on this type of aquifer. In addition, these types of aquifers are perhaps the most easily contaminated, due to the thin unsaturated zone, the absence of a confining layer and the ease of groundwater flow transporting dissolved contaminants.

In complex geological systems such as fractured rock aquifers, the operation of mechanisms associated with MNA have not been so well characterised. In a recent directive, the US EPA considered that in systems where the direction of groundwater flow is difficult to predict, MNA may not be the most cost effective solution as a result of the increased cost of the initial characterisation and monitoring (CIRIA, 1999).

The limited surface area of flow/rock contact in fractured aquifers may also lead one to suspect a reduced opportunity for biodegradation processes. However, TAN in Idaho, US, contains a TCE plume in a fractured basalt aquifer with a deep (64m) water table. The TCE degradation product DCE is found close to the source but not downgradient, indicating anaerobic degradation close to the source driven by organic carbon included within the source itself, progressing to aerobic conditions further downgradient where no degradation takes place (Sorenson et al., 1998). Hinchee (1997) concludes that the same processes that have been observed in unconsolidated sediments at a number of sites are occurring in fractured basalt, and that therefore anaerobic dehalogenation and aerobic oxidation of the less chlorinated solvents should occur. The difference is simply that the characterisation of flow is more problematic in the fractured rock. Additional sites with fractured bedrock dehalogenation are described in Kunkel et al. (1997) and Mahaffey & Dokken (1997).

Aquifer porosity is one of the controls on groundwater velocity, and in fractured strata fracture porosity can be an order of magnitude lower than in porous media (and hence groundwater velocity is correspondingly greater). The likelihood of a receptor existing within the plume area in a fractured rock is therefore many times that of a similar porous media aquifer transmitting a comparable flow volume.

There is little information regarding contamination and the attenuation of contaminants in lower permeability materials. This may simply be because low permeability strata represent a lower risk in terms of impact to a receptor, or that there is a reduced chance of the existence of a receptor in the first instance. DNAPL penetration of unfractured clay is uncommon, since a DNAPL head of around 36m is required to exceed the entry pressure (Jackson, 1998). However, vertical and subvertical fractures and microfractures in clays and clayey materials permit DNAPL intrusion much more easily (an example is reported in Parker et. al., 1998). Dissolved NAPLs also tend to diffuse into clay pore spaces and adsorb to the surface of particles. After this has occurred for a number of years the slow desorption and diffusion out of the clay matrix may represent a long term contaminant source. Schilling et al. (1998) state that in anaerobic conditions beneath an abandoned landfill in the US the "*evidence indicates intrinsic bioremediation of chlorinated volatile organic compounds in the mudstone was pronounced*".

There may be a relationship between permeability and microbial population (Schulze-Makuch, 1998). In general a high proportion of clay was found to correspond to high nitrogen and phosphorous concentrations in the soil and a high bacterial soil population. Conversely, low soil nutrients tended to move the bacteria to groundwater (possibly so that as they became more mobile there was a greater chance of a sufficient nutrient supply). In laboratory tests, increased bacterial populations (relative to high dissolved oxygen conditions) were also measured in groundwater when dissolved oxygen levels were low (reduced to less than 1 mg/l). The specific impacts of variations in bacterial population on the degradation of petroleum hydrocarbons and chlorinated solvents is not discussed, but it would be expected that a reduction in bacterial population would represent a decrease in the potential for biodegradation, assuming the reaction efficiency remains the same.

Microcosm studies of a wetland (high organic) aquifer (Lorah & Olsen, 1998) showed that TCE degradation was fastest under methanogenic conditions (as would be expected), and biodegradation rate constants were two to three orders of magnitude higher than those obtained in microcosm studies using sandy media. In addition, biodegradation occurred at an extremely high rate under sulphate reducing conditions, well in excess of rates reported for less organic rich materials. Complete degradation of ethenes past VC was observed and it is suggested that aerobic degradation of DCE and VC occurs in association with methanotrophic activity around root systems. Degradation rate constants for DCE and VC were similar to those for TCE. This work has implications for groundwater discharging to a wetland and the potential for natural cleanup before impact.

Evidence for the biodegradation of TCE in a carbonate aquifer under anaerobic conditions has been documented by Schilling et al. (1998).

5.3.4 Hydraulic regime

Where legislation and policy permits (but see Section 7.2), MNA through dilution occurs best where there is the greatest volume of underflow compared to contaminant flux, although this situation may lead to a rapidly expanding contaminant plume and may, in any case, contradict various aquifer protection policies. Conversely, however, in low groundwater flow conditions, there is typically more time available for biodegradation or sorption, and contaminant plume migration is limited. In addition, in conditions where limited groundwater flow is associated with materials with a high clay content, there may be factors (for example chemical) influencing the rate of attenuation which are related to the clay itself.

Hydraulic regimes may be complex (see Section 5.2), and even small differences in material permeability, as in the Borden aquifer in Canada, may have significant implications for plume movement. Investigation of a heterogeneous aquifer in the US contaminated with petroleum hydrocarbons showed that NAPL contamination became entrapped preferentially within coarse materials in the saturated zone and finer materials in the unsaturated zone. Therefore, the solute plume was not homogeneous but consisted of a number of sub-plumes, each at different depth intervals, moving at different velocities, and with different contaminant concentrations (Illangasekare et al, 1994). In this situation, which may be common, natural attenuation is likely to occur with varying effectiveness within each sub-plume, and assessment and monitoring must prove receptor protection from each and all of the sub-plumes. The design of monitoring wells has to be particularly stringent, to avoid misleading results due to dilution within the well.

Differences in attenuation rates in areas of saline intrusion have not been well reported. In a study of petroleum contaminated harbour sediments, Coates et al. (1996) suggest that sulphate reduction is often the predominant degradation process, and that in contrast to studies with freshwater sediments, the addition of iron III does not result in iron III reduction and an increase in degradation rate.

5.3.5 Seasonal effects

The potential effects of seasonal changes in flow on a BTEX plume in a shallow sand aquifer in Perth, Western Australia have been investigated through modelling. The results show that seasonal variations in groundwater flow direction have the potential to impact spatial and temporal development of the redox processes involved in the degradation of organic contaminants such as BTEX. The total mass of contaminant degraded does not vary to the extent that localised conditions vary, although these local variations have the potential for significant impact on the assessment of natural attenuation and the potential for natural attenuation where only a limited number of monitoring boreholes are installed and/or monitoring is carried out infrequently (Prommer et al., September 1998).

The dependence of the biodegradation process (particularly for petroleum hydrocarbons and the less chlorinated solvents) on the supply of dissolved oxygen make it susceptible to seasonal changes in groundwater flow and chemistry. For shallow aquifers in particular, the oxygen supply is derived from infiltrating rainwater, so in the wetter months there is more oxygen (dissolved oxygen or other electron acceptors which have become reduced through reaction) available for microbial growth. The effect of changes in infiltration is unlikely to be consistent throughout a contaminant plume, and may therefore lead to variations in chemical conditions within the plume. Other factors (such as temperature) which may affect bacterial activity, may not be so seasonally variable in the subsurface.

Seasonal changes in groundwater flow (both rate and direction) may also affect the rates of biodegradation through chemical variation and through physical changes (faster flow does not leave so much time for degradation to occur). Changes in groundwater direction (and hence plume) may mean an increased contact with microbes and substrates.

Flow volume changes may also have a significant effect on the extent of contaminant dilution within the aquifer, and the impact of any contamination at a receptor (in the summer the groundwater baseflow component may make up a large proportion of surface water flow whereas in the wetter months there may be more dilution within the receptor). Changes in flow volume and direction need not necessarily be natural, but may be a result of seasonal changes in abstraction rates (irrigation in particular is a seasonal groundwater demand).

5.3.6 The effects of temperature

Micro-organisms function within an optimum temperature range, and any biologically mediated attenuation of contaminants will therefore progress only within this range. An increase in temperature within the range will generally result in an increase in microbial activity.

In terms of chemical reaction, an increase in temperature typically results in an increase in reaction rate. On an absolute scale, a reaction that is kinetically possible may not be relevant in the field if the temperature is such that the reaction occurs extremely slowly.

Variations in groundwater temperature are, however, relatively small in the UK, and therefore any attenuation mechanism that is occurring is unlikely to vary significantly due to temperature changes.

Caution should be used when estimating the efficiency of MNA using rates derived from sites in, for example, California or Australia, where groundwater will be warmer than in the UK. Conversion is possible for chemical reaction rates, but this may not be applicable to data describing biodegradation.

5.3.7 The effects of ageing

There is very little published information on the effects of ageing of hydrocarbon contaminants on the potential for attenuation (primarily through biodegradation, but also through sorption and subsequent desorption). However, Sheremata et al. (1998) points out that in some cases, sorption of contaminants to soil particles can reduce their availability for biodegradation, and the longer a contaminant is resident in soils the more resistant it is to desorption and biodegradation.

Laboratory experiments showed that ageing of up to 30 days resulted in a significant decrease in biodegradation, with initially preferential degradation of contaminant from the aqueous (rather than sorbed) phase, followed by preferential sorbed phase degradation 14 days into the experiment. The decrease in aqueous phase degradation was postulated to be due to the increase in dissolved organic matter, a component of which (humic acid) has been shown to result in reduced bioavailability. In addition, there was an increase in the resistance of TCE to desorption over the period of ageing, although conversely, DCE, the product of TCE degradation, became more mobile with time.

The implications of this study to contaminant plumes in the field have not been proven.

For 'recent' contaminants, such as MTBE, microbial evolution may be necessary before biodegradation can occur, and there may therefore be a significant time interval between the contamination event and the onset of biodegradation.

5.3.8 Sorption and biodegradation rates

In moving groundwater, MNA within a risk based framework is likely to be most protective of a receptor where sorption is high and/or biodegradation rates are fastest.

5.3.9 The effects of contaminant concentration

For some contaminants, there is a limit above which the contaminant itself is toxic to the micro-organisms involved in its degradation "*...inhibition of the microbial catalysis of reductive dehalogenation may occur due to high concentrations of dissolved chlorinated hydrocarbons affecting the functioning of anaerobic microbes*" (Jackson, 1998).

It is possible that below this limit the rate of biodegradation is dependent on contaminant concentration, raising such important questions as

- are biodegradation rates and half-lives obtained at one concentration applicable to the same contaminant under the same conditions at other concentrations?
- does the degradation rate vary within a plume due purely to concentration differences, irrespective of other conditions?
- does the degradation rate vary within the plume due to decreasing concentrations with time as natural attenuation proceeds?

Very little information in answer to these questions was encountered during the course of this project, and it is suspected that this is an area requiring further research.

5.3.10 The effects of microbial ecology

The bacteria responsible for the biodegradation of organic contaminants can evolve to degrade contaminants more effectively or to utilise contaminants not previously available. Indeed, there are currently microbial populations that have become so specialised that they will *only* metabolise anthropogenic contaminants such as chlorinated solvents (Mackay, 1999). Therefore, some contaminants previously considered to be recalcitrant (for example, MTBE) may 'become' degradable simply through the evolution of suitable bacteria. At any given site, there is likely to be a time lag before this occurs.

Microbial populations (and hence biodegradation rates) may also vary with aquifer heterogeneity, an issue which is discussed to some extent in Section 5.3.3. For example, population densities may decrease away from the surface, or there may be more bacteria in the aquifer matrix than in fissures.

Again, this is an issue on which there is sparse published information, and it may be an area requiring future research.

5.3.11 The effect of other contaminants

Co-contaminants may have a beneficial impact on the natural attenuation of petroleum hydrocarbons and chlorinated solvents, particularly where attenuation is primarily biological, either by acting co-metabolically or by providing essential substrates (see Sections 5.3.1 and 5.3.13, and Appendix 1).

In general the biodegradation of petroleum hydrocarbons is limited by the supply of electron acceptors such as dissolved oxygen and nitrate (Wiedemeier et al., 1997). Any co-contaminant acting as an electron acceptor would therefore be expected to have a positive effect on the natural attenuation of these contaminants in groundwater.

The biodegradation of chlorinated solvents is typically limited by the supply of electron donors (Wiedemeier et al., 1997), and a co-contaminant acting as an electron donor would be expected to have a positive effect on the natural attenuation of these contaminants in groundwater. The attenuation of chlorinated solvents in association with spills of petroleum hydrocarbons is commonly reported. For example, McQuillan et al. (1998) document a case in which it is clear that limited or no degradation of TCE occurred until the plume overlapped an area contaminated with BTEX, which acted as an electron donor. Extensive attenuation of TCE has been documented at a site at which leachate from a disposal lagoon provided the energy source for co-metabolic reduction (McCarty, 1997). McCarty (1997) also gives an example of methanol and acetate within a plume of PCE acting as electron donors and facilitating degradation to VC.

Similarly, co-contaminants supplying essential nutrients (nitrogen and phosphorous) would be advantageous. In the case discussed by McQuillan et al., it was fortuitous that nitrate concentrations in groundwater were also high as a result of historical contamination with fertilisers.

However, co-contaminants may also compete for electron acceptors/donors or for nutrients. Organic co-contaminants may need to be present as electron donors in greater quantities than would be necessary for the degradation to occur in isolation because other micro-organisms compete for the electron donors (McCarty, 1997). Although compounds which act as electron acceptors under anaerobic conditions may facilitate reductive dehalogenation of chlorinated solvents by supporting the production of electron donors, at higher concentrations they may actually inhibit reductive dehalogenation through competition (Leahy & Skladany, 1998).

Gossett & Zinder (1997), describe competition for the H_2 important in chlorinated solvent reductive dehalogenation. There is evidence to suggest that dechlorinating bacteria may out-compete methanogens, but the relative H_2 affinity between dechlorinators and sulphate reducers is not yet known. The hydrogen source is also important, and it is suggested that compounds such as benzoate (and possibly BTEX) which produce a steady supply of H_2 through degradation are more conducive to successful dechlorination than, for example, lactate or ethanol, which tend to result in short-lived H_2 peaks. Therefore, an assessment of the nature of dechlorinators, the quantities *and qualities* of available electron donors *and* the competition for hydrogen is essential to predict natural attenuation.

Cauwenberghe & Roote (1998) suggest that *"high concentrations of heavy metals, highly chlorinated organics, long chain hydrocarbons or inorganic salts are likely to be toxic to micro-organisms causing reduced efficiency or failure of in situ bioremediation. In other situations, presence of significant quantities of materials more amenable to biodegradation than the target contaminant may render in situ bioremediation ineffective for the needed remediation".*

The co-contaminants themselves may actually prove to be a higher risk than the primary contaminant, and regardless of their impact on the natural attenuation of the petroleum hydrocarbon or chlorinated solvent may preclude the use of MNA as a remedial option. For example, MTBE may not be as degradable in all circumstances as BTEX (although there are references stating the case both ways). The US EPA OSWER (1997) quotes the example of 1.4-dioxane used as an additive to some chlorinated solvents which is more highly toxic, less likely to sorb to aquifer solids and less biodegradable than the solvent itself under given environmental conditions.

5.3.12 The impact of degradation by-products

The degradation of the original contaminant and removal from the groundwater system, although a primary aim of MNA, is not the end of the process. Depending on the relative rates of biodegradation at each stage in the degradation process, the products of degradation may build up in the environment.

The ultimate degradation products, such as chloride, ethane, carbon dioxide etc. are not usually considered to be of concern, but this is not so for all degradation products (for example, VC produced during the degradation of the more highly chlorinated solvents is less easily degraded in anaerobic conditions, is more toxic and is a known carcinogen. (Reported by Environment Canada, quoted in Sheremata et al., 1998)).

McCarty (1997) states:

"Concerns are frequently expressed over the VC formed as an intermediate in reductive dehalogenation of PCE, TCE and DCE in groundwater because VC is a known human carcinogen. It is possible to oxidise VC aerobically, however, with oxygen as an electron

acceptor, or even under anoxic conditions with iron III. In addition, VC is readily and very efficiently co-metabolised by methane, phenol or toluene oxidisers. Here, transformation yields of over 1 gram of VC per gram of methane have been obtained. Thus, at the aerobic fringes of plumes with methane and VC present or where sufficient iron III is present, natural attenuation of VC through oxidation can occur".

Later in the paper when considering attenuation at the St Joseph, Michigan Superfund site in the US, he writes that "*the great extent of aerobic co-metabolic VC transformation in the methane present suggests that aerobic oxidation at the plume fringes is likely to be occurring*".

The RTDF (1997) state "*For a long time, it was commonly believed that VC would accumulate. However, it is now known that VC can be biodegraded under almost all of the potential conditions found in the subsurface because it can undergo direct biodegradation under both aerobic and anaerobic conditions*".

This oxidation of VC (and DCE) at plume fringes, whilst noted regularly in the literature, does not always occur, for example McCarty (1997). In a practical sense, if the receptor is close enough to the contaminant source that oxidation at the plume edges is not sufficient to be protective of human health or the environment with regards to degradation by-products, then MNA is not the optimum remedial method.

Under methanogenic conditions and in the presence of high BTEX concentrations, the rate of methane production from BTEX degradation can be significant (ASTM). Simple mass balance calculations may be possible to estimate the quantities of methane expected at a given site.

It is not only direct degradation products that are increased in the environment as a result of natural attenuation. The changes in redox (and pH) conditions brought about as a result of biological and geochemical interactions may have their own effect. Harris et al (1998) state that the reducing conditions within a contaminant plume are often associated with unacceptably elevated concentrations of dissolved metals (metals such as arsenic and barium which sorb to iron and manganese oxides are released when these oxides are reduced). Metals may subsequently re-adsorb as conditions become more oxidising further downgradient of the source. Leigh et al., (1998) describe an increase in barium concentrations above local drinking water standards associated with the reduction of sulphate, and Carey et al. (1998b) suggest arsenic is included in groundwater analysis when the reductive dissolution of iron hydroxides is suspected. Although this localised increase in metal concentrations may be used as an indicator of the occurrence of natural attenuation, the impact of the increase itself must also be assessed.

5.3.13 Combination with complementary or alternative techniques

Within the Superfund program, MNA has been selected as one of the remedial methods at 73 groundwater contaminated sites, but is the sole treatment option at only six of them ("A Citizen's Guide to Natural Attenuation", US EPA).

The application of MNA is limited, and high concentrations of contaminants are unlikely to be remediated effectively using MNA alone. The use of MNA as a remedial technique is likely to be the most appropriate when used in conjunction with other remedial technologies, or as a follow up to active remediation measures (US EPA OSWER, 1997), for example where a concentration asymptote has been reached resulting from diffusion-limited contamination with NAPLs. MNA is generally not an option at sites with free product in the subsurface (US EPA Office of Underground Storage Tanks, Internet page on Natural Attenuation), and it is now commonly recognised that MNA is most effective alongside some form of source control (e.g. US EPA OSWER, 1997).

The use of MNA alongside other methods is described in many publications, an example of which (Rees, 1998) is included as Appendix 2.

It is vital to consider in detail the effects of engineered remediation techniques on the effectiveness of natural attenuation processes, particularly where the primary attenuating mechanism is biologically mediated. Micro-organisms are sensitive to changes in, for example, pH, temperature and redox conditions, and any adjustments to the groundwater environment are likely to have an impact (either positive or negative) on microbial activity.

Grant Carey writes that "*even minor alterations to redox conditions off-site caused by active on-site remediation may have a significant influence on chlorinated solvent biodegradability downgradient of the site. In a situation where the on-site contaminant source is actively contained, and the electron donors supporting the biodegradation of chlorinated solvents are within the on-site source, there is a risk that the natural attenuation of the plume off-site may be reduced or eliminated*". (Internet, http://gwrp.cciw.ca/internet/gwm-archive/1998/msg00107.html). A study of the effect of changes in redox conditions caused by landfill capping on the degradation of chlorinated ethenes is reported by Carey et al. (1997). Other remedial methods such as groundwater pump and treat systems and air sparging which are known to introduce oxygen to the contaminant plume may remobilise stable chlorinated solvent plumes in anaerobic conditions (Wiedemeier & Pound, 1998).

However, just as there may be a negative impact on natural attenuation through changes in redox conditions, we can also manipulate redox conditions and exploit any positive impact.

A multi-contaminant plume in Germany which had stabilised following groundwater pumping (Willershausen et al., 1998) was successfully remediated through enhanced natural attenuation using a sequential injection methodology to cause changes in redox conditions, in combination with a pump and treat system to prevent plume expansion. Extracted groundwater was treated and enriched with nutrients, oxygen or co-substrates before being discharged to the unsaturated zone and aquifer via infiltration wells. Initially, conditions were made conducive to the biodegradation of the non-chlorinated compounds (e.g. BTEX) through the addition of nutrients and oxygen. Once these compounds had been removed, anaerobic conditions (methanogenic in the centre of the plume) were artificially created in the aquifer through the addition of compounds with high biological oxygen demand. The reductive dehalogenation of the more highly chlorinated solvents progressed for four years, after which time oxygen was reintroduced to accelerate the microbial degradation of by-products under aerobic conditions. Over 24 tons of contaminant was removed and the plume remediated within a period of six years, with natural attenuation accounting for over 90% of the remediation.

This 'enhanced natural attenuation' may also include the introduction of substrates and/or nutrients. Since many petroleum hydrocarbons require oxygen for their degradation, the technological emphasis of engineered bioremediation has been placed on oxygen supply (Committee on In Situ Bioremediation, 1993). The use of nitrate enhancement to accelerate the bioremediation of monoaromatic hydrocarbons in groundwater has been shown to be successful (Eckert et al., 1998), although it is not clear whether this is due to the use of nitrogen as a nutrient or through an increase in the oxidative capacity, or, probably, both.

The addition of specific micro-organisms (engineered or natural) to enhance biodegradation is usually referred to as bioaugmentation, and is outside the scope of this report.

The boundary between enhanced natural remediation schemes and passive or semi-passive remediation is gradational, and there is a full range described in the literature, for example (Barker, 1998) the addition of nitrate through a funnel and gate system to accelerate the biodegradation of a naphthalene plume.

6. THE ASSESSMENT OF NATURAL ATTENUATION

6.1 Established protocols

There is a growing body of information, mainly from the United States, describing the steps to be taken when assessing the role of MNA in groundwater remediation and amassing the evidence required to convince the regulatory agencies, stakeholders such as potential land purchasers, and, where appropriate, the general public. The following protocols have been referenced numerous times in the literature, and are considered currently to be the 'state of the art' in their intended areas of application:

- Technical Protocol for Implementing Intrinsic Remediation with Long Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater. US Air Force Center for Environmental Excellence;
- Technical Protocol for Natural Attenuation of Chlorinated Aliphatic Hydrocarbons in Groundwater Under Development for the US Air Force Center for Environmental Excellence. Overview published in Wiedemeier et al., 1997;
- Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices. RTDF;
- Standard Guide for the Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites. ASTM;
- Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites. US EPA OSWER.

Although the steps outlined in each protocol vary slightly, the following abstracted from the Wiedemeier overview outlines the typical stages recommended in the adoption of MNA:

- review available site data and develop a preliminary conceptual model including the identification of receptors;
- screen the site and assess the potential for MNA (initial screening flowchart presented as Figure 11, (Wiedemeier et al., 1997));
- collect additional site characterisation data to support MNA, as required;
- refine the conceptual model, complete pre-modelling calculations and document indicators of natural attenuation;
- simulate natural attenuation using analytical or numerical solute fate and transport models that allow incorporation of a biodegradation term, as necessary;
- conduct an exposure-pathway analysis;

- evaluate the predictability and potential efficiency of supplemental source removal options;
- if MNA with or without source removal is acceptable, prepare a long term monitoring plan;
- present findings to regulatory agencies, and obtain approval for remediation by MNA.

A flow chart is presented as Figure 12 (Wiedemeier et al., 1997). In respect of the latter point, it should be noted that in the UK, the Environment Agency would encourage early discussion rather than becoming involved at the later stages of the process.

Much of the information presented within each protocol, particularly the background to the processes involved and the overview of site investigation aims and methodology, is general enough to be applied in the UK. However, the protocols may not be applied in their entirety, since some sections are aquifer-specific, and it should be noted that one of the main protocols (the US AFCEE protocol for chlorinated solvents) is not considered to apply outside the USAF, and may not be appropriate for use by the US EPA (RTDF Internet Page, http://www.rtdf.org/b11397).

An assessment of the assimilative capacity of the site area is important in the prediction of the potential for natural attenuation and its effectiveness over time. It may be achieved through the quantification of the contaminant mass and the available electron acceptors/donors (whichever is the limiting factor).

As an example for aerobic oxidation: with an O_2 to benzene mass ratio of 3.1:1, 0.32 mg/l benzene is degraded per 1 mg/l O_2. If the background concentration of dissolved oxygen is 4 mg/l, the assimilative capacity for aerobic degradation is $(0.32/1) \times 4 = 1.28$ mg/l. This is repeated and summed for all other mechanisms (such as denitrification).

"The challenge is to obtain a quantitative understanding of the underlying processes that govern the impact of a spill of organic liquids in an aquifer, the time for the residual source to dissolve, the evolution of contaminant peak concentrations, the ultimate volume of aquifer being contaminated by the dissolved organics and the time required for biodegradation processes to restore the natural aquifer" (Schirmer et al., September 1998).

6.2 Lines of evidence

It is the responsibility of the problem holder to prove (beyond reasonable doubt) that a MNA approach to remediation is acceptable and that there will be no adverse impacts on on-site or off-site receptors (CIRIA, 1999).

