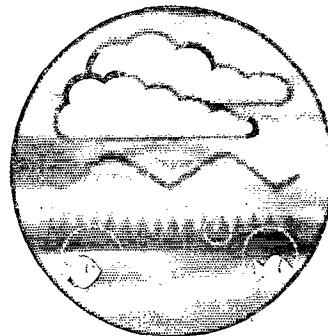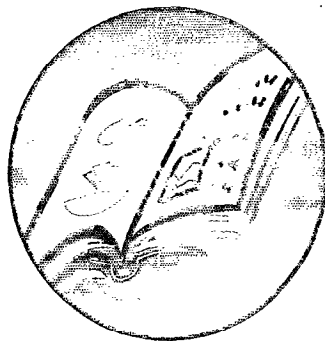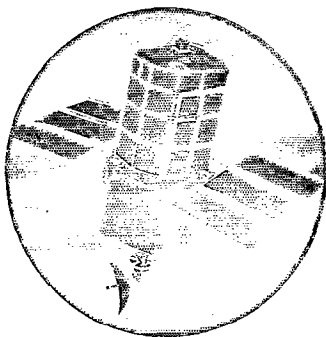# Guidelines and Protocols for Investigations to Assess Site Specific Groundwater Vulnerability

Research and Development

Project Record
P2/042/01

ENVIRONMENT AGENCY

All pulps used in production of this paper is sourced from sustainable managed forests and are elemental chlorine free and wood free

Guidelines and Protecols for Investigations to Assess Site Specific Groundwater Vulnerability

R&D Project Record P2/042/01

M P Boland, BA Klinck, N S Robins, M E Stuart and E J Whitehead

Research Contractor:
British Geological Survey

Publishing Organisation:
Environment Agency
Rio House
Waterside Drive
Aztec West
Almondsbury
Bristol BS32 4UD

Tel: 01454 624400   Fax: 01454 624409

ISBN:1 85705 147 5

© Environment Agency 1999

Dissemination status
Internal: Released to Regions
External: Released to the Public Domain

Statement of use
This report summarises the findings of work carried out towards the implementation of the Groundwater Regulations 1998. The information within this document is for use by Environment Agency staff and others involved in the management of activities that could pose a threat to groundwater quality from List I and List II substances.

Research contractor
This document was produced under R&D Project P2-042 by:

British Geological Survey
Maclean Building
Crowmarsh
Wallingford
Oxon
OX10 8BB

Tel: 01491 838800   Fax: 01491 692345

Environment Agency Project Leader
The Environment Agency's Project Leader for R&D Project P2-042 was:
Jonathan Smith, National Groundwater & Contaminated Land Centre

R&D Project Record P2/042/01

CONTENTS

LIST OF FIGURES

LIST OF TABLES

GLOSSARY

'Acceptable concentration'	Concentration lower than the permitted concentration by a factor taking account of uncertainty in the assessment
Alicyclic	Aliphatic cyclic hydrocarbons
Chelate	Ligand with more than one coordination site
Chemisorption	Type of sorption involving a chemical process
Colloid	Permanent aqueous suspension of molecules too large to form a true solution
Default	Here refers to generic values used by modelling packages where specific data is not entered
Diol	Alcohol with two hydroxyl groups
Distribution coefficient	See partition coefficient
DNAPL	Dense non-aqueous phase liquid
Hydrolysis	Chemical reaction with water
Hydrophobic	Having affinity with water
Inner sphere	Innermost layer of ligands
Isomers	Compounds with the same chemical formula but different structures
Isoprenoid	Long chain hydrocarbons with a repeating side chain structure
Isotherm	Equation relating the amounts of a substance in the free (aqueous or gas) phase and the sorbed phase
Ligand	Molecule coordinated to a central atom or ion usually by a difference in charge
Lipophilic	Having affinity for the organic phase. Similar to hydrophobic
Macromolecular	Having very high molecular weight
Monoaromatic	Hydrocarbons containing 1 aromatic ring, for example, benzene
Partial vapour pressure	The vapour pressure of a component above a solution. Reflects the tendency of the substance to escape from the aqueous phase to the gas phase.
Partition coefficient	Ratio of the distribution of a substance between two phases
'Permitted concentration'	Maximum concentration of List I or II substance allowed in infiltration at the base of the unsaturated zone as specified by the EA
Primary alcohol	Alcohol with the hydroxyl group at the end of the hydrocarbon chain

Reductive dechlorination	Biologically mediated sequential replacement of chlorine atoms by hydrogen atoms on, for example, chlorinated solvents under reducing conditions
Sorbate	See sorption
Sorbent	See sorption
Sorption	Process removing a solute (the sorbate) from solution by interaction with solid matter (the sorbent)
Pyrethroid	Non-systemic contact insecticides similar to those originally derived from pyrethrum flowers
NAPL	Non-aqueous phase liquid

EXECUTIVE SUMMARY

The Groundwater Regulations 1998, which became fully active on 1 April 1999 require that activities are controlled to prevent the entry of List I substances into groundwater, and to minimise the entry of List II substances in order to prevent pollution of the receiving groundwater. In the case of deliberate disposal or discharge onto or into land of materials containing List I or List II substances, an authorisation is required.

Authorisation for the disposal or discharge of List I and II substances can only be granted following a 'prior investigation' which demonstrates that List I substances will not enter groundwater, and List II substances will not cause pollution of groundwater. This document has been produced to assist both Agency staff and potential applicants understand the issues that need to be considered as part of a 'prior investigation' under the Groundwater Regulations, in order to ensure that a consistent and reasonable approach is taken to assessing the likely impacts on groundwater.

A phased approach to evaluating groundwater vulnerability has been adopted for the soil and unsaturated zone, which allows appropriate decisions to be made at each phase. This is designed to allow decisions to be made on discharges where the evaluation is straightforward with a limited amount of data, whilst increasingly complex decisions are supported with an increased amount of site investigation data. Most simple applications will be dealt with at Phases 1a and 1b of the assessment, while more complex applications for the disposal of List I/II substances are essentially supported by more intensive investigations detailed in Phases 2a and 2b. In this way it is intended to ensure that the data collection exercise is in proportion to the potential risk that the proposal represents.

Phase 1a investigation requires only the information on the application form, and the 1:100,000 scale Groundwater Vulnerability Maps. This allows rejection if a risk to surface water is demonstrated or acceptance if no risk to surface water is shown and if there is no aquifer present. Phase 1b also requires information from the geological map and/or borehole records and scores risk to groundwater. Applications can be accepted at this phase where the aquifer has sufficient clay cover or rejected if cover is limited or absent. It is anticipated that the majority of applications would be dealt with at this level. Marginal cases would be referred to Phase 2, as would applications in more sensitive locations and those involving List I substances.

Phase 2 is subdivided into consideration of attenuation in the soil (Phase 2a) and the unsaturated zone beneath the soil layer (Phase 2b). A suitable contaminant transport model is used to calculate the concentration of contaminants leaving the base of the soil (Phase 2a) or the unsaturated zone (Phase 2b) using generic data. These concentrations are then compared to values specified by the Environment Agency.

Where the modelled concentration at the base of the unsaturated zone does not meet the criteria, the application will not be accepted unless the applicant can demonstrate to the satisfaction of the Environment Agency using site-specific data for soils, the aquifer and the contaminant that disposal would not produce unacceptable concentrations at the water table. This would require collecting primary data using standard methodologies such as those prescribed by the BSI and applying these to the model. It is probable that this would involve invasive site investigation.

KEY WORDS

Groundwater; vulnerability; site-specific; List I; List II; discharge; protocols;

1. INTRODUCTION

1.1 Background

The Groundwater Regulations 1998, which became fully active on 1 April 1999, respond to the requirements of the EC Directive on the Protection of Groundwater against Certain Dangerous Substances (80/68/EEC). The Regulations require that activities are controlled to prevent the entry of List I substances into groundwater, and to minimise the entry of List II substances in order to prevent pollution of the receiving groundwater. In the case of deliberate disposal or discharge onto or into land of materials containing List I or List II substances, an authorisation is required. List I and II substances are shown in Table 1.1.