It is now commonly accepted in the US that to support the effective application of remediation through MNA, three lines of evidence are required (US EPA and the AFCEE (Wiedemeier et al., (1995 and 1996), Chapelle, (1997) and Wiedemeier et al., 1997) and RTDF, 1997):

1. An observed reduction in contaminant concentrations along the flowpath downgradient from the contaminant source;
2. A documented loss of contaminant mass at field scale using chemical and geochemical analytical data (e.g. decreasing parent contaminant concentrations, increasing concentration of biodegradation by-products, changes in concentration of electron acceptors and donors, increasing concentration of metabolic by-products) and/or a conservative tracer and a rigorous estimate of the residence time along the flow path to document contaminant mass reduction and to calculate biological decay rates at the field scale;
3. Microbiological laboratory data (e.g. microcosm studies) that support the occurrence of biodegradation and give biodegradation rates.

Wiedemeier (1997) suggests that to support the use of MNA at most sites, the investigator is likely to have to demonstrate that contaminant mass is being destroyed (probably through biodegradation) rather than diluted or transferred to another medium (which may be occurring if only the first line of evidence is covered). Thus the investigator must obtain at least the first two lines of evidence or the first and the third.

It must be noted, in reference to the third line of evidence, that bacteria from natural environments display markedly different properties to those observed during culture in the laboratory (Edwards et al., 1998) due to disturbance of the aquifer materials and micro-organisms, and due to the relative abundance of nutrients. Schirmer et al., (September 1998) state that "*the apparent kinetic degradation rates at the field scale are often smaller when compared to laboratory derived kinetics. The cause of this apparent discrepancy lies primarily in the transport characteristics and heterogeneities at the field scale which are not commonly observed in the laboratory....Nutrients, supplied in excess in the laboratory, are often limiting in the field*". Zeyer et al. (1995) suggest that measurement of trace intermediates, such as fumarate derivatives, may show micro-organism activity. Site specific and in situ evidence is preferable.

A Dutch study of 15 sites in Holland where the plume included PCE and degradation products showed that sites could be classified into one of four groups (Table 2):

Table 2. Dutch site classification.

Ratio VC:DCE	**SO_4^{2-}**	**DOC**	**Complete reductive dehalogenation**
> 0.1	<5 mg/l	>10 mg/l	likely
< 0.05	<5 mg/l	<10 mg/l	may be possible
< 0.05	>20 mg/l	<10 mg/l	unlikely
< 0.05	>20 mg/l	>10 mg/l	unlikely

(adapted from Tonnaer et al., 1998).

The groupings are intended to provide a quick, rough method for an initial assessment of the potential for natural attenuation at a given site, although it is pointed out that the method is still under development, it is not known whether it will apply to soils outside the Netherlands, and the collection of additional data is not precluded.

6.3 Site characterisation and monitoring

In order to implement MNA for the remediation of groundwater, it is essential to fully understand the physical, chemical and biological processes occurring. This necessitates a thorough investigation of the site's geology and hydrogeology, the location, nature and extent of contaminant(s) source and plume, site specific groundwater chemistry both within and outside the plume, and potential contaminant pathways to receptor(s) of concern. This can represent a significant cost implication, and Wiedemeier (1997) quotes that analytical costs are increased by around 10 to 15% over standard site investigation. These costs are regularly retrieved where MNA is selected as the optimal remediation technique. Key parameters to be considered in site characterisation are set out by CIRIA (1999) (Table 3):

Table 3. Site characterisation parameters.

Requirements	**Parameter**
Source Characterisation	• Type of contamination • Presence of additives (e.g. MTBE at petroleum release sites) and co-contaminants • Date of release • Volume of release • Extent of phase separation e.g. for BTEX
Hydrogeology	• Regional hydrogeology • Site stratigraphy • Depth to groundwater • Seasonal variation in groundwater elevation • Unsaturated zone thickness • Hydraulic conductivity • Aquifer porosity • Aquifer thickness
Plume Characteristics	• Delineation of soluble plume • Organic carbon content of aquifer • Degradation products
Assessment of Biodegradation	(list of determinands provided later in this chapter)
Risk Assessment	• Location of potential receptors • Patterns of aquifer use (current and future) • Location of groundwater recharge and discharge areas

It has been suggested (US EPA, quoted in CIRIA, 1999) that all monitoring programmes should be designed to accomplish the following:

- demonstrate whether natural attenuation is occurring according to expectations (i.e. whether or not the conceptual model is correct);
- identify any potentially toxic transformation products resulting from degradation;
- determine if a plume is expanding (either downgradient, laterally or vertically);
- ensure no impact to downgradient receptors;
- detect new releases of contaminants to the environment that could impact the effectiveness of the MNA remedy;

- demonstrate the efficacy of institutional controls that were put in place to protect potential receptors;
- detect changes in environmental conditions (e.g. hydrogeological, geochemical, microbiological or other changes) that may reduce the efficacy of any of the natural attenuation processes;
- verify attainment of remedial objectives.

As described in the previous section, it would be prudent to complete an initial screening of the site to assess the suitability of MNA for the remediation of contaminated groundwater prior to initiating a large scale and costly exercise which may later prove to be fruitless (Blickle et al., 1998). Wiedemeier (1997) proposes a points system for the initial screening exercise, which should be referenced at sites where MNA is being considered.

In terms of adequate monitoring sufficient to characterise the site and provide the required data, Wiedemeier (1997) suggests a *minimum* of six groundwater monitoring boreholes; one upgradient of the contaminant spill, one within the NAPL source area, two directly downgradient of the source area within the dissolved contaminant plume, one directly downgradient of the source area but beyond the limits of the contaminant plume, and finally one downgradient of the source but laterally offset from the direction of groundwater flow, beyond the lateral extent of the contaminant plume. A similar arrangement is pictured in the RTDF document (RTDF, 1997), and is presented herein as Figure 13. It should be noted that each site must be assessed on its merits and the number of monitoring points might vary considerably.

The data collected in the site screening exercise can be used to help design any further site investigation considered necessary. Site screening data and data from the detailed investigation (if completed) can be used to simulate the transport and fate of contaminants in a site specific manner (see Appendix 3 for further details), in order to predict the position and migration of the contaminant plume with time.

Wiedemeier has classified chlorinated solvent plumes behaviour into three basic types, based on the amount of chlorinated solvent, the amount of biologically available organic carbon, the distribution and concentration of natural electron acceptors (oxygen, nitrate etc.) and the types of electron acceptors used (Wiedemeier et al., 1997 and Wiedemeier & Pound, 1998). Any single plume may exhibit different types of behaviour within different areas.

- Type 1 behaviour is characterised by the reductive dehalogenation of chlorinated solvents where anthropogenic organic carbon is acting as a primary substrate for microbe growth resulting in the production of hydrogen, which drives reductive dehalogenation. This behaviour results in the rapid and extensive degradation of the more highly chlorinated solvents such as PCE, TCE, TCA, CT and DCE. In determining the longevity and effectiveness of natural attenuation in these circumstances, the quantity of electron donor must be assessed. It is also important to consider the role of competing electron acceptors such as dissolved oxygen, nitrate and sulphate, and whether VC is oxidised or reduced;

- Where there are relatively high concentrations of natural organic carbon which is biologically available, this carbon source is used by micro-organisms as a primary substrate, and this is what drives dehalogenation. This Type 2 behaviour is generally slower than Type 1 degradation, but can be rapid under the correct conditions. Again, the supply of electron donor, the role of competing electron acceptors and the fate of vinyl chloride must be assessed;

- Type 3 behaviour dominates where there is low natural or anthropogenic carbon, and dissolved oxygen concentrations are higher than about 1 mg/l (aerobic conditions). In these circumstances the reductive dehalogenation of the chlorinated solvents will not occur, although vinyl chloride may be rapidly oxidised.

An example of site conditions exhibiting both Type 1 and 3 behaviour is presented as Figure 14.

6.3.1 Determinands

In both site screening and detailed site characterisation, analysis of a number of parameters may indicate the type and extent of degradation process(es) occurring. Table 4 highlights those determinands that would generally be recommended in a site investigation programme, and has been adapted, in part, from the various protocols available.

Table 4. Determinands for site investigation.

Determinand	**Indication/Reason**
Primary spill contaminants	Assists in the delineation of the contaminant plume and contaminant concentrations. (Soil & Water)
Degradation products of primary spill contaminants	Evidence for the biodegradation of the primary contaminant. cis-DCE is a particularly good indicator of the biodegradation of PCE/TCE since in synthetic DCE the *trans-* isomer predominates. Similarly, the ratio of o-xylene to the m and p isomers would be expected to increase as BTEX degrades. (Water)
Dissolved Oxygen	The electron acceptor most thermodynamically favoured by micro-organisms for the degradation of natural or anthropogenic organic carbon. Concentrations less than 1 mg/l generally indicate an anaerobic environment. At DO greater than about 0.5 mg/l anaerobic bacteria generally cannot function, and reductive dehalogenation of chlorinated solvents is unlikely to occur. It will not occur at concentrations greater than 1 mg/l. Petroleum hydrocarbons and vinyl chloride may be oxidised aerobically at DO concentrations in excess of 1 mg/l. (Water)
Nitrate	Substrate for microbial respiration (electron acceptor) if oxygen is depleted. At concentrations in excess of 1 mg/l, nitrate may compete with reductive pathway. (Water)
Nitrite	Results from nitrate reduction (denitrification). (Water)
Iron III	An analysis of biologically available iron III can be used to estimate the potential for attenuation where iron III is reduced. Iron III may be used as an electron acceptor during anaerobic degradation of electron donors where dissolved oxygen and nitrate are depleted. (Soil)
Iron II	Iron II may indicate the anaerobic biodegradation of petroleum hydrocarbons where dissolved oxygen, nitrate and manganese are depleted (iron III is used as an electron acceptor), although precipitation when combined with other substances may lead to an underestimate of the quantities produced. At concentrations greater than about 1 mg/l, reductive pathway is possible. (Water).
Manganese IV	In some circumstances, manganese IV may be used as an electron acceptor during anaerobic degradation of electron donors where dissolved oxygen and nitrate are depleted. (Soil)
Manganese II	Manganese II may indicate the anaerobic biodegradation of petroleum hydrocarbons where dissolved oxygen and nitrate are depleted (manganese IV is used as an electron acceptor). (Water)
Sulphate	Substrate for anaerobic microbial respiration (electron acceptor). At concentrations in excess of 20 mg/l, sulphate may compete with reductive pathway. (Water)

Sulphide	Results from sulphate reduction. At concentrations greater than about 1 mg/l, reductive pathway is possible. May not be detected even if sulphate reducing bacteria are active because it can react with various oxygenated chemical species and metals. (Water).
Methane	The presence of methane in groundwater is indicative of strongly reducing conditions, and when present (say in excess of 0.1 mg/l) suggests biodegradation of organic carbon via methanogenesis. At concentrations in excess of about 1 mg/l, VC is likely to accumulate, and at concentrations less than 1 mg/l VC will oxidise. (Water)
Dissolved hydrogen	Indicates the terminal electron accepting process, and can be used to predict the possibility for reductive dehalogenation. At DH greater than about 1nM the reductive pathway is possible and VC may accumulate. At concentrations less than 1 nM vinyl chloride can be oxidised. The procedure is described in Chapelle (1997). (Water) Wiedemeier (1997) quotes dissolved hydrogen concentrations for terminal electron acceptor processes as follows: <0.1 nM/l indicates denitrification 0.2 to 0.8 nM/l indicates iron III reduction 1 to 4 nM/l indicates sulphate reduction >5 nM/l indicates methanogenesis
Organic carbon	The total organic carbon (natural or anthropogenic) gives an indication of the supply of primary substrate, and hence the potential for reductive dehalogenation of chlorinated hydrocarbons. A concentration greater than about 20 mg/l in groundwater is likely to be sufficient to drive dehalogenation of chlorinated solvents. Also gives an indication of the retardation (sorption) potential of the soil. (Soil & Water)
pH	Both aerobic and anaerobic processes are pH sensitive. pH between 5 and 9 is the tolerated range for the reductive pathway. A difference in pH between contaminated and uncontaminated groundwater may indicate biological activity is occurring. (Water)
Alkalinity	Used to measure the buffering capacity of groundwater (against acids produced in both aerobic and anaerobic biodegradation), and, since it results from the interaction of CO_2 with aquifer minerals, can also be used to estimate the amount of CO_2 produced during biodegradation. The biodegradation of petroleum hydrocarbons results in an increase in groundwater alkalinity. (Water)

Eh	Indicates the redox state of the groundwater and hence the types of attenuation processes which may occur. <50 mV indicates reductive pathway possible. (Water)
Temperature	Affects the solubility of chemicals involved in oxidation-reduction processes, particularly oxygen. Biochemical processes are accelerated at temperatures in excess of 20^0C, and may be inhibited at temperatures in groundwater below about 5^0C. Temperature may be used as an indicator of when the monitoring borehole has been purged sufficiently to remove stagnant water. (Water)
Chloride	Produced during biodegradation of chlorinated solvents, and may be used as a tracer to estimate biodegradation rates, or, on some cases, the extent of dilution. (Water)
Sodium	Can be used to assess whether chloride is associated with, for example, road salt. (Water)
Ethane/ethene	Produced during reductive dehalogenation of chlorinated solvents. (Water)
Volatile Organic Compounds	Analysed to indicate the extent of contamination (both primary contaminant and degradation by-products), the contaminated mass present and the need for source removal. Also used as primary line of evidence (contaminant mass decrease). (Soil & Water)
Carbon Dioxide	Used as an electron acceptor where concentrations of dissolved oxygen, nitrate, iron III, and sulphate are depleted (in methanogenesis, an anaerobic biodegradation process). Concentrations greater than twice background concentration may indicate that CO_2 is present as an ultimate degradation product of both petroleum hydrocarbons and chlorinated solvents. (Water)
Volatile Fatty Acids	A carbon (and hence energy) source, often found in landfill leachate. Also an intermediate resulting from the biodegradation of aromatic compounds, indicated by concentrations greater than around 0.1 mg/l. (Water)
Bacterial Studies	Apart from indicating that bacteria at the site have the potential to degrade contaminants, other bacterial properties may indicate biodegradation - an increase in the numbers of bacteria within the plume above usual conditions, or bacteria within the plume being able to metabolise the contaminant where bacteria outside the plume cannot. An increase in the number of protozoa (which feed on bacteria) within the plume may also indicate biodegradation.
Carbon Isotopes	Isotopic ratios of the inorganic carbon (carbon dioxide, carbonate ion and related compounds) showing that the contaminant has been transformed to inorganic carbon are a strong indicator of biodegradation. Can also be used to examine plume zonation (Landmeyer et al., background file). (Soil & Water)

Acetate	During methanogenesis, may act as an electron acceptor.
Oxygenates such as MTBE, ethers, acetic acid, methanol and acetone	May be contaminants, and/or may act as electron donors for the dehalogenation of chlorinated solvents. (Water)
Arsenic	(an indicator of Iron III reduction)
Other metals	may be released through changes in redox conditions within a plume, and may hence be an indicator of natural attenuation.

Notes on the definition of redox zones using the parameters described above, and a detailed example are given in Chapelle (1997).

Rugge et al. (1998) have compared the field results of a natural gradient injection test with the results of in situ microcosms and laboratory batch experiments for a range of petroleum hydrocarbons and chlorinated solvents. They conclude that in general the results were in good accordance, with differences due in the main to different experimental periods. It is suggested that the in situ microcosms are useful for studying compounds with lag periods shorter than 50-100 days, and that the batch tests are a cost effective method of examining compounds with varying degradation rates or for mixtures of compounds with a range of lag periods.

6.4 Representation of monitoring results

The representation of monitoring results in a way that can be easily interpreted is an issue which has long been discussed. Methods have included tabulation of data, the construction of contour plots showing groundwater head or concentrations of contaminants of concern, and concentration histograms plotted on a plan of the site.

In many instances, but perhaps in natural attenuation studies in particular, these methods offer no satisfactory method of demonstrating in a consistent manner the large number of factors that are closely interrelated.

SEQUENCE, a relatively new software tool (see Appendix 3), goes some way towards addressing these issues. Essentially, contaminant concentration data are plotted on multi-axis diagrams, which may then be overlaid on a site or potentiometric diagram. The number of axes and the contaminants plotted may be adjusted to suit the system under study (for example, the concentrations of electron donors and daughter products may be important at a chlorinated solvent contaminated site whereas ammonia and List I substances may be of more concern in a landfill leachate plume). Axis scales may be linear or log, and may increase or decrease away from the origin.

Representative SEQUENCE diagrams are given as Figure 15, and further details may be found in Appendix 3. Examples of sites at which SEQUENCE has been used to evaluate the natural attenuation of BTEX and chlorinated ethenes are given on the web page and in Harris et al., 1998 and Carey et al., 1998a.

6.5 Public and regulatory acceptance

It is incumbent upon the proponent of MNA to convince the regulatory agencies, all stakeholders and (if appropriate) the general public that it provides the most satisfactory remediation strategy for contaminated groundwater at a given site. Stakeholders may include not only the current owners and residents of the site, but potential owners, developers, residents and neighbours (perhaps long into the future) and financial institutions. The value of a contaminated site may be dependent upon the acceptance of MNA as a remedial option.

Proof of the efficiency of MNA is dealt with to a great extent through the methods of thorough site characterisation, plume modelling and monitoring outlined in Sections 6.1 to 6.3, and in adherence to the various protocols available. The scientific principles behind these techniques are unlikely to be understood and appreciated by all stakeholders, so, in addition, public and regulatory acceptance is reliant upon clear and timely communication with all parties, and the installation of contingency control measures (within an appropriate monitoring strategy) in the event that conditions deviate from those predicted.

Inherent within these principles is the issue of risk perception, which is, in itself, a complex issue. Communication has to be targeted so each audience can acquire a clear and unbiased picture of the way in which the use of MNA is likely to affect them. No matter how good the science, if there are financial institutions involved and they aren't happy with the use of MNA, then development that relies upon groundwater remediation is unlikely to proceed. The reader is referred to Adams (1995) for further information on risk and risk perception.

On a more practical note, the following regulatory conditions have been imposed in various States in the US (CIRIA, 1999):

- property boundaries often used as points of compliance, beyond which MNA is not permitted;
- movement across property boundaries is only permitted with the consent of the affected landowners;
- institutional controls on the use of groundwater may be imposed while a plume is undergoing natural attenuation;
- monitoring until biodegradation is demonstrated;
- monitoring until water quality criteria have been met;
- monitoring for a minimum of two years;
- closure without monitoring if there are no nearby receptors;
- the use of a sentinel well one year travel time upgradient of the nearest downgradient receptor and five years travel time downgradient of the plume margin.

Monitoring until the risk no longer needs to be managed may be another option. Demonstration of a reduction in contaminant mass rather than concentration (possible through dilution and dispersion) is usually required.

7. NATURAL ATTENUATION IN THE UK

7.1 Current experience

Although the natural attenuation of chlorinated solvents and petroleum hydrocarbons is undoubtedly occurring in the UK, there is far less published information relating specifically to this country than to North America and parts of Europe. Research into the effectiveness of natural attenuation is being carried out, notably at one or two institutions. In particular the Groundwater Protection and Restoration Group based at Sheffield University has an active research group and work group defining research needs. They also hold an annual seminar or workshop, and have set up the 'Network on Natural Attenuation in Groundwater and Soil' (NNAGS) on the Internet for the exchange of information.

Of the industrial representatives, consultants, researchers and remediation contractors contacted as part of this study, many felt that the natural attenuation of chlorinated solvents and/or petroleum hydrocarbons was playing a major role in the remediation of groundwater at a number of sites in the UK. However, since there had been no requirement for the extensive monitoring and characterisation necessary to prove the operating processes, this work had not been carried out and there was consequently limited 'hard' data.

There are few published cases where natural attenuation has been well documented in the UK, and of these, most do not relate to petroleum hydrocarbons or chlorinated solvents (e.g. Thornton et al., September 1998 (phenol, cresols and xylenols, NH_4), Davison & Lerner, 1998 (phenol and ammonium), and Thornton, March 1998 (phenolic and N-containing compounds)). We have come across no published cases where MNA has been specifically selected as a remedial option in the UK.

However, BP International have provided details of a UK case study where natural attenuation has been used. A brief description of the subject site and contaminants is given below.

7.1.1 UK Case Study

The site is located on a minor sandy aquifer in an area that has no sensitive receptors. Some time during the 1960s there was a spill of benzene and toluene of sufficient size for migration of contamination to the water table to occur. Little investigation of the impact of the spill was undertaken at the time but the impact of the spill was investigated in the early 1990s. Initial work and the data collected was inconsistent and problems associated with laboratory analyses and sample collection protocols where found to be at blame. However, from mid 1995 a consistent sampling protocol and a suitable laboratory technique had been identified that allowed the routine collection of data in a form that could be used to assess the role of MNA. Shallow source zone removal was undertaken at the beginning of 1996.

The groundwater is typically 3.5 m below ground level, and is both unconfined and semi-confined beneath the site. Groundwater velocities (unretarded) are in the order of 30-60 m per year, with a hydraulic gradient of around 0.24%. The plume depth is around 9-15 m below ground level. The core of the plume is some 2-3m thick, with some minor residual hydrocarbon contamination above and below the main plume. Detailed multilevel sampling has not been undertake but there is no evidence that the main plume is plunging.

In order to evaluate the use of MNA as a remedial strategy, BP used the ASTM protocols for investigating the lines of evidence needed to promote this remedial method. Initially, 21 monitoring wells were established, but the long term monitoring has, in later years, relied primarily on around 17 well locations.

The investigation and subsequent monitoring demonstrated a number of facts, which, when taken together provided sufficient evidence for the technique to be applied as the primary remedial option. The primary findings were:

- the plume front was stable;
- the area of the plume was reducing;
- the plume front moved only 50 m from the spill site in 30 years;
- the average benzene concentration (across the entire plume) has fallen from 40 mg/l circa 1995 to 12 mg/l circa 1998. During this same period the plume area has reduced by 50%;
- toluene comprised the major component of the original spill but is now absent, suggesting it has all degraded;
- the rate of degradation is greatest at the plume edges and lowest in the centre, with the highest rates being at the upstream edge.

Secondary lines of evidence included:

- measurement of viable anaerobic bacteria and sulphate reducing bacteria within the plume (105 and 104 per ml respectively);

- measurement of redox conditions directly and indirectly.

Overall the amount of sulphate in the groundwater (with the strong indication that sulphate reducing bacteria were present) allowed a calculation that at least 43 mg/l of benzene could be biodegraded (without recourse to dissolved oxygen and nitrate reduction which could be active at the plume edges).

The entire monitoring study has been continuing for 5 years and there is ample evidence that the plume has significantly shrunk in this time scale.

It is evident, however, that a significant amount of time and effort has been extended in undertaking the monitoring and the interpretation of results in order to provide sufficient evidence for the use of MNA to be used as the prime groundwater remediation method. However, BP consider the cost of monitoring, instigating the appropriate protocols, site research and regulatory discussion are expected to be less than direct and active intervention.

The authors of this review report are grateful for the assistance provided by BP International in providing details of this (as yet) unpublished work.

7.2 The applicability of international data and experience to remediation in the UK

Given the body of information relating to the natural attenuation of chlorinated solvents and petroleum hydrocarbons abroad, and the relative sparcity of similar data for UK aquifers, the challenge we face is to examine to what extent the lessons learned in other countries applies in conditions experienced in this country.

There can be no doubt that natural attenuation occurs at some sites even if the precise biochemistry is not fully researched. Further, if the conditions at a site are favourable with respect to redox conditions, electron donors/acceptors and nutrient supplies, then natural attenuation would be expected to be effective and MNA may be viable as a remedial option.

Similarly, the general principles behind site characterisation apply in all UK circumstances. A thorough understanding of the processes involved in natural attenuation and the physical, chemical and biological conditions at the site in question alongside a defensible risk assessment will lead to a reliable assessment of the potential for MNA as a remediation method, whatever country the site is in.

Nevertheless, there are fundamental differences between the properties of the major UK aquifers and the aquifers generally described in the literature, raising important questions. For example:

- how does rapid fissure flow in the Chalk affect the potential for natural attenuation ?
- does the behaviour of the matrix porewater, peculiar to Chalk, change the conditions under which natural attenuation would be expected to be effective ?
- does natural attenuation of petroleum hydrocarbons and chlorinated solvents occur any differently in groundwater in the Sherwood Sandstone at depth than in shallow sandy aquifers ?
- does the considerable seasonal variation in water table elevation at many sites across the UK have any impact ?
- how different is the potential for natural attenuation in low permeability materials in the UK, particularly the drift in the northern part of the country ?

Burgess et al. (1998) have completed a study of a site in southern England at which contaminant diffusion into the Chalk matrix in the seasonally unsaturated zone has occurred (both chlorinated solvents and chloride). Concentrations in matrix porewater are significantly higher than in background groundwater, and in general, chlorinated solvents show a peak (vertically) close to the seasonal water level low. A model has been produced to predict long term elution of contaminants from matrix porewater in the seasonally unsaturated zone.

Differences between the UK and countries abroad may also be apparent in regulatory constraints and socio-political factors, rather than technical or scientific plausibility. For example, the regulatory climate in the UK may preclude the selection of MNA as a remedial option where the plume extends beyond the site boundary, or, until public education has progressed, 'allowing' contaminant plumes to remain within groundwater without active remedial measures may be too emotive an issue.

7.3 Why hasn't natural attenuation been a regular choice for remediation so far in the UK?

Celtic Technologies (pers. comm.) report that MNA has been used in a number of cases and has been accepted by the Environment Agency, although no written information has been received from Celtic.

In general, although natural attenuation is usually accepted as occurring, MNA has not been reported by consultants, contractors or industrial representatives as the selected remedial technique for a number of reasons:

- there has been insufficient monitoring to prove natural attenuation;
- little thought was given to MNA and other remedial options have been considered in preference;
- the necessary investigation would have been too costly;
- proof of natural attenuation was not required (and therefore not obtained), since other remediation options were available;
- the site sensitivity didn't justify extensive monitoring;
- most refuelling stations are too small to contain the contaminant plume within the ownership boundary, and companies are not always willing to undertake off-site monitoring;
- there has been difficulty in isolating or distinguishing the source and plume from other effects, other sources and other plumes etc. Indeed, where a number of potential spills (or source areas) are involved, as may be the case in large industrial areas, it might be difficult to follow the strict protocols and to demonstrate contaminant mass reduction.

Slater et al. (1998), propose a possible solution to the latter problem using carbon isotopes to isolate sources and to identify degradation processes.

7.4 Regulatory context; the Groundwater Regulations 1998

7.4.1 Pollution prevention

The Groundwater Regulations (1998) introduced on 1 January 1999, fully transposing the EC Groundwater Directive (80/68/EEC), prohibit the introduction of List I substances to groundwater, and limit the introduction of List II substances to avoid pollution of that groundwater.

Within this context, therefore, reliance on the natural attenuation of List I contaminants (and probably List II) within groundwater is unlikely to be permitted in a planned remedial strategy where contaminants have not yet reached the water table (attenuation must occur within the unsaturated zone before the contaminant reaches groundwater). A more pragmatic approach, in which the impact on downgradient receptors is assessed, is still relevant for existing/historical groundwater plumes, and in these cases the assessment of natural attenuation remains unaffected by the new regulations.

7.4.2 Remediation of contamination

UK policy on the remediation of contaminated groundwater and soils has long been to remediate to a standard that is fit for the purpose of the site and the local environment, as opposed to a multifunctional approach. Remediation of sites and/or groundwater under the planning process (Town and Country Planning Act 1990) or through Part IIA of the Environmental Protection Act 1990 or section 161A of the Water Resources Act 1990 will continue to emphasise the importance of a risk based approach, and will allow the adoption of MNA where it is shown to adequately manage the risks associated with the contamination.

8. SUGGESTIONS FOR FURTHER RESEARCH

In terms of the applicability of MNA as a remedial option in the UK there is obviously great scope for research. The theoretical basis for the reactions involved has been well covered in international publications, and in general the UK suffers from a lack of practical field studies demonstrating that the accepted theory is relevant to UK aquifers (both Major and Minor, shallow and deep systems). A body of well studied and well documented UK sites demonstrating both those occasions where MNA has been effective and those where it would have failed to be protective of human health and the environment, would lend more confidence to future decisions to implement MNA as a remedial technique at UK sites. Similarly, there is a need for collated information on degradation rates of specific compounds under the aquifer conditions encountered in the UK so that first pass screening exercises may be based on more realistic figures.

As a related issue, it is understood that process of producing a protocol for the assessment and acceptance of MNA specific to the UK is in progress.

Other more specific issues for which it is suggested that further research is required are detailed below:

- This study has focused on the attenuation of chlorinated solvents and petroleum hydrocarbons in groundwater. Similar studies examining the attenuation of other compounds, and the natural attenuation potential within the unsaturated zone or of free phase NAPLs would provide an invaluable basis for the implementation of MNA under other conditions. In this context, there is a body of data relating to PAHs, phenols etc. and to petroleum additives (although a study of the natural attenuation of MTBE is currently being completed at Sheffield University). Hinchee (1997) states that "*it is conceivable that an as yet unidentified process exists that degrades NAPL in situ... which could result in a much more significant mass removal that the dissolution process followed by degradation in groundwater. This is an area which has been largely overlooked*";

- Further investigation into the questions posed in Section 7.2 is vital in order to predict the effectiveness of MNA in UK aquifers. What properties of the Chalk lead to deviations from published theory? What about the Sherwood Sandstone at depth? etc. As stated above, there is a tremendous need for well documented case studies for these aquifers;

- A great deal more information is required on the attenuation (particularly biodegradation and sorption) of compounds within low permeability media. This has implications for landfill sites lined with clays or situated over clays, and for other contaminated sites situated within the large area of the UK overlain by low permeability Glacial Till material;

- Questions raised in Sections 5.3.9 and 5.3.10 regarding non-constant degradation rates due to variations in contaminant concentration or microbial population require further examination;

- Sorption onto specific sites of some mineral phases, and probably also to solid organic phases (such as humics), may facilitate the breakdown of some organic contaminants. It is possible, for example, that polar organic compounds sorbed at charged sites on minerals (e.g. smectite) may be more susceptible to breakdown than when in free solution. Similarly, non-polar organics (e.g. hydrophobic phases) may become more susceptible to breakdown in aqueous conditions when sorbed on solid organic phases with some charge distribution and tendency to take part in electron transfer processes. Sorbed organics would presumably have different Infra Red spectra and other bond properties that could be characterised remotely, at least under microcosm conditions;

- Sorption of organic contaminants onto clays and iron-oxides is not well understood; it is known that sorption may be kinetically slow and also that it may be irreversible (or at least desorption may be slow). The sites where active sorption takes place, and also the locations of degradation by-products (assuming that breakdown might be enhanced when the compound is sorbed), could be investigated by selective extraction of core samples from contaminated sites. The particular aim with respect to natural attenuation would be to confirm that parent compound and 'inferred' daughter products are actually related through their locations in specific sorption sites. The sequential extraction procedures would need to be designed to be selective of mineral phases and/or sites (there are well established procedures here, e.g. extracting just iron-oxides, or clays, or humics) and also to ensure that only the organics associated with those sites were extracted. Selective extraction procedures could also be used in investigating the solid phases in lab or microcosm studies, but it is envisaged that there would be most interest in characterising where organics and daughter products were located in a natural system that had been subjected to long-term contamination and had reached some sort of natural attenuation 'equilibrium' state with full interdependence of the organic, inorganic and microbial reactions;

- It is important to complete an assessment of the effects of co-contaminants, and a quantitative comparison of degradation rates for common contaminants in single and multiple contaminant plumes;

- The role of iron minerals in natural attenuation may be particularly important in British groundwater systems where the host rocks (old rocks with a long diagenetic history) usually have a 'mature' iron mineral assemblage. There is an obvious contrast between Triassic sandstone, with abundant crystalline iron oxide, and Chalk with scattered siderite, marcasite and poorly characterised iron oxide.

- It is necessary to investigate the efficacy and availability of natural iron-containing minerals (both iron II and iron III) and associated redox conditions and microbial populations, in promoting natural attenuation. For example, iron III minerals might be localised electron-acceptors (on mineral surfaces and in micropores) in otherwise reducing groundwaters, thus facilitating oxidative degradation of hydrocarbons (e.g. benzene, toluene). Iron III-reducing bacteria might enhance, or compete with, sulphate reducing bacteria in facilitating the breakdown of electron donors;

- Iron II minerals are expected to be effective in promoting reductive dehalogenation, though presumably not as efficiently as zero-valent iron. They might also be an important intermediary in controlling oxidative degradation of hydrocarbons and other contaminants following artificial oxygenation. Rather than directly oxidising the contaminants, oxidative 'capacity' might be stored by conversion of iron II to iron III compounds, and then the oxidising facility released slowly via microbial processes using iron III as the terminal electron acceptor;

- It would be possible to devise investigations that study the roles of iron compounds and iron related micro-organisms, although the interpretations are likely to be inferential rather than definitive;

- There may be a difference in the degradation rates of common contaminants in the dissolved phase and the sorbed phase. One may dominate the other;

- Low partial pressures of hydrogen are produced in various microbial fermentations under anaerobic conditions. The hydrogen, though in low abundance, can act as an electron donor in reductive degradation of some compounds, also the reaction of hydrogen with oxygen at the aerobic-anaerobic interface in a groundwater system can supply energy for other transformations to occur. For example, the conversion of longer chain fatty acids to acetate in landfills is believed to require these low but significant concentrations of hydrogen. Measuring hydrogen fugacity (i.e. partial pressure) may be a way of categorising the transformations that are proceeding in a subsurface environment; different fugacities may define different microbial populations and organic reactions and thus constrain the active natural attenuation processes. However, Libelo et al. (1998) describe a case where variations in redox zones and degradation processes were not distinguished through dissolved hydrogen measurements;

- It is known that laboratory studies are not always representative of conditions in the field since it is not always possible to take account of factors such as competition from other species and aquifer heterogeneity. The relationship between field and laboratory data requires further exploration so that future (cheaper) laboratory studies (such as microcosm studies) may be used to best advantage. Rugge et al. (1998) have completed one such study;

- ^{36}Chlorine in atmospheric fallout has been enhanced considerably since the early 1960s because of nuclear bomb testing. Thus shallow ‘recent’ groundwaters are expected to have higher ^{36}Cl than older deeper groundwaters, analogously to the enhancement of tritium. Chlorinated anthropogenic compounds are likely to derive their chlorine from evaporite halite or marine chloride, both of which have very low or zero ^{36}Cl contents. Therefore breakdown of these compounds in groundwater will tend to raise dissolved chloride concentrations and to dilute the ‘bomb’ ^{36}Cl concentrations. However uncertainties in the pre-existing variability of ^{36}Cl are likely to obscure the identification of chloride dilution arising from contaminant breakdown, therefore ^{36}Cl does not provide an effective general approach to studying natural attenuation. Moreover it has to be noted that analysis of environmental ^{36}Cl is an expensive technique;

- ^{37}Chlorine is one of two stable Cl isotopes that are ubiquitous in nature (the other predominant isotope is ^{35}Cl). The ratio ^{37}Cl /^{35}Cl varies over a rather small range in nature. It has now been established that slightly larger variations exist in anthropogenic chlorinated compounds. There is also the possibility (that is not, as yet, proved as far as we know) that microbial transformations of such compounds might fractionate the isotopes further. Thus stable Cl isotopes are potentially a more useful tracer of natural attenuation than ^{36}Cl. At least one university group (at Reading) is already doing research on stable Cl isotope evidence for geosphere transformations;

- Stable isotopes (e.g. ^{37}Cl and others e.g. ^{13}C, ^{15}N) could also be enriched in purpose-synthesised organic compounds that would be used in microcosm or other lab or field experiments, to study degradation rates. Stable isotope ratio changes could be cost-effective and unique tracers of some natural attenuation processes. Obviously, use of artificially-enhanced radioactive ^{36}Cl would be prohibited in any in situ natural attenuation experiment;

- The ^{13}C/^{12}C ratio in organic compounds is around -25 per mil (parts per thousand) deviation from the carbonate standard ratio; this derives from the fact that organic compounds are synthesised mostly from natural hydrocarbons. This stable C isotope ratio can be modified in substrate and daughter compounds during natural processes by isotope fractionation, especially if there is microbial intervention. It had been thought that the fractionations would be of negligible significance for characterising breakdown products and pathways, however there is a growing amount of research that suggests that these isotopes might be valuable tracers of these processes. The developments in compound-specific isotope analyses, small sample handling methods, and improved (and cheaper) automated stable isotope analyses have made this method of investigation potentially cost-effective. For natural attenuation studies, stable C isotopes offer possibilities of tracing daughter products back to precursor compounds, and of carrying out mass balance studies of the 'total carbon system' (although it is envisaged these being only semi-quantitative at best).

- ^{14}Carbon is sometimes used to label organic compounds for laboratory and microcosm studies. Potentially the same could be done (and probably has been done) in field studies of natural attenuation. Most organic compounds (unlabelled) will have zero ^{14}C because of their derivation from natural

> hydrocarbon feedstock. When they degrade, the resultant CO_2 will be added to the existing alkalinity and will dilute the atmosphere-derived ^{14}C in groundwater. Thus potentially the changes ^{14}C in polluted groundwater might trace natural attenuation processes, however there is inherent variability of natural ^{14}C, therefore characterisation of this would be a necessary precursor. Natural attenuation studies in the field with either natural or labelled ^{14}C would require careful evaluation. Slater et al. (1998), report on the use of carbon isotopes to isolate sources and to identify degradation processes, and are known to have carried out related work in this field.

There may be a role for the money raised through landfill tax in the progression of those areas of research which would have application in the assessment or use of MNA in relation to landfill sites, such as attenuation within low permeability materials (e.g. landfill liners), or in the unsaturated zone beneath landfill sites.

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GLOSSARY

The following terms have been defined in the various protocols available:

Abiotic Occurring without the involvement of micro-organisms.

Advection Transport of molecules dissolved in water along the groundwater flow path at an average expected velocity.

Aerobe Bacterium that uses oxygen as an electron acceptor.

Aerobic Environmental conditions where oxygen is present.

Aerobic Respiration Process whereby micro-organisms use oxygen as an electron acceptor to generate energy.

Aliphatic Hydrocarbon A compound built from carbon and hydrogen atoms joined in a linear chain. Petroleum products are composed primarily of aliphatic hydrocarbons.

Anabolism The process whereby energy is used to build organic compounds such as enzymes and nucleic acids that are necessary for life functions. In essence, energy is derived from catabolism, stored in high energy intermediate compounds (such as adenosine triphosphate (ATP), guanosine triphosphate (GTP) and acetyl-coenzyme A), and used in anabolic reactions that allow a cell to grow (quoting Chapelle, 1993).

Anaerobic Environmental conditions where oxygen is absent.

Anaerobic Respiration Process whereby micro-organisms use a chemical other than oxygen as an electron acceptor. Common “substitutes” for oxygen are nitrate, sulphate, iron III, carbon dioxide and other organic compounds (fermentation).

Anthropogenic Man made.

Aquifer A geological formation that stores and readily transmits water.

Aquitard A geological formation of low permeability that does not readily transmit groundwater.

Aromatic Hydrocarbon A compound built from carbon and hydrogen atoms joined in an unsaturated ring (e.g. benzene ring).

Assimilative Capacity A semi-quantitative estimate of the potential mass of contaminant per unit volume of groundwater that can be metabolised by aerobic and anaerobic biodegradation under existing site conditions.

Attenuation Rate Measured reduction in concentration or mass of compound with time or distance expressed as an amount of reduction per unit time or unit distance.

Bacterium A single celled organism of microscopic size. Bacteria are ubiquitous in the environment inhabiting water, soil, organic matter and the bodies of plants and animals.

Biochemical Produced by or involving chemical reactions of living organisms.

Biodegradation Biologically mediated conversion of one compound to another.

Bioremediation Use of micro-organisms to control and destroy contaminants.

Biotransformation Microbiologically catalysed transformation of a chemical to another product.

BTEX Benzene, toluene, ethyl benzene and xylene. Primary constituents of petrol (gasoline).

Catabolism The process whereby energy is extracted from organic compounds by breaking them down into their component parts.

Co-metabolism The process in which a compound is fortuitously degraded by an enzyme or cofactor produced during microbial metabolism of another compound. The co-metabolised compound cannot serve as an energy source for the micro-organisms.

Chlorinated Solvent A hydrocarbon in which chlorine atoms substitute for one or more hydrogen atoms in the compound's structure. Chlorinated solvents are commonly used for grease removal in manufacturing, dry cleaning and other operations.

Conceptual Site Model A written or pictorial representation of an environmental system and the biological, physical and chemical processes that determine the transport of constituents of concern from sources through environmental media to environmental receptors within the system.

Corrective Action Action taken to identify and clean up a release of contaminant. These activities include site assessment, interim remedial action, remedial action, operation and maintenance of equipment, monitoring of progress and termination of the remedial action.

Daughter Product A compound that results directly from the biodegradation of another. For example, *cis*-1,2-dichloroethene is commonly a daughter product of trichloroethene.

Dechlorination See **Reductive Dechlorination**.

Degradation Destruction of a compound through biological or abiotic reactions.

Dehalogenation See **Reductive Dehalogenation.**

Dehydrohalogenation The elimination of H-X resulting in the formation of an alkene.

Desorption The opposite of sorption; the release of chemicals attached to solid surfaces.

Diffusion The process whereby molecules move from areas of high concentration to areas of low concentration as a result of Brownian motion.

Dihalo-elimination Reductive elimination of two halide substituents resulting in the formation of an alkene.

Dilution The combined processes of advection and dispersion result in a net dilution of the molecules in groundwater.

Dispersion The spreading of molecules along and away from the expected groundwater flow path during advection as a result of mixing of groundwater in individual pores and channels.

DNAPL See **Non-Aqueous Phase Liquids**

Electron A negatively charged subatomic particle that may be transferred between chemical species in chemical reactions. Every chemical molecule contains electrons and protons (positively charged particles).

Electron Acceptor An element or compound that is reduced by receiving electron(s) produced by the oxidation of an organic compound through microbial metabolism or abiotic chemical oxidation processes. Common electron acceptors in groundwater are oxygen, nitrate, iron III, sulphate and carbon dioxide. In some cases the chlorinated aliphatic hydrocarbons such as PCE, TCE, DCE and VC can also act as electron acceptors.

Electron Donor A compound that supplies or loses electrons (and is therefore oxidised) in oxidation-reduction reactions. In bioremediation, organic compounds serve as electron donors. Less chlorinated solvents can also act as electron donors.

Electrophile A reactive species that accepts an electron pair.

Elimination Reaction where two groups such as chlorine and hydrogen are lost from adjacent carbon atoms and a double bond is formed in their place.

Epoxidation A reaction where an oxygen molecule is inserted into a carbon-carbon double bond and an epoxide is formed.

Expanding Plume Configuration where the solute plume margin is continuing to move outward or downgradient from the source area.

Facultative Anaerobes Micro-organisms that use (and prefer) oxygen when it is available, but can also use alternative electron acceptors such as nitrate under anaerobic conditions when necessary.

Fermentation Microbial metabolism in which a particular compound is used both as an electron donor and an electron acceptor resulting in the production of oxidised and reduced daughter products.

Geochemical Produced by or involving non-biochemical reactions of the subsurface.

Growth Substrate An organic compound upon which bacteria can grow, usually as a sole carbon and energy source.

Heterotroph Organism that uses organic carbon as an external energy source and as a carbon source.

Hydraulic Conductivity The relative ability of a soil, sediment or rock to transmit water.

Hydrogenolysis A reductive reaction in which a carbon-halogen bond is broken and hydrogen replaces the halogen substituent.

Hydroxylation The addition of a hydroxyl group to a chlorinated aliphatic hydrocarbon.

Inorganic Compound A chemical that is not based on covalent carbon bonds. Important examples are metals, nutrients such as nitrogen and phosphorous, minerals and carbon dioxide.

Institutional Controls The restriction on use or access (for example fences, deed restrictions, restrictive zoning) to a site or facility to eliminate or minimise potential exposure to a constituent of concern.

Lithotroph Organism that uses inorganic carbon such as carbon dioxide or bicarbonate as a carbon source and an external source of energy.

LNAPL See **Non-Aqueous Phase Liquids**

Metabolic By-Product A product of the reaction between an electron donor and an electron acceptor. Metabolic by-products include volatile fatty acids, daughter products of chlorinated aliphatic hydrocarbons, methane and chloride.

Metabolic Intermediate A chemical produced in one step of a multi-step biotransformation.

Metabolism The chemical reactions in living cells that convert food sources to energy and new cell mass.

Methanogen A micro-organism that exists in anaerobic environments and produces methane as the end product of its metabolism. Methanogens use carbon dioxide or simple carbon compounds such as methanol as an electron acceptor.

Microcosm A laboratory vessel set up to resemble as closely as possible the conditions of a natural environment.

Micro-organism An organism of microscopic or submicroscopic size. Bacteria are micro-organisms.

Mineralisation The complete degradation of an organic compound to carbon dioxide, water, and, in some cases, inorganic ions.

Monitoring Point A monitoring well or other monitoring device placed in a selected location for observing parameters such as liquid level or pressure changes or for collecting liquid samples.

Monooxygenase A microbial enzyme that catalyses reactions in which one atom of the oxygen molecule is incorporated into a product and the other atom appears in water.

Non-Aqueous Phase Liquids (NAPLs) Organic liquids maintained in a separate phase from water. May be lighter than water (LNAPL) or denser than water (DNAPL).

Nucleophile A chemical reagent that reacts by forming covalent bonds with electronegative atoms and compounds.

Obligate Aerobe Micro-organisms that can only use oxygen as an electron acceptor. Thus the presence of molecular oxygen is a requirement for these microbes.

Obligate Anaerobes Micro-organisms that grow only in the absence of oxygen; the presence of molecular oxygen either inhibits growth or kills the organism. For example, methanogens are very sensitive to oxygen and can live only under strictly anaerobic conditions. Sulphate reducers on the other hand can tolerate exposure to oxygen, but cannot grow in its presence (quoting Chapelle, 1993).

Oxidation Loss of electrons from a compound, such as an organic contaminant. The oxidation can supply energy that micro-organisms use for growth. Often (but not always) oxidation results in the addition of an oxygen atom and/or the loss of a hydrogen atom.

Oxygenase An enzyme that introduces oxygen into an organic molecule.

Petroleum Hydrocarbon A chemical derived from petroleum by various refining processes. Examples include petrol (primarily BTEX), fuel oil and jet fuel.

Plume Volume or zone of groundwater where dissolved constituents of concern are present.

Point of Compliance Location(s) selected between the source area(s) and potential point(s) of exposure where concentrations of constituents of concern must be at or below the determined groundwater target levels.

Primary Substrate The electron donor and electron acceptor that are essential to ensure the growth of micro-organisms. These compounds can be viewed as analogous to the food and oxygen that are essential for human growth.

Receptor Persons, structures, utilities, ecological systems and water supply wells that are or may be adversely affected by a release of contaminant.

Reduction Transfer of electrons to another compound, which is then oxidised.

Reductive Dechlorination The removal of a chlorine atom or atoms from an organic compound and replacement with hydrogen atoms (see reductive dehalogenation).

Reductive Dehalogenation A variation on biodegradation in which microbially catalysed reactions cause the replacement of a halogen atom on an organic compound with a hydrogen atom. The reaction results in the net addition of two electrons to the organic compound.

Remedial Goals Remediation objectives established to protect human health and the environment. Remedial goals may be concentration based target levels applied at specific points throughout the plume, or performance based criteria such as demonstrated containment of the solute plume or demonstrated reduction in concentrations of constituents of concern over time within the plume or with distance from the source area.

Remediation/Remedial Action Activities conducted to protect human health, safety and the environment. These activities include evaluating risk, making no further action determinations and monitoring, and designing and operating cleanup equipment.

Respiration The process of coupling the oxidation of organic compounds with the reduction of inorganic compounds such as oxygen, nitrate, iron III, manganese IV and sulphate.

Sentinel Well Monitoring point(s), established at a location(s) between the leading edge of a contaminant plume and a sensitive receptor to ensure that there will be time for other remedial action to be taken if the plume does migrate beyond predicted boundaries.

Shrinking Plume Configuration where the solute plume margin is receding back towards the source area over time and the concentrations at points within the plume are decreasing over time.

Solvolysis A reaction in which the solvent serves as the nucleophile.

Sorption Attachment of a substance to the surface of a solid by physical or chemical attraction.

Source Area The location of free phase liquid hydrocarbon or the location of the highest soil and groundwater concentration of constituents of concern.

Stabilisation Process in which chemical molecules become chemically bound by a stabilising agent (e.g. clay or humic materials) reducing the mobility of the molecule in groundwater.

Stable Plume Configuration where the solute plume margin is stationary over time and concentrations at points within the plume are relatively uniform over time, or may decrease over time.

Substitution A reaction in which one substituent on a molecule is replaced by another.

Substrate A compound that micro-organisms can use in the chemical reactions catalysed by their enzymes.

Sulphate Reducer A micro-organism that exists in anaerobic environments and reduces sulphate to hydrogen sulphide.

Toxicity The inherent and relative ability of a substance to cause a deleterious effect in an organism.

Volatilisation The transfer of a chemical from the liquid to the gaseous phase (as in evaporation).

APPENDIX 1

PROCESSES INVOLVED IN NATURAL ATTENUATION

APPENDIX 1 - PROCESSES INVOLVED IN NATURAL ATTENUATION

Although commonly used interchangeably with the idea of biodegradation and the remediating effects of microbes, the reduction in contaminant mass, concentration, volume, flux, mobility or toxicity identified as the basis of natural attenuation can occur through a number of processes, and, indeed, can progress effectively without biodegradation (Wiedemeier & Pound, 1998). However, Barker (1998) states that *"While dispersion and sorptive retardation contribute to contaminant attenuation, chemical or biological reaction is usually required to meet the stringent remedial objectives usual for organic contaminants"*.

The processes through which the natural attenuation of contaminants occurs are described in the following sections. The dominant attenuating process will depend on the interaction between the major contaminant, other co-existent contaminants and given site conditions.