Table 1.1 Summary of the substances controlled under the Groundwater Regulations, 1998

List I

- Organohalogen compounds and substances which may form such compounds in the aquatic environment
- Organophosphorus compounds
- Organotin compounds
- Substances which possess carcinogenic, mutagenic or teratogenic properties in or via the aquatic environment
- Mercury and its compounds
- Cadmium and its compounds
- Mineral oils and hydrocarbons
- Cyanides

List II

- The following metals and metalloids and their compounds:

Antimony	Chromium	Nickel	Tin
Arsenic	Cobalt	Selenium	Titanium
Barium	Copper	Silver	Uranium
Beryllium	Lead	Tellurium	Vanadium
Boron	Molybdenum	Thallium	Zinc

- Biocides and their derivatives not appearing in List I
- Substances which have a deleterious effect on the taste or odour of groundwater, and compounds liable to cause the formation of such substances in water and to render it unfit for human consumption
- Toxic or persistent organic compounds of silicon, and substances which cause the formation of such compounds in water, excluding those which are biologically harmless or which are rapidly converted in water into harmless substances
- Inorganic compounds of phosphorus and elemental phosphorus
- Fluorides
- Ammonia and nitrites

Groundwater is an important and finite resource, and like all other controlled waters must be protected from pollution. To this end the 'Policy and Practice for the Protection of Groundwater' was published by the former National Rivers Authority, and has recently been updated and reissued by the Environment Agency (Environment Agency, 1998). The Groundwater Regulations 1998 augment a formal system for the control of discharges of List I and List II substances to groundwater. No List I substances are allowed to be discharged to groundwater, whereas low concentrations of List II substances may be tolerated provided that pollution of the groundwater does not occur. The Regulations supplement existing powers under the Environmental Protection Act 1990 and the Water Resources Act 1991.

Authorisation for the disposal or discharge of List I and II substances can only be granted following a 'prior investigation' which demonstrates that List I substances will not enter groundwater, and List II substances will not cause pollution of groundwater. This document has been produced to assist both Agency staff and potential applicants understand the issues that need to be considered as part of a 'prior investigation' under the Groundwater Regulations, in order to ensure that a consistent and reasonable approach is taken to assessing the likely impacts on groundwater.

1.2 Objectives

The overall objectives of the project are:

> To prepare guidance on the requirements for investigations and data collection when undertaking 'prior investigation' of groundwater vulnerability as required by the Groundwater Regulations 1998. To advise on the most appropriate methods of analysis and to prepare a protocol for assessing the actual risk to groundwater.

These can be broken down into 6 component parts. The first three of these are essentially information and data gathering tasks, the fourth and fifth are to evaluate methods and intensity of investigation and the sixth and final task is to bring the information together to form a hierarchical methodology for assessing vulnerability. This is the protocol. The objectives that these activities should satisfy are:

Identify the processes that are relevant to different types or groups of contaminants in Lists I and II within the unsaturated zone

These processes are all well documented in the international scientific literature. They include:

- processes affecting entry of the contaminant to the subsurface such as the formation of immiscible phases, with obvious implications for rapid transport to the water table,

- processes of contaminant attenuation within the unsaturated zone: volatilisation, sorption, microbial and chemical degradation or transformation,

- processes of contaminant mobilisation once within the unsaturated zone, for example complexation of metals or less-soluble organics by mobile organic material,

Aquifer	Type	Score
MINOR AQUIFERS continued		
Weald Clay (sandstones and limestones)	mixed	2
Tealby Limestone	fractured	1
Claxby Formation	fractured	1
Tunbridge Wells Sands	intergranular	3
Wealden Beds (sands)	intergranular	3
Wadhurst Clay Formation (sands)	intergranular	3
Ashdown Beds (except clay)	intergranular	3
Purbeck (sands)	intergranular	3
Portland Sands	intergranular	3
Corallian Group (except Yorkshire and Osmington Oolite)	fractured	1
West Walton Formation (limestone)	fractured	1
Kellaways Sand/Osgodby Formation	intergranular	3
Cornbrash Formation	fractured	1
Ravenscar Group	mixed	2
Blisworth Limestone	fractured	1
Glentham Formation (limestones)	fractured	1
Fuller's Earth Rock	fractured	1
Northampton Sand	intergranular	3
Upper Lias (Yeovil/Bridport Sands)	intergranular	3
Junction Bed	fractured	1
Marlstone Rock Formation	fractured	1
Dyrham Formation	intergranular	3
Lower Lias (limestones)	fractured	1
Blue Lias	fractured	1
White Lias/Langport Member	fractured	1
Sandstones in Mercia Mudstone Group	fractured	1
Permian breccias and conglomerates (south-west England)	mixed	2
Basal Permian Sands	mixed	2
Coal Measures (including Barren Measures)	fractured	1
Millstone Grit	fractured	1
Culm	fractured	1
Carboniferous Limestone (limestones in northern England, Yoredales, Limestone Shales)	fractured	1
Devonian sandstones	fractured	1
Silurian limestones	fractured	1
volcanic rocks	fractured	1

1.3 Concept of Groundwater Vulnerability

Groundwater vulnerability (to contamination) is the likelihood of contaminants reaching the water table after introduction at some point at the ground surface. In the current terminology of risk assessment, a receptor is only at risk if there exists both a hazard (e.g. a pollutant) and a pathway by which that hazard might be transmitted to the receptor (groundwater). Groundwater vulnerability is a measure of the significance of a pathway and a receptor. In the context of the Groundwater Regulations, discharge of one or more List I or List II substances constitutes a hazard, whilst the underlying groundwater constitutes the receptor. The investigation addresses the pathway in order to evaluate whether contaminants will reach the watertable, and what form and concentration they will be in. It therefore concentrates on an understanding of the processes that may take place in the soil and the unsaturated zone of the aquifer.

Groundwater vulnerability is a function of the intrinsic properties of the overlying soil and the unsaturated zone of the aquifer, with the risk of groundwater pollution dependent on the interaction of groundwater vulnerability (hydrogeology) and the contaminant properties (contaminant physico-chemistry). The Environment Agency (EA 1998) take this forward to define groundwater vulnerability as a function of:

- the nature of the overlying soil;

- the presence and nature of any overlying superficial or glacial deposits;

- the nature of the geological strata forming the aquifer;

- the thickness of the unsaturated zone or thickness of confining beds.

However, predicting the movement and fate of a pollutant arriving at the ground surface is difficult and complex. A pesticide sprayed in dilute aqueous form onto agricultural land may be broken down into harmless compounds by biological activity in the soil quite quickly. Disposal of the same pesticide in concentrated form to landfill may result in relatively rapid penetration into an aquifer without any significant degradation.

The thickness of the unsaturated zone and the potential it offers for pollutant attenuation by physical, chemical or biological processes makes it the key to resolving site-specific groundwater vulnerability issues. In the absence of fractures and other potential by-pass features, unsaturated flow is normally slow and intergranular in a chemically aerobic and usually neutral or alkaline environment. There is considerable potential for:

- interception, sorption and elimination of pathogenic bacteria and viruses;

- attenuation of heavy metals, and other inorganic chemicals, through precipitation, sorption or cation exchange;

- sorption of many, and biodegradation of some, natural and synthetic organic compounds.

However, the ability of the unsaturated zone to attenuate pollutants is difficult to predict and it depends on:

- the hydraulic loading of the discharge;

- the physico-chemical nature of the substances released, and;

- the biochemical environment, physical properties and thickness of the unsaturated zone.

In effect, persistent and mobile substances are only delayed on their transit to the water table whereas attenuation of less persistent compounds is enhanced the greater the unsaturated zone thickness. These same effects are most active in the soil zone where biological activity is greatest. However, where the waste is discharged below the soil zone (to soakaway or discharge pit) the soil horizon is by-passed.

1.4 Methodology

A phased approach to evaluating groundwater vulnerability has been adopted for the soil and unsaturated zone. An assessment is made at the end of each phase; the application for authorisation under the Groundwater Regulations 1998 will be given or refused a consent where a clear result is obtained at the end of the first phase. This is designed to allow decisions to be made on the discharges with least risk but supported by a limited amount of data, whilst increasingly complex decisions are supported with an increased amount of site investigation data. An outline flow chart is shown in Figure 1.1 and summary data requirements in Table 1.2.

Most simple applications will be dealt with at Phase 1 of the assessment protocol, while more complex applications for the disposal of List I/II substances are essentially supported by more intensive investigations detailed in Phases 2a and 2b. In this way it is intended to ensure that the data collection exercise is in proportion to the potential risk that the proposal represents.

The conclusion for any application may result in one of three options:

- acceptance of the proposal to discharge where there is no perceived risk;

- outright refusal of the proposal to discharge where the there is a clear unacceptable risk;

- referral of the proposal to discharge for consideration at Phase 2 in all other cases.

Phase 1a assessment requires only the information on the application form, and the 1: 100,000 scale Groundwater Vulnerability Maps. It is anticipated that the majority of applications would be dealt with at Phase 1 level. In some cases a rapid supplementary assessment based on desk access to basic information on topography, land use, land drainage, surface waters, and soils can be made. The approach has been designed in anticipation of GIS type data storage and handling facility being available for use throughout the Environment Agency in due course. In the mean time the protocol deals with manual gathering of relevant information. The source-pathway-receptor methodology is used and applications will be

given consent where either there is no receptor (groundwater) or surface water or no pathway to surface water can be shown. Where a pathway and a receptor can be defined for surface water the application is refused. Where an aquifer is present the application passes to Phase 1b.

In Phase 1b the groundwater vulnerability is assessed using relevant information from soil and geological maps, and borehole records. Where there is no Major or Minor Aquifer present the application can be accepted. Where an aquifer is present but there is insufficient clay cover the application may be refused or additional investigations undertaken to quantify better the attenuating properties of the soil and unsaturated zone. Other cases would be referred to Phase 2. Applications in more sensitive locations or involving a significant loading of List I substances are also considered to require assessment at Phase 2.

Phase 2 is subdivided into consideration of attenuation in the soil (Phase 2a) and the unsaturated zone beneath the soil layer (Phase 2b). The properties of the contaminant, the method of disposal and the properties of the subsurface are all taken into account. A suitable contaminant transport model is used to calculate the concentration of contaminants leaving the base of the soil (Phase 2a) or the unsaturated zone (Phase 2b). These are termed the modelled concentrations in this report. These impacts are then compared to criteria specified by the EA. It is necessary to provide a safety margin which allows for the uncertainties in the assessment process.

These phases are based on the application of models such as the CONSIM model to determine the nature and loading of material likely to arrive at the water table. Such models assume that discharge is maintained at a level at which the unsaturated zone remains unsaturated. Data inadequacy is covered by a range of literature values, so that model results will inevitably comprise ranges rather than single values. It is assumed that an application at this level would involve an expert to prepare the technical simulation or that it would be carried out by experts in the employment of the applicant. The protocol describes the mechanics of the Phase 2 evaluation and the ranges of values for specific materials which may result in acceptance, referral or refusal.

Where the modelled concentration at the base of the unsaturated zone does not meet the criteria following modelling of both the soil and unsaturated zones, then the application will not be accepted unless the applicant can demonstrate to the satisfaction of the Environment Agency using site-specific data for soils, the aquifer and the contaminant that disposal would not produce unacceptable concentrations at the water table. This would require collecting primary data using standard methodologies such as those prescribed by the BSI (see BSI in reference list in Section 7) and applying these to the model. It is probable that this would involve invasive site investigation.

Where the modelled concentration is still unacceptable consideration of the effect of dilution by the receiving groundwater may be taken into account for List II substances but is not relevant in respect of List I substances.

Contaminant transport and attenuation processes are reviewed in Chapter 2. This chapter also contains source information on relevant contaminant properties. Desk study information sources for soils and aquifers are reviewed in Chapter 3. Chapter 4 contains a review of existing guidance on site characterisation and monitoring.

Table 1.2   Phased approach for assessing site-specific vulnerability

Phase	Process	Data requirement	Comment
1a	Initial assessment of surface and groundwater risk	Questionnaire and vulnerability map	Expect majority of applications to be passed in this phase
1b	Ranking of groundwater vulnerability	Geology and hydrogeology maps Borehole records	
2a	Assessment of attenuation processes in soil using models	Contaminant properties Soil characteristics Hydraulic loading Appropriate model	Initial assessment may use generic data from standard sources. Where existing data is inadequate site-specific/ contaminant-specific data will need to be collected from site investigations
2b	Assessment of attenuation processes in unsaturated zone using models	Contaminant properties Aquifer characteristics Hydraulic loading Appropriate model	

The procedures appropriate to use within Phase 1 and 2 are discussed in more detail in Chapter 5 and the formal protocol to be followed is presented in Chapter 6.
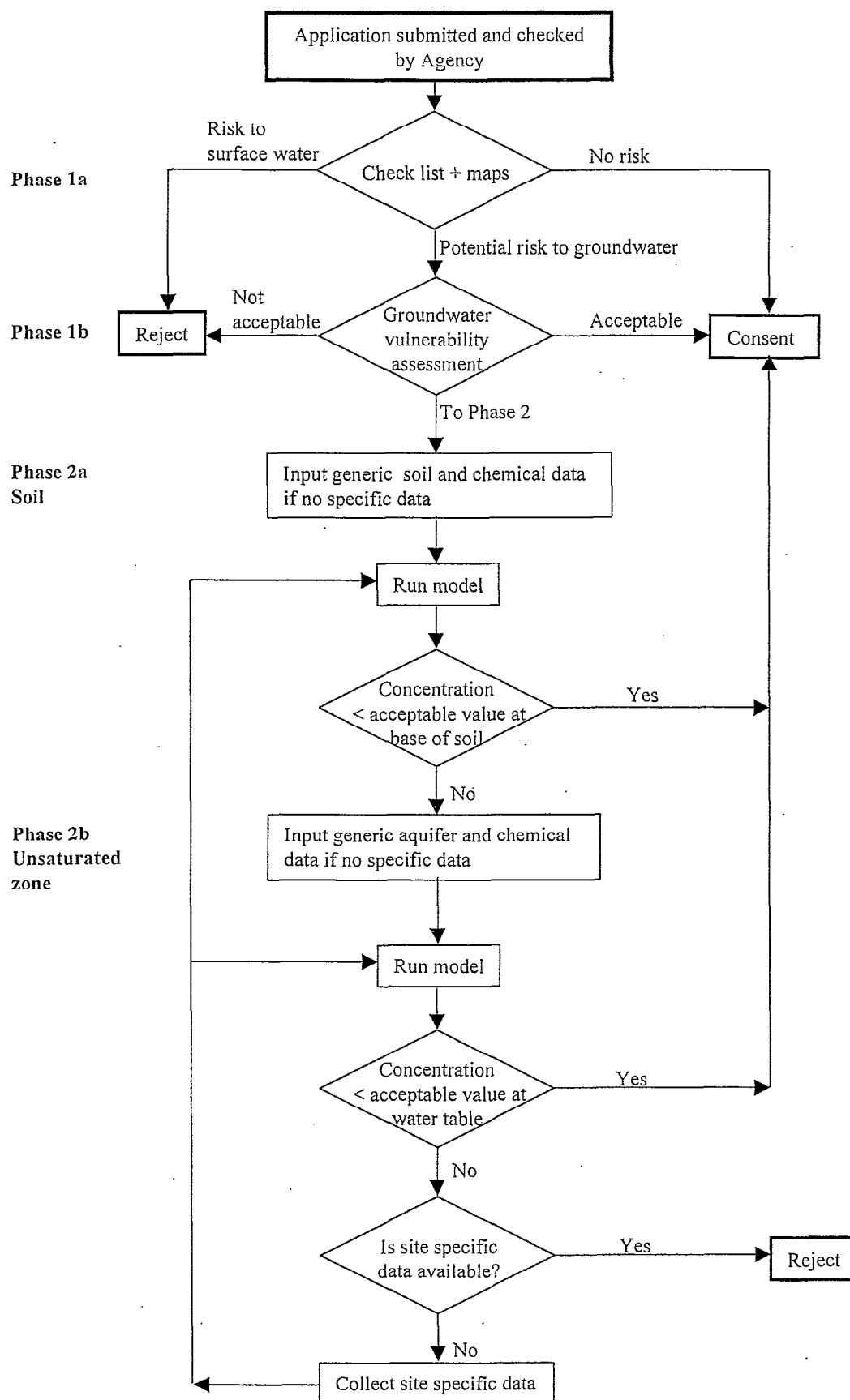
Figure 1.1 Summary chart for phased approach to assessing authorisations under the Groundwater Regulations 1998

2. CONTAMINANT TRANSPORT PROCESSES IN THE SOIL AND UNSATURATED ZONE

2.1 Entry to the subsurface

This chapter reviews the potential mechanisms of entry of List I and II contaminants to the subsurface and the attenuation mechanisms operating in the unsaturated zone. Two types of scenario are considered: the application of waste materials, such as sewage sludge and animal slurry, to land for agricultural benefit or for disposal; and the accidental penetration directly to the subsurface of fuels and industrial chemicals from accidents or leaks, for example from car park drainage to soakaway.

The application of sewage sludge to farmland for agricultural benefit currently represents the single largest outlet for sewage sludge in the UK and accounts for 44% of the sludge produced (MAFF 1993). With increased amounts of sludge being produced and the end of disposal at sea in December 1998, the water industry is likely to seek to recycle increasing quantities. The disposal of spent and waste pesticides (for example sheep dip) to land is permitted under the MAFF Code of Good Agricultural Practice for the Protection of Water (1998). The current switch away from organophosphates to the synthetic pyrethroids in sheep dip formulations poses an increased risk to the environment since these latter compounds are generally much more toxic to fish and invertebrates.

For soil application, attenuation of contaminants in the organically rich and highly microbially active soil will occur before the unsaturated zone is reached. Where entry of contaminants to the unsaturated zone is direct, for example, from soakaway drainage, attenuation by the soil cannot be assumed and the attenuation capacity of the unsaturated zone alone must be assessed. In dual porosity media, such as the major Chalk and Triassic Sandstone aquifers of the UK, where there is the potential for a significant proportion of infiltration to reach the aquifer by by-pass or fissure flow, it is considered that it must be possible for contaminants to reach the water table with little or no attenuation. In these cases, the rapid penetration of the aquifer by chemicals forming an immiscible phase must also be considered.