A1.1 Dilution, dispersion and diffusion

Dilution, dispersion and diffusion are physical processes which reduce the concentration of a contaminant, but do not affect its mass, toxicity or mobility. The volume of contaminated groundwater actually increases.

Nonetheless, in many instances, dilution within clean groundwater is likely to be the dominant attenuation mechanism where small quantities of contaminant reach an aquifer with a relatively large underflow. Additional dilution may occur where a contaminant plume discharges to a 'clean' surface water body, and, for shallow aquifers in particular, dilution by uncontaminated infiltration away from the source area is also likely to be a significant factor in attenuation.

Mechanical dispersion causes contaminant dilution through the spreading of contaminant molecules beyond strictly advective movement. This occurs as a result of tortuosity at the micro scale, variations in aquifer permeability and pore size, and frictional variations within the pore space. Dispersion has both a longitudinal and transverse component. Dispersion may also be caused through density differences between the contaminant plume and surrounding groundwater. Although not strictly dispersion, spreading of the contaminant plume through seasonal or other variations in groundwater flow direction may be observed in the field when monitoring is carried out at discrete time intervals.

Diffusion is relevant to the natural attenuation of groundwater contaminants in three ways:

- it will occur at the edges of a contaminant plume where the concentration gradient causes movement of contaminant molecules into uncontaminated groundwater; again, another form of dilution. In any environment other than very low permeability media, diffusion in this context is likely to be insignificant as a contaminant movement mechanism;
- diffusion into low permeability material has been shown, through mathematical simulation, to be significantly faster than diffusion out of those same materials (Grathwohl (1998), assuming PCE, TCE and naphthalene), an effect attributed to 'pseudo-hysteresis' which will contribute ultimately to contaminant dilution in groundwater;
- diffusion into low permeability materials can result in an extremely long lasting contaminant source for groundwater in adjacent aquifers. The mathematical simulation described by Grathwohl (1998) shows significant contaminant concentrations persisting 100 years following initial contamination. Similar effects may be expected through fissure/matrix interactions in dual porosity systems.

A more detailed description of dilution, dispersion and diffusion may be found in any standard hydrogeological text, such as Freeze & Cherry (1979).

A1.2 Volatilisation

Chlorinated solvents are volatile organic compounds (VOCs), with the less chlorinated compounds having a tendency towards higher volatility.

Many petroleum hydrocarbons have volatile components, with the shorter chain lengths having a tendency towards higher volatility.

In terms of groundwater contamination, the volatilisation of components to soil gas represents the removal of contaminant mass, although contaminant destruction does not occur (mass is simply transferred from one medium to another). The extent to which volatilisation occurs is dependent on both the physico-chemical characteristics of the contaminant and site specific conditions such as temperature, depth to groundwater, porosity and soil type. Since the area of the groundwater system exposed to soil gas is relatively small, it is unlikely to represent a significant reduction in dissolved contaminant concentration (Wiedemeier, 1995). In fact, volatilisation accounts for a total mass loss of about 5-10% benzene at a typical site (US EPA OUST Internet page on Natural Attenuation).

Volatilisation is important for fresh spills of petroleum products, for older but highly volatile petroleum constituents, for free phase product and for high levels of dissolved constituents of concern. As time passes after a release, this mechanism becomes less important (ASTM, 1998).

In some cases, the transfer of contaminant mass may cause additional risk, for example the build-up of volatile components within enclosed spaces.

A1.3 Retardation

The rate of movement of a contaminant plume may be reduced compared to advective groundwater flow through a number of mechanisms. It is usual to describe this reduction in contaminant velocity using a retardation factor, which is simply the ratio of contaminant velocity to the velocity of a conservative (or unretarded) species.

The primary abiotic retardation mechanism for organic contaminants is sorption, where contaminants become fixed (sorb) to, or diffuse into, the soil matrix. Contaminant mass is removed from the dissolved phase, but the reaction is frequently reversible (albeit extremely slowly in some instances) and does not therefore represent a permanent mass reduction. Like diffusion, slow desorption ultimately results in higher dilution than for the original unsorbed contaminant, but may also result in an extremely long lasting contaminant source which is difficult to remediate using conventional techniques such as pump and treat.

The extent of contaminant sorption to the solid phase can also influence the efficiency of other attenuating mechanisms, such as volatilisation, chemical reaction and biodegradation (ASTM, 1998).

Organic contaminants sorb preferentially to the soil organic fraction or to clay minerals, neither of which tend to be associated with areas of high groundwater flow.

A retardation factor greater than around 1.5 to 3.0 for a BTEX plume suggests that processes other than sorption are acting (ASTM, 1998).

A1.4 Other Abiotic Reactions

Apart from sorption, other non-biologically mediated reactions may act to attenuate organic contaminants in groundwater, converting them to a less mobile, less reactive or less toxic form (stabilisation).

These reactions include hydrolysis (reaction with either a water or a hydroxide ion to produce an alcohol), substitution (reaction with another anion as the nucleophilic agent), elimination (two adjacent groups within the molecule are lost resulting in the formation of a double bond) and oxidation/reduction (redox) reactions involving the transfer of electrons.

However, for petroleum hydrocarbons such as BTEX, the abiotic reactions are not important in the subsurface environment (ASTM, 1998). TCA is the only chlorinated solvent chemically breaking down within 10-20 years, which may be considered a feasible time for remediation programmes (McCarty, 1997). In this process, TCA forms 1,1-DCE (~20%) and acetic acid (~80%), and the reaction is very temperature dependent.

A1.5 Biodegradation

Reduction/oxidation (redox) reactions are the key to the degradation of hydrocarbon contaminants in groundwater. Although thermodynamically favourable, however, most of the reactions involved in the reduction and oxidation of chlorinated aliphatic hydrocarbons do not proceed abiotically (Wiedemeier et al., 1997), and biodegradation is usually the predominant process of natural attenuation at chlorinated solvent sites (RTDF, 1997). For petroleum hydrocarbons, biodegradation is considered to be the primary mechanism by which the solute mass is removed (ASTM, 1998).

'A bacterium's purpose in life is to become bacteria' (RTDF Internet printout, January 1998), and like any other biological entity, micro-organisms obtain the carbon and energy they require for survival, growth and reproduction through the transformation of organic molecules (substrates).

The energy is released during the movement of electron(s) from the organic carbon source (electron donor) through a series of enzyme catalysed oxidation-reduction reactions. In uncontaminated groundwater, naturally occurring organic carbon such as leaf litter residue is utilised as the carbon source, but micro-organisms are equally able to use the organic carbon contained in leaked fuel hydrocarbons, or other organic compounds (such as volatile fatty acids) found in landfill leachate. The less chlorinated solvents, such as DCE, VC, DCM, chloromethane, 1,2-DCA and chloroethane, may also act as a carbon source under aerobic and occasionally under ferric iron reducing conditions (Gossett & Zinder, 1997, Wiedemeier et al., 1997 and Bradley & Chapelle, 1997), although it is generally believed that the highly chlorinated compounds do not (Wiedemeier et al., 1997).

The metabolic intermediates resulting from electron movement are either converted to biomass or are completely oxidised to carbon dioxide and water; hence the organic carbon source itself is degraded.

Organic Carbon Source + Micro-organisms + Nutrients

↓

Enzyme Catalysed Oxidation-Reduction reactions

↓

Energy +Biomass + $\mathbf{CO_2 + H_2O}$

The process requires an ultimate electron sink (terminal electron acceptor) for the transferred electrons.

A1.5.1 Aerobic respiration (contaminant as electron donor)

Typically the electron acceptor is dissolved oxygen, and the process of carbon substrate degradation and reduction of the electron acceptor is known as aerobic respiration.

The following equations are examples of aerobic biodegradation/respiration:

$2C_6H_6 + 15O_2 \Rightarrow 12CO_2 + 6H_2O$ (Benzene)

$Cl_2C_2H_2 + 2O_2 \Rightarrow 2CO_2 + 2H^+ + 2Cl^-$ (DCE)

$ClC_2H_3 + 5/2O_2 \Rightarrow 2CO_2 + H_2O + H^+ + Cl^-$ (VC)

The aerobic metabolism of BTEX has been widely documented, both in the field and in the laboratory (microcosm studies), and it is likely that the micro-organisms capable of aerobic degradation are nearly ubiquitous in subsurface environments (ASTM, 1998). Almost all types of fuel hydrocarbons can be biodegraded under aerobic conditions (Borden et al, quoted Wiedemeier et al., 1995), yet only a few of the chlorinated solvents (the less chlorinated compounds) degrade aerobically (Wiedemeier et al., 1999).

A1.5.2 Anaerobic respiration (contaminant as electron donor)

Once the concentration of dissolved oxygen in the system has become exhausted (or, in practice reduced to below about 0.5 to 1.0 mg/l), other oxidising agents are used as electron acceptors, in a process known as *anaerobic* respiration. The energy released during electron transfer is different for each oxidising agent, and since the more energetic reactions are favoured, the reactions proceed sequentially (in order of decreasing energy) until each electron acceptor is exhausted. In order of preference the electron acceptors typically utilised in anaerobic respiration are nitrate, ferric iron, sulphate or, in extremely reducing conditions, carbon dioxide. Occasionally, other degradation mechanisms such as manganese reduction may dominate if the physical and chemical conditions in groundwater are favourable (Wiedemeier et al., 1995).

The reactions progress according to the following example equations in which benzene is assumed to be the primary substrate:

$6NO_3^- + 6H^+ + C_6H_6 \Rightarrow 6CO_2 + 6H_2O + 3N_2$ Denitrification
$30Fe(OH)_3 + 60H^+ + C_6H_6 \Rightarrow 6CO_2 + 78H_2O + 30Fe^{2+}$ Iron III reduction
$15SO_4^{2-} + 30H^+ + 4C_6H_6 \Rightarrow 24CO_2 + 12H_2O + 15H_2S$ Sulphate reduction
$4C_6H_6 + 24H_2O \Rightarrow$ *intermediate step* $+ 3CO_2 \Rightarrow 15CH_4 + 12CO_2 + 6H_2O$ Methanogenesis

Under the right environmental conditions, chlorinated hydrocarbons can also act as electron acceptors in a process known as reductive dehalogenation, typically occurring under sulphate reduction or methanogenic conditions (see Section A1.5.3).

The anaerobic degradation of TEX has been widely demonstrated, and although there are conflicting reports for benzene (Wiedemeier et al. (1995), quoting several authors) an increasing number of studies are showing that the anaerobic degradation of benzene is possible (ASTM, 1998, with many examples quoted in Wiedemeier et al., 1999). Under nitrate reducing conditions the degradation of TEX has been shown to progress in the following order: toluene, p-xylene, m-xylene, ethylbenzene, and finally o-xylene.

The oxidation of vinyl chloride is the only known example of the oxidation of chlorinated solvents under anaerobic conditions (Wiedemeier et al., 1999).

The *rate* of degradation tends to decrease substantially with the use of energetically less favourable electron acceptors (Prommer et al., September 1998). Oxidation and denitrification produce a great deal of energy, and aerobic biodegradation has consequently been described as the most dominant form of natural attenuation of petroleum hydrocarbons where plumes are being actively destroyed (J T Wilson et al., 1997).

Iron III and manganese IV reduction produce less energy than oxidation and denitrification, sulphate reduction a great deal less again, and methanogenesis releases only a limited amount (J T Wilson et al., 1997). Anaerobic biodegradation may therefore be slower than aerobic degradation by a factor of ten to several hundred (US EPA OUST Internet page on Natural Attenuation)), and contaminant input to groundwater (through, for example, the dissolution of the NAPL source) may well occur at rates which exceed the destruction of hydrocarbon. For this reason, the anaerobic (particularly sulphate reducing and methanogenic) degradation of petroleum hydrocarbons has generally been considered not to occur for practical purposes (e.g. Prommer (September 1998), quoting Thierrin et al.). In contrast to this view, Wiedemeier et al. (1999) state that more recently it has come to be understood that because the pool of anaerobic electron acceptors is far greater than the supply of oxygen within a contaminant plume, anaerobic biodegradation may actually account for a large proportion of the total contaminant mass removal over the life of the plume.

The biodegradation (both aerobic and anaerobic) of organic carbon sources is limited by the availability of electron acceptors. Since in most natural systems there is a large supply of electron acceptors, where the degradation of petroleum hydrocarbon does occur it typically continues until all contaminant is destroyed (Wiedemeier et al., 1997).

Measured differences in the concentration of oxygen, nitrate/nitrite, ferric/ferrous iron, sulphate/sulphide and methane within and upgradient of the contaminant plume are indicators of biodegradation occurring through the mechanisms described above.

A1.5.3 Dehalorespiration, or reductive dehalogenation (contaminant as electron acceptor)

Occasionally and under the correct environmental conditions, the electron acceptor can be a chlorinated solvent, rather than oxygen, nitrate or ferric iron etc. The term dehalorespiration has been used to describe the use of chlorinated solvents by micro-organisms as electron acceptors (Wiedemeier et al., 1999). This involves two electrons. One electron combines with a proton (hydrogen ion) to form a hydrogen atom which replaces a chlorine atom in the solvent, and the second is added to the chlorine atom after removal to form a chloride ion (J T Wilson et al., 1997). Chlorine atoms are removed sequentially from the chlorinated solvent, and since the solvent is reduced through this process it is known specifically as reductive dechlorination (or a little more generally, dehalogenation). The process is illustrated in diagrammatic form on Figures 5 to 7 in the main text. Reductive dehalogenation is the most important process for the natural biodegradation of the more highly chlorinated solvents (Wiedemeier et al., 1997), and may be important for the less chlorinated compounds, depending on environmental factors (Wiedemeier et al., 1999).

Ideally reductive dehalogenation would progress to completion, or to non-toxic products (for example, PCE to TCE to DCE to VC to ethene (and further to CO_2)). However, since during reductive dehalogenation the chlorinated solvent is acting as an electron acceptor, the presence of an indirect electron donor (the carbon source which acts to provide the dissolved hydrogen, the direct electron donor) is essential, and in many aquifers the process tends to be limited by the availability of naturally occurring organic carbon. Attenuation occurs most successfully where a secondary source of organic carbon exists (such as petroleum hydrocarbons or landfill leachate).

The efficiency of reductive dehalogenation appears to differ under methanogenic, sulphate reducing, iron III reducing and nitrate reducing conditions (Chapelle, 1997). Since the chlorinated solvent is competing with other electron acceptors, it seems reasonable to assume that the efficiency with which reductive dehalogenation occurs depends on the amount of energy released compared with other electron accepting processes (in the same way as denitrification is preferred over iron III reduction, for example). Dehalogenation is not a single reaction, but a series of reactions affecting a large number of different compounds, and the efficiency with which dehalogenation takes place may best be understood by treating each reaction separately.

The more oxidised (chlorinated) solvents, such as PCE and TCE are the most susceptible to reductive dehalogenation, and the rate of dehalogenation has been seen to decrease as the degree of chlorination decreases (Wiedemeier et al., 1997, & Stephens et al., 1998). Dehalogenation of the more highly chlorinated compounds therefore appears to release more energy (and is thus more favourable) than dehalogenation of the less chlorinated solvents. This is borne out by the fact that the dehalogenation of PCE and TCE to DCE, or carbon tetrachloride to chloroform and carbon dioxide can occur under mildly reducing conditions such as nitrate or iron III reduction, whereas the transformation of DCE to VC or VC to ethene seems to require the more strongly reducing conditions of methanogenesis (McCarty, 1997, & Chapelle, 1997).

Nevertheless, general statements may be made such as "*reductive dehalogenation is best under sulphate reduction or methanogenic conditions, although it may occur under nitrate and iron III reducing conditions*" (Wiedemeier et al., 1997) and "*it appears that reductive dehalogenation occurs most rapidly, and affects the widest range of chlorinated solvents* [but this does not mean all the chlorinated solvents] *under methanogenic conditions*" (Wiedemeier et al., 1997, Stephens et al., 1998, Lorah & Olsen, 1998).

The *occurrence* and the *rate of occurrence* of dehalogenation are not the same, and the decrease in the rate of dehalogenation as the degree of chlorination decreases has implications for the practicality of dehalogenation in the field. Whilst methanogenic conditions are considered favourable for the reductive dehalogenation of the less chlorinated compounds, the reaction is extremely slow - slower than the rate of oxidation of these compounds under aerobic conditions. In microcosm studies, Lorah & Olsen (1998) showed that while TCE degraded anaerobically, DCE (predominantly cis-DCE) and VC accumulated. Conversely, in aerobic conditions, TCE did not degrade, but the half-lives of DCE and VC were comparable to those of TCE under anaerobic conditions. Consequently it is generally accepted that for practical purposes, aerobic conditions are required for the biodegradation of the less chlorinated compounds. This is discussed in more detail in Section 5.3.2.

Variations in the efficiency of reductive dehalogenation may also be due to different bacterial populations required at each stage and/or competition between bacterial populations (Otten et al. (1998) quoting others). Tonnaer et al., (1998) describe sites in the Netherlands at which it is suggested that two populations of micro-organisms were involved in the reductive dehalogenation of PCE, one degrading PCE to TCE and DCE, and another completing DCE to VC to ethene degradation. The first stage seems to occur in all anaerobic aquifers (bacteria present) but the second step is less easy, and in Holland sulphate reducing conditions are essential. In addition, competitive exclusion can occur between microbial sulphate reducers, methanogens and reductive dechlorinators (Wiedemeier et al., 1997).

It should also be noted here that a number of authors (e.g. Stephens et al., 1998, Lorah & Olsen, 1998, Weigand et al., 1998) state that through reductive dehalogenation the *cis*-1,2-DCE isomer is by far the most prevalent (around 80-90% of the total DCE). Since in synthetic DCE the *trans-* isomer predominates (Weissenborn et al., 1998), an increased proportion of the *cis-* isomer in the field is often an indication of biodegradation of the more highly chlorinated solvents occurring, as opposed to evidence of a DCE spill.

A1.5.4 Fermentation (contaminant as both electron donor and electron acceptor)

In the process of fermentation, the organic contaminant being degraded acts as both an electron donor and as an electron acceptor. During fermentation, micro-organisms catalyse a series of electron transfers which result in the transformation of organic compounds to products such as acetate, water, carbon dioxide and hydrogen. The hydrogen product is extremely important, since it can be used in dehalorespiration. Methanogenesis is perhaps the most obvious fermentation reaction at contaminated sites, and is an important mechanism in the complete degradation of petroleum hydrocarbons (Wiedemeier et al., 1999).

A1.5.5 Co-metabolism

Co-metabolism is the process in which a compound is fortuitously degraded by an enzyme or co-factor produced during the microbial metabolism of another compound. The co-metabolised compound cannot serve as an energy source for the micro-organisms, and the organism receives no known benefit from the degradation of the compound (Wiedemeier et al., 1997).

Since the reductive dehalogenation of chlorinated solvents occurs indirectly as a result of the use of organic carbon by micro-organisms, the process has been described as a form of anaerobic co-metabolism (Stephens et al., 1998). However, Wiedemeier et al. (1999) distinguish between reductive dechlorination as described in Section A1.5.3, and reductive dechlorination through true co-metabolic routes involving enzymes and co-factors, as noted, for example, in Stephens et al. (1998) and RTDF (1997). The co-metabolic process is described as slow and incomplete (Gossett & Zinder, 1997), and very limited under natural conditions (Wiedemeier et al., 1999).

Vinyl chloride has been noted as readily and very efficiently co-metabolised by methane, phenol or toluene oxidisers, with transformation yields of over 1 gram of VC per gram of methane being obtained (McCarty, 1997).

A1.5.6 Nutrients

In addition to an organic carbon source, micro-organisms require hydrogen, sulphur, nitrogen and phosphorous. In soils and aquifer materials contaminated with most organic compounds, carbon and hydrogen are not typically limiting because they are the major components of organic compounds, and sulphur is generally available in sufficient quantities for growth. Thus, the major limiting elements are nitrogen and phosphorous. The carbon/nitrogen/phosphorous ratio usually considered ideal is 300-100:10:1-0.05, although this ratio may vary depending on the nature of the contaminants (Godsey, 1994). Edwards et al. (1998) also note that "*most natural environments are severely nutrient limited and most bacteria exist in a prolonged state of starvation punctuated by occasional periods of nutrient excess*". However, Wiedemeier (1995) states that the rate of biodegradation in the subsurface environment is typically not limited by the supply of these nutrients.

In addition, environmental conditions such as pH and temperature must be correct for each micro-organism involved in the different stages of organic carbon breakdown.

A1.6 Phytoremediation

Phytoremediation, or the remediation of contamination through plant matter is well known in terms of the removal of heavy metals and other contaminants in reedbeds. In addition, plants have been used to accumulate metals from soils, to promote degradation of toxic organic compounds such as munitions compounds, polychlorinated biphenyls, polyaromatic hydrocarbons and pesticides (Strand et al. (1998) quoting a number of references). The paper discusses the removal of fully chlorinated alkanes (such as carbon tetrachloride) and the less chlorinated alkenes (such as TCE) through complete degradation to carbon dioxide and chloride, using hybrid poplar trees. A significant reduction in contaminant mass (95%) in groundwater was measured in pilot studies. In addition, transpiration of the contaminants was less than 5% of the total removal, suggesting that mass transfer alone was not the predominant attenuating process.

Order of magnitude cost savings could be made by using phytoremediation compared to conventional destructive treatment (Strand et al., 1998). However, there are limitations. Where trees are not naturally growing above contaminant plumes, large areas of planting are required to draw water from all depths of contaminated plumes, particularly since trees only take up water from the capillary fringe above the water table (although it could be argued that large areas of tree planting are not an environmental disadvantage, it could be particularly impractical in industrialised or built up areas).

A1.7 Summary

Table A1.1 summarises the feasibility of various biodegradation processes for selected chlorinated solvents:

Table A1.1. Degradation of Common Chlorinated Solvents Under Aerobic and Anaerobic Conditions (RTDF, 1997).

	PCE	TCE	DCE	VC	1,1,1-TCA	CT	TCM	DCM
Aerobic Biodegradation								
Primary substrate	N	N	Y*	Y	N	N	N	Y
Cometabolic degradation (methane or alkanes)	N	Y	Y	Y	Y*	N	Y	Y
Cometabolic degradation (aromatics)	N	Y	Y	Y	N	N	N	N
Cometabolic degradation (ammonia)	N	Y	Y*	Y*	Y	N	Y	Y
Anaerobic Biodegradation								
Primary substrate	N	N	N	Y	N	N	N	Y
Co-metabolic degradation (denitrification)	Y*	Y*	Y*	Y*	N	Y	Y*	Y
Co-metabolic degradation (iron reduction)	Y	Y	Y	Y	Y	Y	Y	Y
Co-metabolic degradation (sulphate reduction)	Y	Y	Y	Y	Y	Y	Y	Y
Co-metabolic degradation (methanogenesis)	Y	Y	Y	Y	Y	Y	Y	Y
Abiotic Transformation	N	N	N	N	Y	Y*	N	N

Y: Occurs, consensus opinion in the literature

Y: May occur, limited evidence or conflicting information*

N: Does not occur, consensus opinion in the literature

But there are less optimistic versions of this available:

Table A1.2. Evidence for Degradation Based on Bench Scale Testing (Leahy, 1998):

	PCE	TCE	1,1-DCE	CE	TCA	CT	TCM	DCM
Simple Anaerobic	N	N	N	-	LIM	Y	-	-
Sulphate Reducing	LIM	N	N	-	LIM	Y	LIM	-
Methanogenic	Y	Y	N	-	Y	Y	LIM	-

Y: Occurs

N: Does not occur

LIM: Limited evidence for degradation was observed, e.g. daughter products

-: Insufficient data available to draw conclusion

Table A1.3. Conditions for Biotic and Abiotic Transformations of Chlorinated Solvents (McCarty, 1998).

	PCE	TCE	TCA	CT
Biotic - Aerobic				
Primary Substrate	N	N	N	N
Co-metabolism	N	Y	Perhaps	N
Biotic - Anaerobic				
Primary Substrate	Y	Y	Perhaps	Perhaps
Co-metabolism	Y	Y	Y	Y
Abiotic	N	N	Y	Perhaps

Y: Occurs

N: Does not occur

The occurrence of the reductive transformation of chlorinated solvents, summarised by McCarty (1997) is shown as Table A1.4.

Table A1.4. Occurrence of the Reductive Transformation of Chlorinated Solvents

	Redox Condition			
	All	*Denitrification*	*SO_4Reduction*	*Methanogenesis*
Carbon tetrachloride		to CF	to CO_2+Cl^-	
1,1,1-Trichloroethane	to 1,1-DCE + CH_3COOH		to 1,1-DCA	to CO_2+Cl^-
Tetrachloroethene			to 1,2-DCE	to ethene
Trichloroethene			to 1,2-DCE	to ethene

APPENDIX 2

AN EXAMPLE OF THE USE OF MNA ALONGSIDE OTHER REMEDIATION METHODS

Natural Attenuation as Remedial Design Treatment Element

by

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Abstract: *A integrated site-wide groundwater remedial approach using natural attenuation as a remedial treatment element was developed for the Caldwell Trucking Company Superfund Site (Site), located in Fairfield, New Jersey. Based on new information and the growing acceptance of natural attenuation, the USEPA approved a modification to the existing remedial design/remedial construction schedule, to allow for the use of natural attenuation to treat the main body of the predominantly chlorinated organics plume (along with source and receptor remedial elements) on a trial basis with hopes of ultimately replacing the ROD selected pump and treatment remedy.*

BACKGROUND

The United States Environmental Protection Agency (USEPA) listed the Site (Figure 1) on the National Priorities List (NPL) in 1983 and finalized the Remedial Investigation and Feasibility Study (RI/FS) in June 1986 (Initial RI/FS). A Record of Decision (ROD) was then issued by USEPA following the Initial RI/FS (1986 ROD) to address remediation of the near source area soils and sludges. A second RI/FS was completed by USEPA in 1989 (Second RI/FS) and a subsequent ROD was issued (1989 ROD). The remedy selected by the 1989 ROD (Remedy II) dealt with groundwater contamination. A "Modified Remedy" was adopted by USEPA in 1993 following several Explanations of Significant Differences (ESDs). Briefly, the Modified Remedy included the following:

- Installation of groundwater recovery wells to intercept contaminated groundwater within the 10,000 parts per billion (ppb) trichloroethylene (TCE) contour; and,
- Remediation of the contaminated Seep Area and tributary to Deepavaal Brook by means of upgradient groundwater pumping and treatment.