2.2 Dilution and dispersion

These processes control the distribution (spreading) of solutes within the saturated zone, but are necessary in this context as they are used in most pollutant transport models. They also have relevance where a concentration target has to be met (i.e. for List II substances).

Advection (or plug flow) - dissolved substances (solutes) are carried along by the flow of the water under a hydraulic gradient. Non-reactive (conservative) substances travel at the same rate as the water; reactive solutes may be retarded by other processes, in which case they travel more slowly than the water. Excluded substances, those which cannot enter small pores, may travel faster than the average rate of water movement.

Water can only flow once the moisture content exceeds the field capacity, as until this point is reached all the water is held to the surfaces of the porous medium by surface-tension

forces. Further information about the flow of water in the unsaturated zone is given in texts such as Fetter (1993) and Bedient et al. (1994).

Advection is described by the following equation. The average linear water velocity, v_z, is defined as the rate of flow of water across a unit cross-sectional area of the porous medium:

$$v_z = \frac{K}{n_e}\frac{dh}{dl}$$

where: v_z = average linear velocity in z direction (distance/time)
 K = hydraulic conductivity (distance/time)
 n_e = effective porosity
 dh/dl = hydraulic gradient (distance/distance)

The volume of water flowing across the unit area is equal to the average linear velocity times the effective porosity (porosity available for flow). The 1D advected mass flux of solute, F_z, is then determined by multiplying the quantity of water by the concentration of solute:

$$F_z = v_z\, n_e\, C$$

where: F_z = mass flux of solute per unit area
 C = solute concentration (mass/volume)

Mechanical dispersion - water flowing through a porous media travels at various velocities. This is because: some paths through the pore network are longer than others, so travel times are slower; flow is faster in the centre of pores than near the edges due to frictional drag; and the size of pores and pore throats varies, with faster flow in larger pores. Waters of different solute concentrations therefore become mixed as flow occurs. Mixing of contaminated water with uncontaminated water dilutes the concentration of contaminant. Dispersion is less significant in the unsaturated zone than the saturated as flow is slower.

Coefficients of mechanical dispersion can be calculated by multiplying dynamic dispersivity (an intrinsic property of the porous medium) by the average linear velocity (Fetter 1993):

Coefficient of longitudinal mechanical dispersion = $\alpha_i\, v_i$

where: v_i = the average linear velocity in the i direction (distance/time)
 α_i = the dynamic dispersivity in the i direction (distance)
and
Coefficient of transverse mechanical dispersion = $\alpha_j\, v_j$

where: v_j = the average linear velocity in the j direction (distance/time)
 α_j = the dynamic dispersivity in the j direction (distance)

Molecular diffusion - when a concentration gradient is present molecules of solute move from regions of higher concentration to those of lower concentration. Although diffusion is generally very slow in comparison to mechanical dispersion, it can be a significant process over long timescales particularly as diffusion occurs even in the absence of flow. It can also be highly significant in dual porosity systems which have preferential flow pathways such as fractures as well as matrix porosity. In such systems, recharge of contaminated water may occur primarily via the fractures (i.e. flow bypasses the matrix). However, contaminants can

diffuse into the matrix, lowering the concentration of contaminant in the mobile fissure water, and then gradually diffuse back into the mobile water over time. This process does not remove contaminant, but is a retardation mechanism (the transport of the contaminant is slower than that of the mobilising water). The resulting delay in reaching the water table may enhance other processes which do reduce the contaminant mass by allowing more time for them to occur.

The mass flux of solute produced by diffusion is determined by the diffusion coefficient of the solute and the concentration gradient, as described by Fick's first law:

$$F = - D_d (dC/dx)$$

where: F = mass flux of solute per unit area per unit time
D_d = diffusion coefficient (area/time)
dC/dx = concentration gradient (mass/volume/distance)

D_d is temperature dependent (Fetter 1993).

Fick's second law is used when concentrations are changing with time:

$$\frac{dC}{dt} = D_d \frac{d^2C}{dx^2}$$

where: dC/dt = change in concentration with time (mass/volume/time)

However, Fick's Laws do not account for the tortuous routes that water and solute molecules take through a porous media; for this reason an effective diffusion coefficient, D^*, is calculated (Fetter 1993). The effective diffusion coefficient is equal to the diffusion coefficient multiplied by a tortuosity coefficient, ω:

$$D^* = \omega D_d$$

Hydrodynamic dispersion - as mechanical dispersion and molecular diffusion both have the effect of diluting the contaminant concentration they are commonly considered together as hydrodynamic dispersion. Although the contaminant concentration is reduced by the action of hydrodynamic dispersion, the total mass of contaminant in solution is unchanged (but contained within a greater volume of water).

The parameters which describe diffusion and mechanical dispersion are combined to produce the hydrodynamic dispersion coefficient, D (Fetter 1993):

$$D_L = \alpha_L v_L + D^*$$

$$D_T = \alpha_T v_T + D^*$$

where: D_L = longitudinal hydrodynamic dispersion coefficient (parallel to the main flow direction)
D_T = transverse hydrodynamic dispersion coefficient (perpendicular to the main flow direction)
α_L = longitudinal dynamic dispersivity
α_T = transverse dynamic dispersivity

2.3 Attenuation mechanisms

2.3.1 Approach

Various processes may occur which reduce the amount of mobile contaminant during the transport of contaminants through the unsaturated zone to an underlying aquifer. These processes can significantly reduce the vulnerability of the groundwater to contamination. Whether or not they occur, and to what extent, are determined by both the nature of the contaminant(s) and the characteristics of the subsurface environment. This review of contaminant transport in the unsaturated zone describes the various attenuation processes that may occur. The transport behaviour of the specific groups of contaminants comprising Lists I and II of the EC Groundwater Directive (80/68/EEC) is discussed in text boxes accompanying the main review.

The processes which affect contaminant transport can be subdivided into three groups: physical, geochemical, and biochemical processes. Some of these processes remove the contaminant from the subsurface altogether (for example degradation); some transfer contaminant from the mobile phase to an immobile phase (retardation) and some may simply redistribute contaminant within the mobile phase. The impact of these various processes on the arrival of a contaminant pulse is shown schematically in Figure 2.1, superimposed on the normal physical dispersion.

2.3.2 Physical processes

Filtration - the mechanical straining of suspended particles depends upon the size of pore throats relative to the size of the particles. Suspended particles may originate from the soil zone, precipitation from the pore water, microbes, and so on.

Volatilisation - partitioning of volatile substances (e.g. benzene) into the vapour phase reduces the amount of contaminant present as an immiscible liquid or in the aqueous phase, although typically not substantially (Vrba & Zaporozec 1994). The Henry's law constant is the proportionality factor between the partial vapour pressure of a solute above its aqueous solution and its concentration in aqueous solution (Fetter 1993). Substances with higher values of Henry's law constant tend to be more volatile. The water-air partition coefficient is a similar parameter, equal to the ratio of the aqueous solubility of a substance to the saturated vapour concentration of the pure compound. "Those compounds with low water-air partition coefficients, such as the alkanes, favour the vapour phase, whereas those with high water-air partition coefficients, such as benzene, favour the aqueous phase" (Fetter 1993).