The Modified Remedy was to comply with the following applicable or relevant and appropriate requirements (ARARs): New Jersey Surface Water Discharge Regulations should be meet by the treated groundwater, the off-gas from the volatile stripping process will meet the New Jersey Administrative Code 7:27 Air Emission Regulations, and if the Remedial Action (RA) will adversely affect the nearby wetlands, the New Jersey Fresh Water Wetlands Statutes and Regulations will also be complied with. However, the 1989 ROD included a TI waiver of compliance with Federal and State Safe Drinking Water Act MCLs.

Site Setting

Previous investigations conducted at the Site successfully defined the Site geology and hydrogeology. Figure 2 presents a conceptual rendering of the Site hydrogeologic setting, where groundwater flows north-northeast, from upgradient areas of the site towards the Passaic River through mixed glacial sediments and fractured bedrock. Prior to discharge to the major river body, groundwater discharges occasionally to small tributary creeks of the Passaic River, and at a seep area.

The Site geology is primarily unconsolidated deposits overlying bedrock. The overburden unconsolidated deposits thicken with distance northwestward from beneath the Site. Two water-bearing units, separated by an intervening confining unit were defined within the unconsolidated deposits (Zones A and B). Zone A, consists of sands and silty sands, ranging in thickness from less than 4 feet in the east of the Site area to as much as 40 feet in the northwest. Zone B consists of silty sands, sands and gravel, with cobbles and boulders in localized areas. Zone A is separated from the Zone B by a silty clay and clay unit. The clay unit ranges in thickness from zero feet at its edge in the southeast, where it lies on top of the Bedrock Units, to about 20 feet to the northwest of the Site.

The bedrock underlying the overburden units comprises the Second Watchung basalt of the Preakness Formation. The upper part of the basalt flow is vesiculated and heavily fractured. Deeper within the basalt flow, the rock is significantly more intact. In the Site area, groundwater flow through bedrock occurs primarily in fractured and vesiculated portion, designated the Shallow Zone C. The Shallow Zone C is hydraulically quite conductive, and along with Zone B of the Overburden Units, serves as the principal groundwater flow zone for the deeper groundwater flow components.

The primary source of groundwater contamination was two former sewage disposal lagoons, the Central Lagoon and the North Lagoon. These lagoons, in existence since the 1950's, were used as infiltration lagoons for clarified domestic and industrial septic waste. Lesser sources of contamination have been identified adjacent to the Site. The principle dissolved constituent at the Site is TCE, with lesser PCE and 1,1,1 TCA. Contaminated groundwater enters Zone B near the source areas where the clay unit is absent, and flows predominantly through Zone B and then into and through Shallow C Zone. Based on limited pumping test data, groundwater is estimated to travel at rates from 1 to 2 feet per day in the B Zone, and up to 12 feet per day in the C Zone. Overall, the TCE and cis,1,2-DCE plumes (Figures 3A and 3B, respectively) extend, in approximately equal concentrations, some 4000 feet downgradient from the source area towards the flat laying wetland area and the Deepavall Brook. Contaminated groundwater is known to discharge at the "seep area" at similar concentrations to adjacent groundwater monitoring wells.

The current Remedial Design (RD) for the Modified Remedy included an extraction system of four wells pumping at an average flow rate of 180 gallons per minute (gpm). The groundwater was to be treated using equalization, filtration and air stripping. The off-gas from the air stripper was also to be treated prior to discharge to atmosphere. The effluent water for the treatment plant was to be discharged to surface water via dedicated outfall lines. This remedy was design to "contain" the groundwater plume near the source, and in time, return groundwater concentrations in the seep area to background.

FOCUSED FEASIBILITY STUDY

A scope of work was developed that including the re-evaluation of Site groundwater conditions, and the proposed Modified Remedy. The study focused on consideration of the development of a more cost-effective Site-wide groundwater remediation that would meet RAOs and the National Contingency Plan (NCP) criteria. Elements of the re-evaluation included:

- Natural attenuation evaluation; and,
- Source and receptor control measures evaluation.

Natural Attenuation Evaluation

Natural Attenuation was evaluated as part of the Site-wide groundwater remedial approach. Natural attenuation processes, especially biodegradation, are important in the restoration of contaminated soils and groundwater. This is evidenced by the fact that considerable amounts of contaminants introduced into the subsurface over the last century are no longer present, without the benefit of human intervention. The approach to in-situ remediation is the identification of bioremediation mechanisms and demonstrating that an indigenous bacterial population exists under suitable environmental conditions and that degradation has already occurred and is continuing. This can be a preferred remediation because it requires no intervention besides monitoring of the natural progress of biodegradation. In addition to its non-intrusive nature and potential for substantial cost savings, in-situ remediation reduces the possibility of exposure to the contaminants, thereby lowering the risk to potential receptors.

Numerous guidance provide for the investigation and documentation of in-situ remediation, outlining specific protocol for data collection, groundwater modeling, and exposure assessment in support of intrinsic remediation. Additionally, natural attenuation has been demonstrated for a wide variety of contaminants with biodegradation occurring under both aerobic and anaerobic conditions. In-situ bioremediation has been documented for some of the more persistent, co-metabolic compounds such as chlorinated solvents and PCBs. In-situ remediation may be the treatment option chosen for an entire site, or it may be combined with a number of other treatment technologies.

For the Site re-evaluation, historical data was used in conjunction with and a new round of low stress groundwater sampling, conducted to include sampling of natural attenuation parameters, VOCs and SVOCs (Eckenfelder, 1996). These data were used to establish spatial goechemical trends, provide time series information on the concentration trends, and used in modeling studies to provide rates of natural attenuation.

Results of natural attenuation parameter sampling indicated:

- A zone of reducing conditions immediately downgradient of the source area was defined by Eh conditions ranging between –250 millivolts to +100 millivolts;
- Elevated alkalinity in near source areas four times concentrations reported in distal downgradient areas;
- Decreased dissolved oxygen (DO) concentrations in the reducing area and the subsequent "rebound" of DO concentrations in the downgradient wetlands areas near the seep area;
- Presence of ferrous iron ranging from 0.3 mg/l to 5.1 mg/l in area of reducing conditions; and,
- Elevated carbon dioxide and decreased pH in the area of reducing conditions as compared to more downgradient samples.

Results of VOC sampling indicated:

- Total VOC and TCE concentrations were improving or steady-state with respect to time as evidence by 26 of 29 monitoring wells showing decreasing concentration trends or steady concentration trends as defined by having a change less that 10 percent from the earliest historical data; and,
- A complete degradation series from TCE to cis-1,2-DCE to vinyl chloride and ethene was present along the groundwater flow pathways that lead from the Central and North Lagoon areas.

As shown on Figure 4, the spatial patterns of iron reducing conditions and the presence of vinyl chloride, and the occurrence of ethene at the most downgradient edge of the reducing zone indicated that a robust natural attenuation system was currently operating at the site. In order to quantify the rate of degradation, one-dimensional (1-D) fate and transport modeling was conducted along the centerline of the Central Lagoon plume using the 1-D, advection-dispersion equation with both sorption and 1st-order decay terms. The model was calibrated to 1996 groundwater conditions using a best-estimated source concentration and site specific retardation coefficients for TCE and cis-1,2-DCE.

Overall, results of the natural attenuation evaluation indicated a vibrant biodegradation (fed by organic substrate and bacteria from past sewage disposal practices) that was degrading approximately 40 percent of the estimated 3,000 kg/yr of TCE "entering" the groundwater system.

Source and Receptor Controls

Source control measures (conducted by others) have recently been implemented at the Central and North Lagoon areas, including Soil Vapor Extraction (SVE) and soil stabilization. Of critical importance was the new information provided by the SVE system which indicated that during the first 5 months of operation, the SVE system had removed approximately 5000 lbs of TCE and over 8000 lbs of total VOCs. Ultimately, the total VOC removal from the lagoon areas was about 20,000 lbs. Following SVE, soil stabilization was performed in a cell-wise fashion during which 50 foot square areas were excavated, mixed with cement to an approximate 8 percent by weight mixture, and then replaced in the same cell. The importance of these measures was to both decrease the total source mass potentially available to the environment, and to secure the source from further contributing to the groundwater plume system.

Protecting downgradient receptors at a groundwater to surface water discharge (seep) required looking into technologies to treat groundwater at the localized seep area within the larger groundwater plume. In general, reactive walls containing metallic iron have been shown successful in degrading chlorinated organic compounds in groundwater. This method of treatment developed from research initiated at the Institute for Groundwater Research, University of Waterloo, involves placing granular iron in in-situ permeable zones across the path of groundwater contaminated with VOCs. As the contaminated groundwater flows through the reactive permeable zone, the chlorinated solvents react with the granular iron and are reduced to nonchlorinated species. This technology was found to be applicable for the conditions encountered at the Site. Golder Sierra LLP was eventually commissioned to place a vertical reactive wall in the B Zone using oriented vertical fracturing technology just upgradient of the seep.

Alternative Plan

After the Site re-evaluation, an "Alternative Remedy" to the pump and treatment Modified Remedy was proposed to the USEPA and the NJDEP. This remedy consisted of:

- Natural attenuation of the main body of the plume in that area between the source control and the receptor (seep area) control remedies;
- A sub-surface vertical reaction iron wall to treat groundwater prior to its discharge at the seep; and,
- Continued source control measures.

This remedy was compared against the Modified Remedy using the NCP Criteria and Site-specific RAOs. Comparisons showed that the Alternative Plan was as protective of human health and the environment. The Alternative Remedy was equivalent to the Modified Remedy in compliance with ARARs, was more reliable, implementable with less disruption to the surrounding community, and could be constructed and operated at considerably less cost. The Alternative Remedy eliminates direct risk at the seep and compared to the Modified Remedy, removes contaminant mass in groundwater more quickly and in greater mass than the pump and treatment system.

ACKOWLEDGMENTS:

The author wishes to thank the USEPA Project Manager for the Site, Mr. Richard J. Robinson, for his support of the Alternative Remedy. Additional thanks go to the NJDEP, and Ms. Carole Peterson (Chief, New Jersey Remediation Branch, USEPA) for the opportunity to delay construction of the Modified Remedy such that the Alternative Remedy could be implemented on a trial basis. Finally, thanks go to Mr. John E. Vidumski of DuPont Specialty Chemicals for his enthusiasm and direction in moving forward with the use of innovative technologies for site remediation.

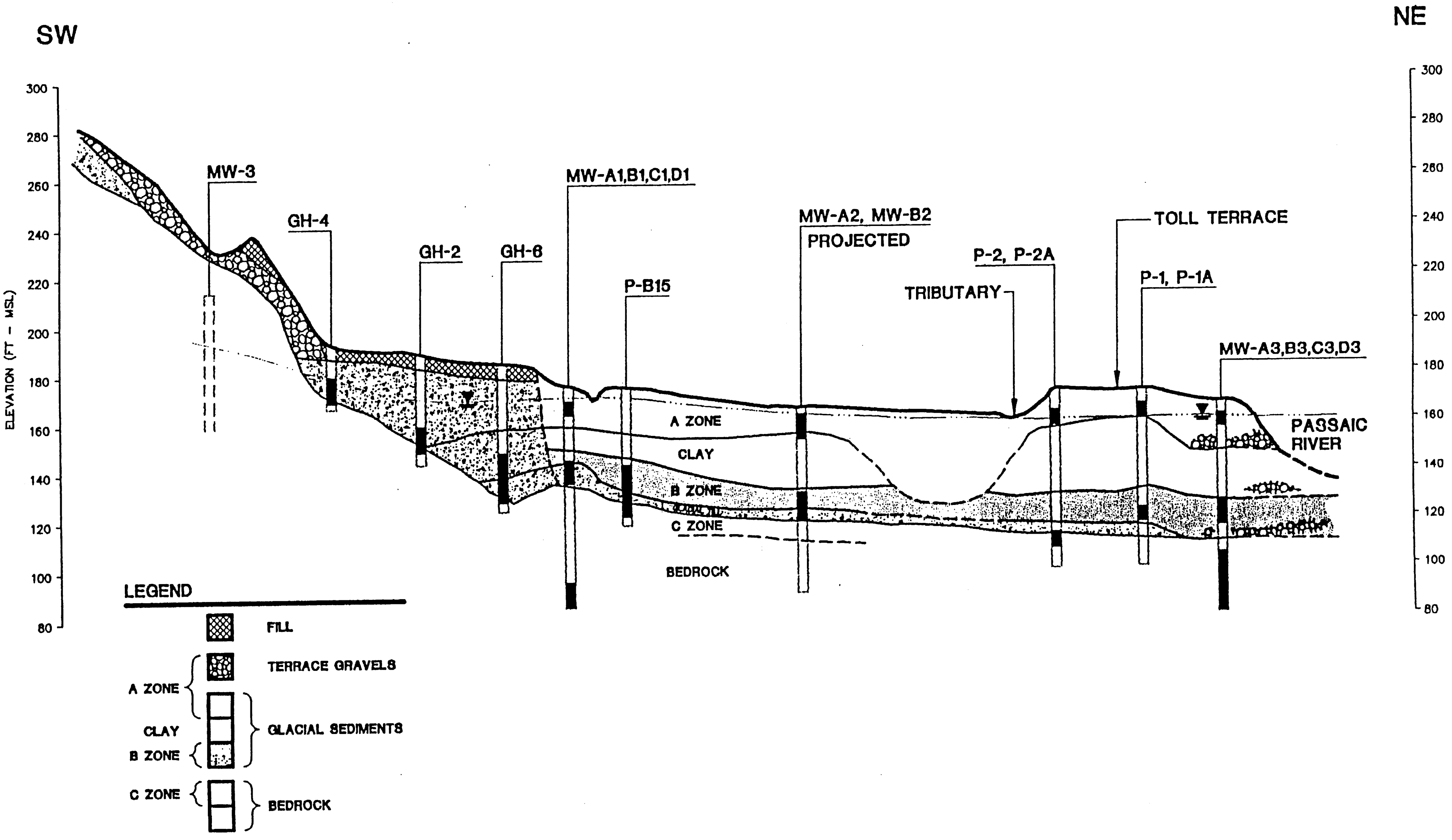


FIGURE 2 - Geologic Cross Section

NOT TO SCALE

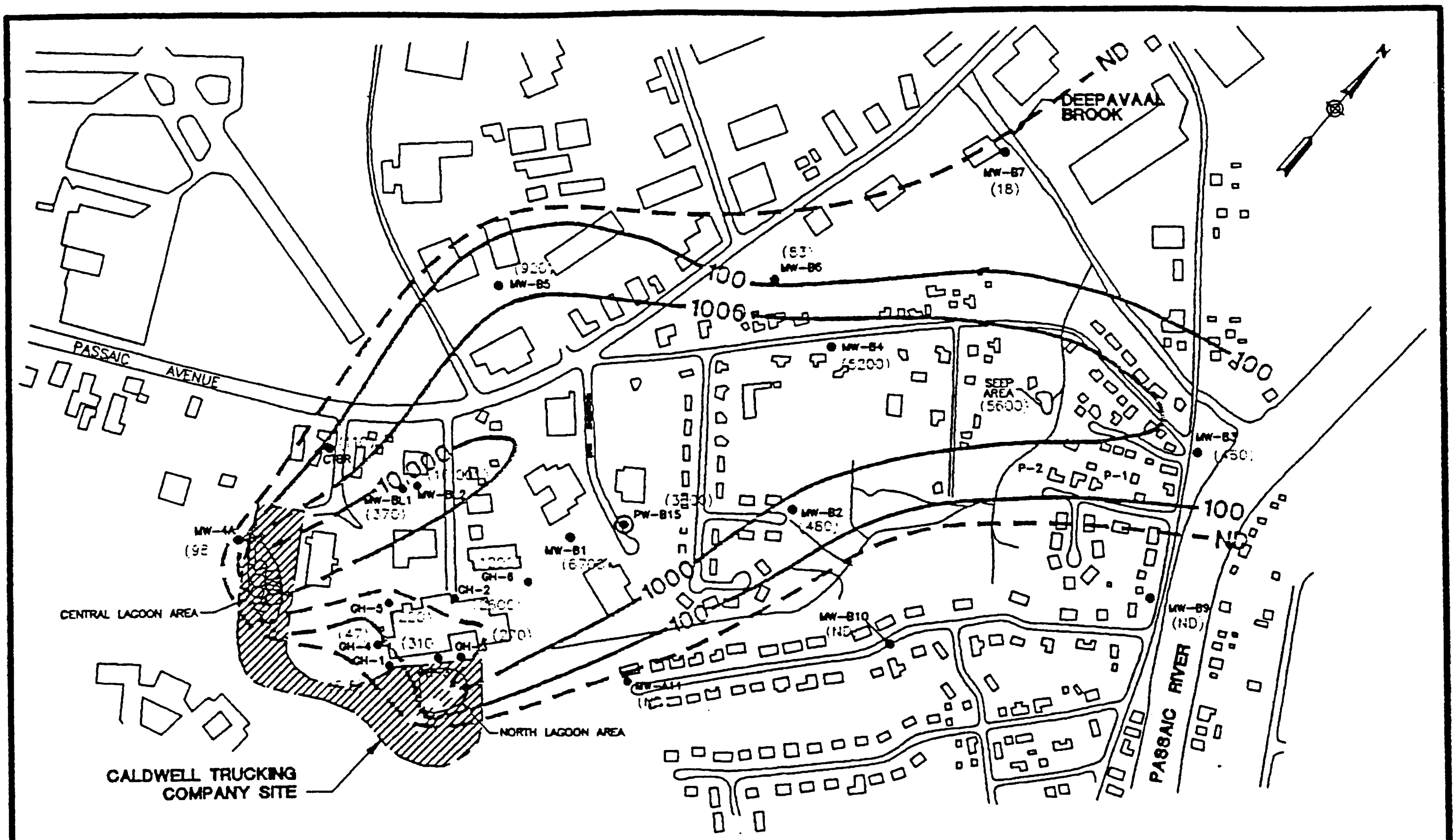


FIGURE 3A - Zone B Trichloroethene (TCE) ug/l October-November 1996

NOT TO SCALE

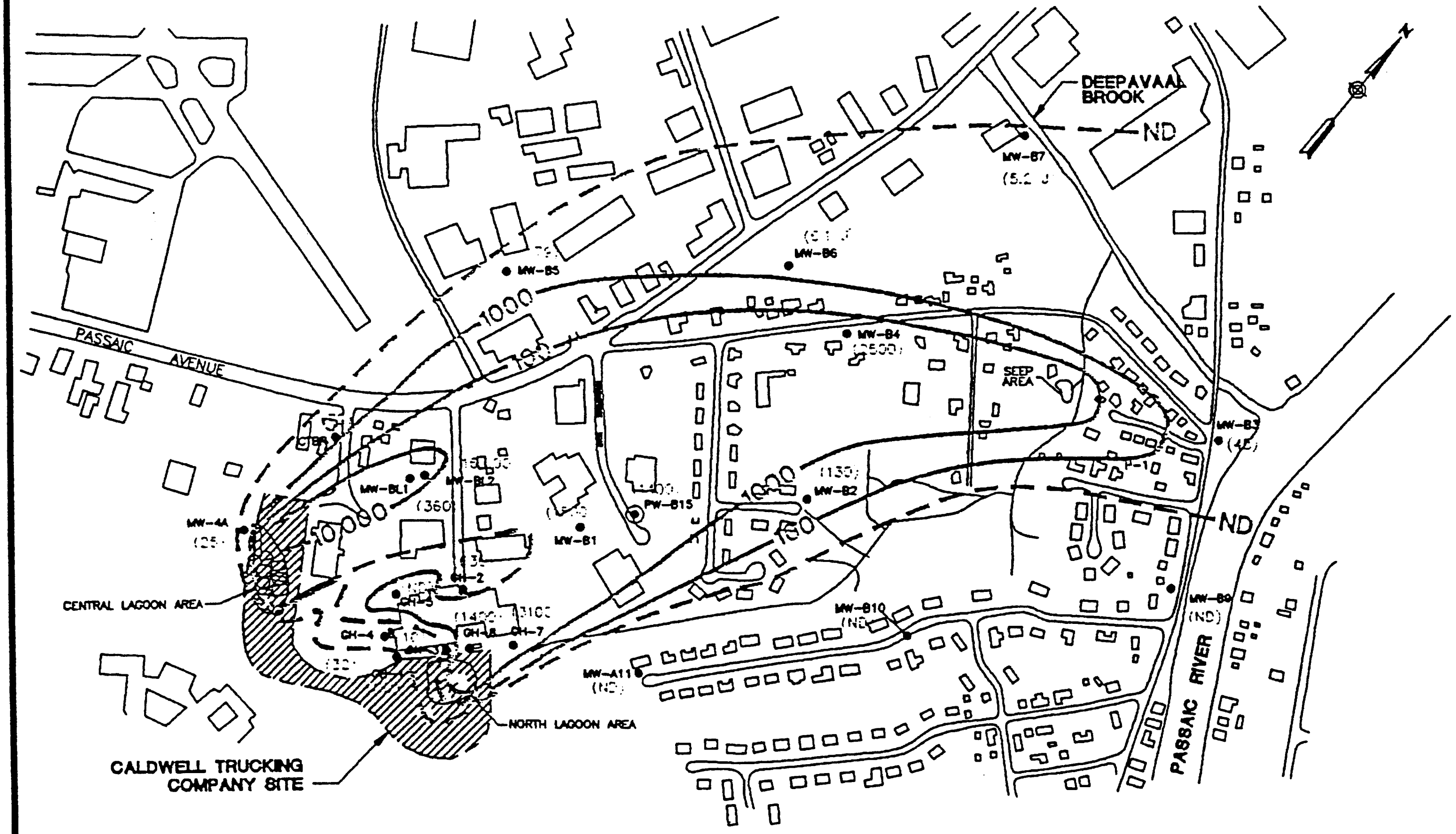


FIGURE 3B - Zone B cis-1,2-DCE ug/l October-November 1996

NOT TO SCALE

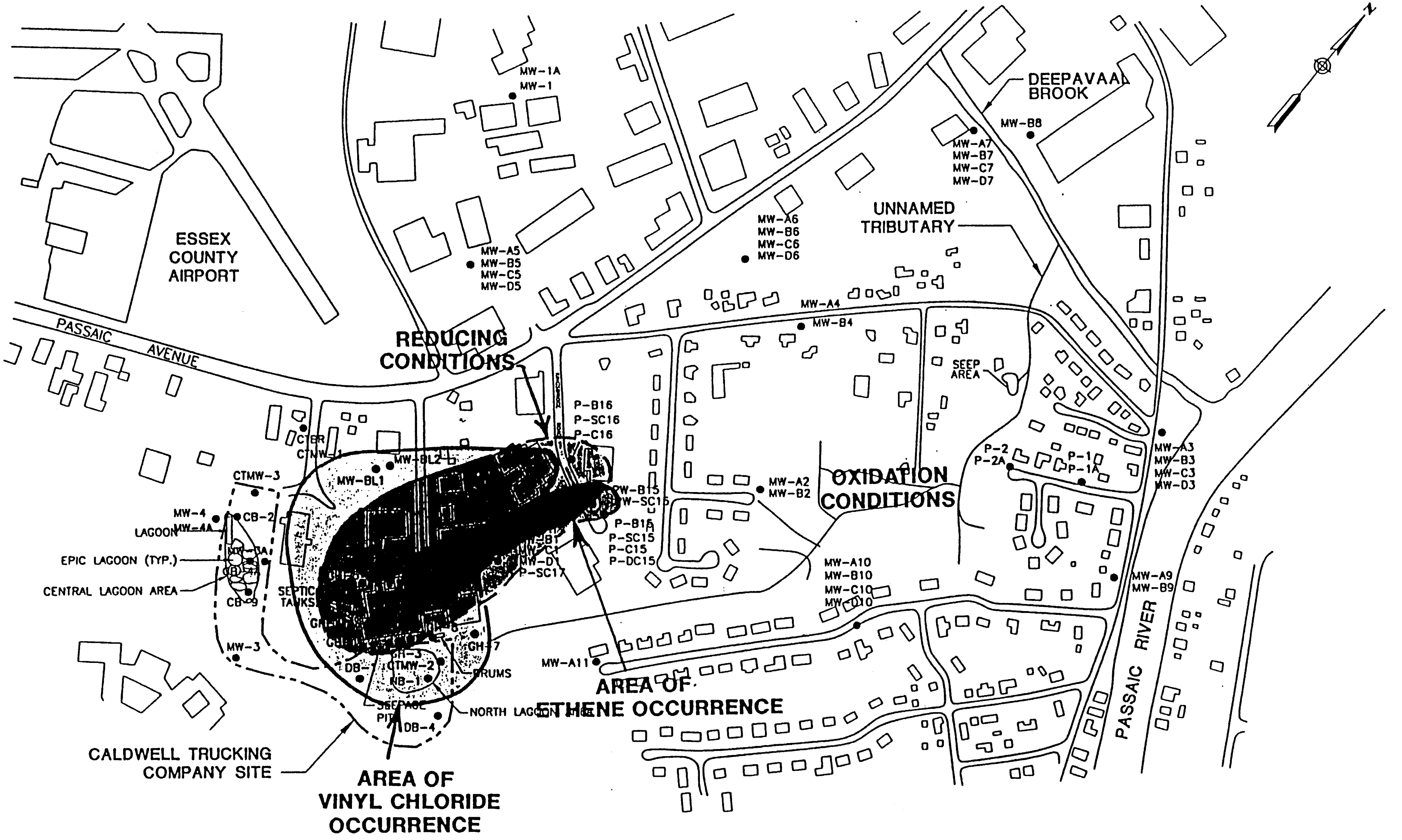


FIGURE 4

Reductive Zone and Area of Vinyl Chloride and Ethene Occurance

NOT TO SCALE

APPENDIX 3

SOFTWARE AVAILABLE FOR THE ASSESSMENT OF NATURAL ATTENUATION

APPENDIX 3 - SOFTWARE AVAILABLE FOR THE ASSESSMENT OF NATURAL ATTENUATION

A3.1 General

A key element in the use of MNA as a remedial option for groundwater is the reliable prediction of the fate and concentration of contaminants within the plume with time. This may be achieved through the use of analytical equations, probably in spreadsheet form, or through commercially available numerical and analytical models.