Gas transport - gases that form when contaminants decay (e.g. nitrogen, carbon dioxide) or volatilise can travel by diffusion, and may leave the system by diffusion across the subsurface/atmosphere interface. Gases may also be transported by advection if a density gradient is present (Hughes Conant et al. 1996), or if there are pressure gradients within the aquifer. Aquifers tend to 'de-gas' when regions of low atmospheric pressure ('depressions') pass over. Variations in the level of the water table may lead to pumping of the air in the unsaturated zone.
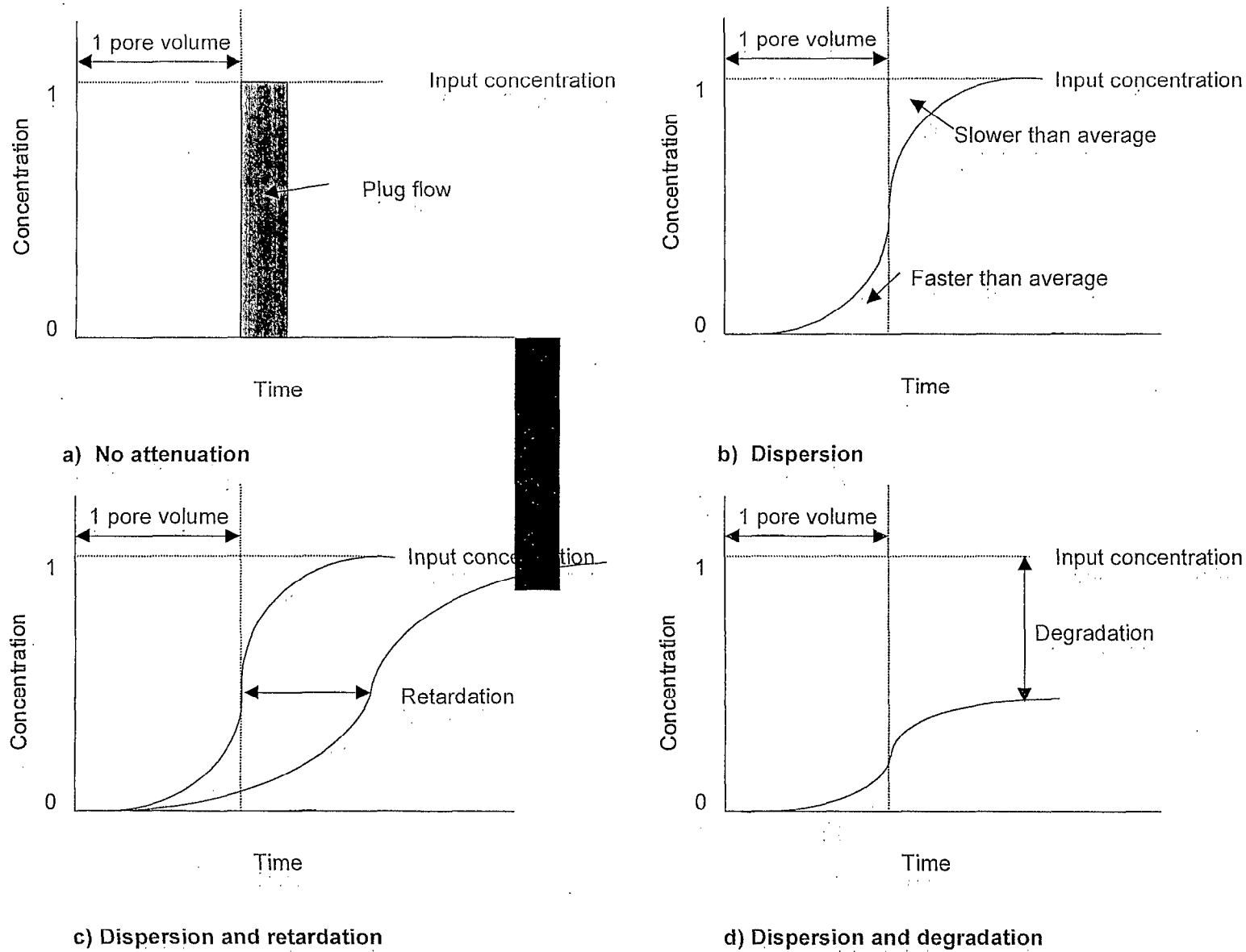
a) No attenuation

b) Dispersion

c) Dispersion and retardation

d) Dispersion and degradation

Figure 2.1 Schematic diagrams of impact of attenuation processes on a contaminant pulse

2.3.3 Geochemical processes

Sorption-desorption - the term sorption encompasses various processes by which solutes are removed from solution by interactions with solid matter (e.g. the soil/rock through which the water is flowing). Adsorption is the attachment of a solute to a solid surface, whereas absorption is the movement of a solute into the structure of a porous particle where it sorbs onto an internal surface. The term 'sorption' is often used to cover both adsorption and absorption. If the solute replaces a previously sorbed ion, the process is termed ion exchange. Sorption reactions generally result from electrostatic forces; if the solute becomes chemically bonded to a solid, the process is termed chemisorption.

The term 'partitioning' describes the process by which a solute becomes distributed between two or more phases, such the solid and dissolved or gaseous phases. The extent to which sorption removes solutes from solution depends on a number of factors:

- the nature of the solute - some substances, such as the chloride ion, do not tend to undergo sorption, while other contaminants, such as heavy metals, tend to be strongly sorbed.

- the concentration of the solute- the greater the amount in solution, the greater the quantity sorbed, although normally the proportion of sorbed decreases with increasing solute concentration. The relationship between the amount sorbed and the concentration in solution is called the 'adsorption isotherm'.

- the nature and concentration of other solutes - there may be competition for suitable sorption sites, or the presence of other solutes may produce a synergistic effect which increases the amount of sorption.

- the nature of the soil/rock matrix - there are a finite number of sites available for sorption, and different substances sorb to different types of site. In general, the sorption capacity of a substance is higher the larger the specific surface area (controlled by grain size) and the greater the proportion of clay minerals, organic matter and oxyhydroxides. Organic matter and iron/manganese oxyhydroxides are commonly present as coatings upon the surfaces of larger particles such as quartz.

- the subsurface environmental conditions - pH and redox potential (Eh) significantly influence the extent of sorption. For example, many heavy metals are more soluble at lower pH, so a smaller proportion will be sorbed in lower pH environments. However, this is not the case for metals present as oxyanions, such as chromate, arsenate, selenate etc (Figure 2.2).

- the flow rate of the water - the more time the water spends in contact with the matrix, the more likely it is that equilibrium partitioning will be attained.

The sorption behaviour of a particular substance with regards to a certain sorbent can be described in a quantitative manner by its distribution coefficient, K_d. This term describes the equilibrium partitioning behaviour, and is generally measured in the laboratory. The methods used to evaluate K_d are described in Fetter (1993). Values of K_d are specific to particular solute/sorbent systems, and to other conditions such as temperature, pH and solute concentration; published values should therefore be used with caution. K_d is defined by the equation:

		pH							
		3	4	5	6	7	8	9	
Oxides	Cations	▨	▨	▨	▨	▨	▨	▨	Hg^{2-}, Pb^{2+}
			▨	▨	▨	▨	▨	▨	Cu^{2+}
				▨	▨	▨	▨	▨	Zn^{2+}, Co^{2+}
					▨	▨	▨	▨	Cd^{2+}
						▨	▨	▨	Mn^{2+}
							▨	▨	Ca^{2+}, Mg^{2+}
	Anions	▨	▨	▨	▨				AsO_4^{3-}
				▨	▨	▨	▨		AsO_3^{3-}, SeO_4^{3-}, CrO_4^{2-}, PO_4^{3-}
Organic Matter	Cations	▨	▨	▨	▨	▨	▨	▨	Hg^{2+}, Pb^{2+}, Al^{3+}
			▨	▨	▨	▨	▨	▨	Cu^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}
				▨	▨	▨	▨	▨	Ca^{2+}, Mg^{2+}
	Anions	No variation							
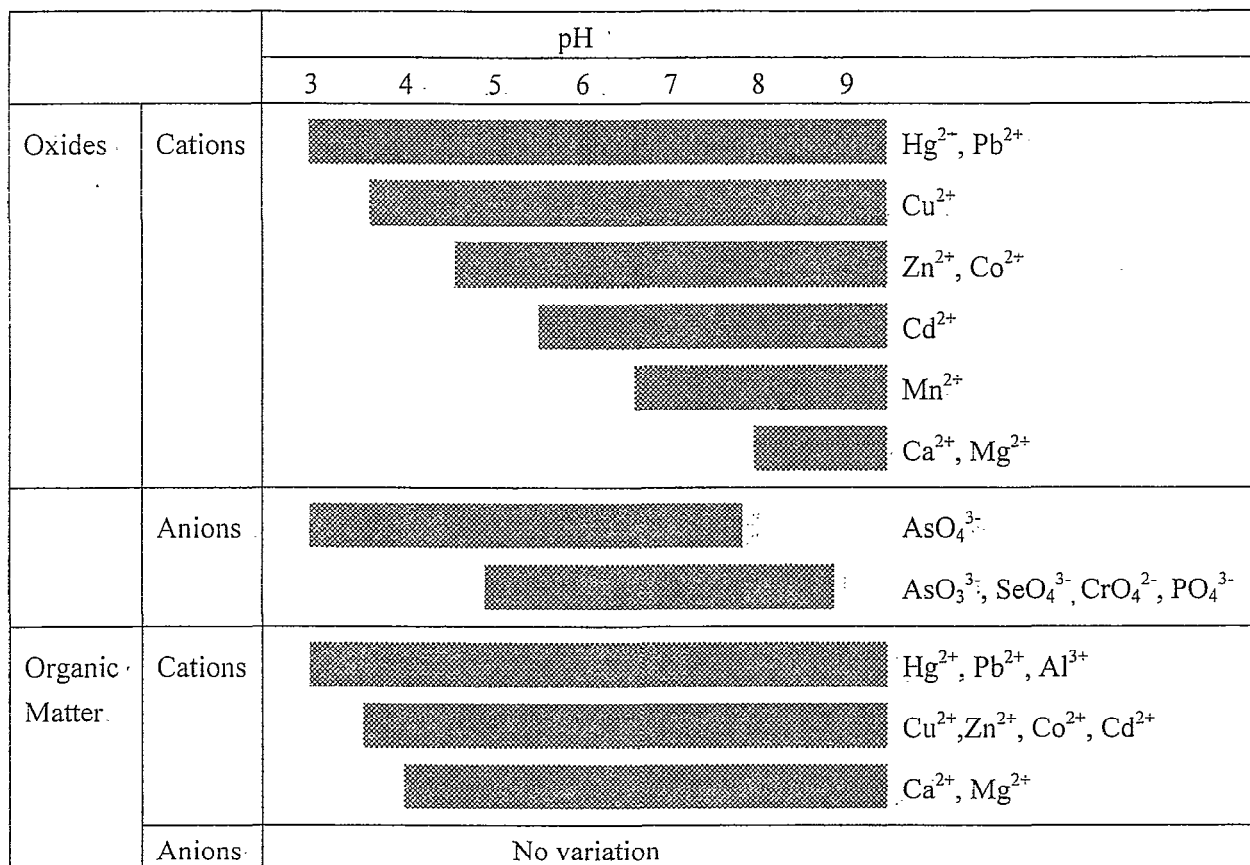
igure 2.2   pH at which metal ion sorption on oxides and natural organic matter is
significant