Four different types of models have been developed:

- Saturated flow models describe where and how fast the water and dissolved contaminants flow through the saturated zone;
- Multiphase flow models characterise the situation in which two or more fluids, such as water and non-aqueous phase contaminant or water and air exist together in the subsurface;
- Geochemical models analyse how a contaminant's chemical speciation is controlled by the thermodynamics of the many chemical and physical reactions that may occur in the subsurface;
- Biological reaction rate models represent how quickly the micro-organisms transform contaminants.

Because so many complex processes interact in the subsurface, ultimately, two or more types of model may be required for a complete evaluation.

(Committee on In Situ Bioremediation, 1993).

The aim of all contaminant modelling within a MNA strategy should be primarily to:

- predict the future extent and concentration of the dissolved plume by simulating the combined effects of advection, dispersion, sorption and biodegradation;
- to assess the potential for downgradient receptors to be exposed to contaminant concentrations in excess of regulatory or risk based levels intended to be protective of human health and the environment;

- to provide technical support for the MNA remedial option at post modelling regulatory negotiations to help design a more accurate verification and monitoring strategy and to help identify early source removal strategies.

(Wiedemeier et al., 1997)

Two issues should always be critically examined when considering the use of models or when relying upon their results. Firstly, has the model undergone sufficient validation to be used with confidence, and secondly, what are the limitations of the model package (CIRIA, 1999). Inevitably, models make assumptions and simplifications regarding the natural environment, and it is up to the model user to determine that these assumptions are valid for use at the site in question. In some instances the complexities of the hydrogeological regime may preclude the use of modelling to the extent that accurate predictions become virtually impossible. In such circumstances, reliance on MNA may be inadvisable.

The following is a list of examples of software that may assist in the prediction of contaminant plume movement or the documentation of the effectiveness of MNA. The list is not intended to be exhaustive (simply a list of software that we have come across during the literature searches), and in the production of this report we have not conducted a critical review of the software. Nevertheless, the majority of the listed software has been designed with contaminant plume analysis in mind (and in some cases specifically with the assessment of MNA/bioremediation). Most are free over the Internet, and there are more listed by Wiedemeier (1997 and 1999).

A3.2 BIO3D

According to Schirmer et al. (1998) BIO3D has been developed at the University of Waterloo in Canada as a three dimensional numerical transport model which includes modified Monod kinetics to allow for changing contaminant degradation rates under electron acceptor limiting conditions, substrate toxicity effects (Haldane inhibition) and microbial growth.

A3.3 Biochlor

Based on BioScreen, BioChlor simulates the natural attenuation of chlorinated solvents, and is available free over the Internet through www.gsi-net.com.

A3.4 BIOPLUME II & III

BIOPLUME II is described by Wiedemeier (1997) as "*a two dimensional model for simulating transport of a single dissolved hydrocarbon species under the influence of oxygen-limited biodegradation, first order decay, linear sorption, advection and dispersion. Aquifer may be heterogeneous and anisotropic. Based on the USGS two dimensional MOC model (including a finite difference flow model) by Konikow & Bredehoeft (1978). Oxygen limited biodegradation is a reactive transport process. A public domain code with a menu driven pre-processor and limited post processing abilities*".

BIOPLUME III is the successor to BIOPLUME II, and apart from general improvements, can handle multiple contaminants.

A3.5 BioRedox

BioRedox is based on MT3D, and is described by Richard Murphy of Conestoga-Rovers & Associates who developed the software along with Grant Carey (Environmental Software Solutions) and Paul Van Geel of Carleton University as "*a three dimensional, multispecies reactive transport model that provides an unprecedented level of flexibility for predicting the natural attenuation of petroleum hydrocarbons and chlorinated solvents. BioRedox provides unique capabilities for simulating the sequential transformations of chlorinated solvents as well as the redox-dependent oxidation, methanotrophic co-metabolism and/or reductive dehalogenation of organic pollutants. BioRedox also provides convenient utilities such as a solute properties database, a redox reactions database and innovative visualisation capabilities*" (Internet, http://gwrp.cciw.ca/internet/gwm-archive/1998/msg00107.html).

BioRedox is available free over the Internet, and can be downloaded from http://www.rovers.com/natural_attenuation.htm. An example of a site at which BioRedox has been used to evaluate the natural attenuation of BTEX and chlorinated ethenes is given in Carey et al., 1998a.

A3.6 BIOSCREEN

In the User's Manual (Newell et al., 1998), BIOSCREEN is described as "*an easy to use screening model which simulates remediation through natural attenuation of dissolved hydrocarbons at petroleum fuel release sites. The software, programmed in the Microsoft*

Excel spreadsheet environment and based on the Domenico analytical solute transport model, has the ability to simulate advection, dispersion, adsorption and aerobic decay, as well as anaerobic reactions that have been shown to be the dominant biodegradation processes at many petroleum release sites. BIOSCREEN includes three different model types:

- *solute transport without decay;*
- *solute transport with biodegradation modelled as a first order decay process (simple, lumped-parameter approach);*
- *solute transport with biodegradation modelled as an instantaneous biodegradation reaction (approach used by BIOPLUME models).*

The model is designed to simulate biodegradation by both aerobic and anaerobic reactions. It was developed for the [US] Air Force Centre for Environmental Excellence (AFCEE)".

A3.7 BioTrans

The following is abstracted from the BioTrans Internet page: "*BioTrans is a two-dimensional (vertically averaged) finite element code which models areal transport of multiple dissolved contaminants and oxygen in groundwater due to convection and hydrodynamic dispersion. Adsorption of contaminants is considered and decay may be modelled as a first-order reaction, or as an oxygen-limited process. Transport takes place in the mobile fraction of the pore space with rate-limited mass transfer between mobile and immobile pore space (e.g., fractures and soil matrix, respectively). Mass loading rates to groundwater may be specified by the user or computed internally due to dissolution from a NAPL. Mass may be removed from the groundwater through pumping and by losses through outflow boundaries.*

BioTrans' simulation functionality is comparable with that of BIOPLUME II. It handles biodegradation as a first-order decay process, or as an oxygen-limited process in the same way as BIOPLUME II. However, it can handle more chemical components simultaneously (5 chemical species and oxygen), supports irregular meshes, includes volatilisation loss from NAPL, supports immobile-mobile region mass transfer, and offers soil and fluid property estimators. BioTrans is based on well-established theoretical approaches, and has been subject to limited verification".

More information about BioTrans and how to obtain it can be obtained from their web page:

http://www.mines.colorado.edu/research/igwmc/software/igwmcsoft/biotrans.htm

A3.8 ConSim

ConSim is designed to provide those concerned with the management of land contamination with a means of assessing the risk that is posed to groundwater by leaching contaminants.

The software models contaminant mobilisation and transport, and is intended to use commonly available site investigation data. The probabilistic methodology allows full incorporation of data uncertainty such that the assessment may be rational and consistent.

ConSim includes an assessment of contaminant attenuation through first order biodegradation/radioactive decay and/or retardation (linear sorption) in both the unsaturated zone and aquifer, and through aquifer dilution. Contaminant transport within the aquifer is examined using a modified form of the Domenico analytical equation, such that contaminant impact may be examined at a receptor both directly downgradient of the contaminant source and laterally offset.

ConSim is designed primarily as a conservative risk assessment tool, and has not been designed to model the detailed physical, chemical and biological processes that influence contaminant mobilisation, migration, retardation and attenuation. It has been produced by Golder Associates (UK) Ltd in association with the Environment Agency and is available on a commercial basis.

A3.9 FATE5

In the abstract to their paper, Nevin et al. (1997) describe FATE5 as "*a new groundwater modelling tool developed to assist users with determining site-specific natural attenuation rates for organic constituents dissolved in groundwater. FATE5 is based on and represents an enhancement to the Domenico analytical groundwater transport model (Domenico, 1987). These enhancements include use of an optimisation routine to match results from the Domenico model to actual measured site concentrations, and extensive database of chemical property data, and calculation of an estimate of the length of time needed for a plume to reach steady state conditions. FATE5 was developed in Microsoft Excel and is controlled by means of a simple user-friendly graphical interface.*

Using the Solver routine built into Excel, FATE5 is able to calibrate the attenuation rate used by the Domenico model to match site-specific data. By calibrating the decay rate to site-specific measurements, FATE5 can yield accurate predictions of long term natural attenuation processes within a groundwater plume. In addition, FATE5 includes a formulation of the transient Domenico solution used to help the user determine if the steady state assumptions employed by the model are appropriate. The calibrated groundwater flow model can then be used either to i) predict upper-bound constituent concentrations in groundwater, based on an observed source zone concentration, or ii) back-calculate a lower-bound SSTL [site specific target level] value, based on user-specific exposure point concentration at the groundwater point of exposure".

A3.10 NADSS (Natural Attenuation Decision Support Software)

On their Internet page (http://kemb.uwrl.usu.edu/api/intro.html) Natural Attenuation Decision Support System (NADSS) is described as "*an application software designed to help the user explore the application of natural attenuation at a given UST [underground storage tank] site by aiding the user through a series of logical steps that lead from the initial site assessment phase through data collection and reduction/interpretation phases of a project. NADSS can also be applied in training scenario to generate a quantitative description of intrinsic remediation processes*".

A3.11 PHTRAN

Examples of the use of PHTRAN, a 2D reactive multicomponent model, are described in Prommer et al. (July, 1998).

A3.12 RT3D

The following is an extract from the RT3D web page (http://bioprocess.pnl.gov/rt3d.htm):

"*RT3D is a Fortran 90-based software package for simulating three-dimensional, multi-species, reactive transport in groundwater. The code is based on the 1997 version of MT3D (DOD_1.5), but has several extended reaction capabilities. RT3D can accommodate multiple sorbed and aqueous phase species with any reaction framework that the user wishes to define.*

RT3D is Widely Applicable. With a variety of pre-programmed reaction packages and the flexibility to insert user-specific kinetics, RT3D can simulate a multitude of scenarios. For example, natural attenuation processes can be evaluated or an active remediation can be simulated. Simulations could potentially be applied to scenarios involving contaminants such as heavy metals, explosives, petroleum hydrocarbons, and/or chlorinated solvents.

RT3D is highly flexible. The users can enter their own reaction kinetic expressions or choose from a suite of 8 pre-programmed reaction packages. Pre-programmed packages include:

- *Two Species Instantaneous Reaction (Hydrocarbon & Oxygen);*
- *Instantaneous Hydrocarbon Biodegradation Using Multiple Electron Acceptors* (O_2, NO_3^-, Fe^{2+}, SO_4^{2-}, CH_4)*;*
- *Kinetically Limited Hydrocarbon Biodegradation Using Multiple Electron Acceptors* (O_2, NO_3^-, Fe^{2+}, SO_4^{2-}, CH_4)*;*
- *Kinetically Limited Reaction with Bacterial Transport (Hydrocarbon, Oxygen, & Bacteria);*
- *Non-Equilibrium Sorption/Desorption;*
- *Non-Aqueous Phase Liquid Dissolution Model;*
- *Dual Porosity Model;*
- *Reductive, Anaerobic Biodegradation of PCE/TCE/DCE/VC;*
- *Anaerobic and Aerobic Biodegradation of PCE/TCE/DCE/VC*".

A3.13 SEQUENCE

SEQUENCE is described on the Conestoga-Rovers Association web page (http://www.rovers.com/) as follows:

SEQUENCE (U.S. Patent Pending) is a unique tool that simplifies the analysis and presentation of natural attenuation data. SEQUENCE is based on an innovative approach for visualizing natural attenuation trends for organic chemicals and geochemical indicators, using a modified radial diagram method. Given the simplicity and effectiveness of this visualization approach, SEQUENCE visual aids are well-suited for presentations to technical audiences and to the general public.

SEQUENCE V1.1 was developed by Grant Carey in association with CRA. This version is being released free to the public domain because we believe that the SEQUENCE visualization approach will become an essential tool for evaluating natural attenuation. We are also *developing a Professional version of* SEQUENCE *(V2.0) in conjunctions with Waterloo Hydrogeologic, Inc. with added features that assist in the management of data and preparation of natural attenuation maps.*

SEQUENCE *visual aids may be used to simultaneously show spatial and temporal trends for multiple organic pollutants on one site map. For some sites, this one radial diagram map may provide the primary line of evidence necessary to support natural attenuation as a site remedy. The distinct functionality incorporated into* SEQUENCE *also allows for the preparation of* SEQUENCE *-Redox maps, which may be used to identify trends in geochemical indicators (electron acceptors and metabolic by-products), providing a valuable secondary line of evidence for supporting the occurrence of biodegradation processes.*

SEQUENCE *may also be used for other applications, such as the preparation of visual aids for regular monitoring programs. For example,* SEQUENCE *-Redox maps are well-suited for documenting the geochemical data collected for regular landfill monitoring programs.*

SEQUENCE V1.1 is available free over the Internet, and can be downloaded from http://www.rovers.com/. Version 2.1 is available commercially. Examples of sites at which SEQUENCE has been used to evaluate the natural attenuation of BTEX and chlorinated ethenes are given on the web page and in Harris et al., (1998) and Carey et al., (1998a).

APPENDIX 4

RELATED WEB PAGES

APPENDIX 4 - RELATED WEB PAGES

US EPA Pages:

Homepage
http://www.epa.gov/

Office of Research & Development (ORD), Bioremediation Action Committee. Information on passive and active bioremediation, and recent EPA bioremediation publications.
http://www.epa.gov/ORD/WebPubs/biorem/

Office of Underground Storage Tanks (OUST) information on natural attenuation.
http://www.epa.gov/OUST/cat/natatt.htm
http://www.epa.gov/swerust1/cat/natatt.htm

Office of Underground Storage Tanks (OUST) Homepage, with links to Office of Solid Waste and Emergency Response (OSWER) Policy Directives
http://www.epa.gov/swerust1/directiv/index.htm

NRMRL/SPRD Homepage. Office of Research & Development (ORD) R S Kerr Environmental Research Laboratory (also BIOSCREEN & BIOPLUME III, and links to other useful pages).
http://www.epa.gov/ada/kerrlab.html

Federal Facilities Restoration & Reuse Office (FFRRO), fact sheet on natural attenuation of chlorinated solvents.
http://www.epa.gov/swerffrr/chlorine.htm

Federal Facilities Restoration & Reuse Office (FFRRO), fact sheet on natural attenuation of petroleum hydrocarbons
http://www.epa.gov/swerffrr/petrol.htm

Proceedings of the Dallas Conference on the natural attenuation of Chlorinated Solvents
http://www.epa.gov:80/ordntrnt/ORD/WebPubs/biorem/naturgw.pdf

US EPA Region 4 "Suggested Practices for the Evaluation of a Site for Natural Attenuation (Biological degradation) of Chlorinated Solvents".
http://www.epa.gov:80/region04/wastepgs/oftecser/protoexp.pdf

Other web pages with information on natural attenuation:

Network on Natural Attenuation in Groundwater and Soil (NNAGS)
http://www.shef.ac.uk/~nnags/

Remediation Technologies Development Forum (RTDF) Homepage, including names and contact details for individuals involved in MNA research & practice.
http://www.rtdf.org/
http://www.dep.state.pa.us/dep/deputate/airwaste/wm/remserv/biotreat/Tech_Ref.htm

Groundwater Remediation & Technologies Analysis Center
http://www.gwrtac.org/

Technology Innovation Office. Clean up information
http://clu-in.com

NICOLE (Network on Contaminated Land in Europe)
http://www.nicole.org/

NOBIS, Netherlands research programme on in situ bioremediation
http://www.bouwweb.nl/CUR/NOBIS/

Federal Remediation Technologies Roundtable
http://www.frtr.gov/

Monitored Natural Attenuation Toolbox
http://www.sandia.gov/eesector/gs/gc/na/mnahome.html

Bioremediation Resources on the Internet
http://gw2.cciw.ca/internet/bioremediation/

CSIRO, Perth, Australia
http://www.clw.csiro.au/research/groundwater/remediation/
http://www.clw.csiro.au/CGS/conferences/

Setting limits on natural attenuation
http://www.sgcleanup.com/bio/limits.htm

SEQUENCE and BioRedox
http://www.rovers.com/
http://gwrp.cciw.ca/internet/gwm-archive/1998/msg00107.html

BioTrans
http://www.mines.colorado.edu/research/igwmc/software/igwmcsoft/biotrans.htm

Natural Attenuation Decision Support System (NADSS)
http://kemb.uwrl.usu.edu/api/intro.html

RT3D
http://bioprocess.pnl.gov/rt3d.htm

APPENDIX 5

DEGRADATION RATE CONSTANTS

APPENDIX 5 - DEGRADATION RATE CONSTANTS

The rate at which a petroleum hydrocarbon or chlorinated solvent is degraded in groundwater is dependent on site specific factors such as redox conditions and the availability of nutrients, electron donors or electron acceptors. It is therefore extremely difficult to generalise and to quote 'typical' values of rate constants or half-lives.

Having said that, for sites where no degradation of contaminant has been measured (perhaps for a new spill or leak, or in an initial screening exercise), potential degradation rates may be predicted using values measured at other sites exhibiting similar conditions. Wilson (1998) quotes a series of ranges of degradation rates for common chlorinated solvents, and these are duplicated as Figure A5.1. Wilson also points to a further reference for additional field and laboratory data.

Degradation rates may be calculated from site data using the method described by Buscheck & Alcantar (1995).

The following should also be noted: *"The apparent kinetic degradation rates at the field scale are often smaller when compared to laboratory derived kinetics. The cause of this apparent discrepancy lies primarily in the transport characteristics and heterogeneities at the field scale which are not commonly observed in the laboratory....Nutrients, supplied in excess in the laboratory, are often limiting in the field*". (Schirmer et al., September 1998).

In addition to the above, the following is a brief selection of the many references which quote degradation rates or contaminant half-lives. It is recommended that the full references be consulted to ensure that site conditions do not differ significantly from those in the published studies.

Barker, J F (1998). "Fate of Organic Contaminants in Groundwater: Natural and Enhanced Attenuation". In Groundwater Quality: Remediation and Protection (proc. GQ98, Tubingen, Germany, September 1998. IAHS Publication 250). *(Field, MTBE).*

Bourquin, A W, J V Accashian, J M Mosher and D D Lakin (1998). "Natural Attenuation of Chlorinated Solvent-Contaminated Groundwater". In *Natural Attenuation Chlorinated and Recalcitrant Compounds*, (proc. The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 1998). pp281-286. *(Field, TCE, DCE and VC. Also quotes further references).*

Howard, P H (1985). “Determining 'Real World' Biodegradation Rates”. Environ. Toxic Chem. 4: 129-130.

Howard, P H and A E Hueber (1987). “Biodegradation Data Evaluation for Structure/Biodegradability Relations”. Environ. Toxicol. Chem. 6: 1-10.

Howard, P H, A E Hueber and R S Boethling (1987). “Biodegradation Data Evaluation for Structure/Biodegradability Relations”. Environ. Toxicicol. Chem. 6: 1-10.

Howard, P H, R S Boethling, W M Stiteler, W M Meylan, A E Hueber, J A Beauman and M E Larosche (1992). “Predictive Model for Aerobic Biodegradability Developed from a File of Evaluated Biodegradation Data”. Environ. Toxicol. Chem. 11: 593-603.

Howard, P H, R S Boethling, W F Jarvis, W M Meylan and E M Michalenko (1991). “Handbook of Environmental Degradation Rates”. Lewis Publishers, Ann Arbor, MI.

Lorah, M M and L D Olsen (1998). “Anaerobic and Aerobic Biodegradation of Chlorinated Solvents in a Freshwater Wetland”. In *Natural Attenuation Chlorinated and Recalcitrant Compounds*, (proc. The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 1998). pp27-32.