$$K_d = C_a / C_s$$

where C_a is the concentration in the aqueous phase and C_s is the concentration in the solid phase. This corresponds to the linear part of the Langmuir isotherm (Figure 2.3). Experimental data which do not correspond to this linear relationship may fit the empirical relationship:

$$C_s = K_d \times (C_a)^{1/n}$$

where n is a constant generally >1. This is the Freundlich isotherm.

The organic content of natural sorbents is primarily responsible for the sorption of hydrophobic organic compounds where the organic content exceeds 0.1% (Schwarzenbach and Westall 1985). For such compounds K_d can therefore be expressed in terms of the organic carbon content f_{oc} (as fraction of organic carbon) and an organic carbon partition coefficient K_{oc} where

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

Values of K_d can be derived from reference partition coefficients, such as the n-octanol/water coefficient K_{ow}, using the relationship in the form

$$\text{Log } K_d = \log f_{oc} + \log K_{oc} = \log f_{oc} + a \log K_{ow} + b$$
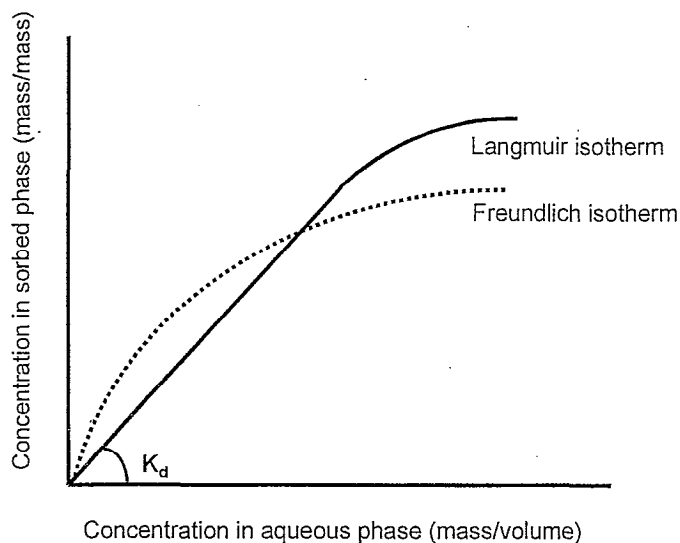
Figure 2.3 Schematic sorption isotherms

where the parameters a and b are determined by the type of compound being sorbed. Values of a and b for some pesticides and other organic compounds are tabulated in Schwarzenbach and Westall (1985).

Sorption processes can be reversible; desorption typically occurs as a response to changing environmental conditions. For example, if water with a low concentration of contaminant flowed through an area of the subsurface which contained much sorbed contaminant, disequilibrium would be created and desorption would take place until equilibrium partitioning was attained again. Thus, contaminants may desorb and re-enter the mobile phase. Reversible sorption therefore retards the transport of the contaminant rather than removing it permanently from the subsurface.

The cation exchange capacity (CEC) of a soil can be used to estimate the importance of ion exchange processes. It is a measure of the soils negative charge density and determines the extent of cation sorption due to electrostatic forces. Greater proportions of organic matter and clay minerals in a soil result in a larger CEC as they have large negative charges (Smith 1996).

Colloidal sorption - in general, the sorption of a contaminant to a solid makes it immobile, and therefore reduces the amount of contaminant in the mobile phase. However, in some systems colloids (very small particles of solid matter, typically less than 2 μm in diameter) are transported in suspension in the moving water. Contaminants that have sorbed onto colloids remain mobile, and so may be transported into the aquifer. Mass transport equations do not always account for this process, so they may overestimate retardation. Colloidal particles may be organic or inorganic; for example, macromolecular components of dissolved organic compounds (DOC), mineral precipitates, and rock/mineral fragments (McCarthy & Zachara 1989). The stability, mobility and reactivity of inorganic colloids depends on factors such as the mineralogy of the subsurface, the pH and ionic strength of the solution, and the nature of sorbates which attach to them (Puls & Powell 1992). Colloids may be immobilised by processes such as filtration or adsorption.

Solution-precipitation - contaminants may precipitate out of solution as solids if the water passes through zones of different physicochemical conditions, e.g. from oxidising to reducing conditions. If the subsurface environment changed again these solids may be dissolved once more, remobilising the contaminant.

Some contaminants can be removed from solution by co-precipitation, i.e. they are incorporated into the structure of a precipitate. For example, when calcite precipitates in the presence of zinc or copper, they may be substituted for calcium in the mineral lattice. Replacement is a similar process whereby a contaminant may be substituted into the structure of a mineral which has already precipitated. Precipitation reactions are only likely to be important for some major ions and are unlikely to be significant for trace metals present in soils as a result of application of sludge or slurries.

Oxidation-reduction (redox) reactions - the redox conditions in the subsurface are commonly spatially variable, for example, biological activity consumes oxygen, so suboxic or anoxic conditions may prevail at depth in aquifers. However, the unsaturated zone is usually oxic. Anaerobic conditions can occur beneath landfill sites or other situations where large amounts of organic substances are present as the presence of organic compounds encourage biological activity.

"Oxidation-reduction reactions involve elements that can exist in more than one valence state" (Fetter 1993). Different forms (species) of such elements are stable in different Eh-pH ranges, which can be determined experimentally or from thermodynamic principles. Figure 2.4 shows the various species of uranium present in aqueous solution depending on Eh and pH. However, microbiological conditions as well as physicochemical ones control the stability of some species because microbes utilise redox reactions to generate energy (see later section). The presence of other solutes can also influence the compounds which are formed under certain Eh-pH conditions. Redox changes can also lead to important changes in the solubility of some redox-sensitive trace metals particularly As, Se and Cr which all form anionic complexes which are stable at the near neutral pHs typical of groundwaters.

Complexation - metal ions in aqueous solution often do not exist as isolated entities but as complexes. A complex is an ion that is a combination of cations with anions or molecules. The anions or molecules are known as ligands. For example, water molecules may be chemically bound to metal cations; the cation is then termed hydrated. These associations increase the stability of the entities involved. If a ligand has more than one site for bonding with a cation then it is termed a chelating agent. Chelating agents may be naturally occurring in the subsurface (e.g. humic and fulvic acids in soils) or anthropogenic compounds.