McCarty, P L (1997). “Biotic and Abiotic Transformations of Chlorinated Solvents in Ground Water”. In Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water, USEPA ORD Document EPA/540/R-97/504, May 1997. pp7-11. *(Abiotic TCA degradation rates).*

McQuillan, D M, B H Faris and B H Swanson (1998). "Intrinsic CoMetabolism of Carbon Tetrachloride with Gasoline: Regulatory Site Closure". In *Natural Attenuation Chlorinated and Recalcitrant Compounds*, (proc. The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 1998) pp 263-268. *(Field, Tetrachloromethane).*

Schilling, K E, J K Sheldon and M D Basel (1998). "Field Evidence For Intrinsic Bioremediation of Trichloroethene in a Carbonate Aquifer". In *Natural Attenuation Chlorinated and Recalcitrant Compounds*, (proc. The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 1998). pp243-248. *(Field, TCE, DCE and VC).*

Weigand, M A, G Gaillot, S Tituskin, J Zhang, K Ramanand and D Graves (1998). "Natural Attenuation of PCE and TCE: A Case Study". In *Natural Attenuation Chlorinated and Recalcitrant Compounds*, (proc. The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 1998). pp287-291. *(Field, TCE).*

Wilson, B H, J T Wilson and D Luce (1997). "Design and Interpretation of Microcosm Studies for Chlorinated Compounds". In Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water, USEPA ORD Document EPA/540/R-97/504, May 1997. pp23-30. (*Microcosm studies, TCE, benzene and toluene).*

FIGURES

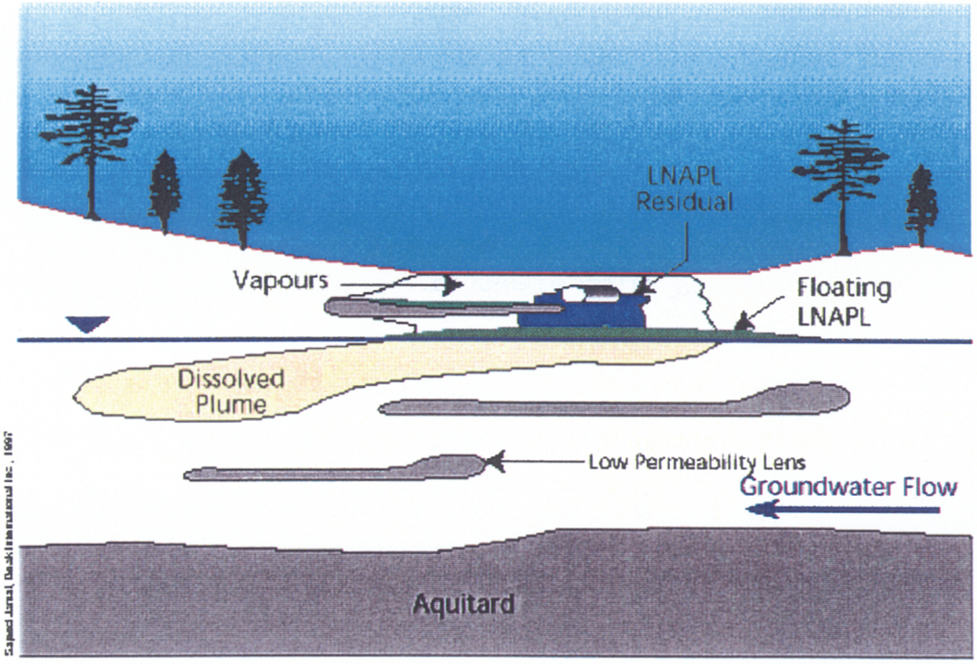


Figure 1. Distribution of Light Non Aqueous Phase Liquids (LNAPLs) in the Subsurface (From RTDF, 1997)

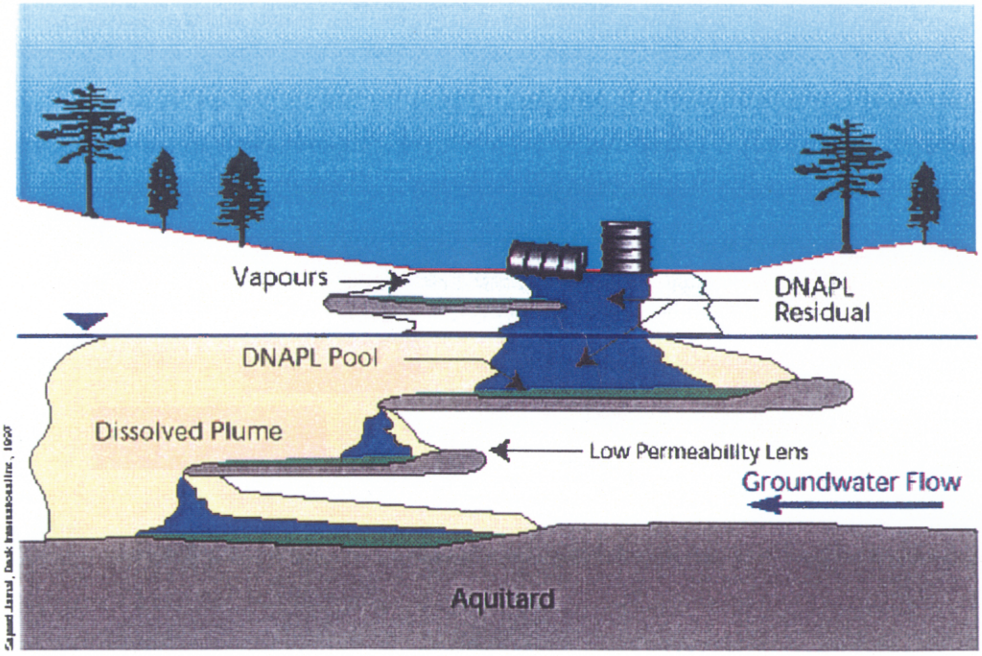


Figure 2. Distribution of Dense Non Aqueous Phase Liquids (DNAPLs) in the Subsurface (From RTDF, 1997)

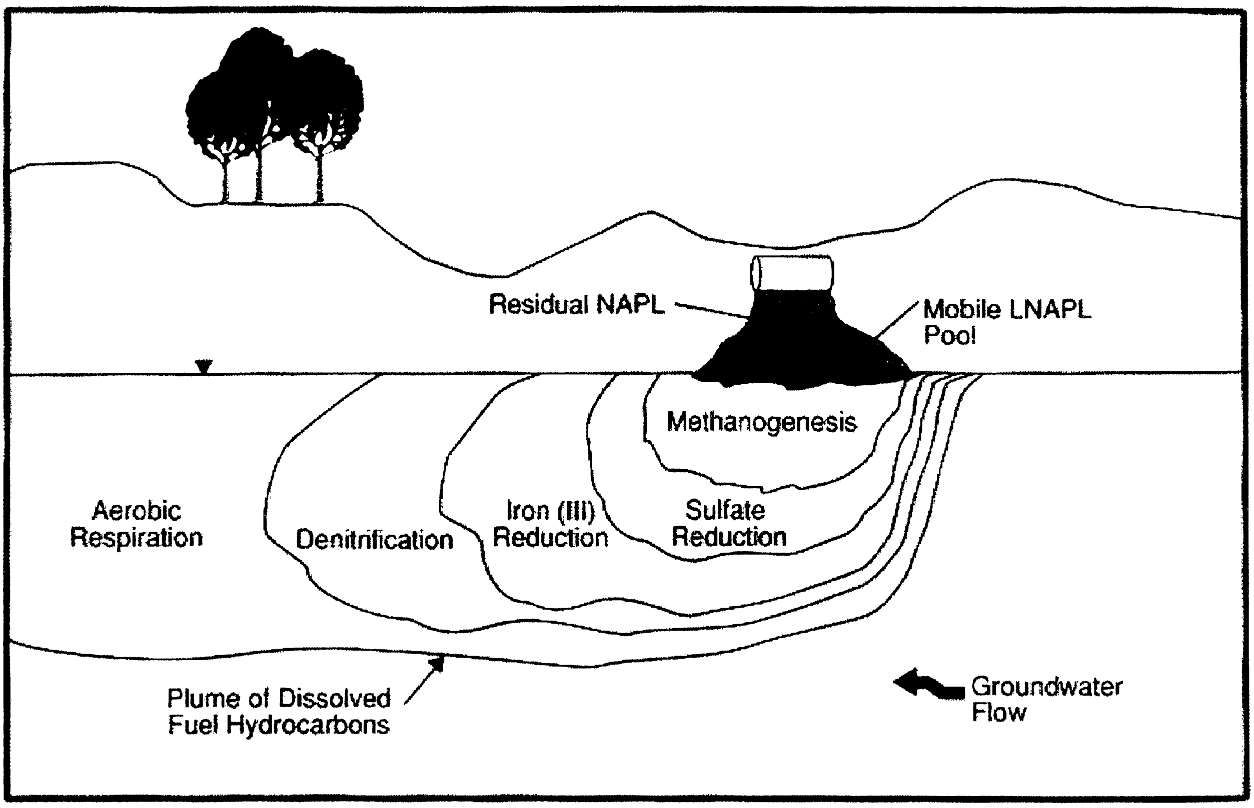


Figure 3. Conceptualisation of electron acceptor zones in the subsurface. (From Wiedemeier et.al. (1999), Adapted from Lovley et al)

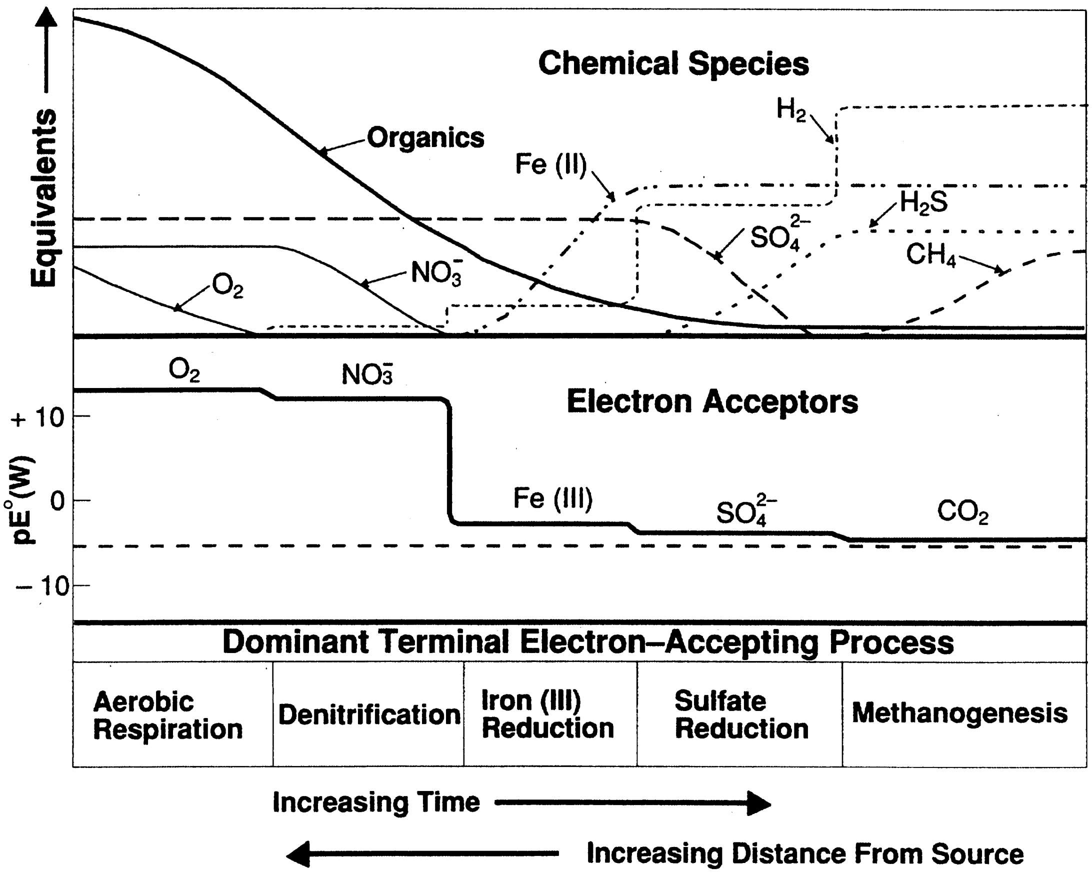


Figure 4. Conceptual model of the geochemical evolution of groundwater contaminated with petroleum hydrocarbons. (From Wiedemeier et.al.,(1999). After Bouwer and McCarty)

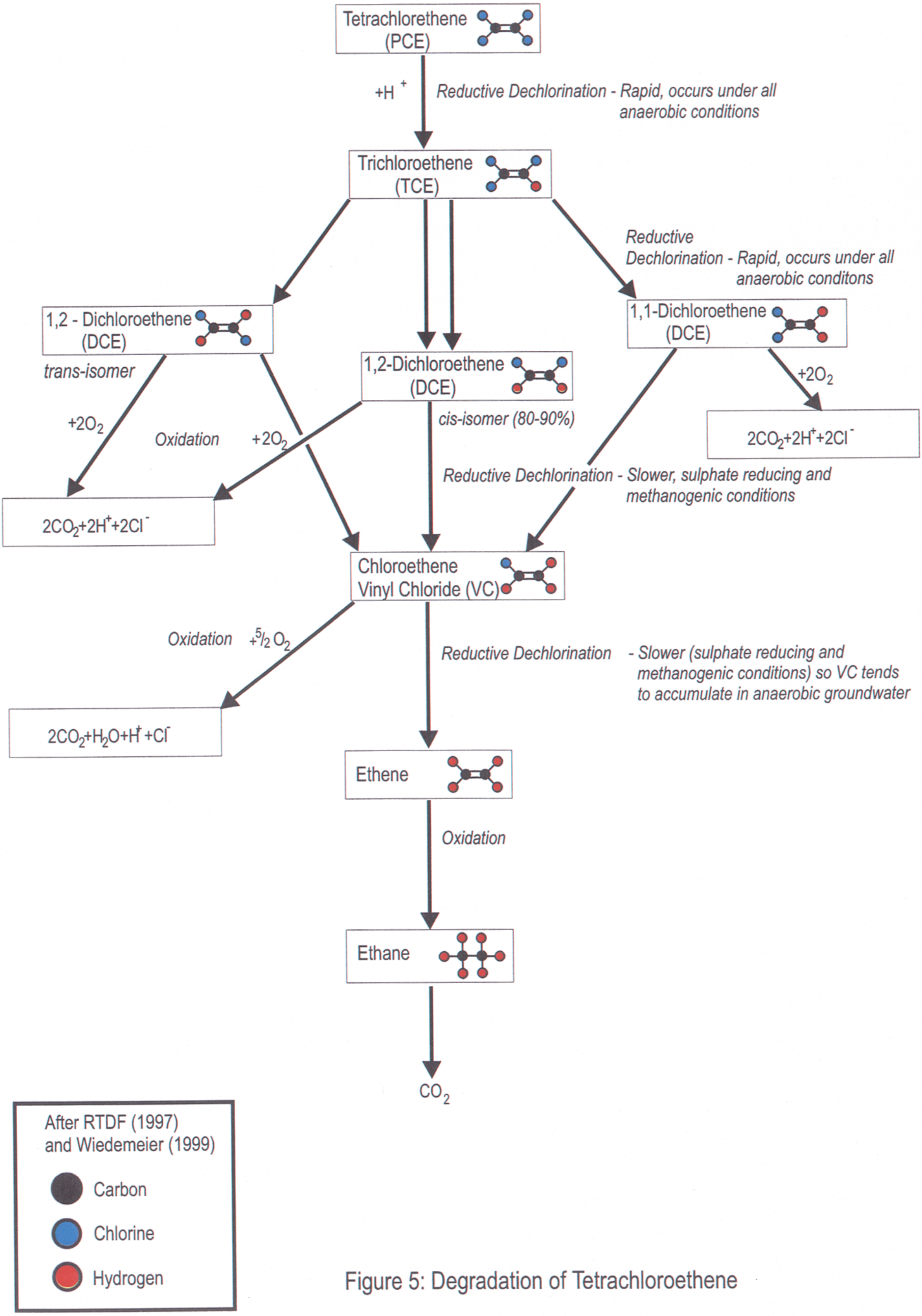
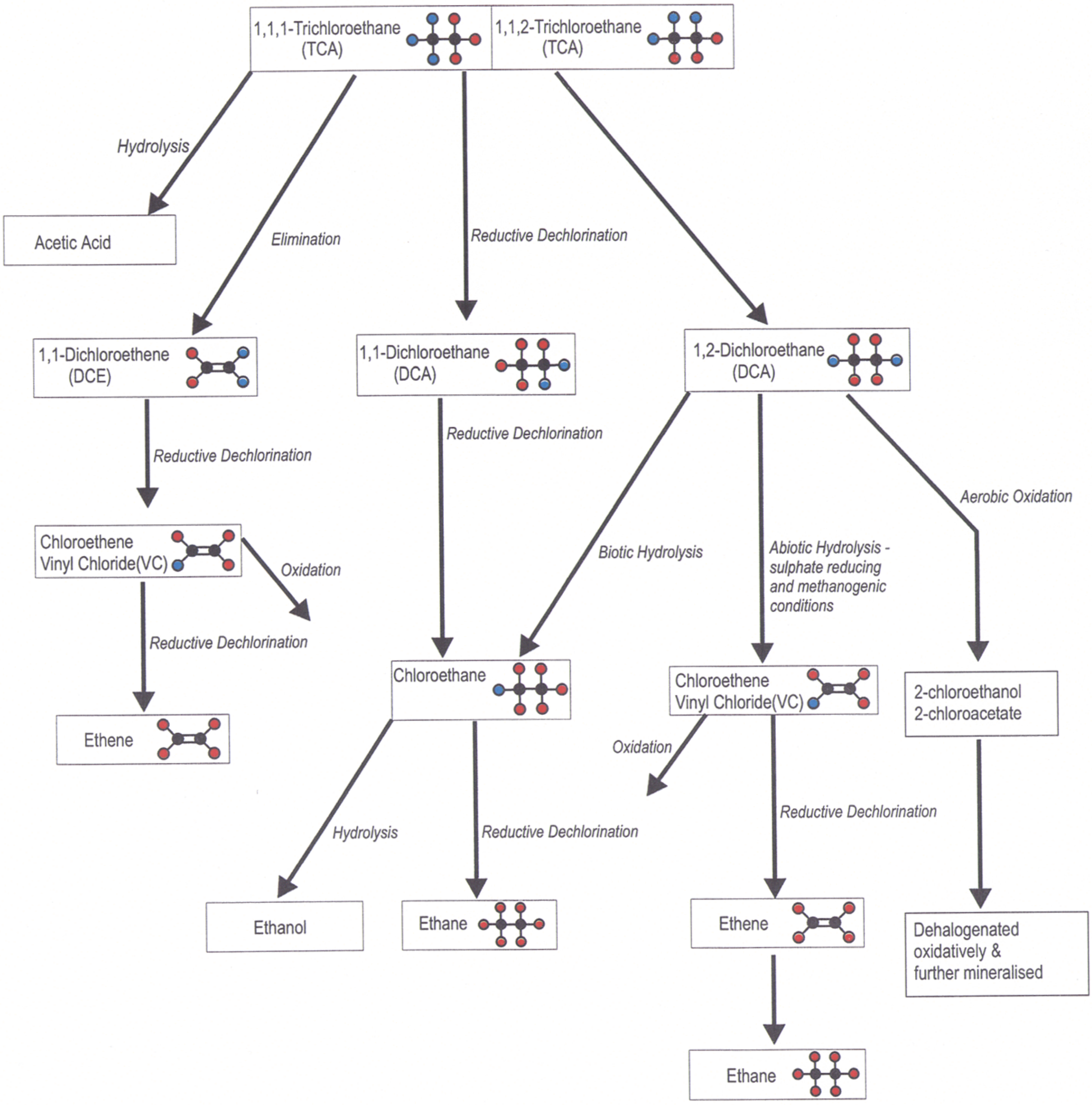


Figure 5: Degradation of Tetrachloroethene



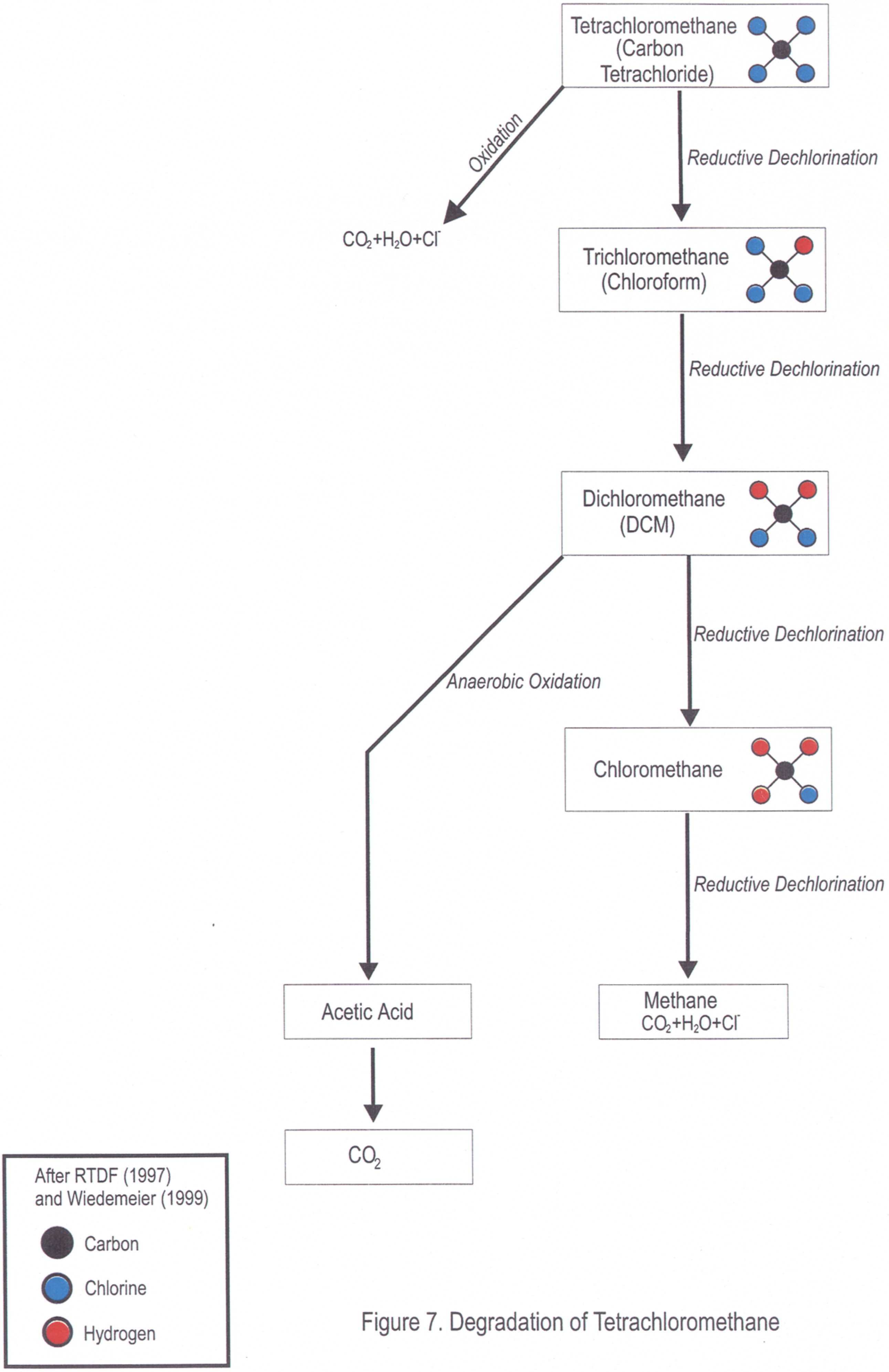
After RTDF (1997), Wiedemeier (1999) and Bosma et al. (1998)

● Carbon

🔵 Chlorine

🔴 Hydrogen

Figure 6. Degradation of Trichloroethane



After RTDF (1997) and Wiedemeier (1999)

Figure 7. Degradation of Tetrachloromethane

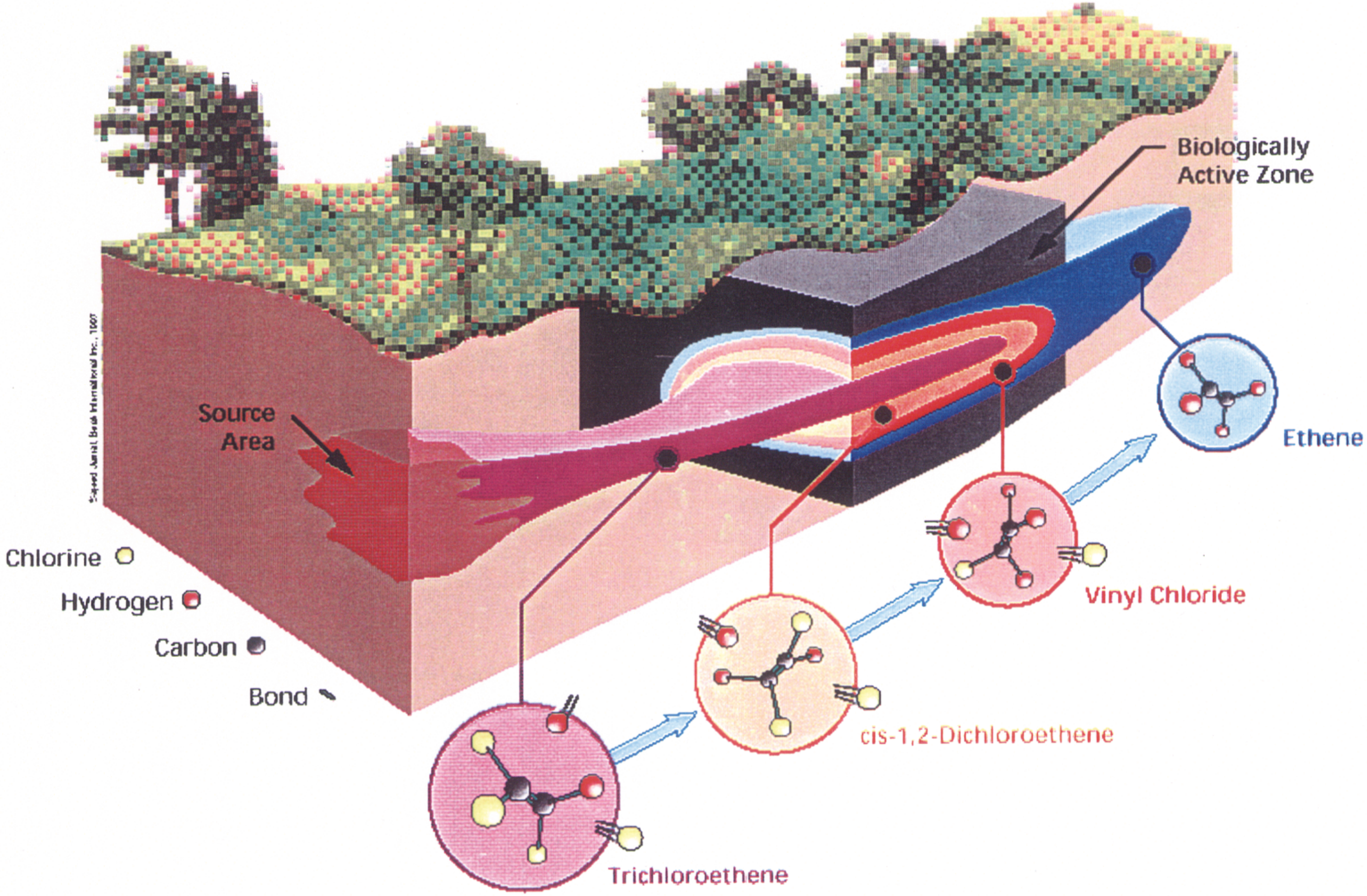
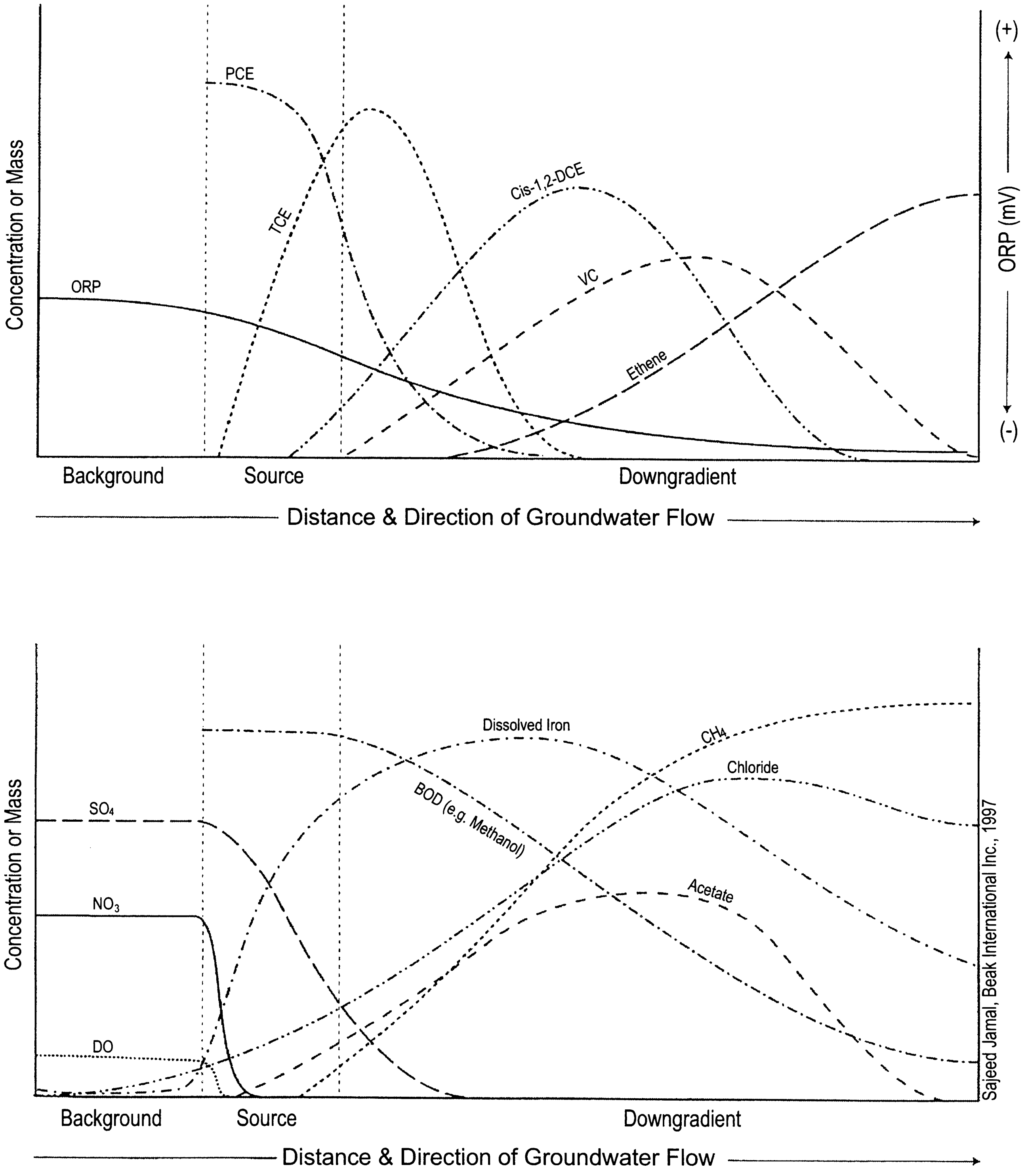


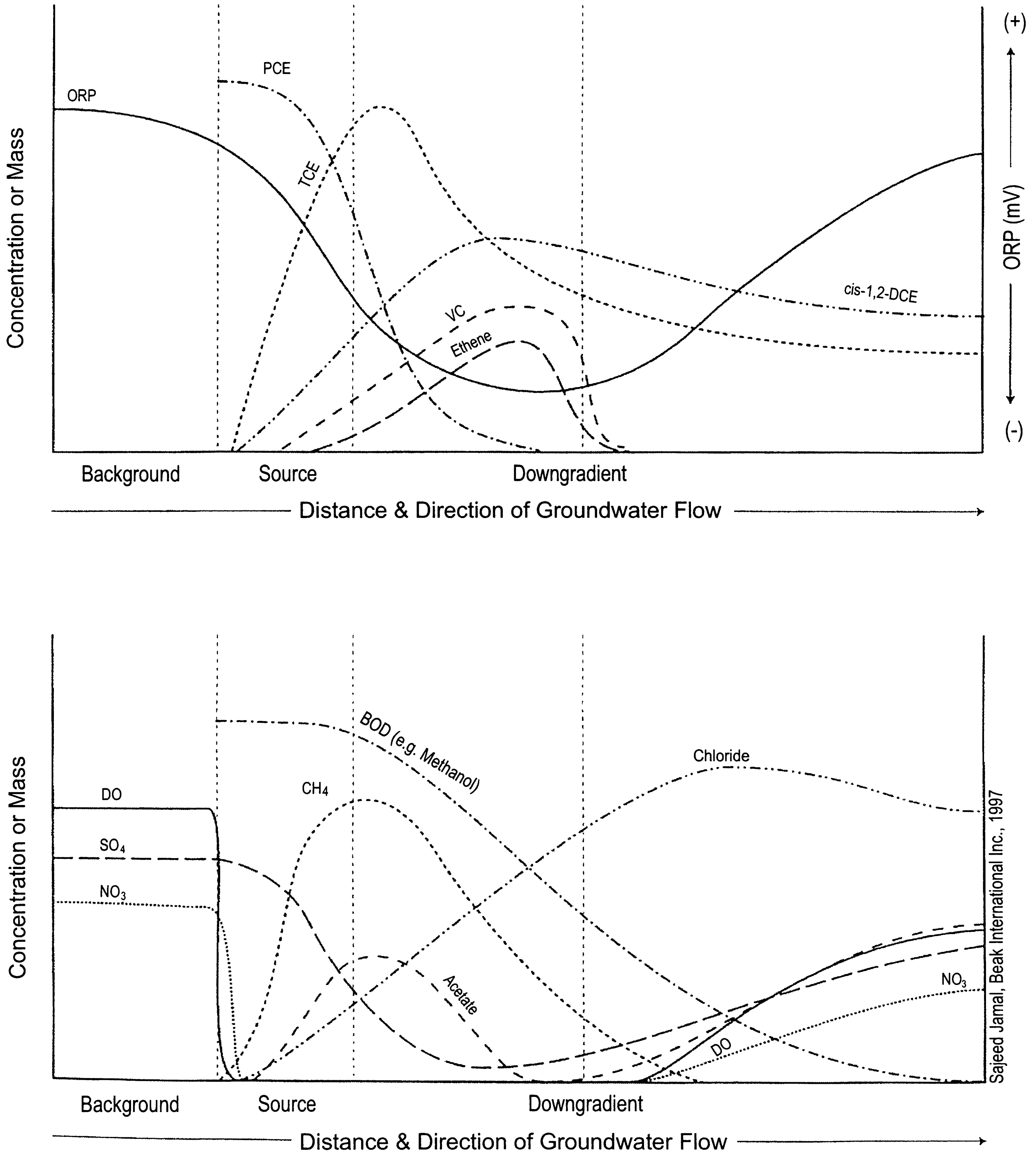
Figure 8. Anaerobic Reductive Dechlorination of a Trichloroethene Plume
(From RTDF, 1997)



Sajeed Jamal, Beak International Inc., 1997

Interpretation: BOD (e.g. Methanol) is supporting the growth of anaerobic bacteria as shown by the production of methane and acetate, and depletion of sulphate. Sulphate-reducing and possibly iron-reducing bacteria appear responsible for the initial dechlorination of PCE through to DCE. As the sulphate concentration decreases, the activity of methanogenic bacteria increases. Under methanogenic/acetogenic conditions 1,2-DCE and VC are dechlorinated to ethene.

Figure 9. Common Patterns of Chlorinated Solvent Biodegradation in an Anaerobic System
(From RTDF, 1997)



Sajeed Jamal, Beak International Inc., 1997

Interpretation: An anaerobic zone has developed in an aerobic groundwater system due to the metabolism of the BOD (e.g. Methanol) in the source area. In the anaerobic zone PCE is dechlorinated to TCE, DCE, VC and finally ethene. Methanogenic, sulphate-reducing, iron-reducing, and acetogenic bacteria are active, and their interactions are responsible for the dechlorination. However, the dechlorination rate is insufficient to cause all of the TCE and DCE to be dechlorinated in the anaerobic zone. These chemicals along with methane, ethane and vinyl chloride migrate into the transition and aerobic zones. In the transition zone the TCE and DCE is partially cometabolised by methanotrophs growing on the methane. Ethene and VC are mineralised to CO_2 by aerobic bacteria in the aerobic zone.

Figure 10. Common Patterns of Chlorinated Solvent Biodegradation in a Sequential Aerobic/Anaerobic System (From RTDF, 1997)

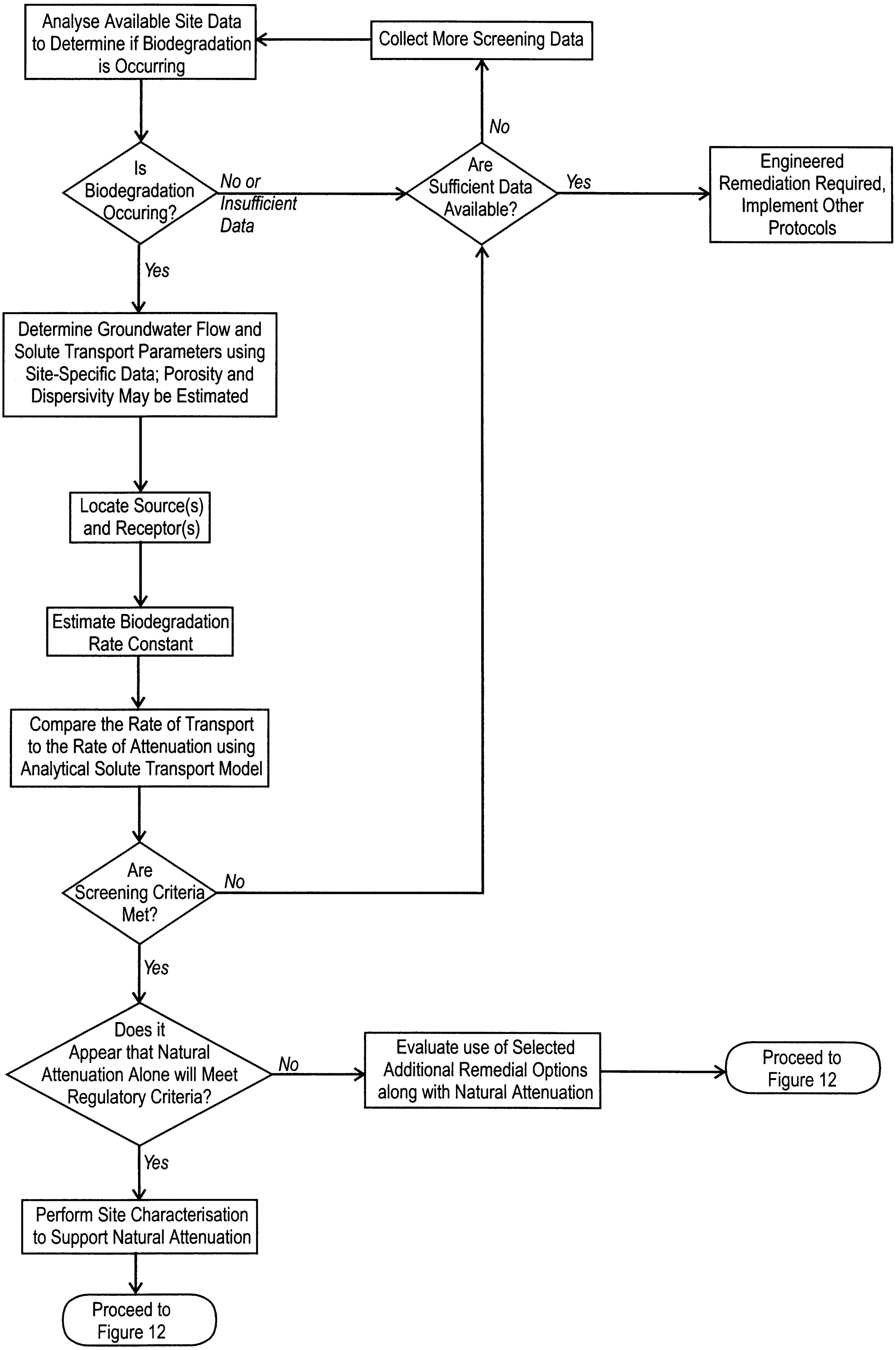


Figure 11. Initial Screening Process Flowchart (From Wiedemeier et.al., 1997)

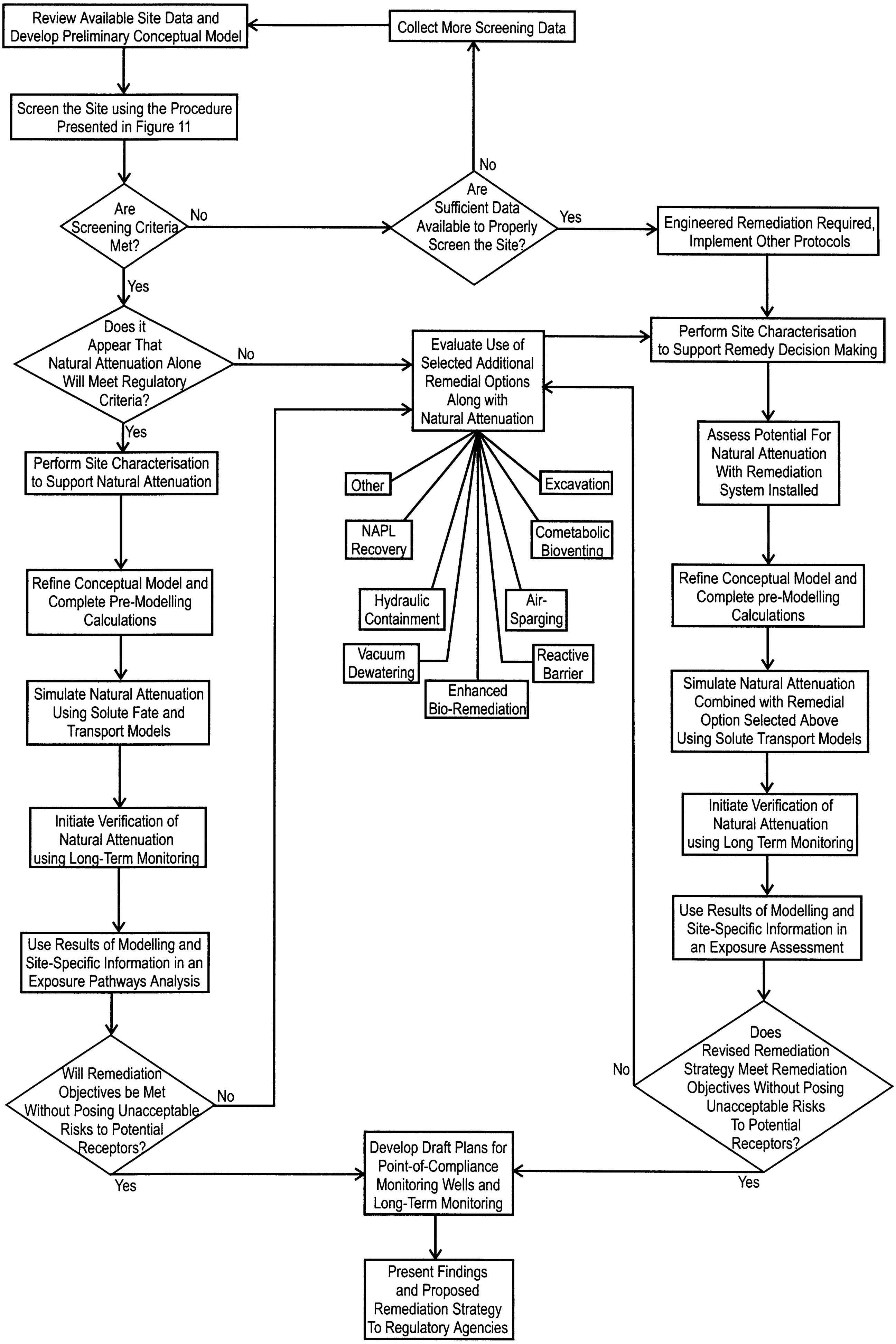
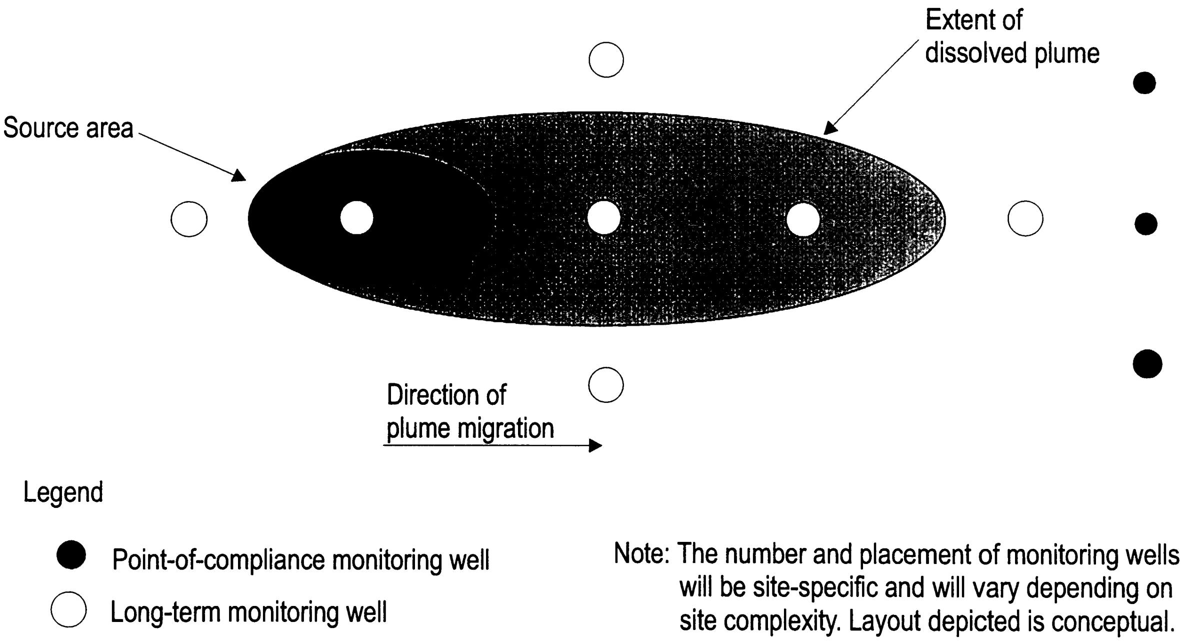


Figure 12. Natural Attenuation of Chlorinated Solvents Flowchart (From Wiedemeier et.al., 1997)



Note: The number and placement of monitoring wells will be site-specific and will vary depending on site complexity. Layout depicted is conceptual.

Figure 13. Theoretical Well Locations for Monitoring Natural Attenuation (From RTDF, 1997)

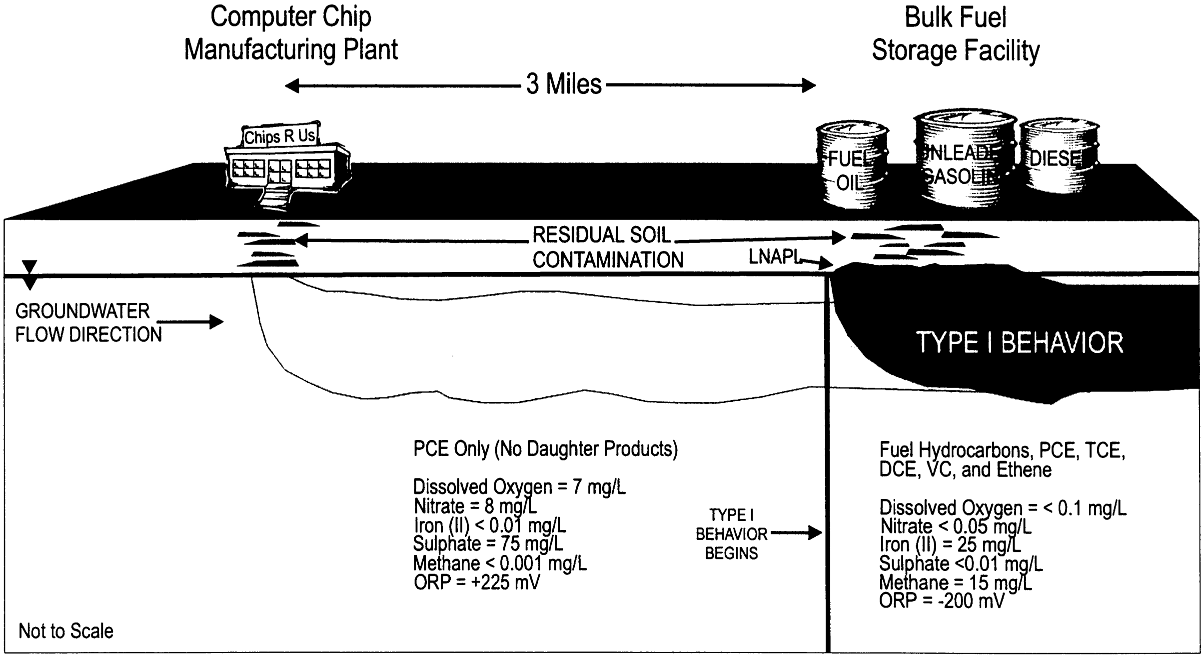


FIGURE 14. Conceptual site model of mixed Type 3/ Type 1 environments (From Wiedemeier et.al., 1999).

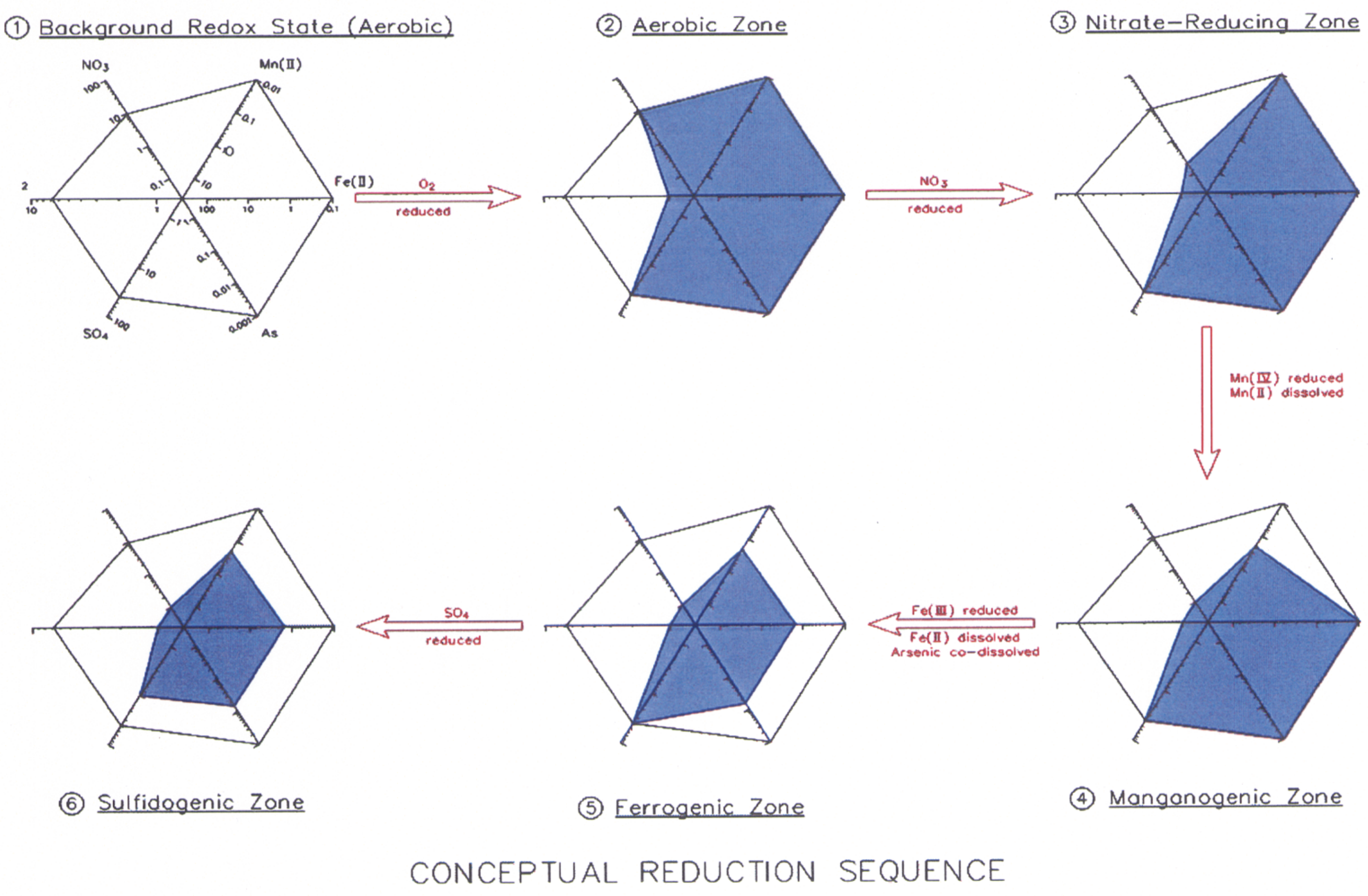


Figure 15. Example SEQUENCE plot. Each redox zone corresponds to a different primary electron acceptor. The SEQUENCE plots illustrate the sequential removal of each electron acceptor from groundwater as biodegradation occurs.

(From Conestoga-Rovers Association web page, http://www.rovers.com/)