Complexation of metal ions with anions or organic matter can result in increased mobility if the complex is soluble (Fetter 1993). Interaction (sorption/complexation) with colloidal materials has also been implicated in the transportation of metals. For example, Ledin et al. (1997) stated that "bacteria may ... affect the mobility and distribution of metals in natural soil environments". Their experiments showed that zinc and strontium, at concentrations representative of those found in nature, were adsorbed by a common soil bacterium, *Pseudomonas putida* (Ledin et al. 1997). These findings confirm those of previous studies reviewed by Ledin et al. (1997) which document metal accumulation by bacteria. Metals may therefore be transported by a colloidal phase in some circumstances, in which case filtration is relevant as an immobilisation mechanism.
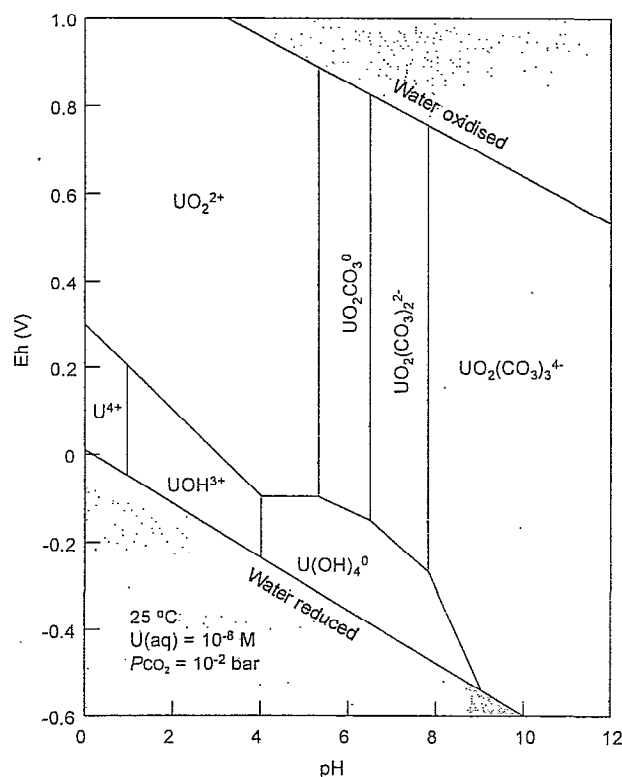
Figure 2.4 Eh-pH diagram for aqueous species for the U-O₂-CO₂-H₂O system in pure water (simplified from Langmuir 1997)

Cadmium mobility

Cadmium (Cd) occurs in aqueous solution as Cd^{2+} (Fetter 1993) and also undergoes sorption and complexation, although Lamy *et al.* (1993) suggest that cadmium is one of the most mobile trace metal in soils. The laboratory experiments performed by Allen *et al.* (1995) showed that values of the partition coefficient K_d increase significantly with increasing pH (over 3 orders of magnitude). The results of Allen *et al.* (1995) also demonstrate the importance of soil composition on pH; at pH 6, K_d values for a series of soils ranged from about 20 to about 1500 ml/g. K_ds were typically larger for soils with higher proportions of clay and/or organic matter.

Cadmium interacts with organic matter; Dunnivant *et al.* (1992) found that increasing the concentration of dissolved organic carbon (DOC) produced an increase in cadmium mobility. Although Dunnivant *et al.* (1992) point out that the concentrations of DOC used in their experiments were typical of landfill leachate, considerably higher than in nature, they state that "even low concentrations of mobile DOC could significantly increase the transport [of cadmium] in groundwater systems".

Hamer *et al.* (1994) found that cadmium can be incorporated into the structure of calcite by solid-phase recrystallisation in zones of calcite dissolution. This process is initiated by sorption of the cadmium onto the calcite, followed by diffusion of the Cd into a surface layer, and finally recrystallisation. Other metals can also fit into the structure of calcite, for example uranium (UO_2^{2+}). These metals are released if the calcite is dissolved.

Acid-base reactions - involve the transfer of protons, and therefore affect the pH of the solution. For example, acids accidentally introduced into the subsurface may be neutralised by reaction with carbonate minerals in the subsurface, such as calcite. This reaction would reduce the impact of the contamination.

Significant processes controlling metal mobility - The mobility of metals in soils is controlled by the rate of water flow and the magnitude of the solid/solution partition coefficient. It is generally restricted by cation exchange and sorption onto soil particles (Fetter 1993). Metals tend to sorb by forming complexes with functional groups of solid surfaces such as iron oxides; a mechanism termed surface complexation. Metals may undergo precipitation (and thus immobilisation) if a mineral is stable in the prevailing conditions (e.g. Eh and pH). However, heavy metals (e.g. Hg, Cd, Zn, Cu) are typically present in such low concentrations that precipitation is inhibited (Schuster 1991) although coprecipitation with other major elements may occur. In general, "conditions that promote mobility include an acidic, sandy soil with low organic and clay content" (Fetter 1993).

Mercury mobility

Mercury (Hg) is not very mobile in the environment due to its strong affinity with soil constituents and the low solubility of its inorganic forms (Fetter 1993; Schuster 1991). The behaviour of mercury in soils has been reviewed by Schuster (1991), whose conclusions are summarised here along with those of some recent studies. Complexation of mercury with OH⁻, Cl⁻, and organic matter is the main control upon mobility as complexation can induce sorption or desorption of Hg (Schuster 1991). The extent of sorption is also determined by pH; Yin et al. (1996) reported that "at low pH [around pH 3], Hg(II) was extensively adsorbed by all [15] soils".

Schuster (1991) reports that complexation with OH⁻ increases the solubility, and thus the mobility, of mercury (Schuster 1991). The presence of chloride can significantly decrease the adsorption of mercury due to the formation of soluble complexes, but only under certain conditions. Yin et al. (1996) found that when the pH value was equal to or greater than pH 6.5, an increase in the concentration of chloride did not significantly affect mercury mobility as under these conditions Hg-Cl complexation formation is negligible. At pH<6.5, the effect of Cl⁻ depended upon the organic matter content of the soil; Cl⁻ only caused a significant decrease in mercury sorption in soils with little organic matter (Yin et al. 1996). When the soil contained larger amount of organic matter, the dominant control of mercury mobility was complexation with dissolved organic matter (Yin et al. 1996).

Mercury can form complexes with both dissolved and solid organic matter. The partitioning of organic matter between aqueous and solid phases is pH-dependent, with a greater proportion dissolved at higher pH (Yin et al. 1996). The extent to which complexation with dissolved organic matter will increase the mobility of mercury in a soil is therefore controlled by the organic matter content and pH of the soil (Yin et al. 1996).

In acidic soils (pH<5), mercury will be sorbed by soil organic matter, while sorption in higher pH soils is dominated by clay minerals and iron oxides (Schuster 1991). "Generally, the strong binding [of Hg to soil organic matter] results in a low availability and mobility of Hg in the soil" (Schuster 1991).

Mobility of anions in soils

Anion mobility is controlled by precipitation, sorption and complexation reactions, which are highly pH dependent (McBride 1994).

Anions such as borate and phosphate are considered to sorb in soils principally as inner sphere complexes. This tends to mean that they are not significantly affected by changes in pH. Phosphate, however, bonds so strongly on soil minerals that it can be considered as immobile. It reacts with adsorbed H^+, Al^{3+} and other soil components to change surface charge or to form insoluble precipitates. For example, phosphate is absorbed at selected sites on calcite which then nucleates as a calcium phosphate solid at the surface. This sorption is non-reversible with the result that phosphate migration through mineral soils to groundwater is rarely detected.

Arsenic has similar chemical behaviour to phosphate, arsenate is chemisorbed by Al and Fe oxides, non-crystalline aluminosilicates and silicate clays. It sorbs most effectively at low pH and consequently its mobility is low in acid soils. In neutral to alkaline soils, particularly those which are sodic, it may be mobile as soluble sodium arsenate. Arsenite sorption is however most effective in the range pH 7-9.

Boron is rated as quite a mobile element. At high pH the borate anion is formed which can be sorbed onto Al and Fe oxides and silicate minerals. In some soils under acid conditions a large fraction of the total boron is water extractable.

Fluorine occurs exclusively as the fluoride anion, F^-, in soils where it complexes strongly with metals such as Al^{3+} and Fe^{3+} (McBride 1994). The ion also chemisorbs strongly on clays and oxides by ligand exchange of surface OH^-. Fluoride is significantly protonated at less than pH 3.2 and maximum sorption takes place at pH 3-5. It has particular affinity for Al^{3+} and forms soluble complexes which give high fluoride mobility in acid soils. In calcareous soils fluoride mobility is low being limited by incorporation into insoluble Ca minerals, such as hydroxyapatite, whereas in sodic soils fluoride mobility is enhanced by the high solubility of NaF.

Cyanide occurs mainly as iron cyanide complexes in soils. Meeusen et al. (1994) found that at pH of 7.5 or greater cyanide is mobile and high concentrations were found in groundwater. Even at pH 4 precipitation was not great enough to prevent Dutch soil standards from being exceeded.

Chemical degradation of organic compounds - Chemical degradation occurs as a result of reactive agents in the environment, most commonly water and oxygen. Molecular oxygen and its more reactive forms, such as ozone and peroxides, are capable of reacting with many compounds to generate oxidation products. In all but the most oxygen-poor environments, oxidative transformations of organic compounds are frequently the most common degradative pathways observed.

Hydrolysis is a chemical transformation process in which a chemical reacts with water. For organic compounds the reaction results in the introduction of a hydroxyl group (-OH) into the compound, with consequent further transformations and toxicity changes (Bedient et al. 1994).

Not all functional groups of organic compounds are susceptible to hydrolysis, but for pesticides hydrolysis is a primary route, for example in the degradation of phosphate ester pesticides such as parathion (Coats 1991).

Photodegradation- Photochemical transformations can result in the degradation of organic micropollutants at the soil surface either directly, where the organic compound forms the absorbing chromophore and is transformed, or indirectly where it acts a sensitiser resulting in the release of free radicals. These radicals in turn react with other organic species. Some otherwise quite persistent chemicals, such as chlorinated solvents, are quite readily degraded in sunlight. The energy available from photochemical absorption is relatively high and can be comparable to chemical bond energies, so the rate of photochemical reactions can be high.

2.3.4 Biochemical processes

Biodegradation - substances can be broken down by reactions that are catalysed by microbes. These reactions generate energy for the organisms involved. The products of these reactions (metabolites) may be as harmful as the original contaminant, or more so. However, the metabolites may also be biodegradable.

Organic compounds may be degraded by many different mechanisms. Many different microorganisms can play a role. These include bacteria, fungi and actinomycetes. The three major mechanisms of biological degradation are:

- Catabolism or direct oxidation where the molecule is utilised as a nutrient or energy source
- Co-metabolism where utilisation is coincidental to normal metabolic functions
- By enzymatic action where microorganisms have secreted enzymes into the soil, such as phosphatases and amidases, which may persist long after the parent cells are dead.

Many compounds undergo a series of biochemical transformations which eventually result in the complete removal of the compound. Most of these processes involve some increased degree of water solubility. Microbial degradation rates are strongly dependent on environmental conditions such as temperature and, in the unsaturated zone, the quantity of water as well as the microbial ecology. The rates are often limited by availability of essential nutrients, such as phosphorus, of readily degradable carbon compounds to support the microbial population or electron acceptors.

For most compounds, aerobic degradation is more rapid than anaerobic degradation and the rate for many compounds is decreased by several orders of magnitude in the absence of oxygen. For example, Eganhouse et al. (1996) found that almost all monoaromatic hydrocarbons persisted in the anoxic zone close to a hydrocarbon spill. Aromatic hydrocarbons were also more persistent than alkanes in the anaerobic environment. However, degradation of more persistent compounds such as chlorinated hydrocarbons and PCBs can be more rapid under anaerobic conditions due to the importance of reductive dechlorination (Suflita and Sewell 1991).

In aerobic degradation, oxygen is not only used as the terminal electron acceptor for microbial respiration but also acts as a reactant in the initial breakdown step. Once oxygen

has been consumed a sequence of other electron acceptors such as nitrate, sulphate or carbon dioxide may support degradation.

The degradability of a compound is usually expressed in terms of its half-life (t⌐7), the time in which the concentration is reduced to half its original value under a given set of conditions. It is assumed that the concentration will fall exponentially (Figure 2.5). The rate of transformation is dependent on a variety of factors, including the physicochemical properties of the compound. Information on persistence in aquifers for a range of organic compounds is contained in Ghiorse and Wilson (1988). Development of an idea for the prediction of pollutant biodegradability from chemical structure is found in Mani et al. (1991).
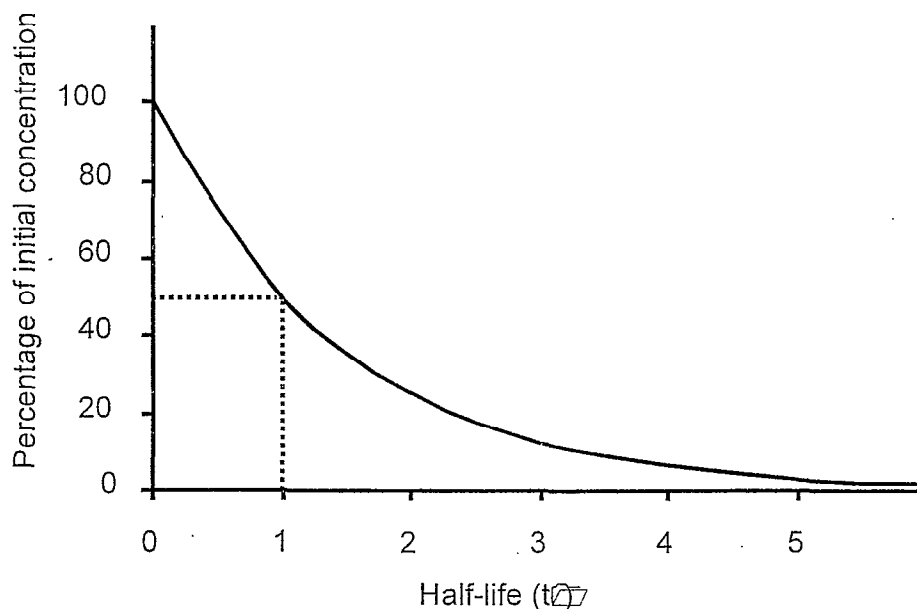
Figure 2.5 Schematic degradation curve

Biodegradation of chlorinated compounds

In contrast to the biodegradation of petroleum hydrocarbons, evidence suggests that only a few chlorinated compounds can be used as growth substrates (RTDF 1997). In aerobic environments compounds are co-metabolised by non-specific microbial oxygenase enzymes. Aerobic co-metabolic biodegradation generally proceeds via an unstable epoxide intermediate that spontaneously decomposes to carbon dioxide, chloride, water and organic by-products such as acetate.

In anaerobic environments compounds act as electron acceptors in a process called reductive dechlorination. Other carbon substrates are required to act as electron donors. Anaerobic biodegradation via sequential dechlorination of the parent proceeds to such products as ethene, ethane and methane. For example, the anaerobic dechlorination of PCE proceeds via TCE, cis1-2,DCE, and vinyl chloride to ethene and ethane. Each successive step in the dechlorination process is theoretically slower than the preceding step and at some sites, biodegradation may not proceed to completion. As a result intermediate compounds may accumulate. It is now known that vinyl chloride can be biodegraded under almost all subsurface conditions.

Biodegradation of petroleum hydrocarbons

Petroleum is an extremely complex mixture of hydrocarbons that degrade at different rates. Within the saturated hydrocarbon fraction (i.e. those compounds which do not contain double bonds), the n-alkanes are normally considered the most readily degraded components and biodegradation of alkanes up to n-C_{44} has been demonstrated (Atlas 1981). This normally proceeds via terminal attack to form a primary alcohol that is further oxidised to shorter chain fatty acids. These acids may then accumulate in the environment.

The highly branched isoprenoid alkanes, such as pristane, undergo oxidation with the formation of dicarboxylic acids. Methyl branching generally increases the resistance to attack. Cycloalkanes are particularly resistant to attack with the complex alicyclics, such as the hopanes, being among the most persistent components of petroleum spillages.

The bacterial degradation of aromatic hydrocarbons normally involves the formation of a diol followed by cleavage and formation of a diacid. Light aromatic hydrocarbons such as benzene, toluene and xylene (BTEX) are subject to degradation in the dissolved state. Liquids are utilised by bacteria at the water interface, whilst solids do not appear to be attacked.

Extensive methyl substitution can inhibit initial oxidation. Degradation rate also varies widely between different isomers of the same compound (Eganhouse 1996). Condensed ring aromatic structures, such as the polyaromatic hydrocarbons (PAH) are relatively resistant to attack and persistence increases with complexity, naphthalene being 1000 times more rapidly degraded than the benzopyrenes (Atlas 1981).

The fate of petroleum hydrocarbons is largely determined by abiotic factors that influence the weathering. The physical state has a marked effect. At low concentrations, hydrocarbons are soluble in water but in most spillages the solubility limit is exceeded. In soils plant materials and soil particles sorb the hydrocarbons and spreading is limited.

There has also been considerable interest in degradation of petroleum hydrocarbons under anoxic conditions (Baedecker et al. 1993; Barbaro et al. 1992) although these conditions are unlikely to be prevalent in the unsaturated zone.

Higgo et al. (1996) demonstrated the difficulty of predicting compound degradation in any given situation, given the variability in groundwater chemistry and sorption as well as biological transformation. Pothuluri et al. (1990) showed the great variability in pesticide degradation rate from the soil, through the unsaturated zone to the water table.

Biotransformation – biologically-mediated reactions may cause changes between species which are relevant to groundwater quality. For example, the speciation of nitrogen changes as a result of redox reactions induced by microbes; nitrate can be reduced to nitrogen gas, with nitrite and nitrous oxide gas forming as intermediates.

Degradation of sheep dip insecticides

Sheep dip insecticides have traditionally been mainly of the organophosphate type, but are being replaced by the synthetic pyrethroids.

Organophosphate insecticides are normally esters, amides or thiol derivatives of phosphorus containing acids. These compounds are chemically reactive and subject to hydrolysis. Biotransformation may be initiated by mixed function oxidases. The reaction products may be more toxic than the parent compounds (Day 1991). For example the biodegradation of parathion:

| Parathion | Diethylthiophosphate | p-nitrophenol |
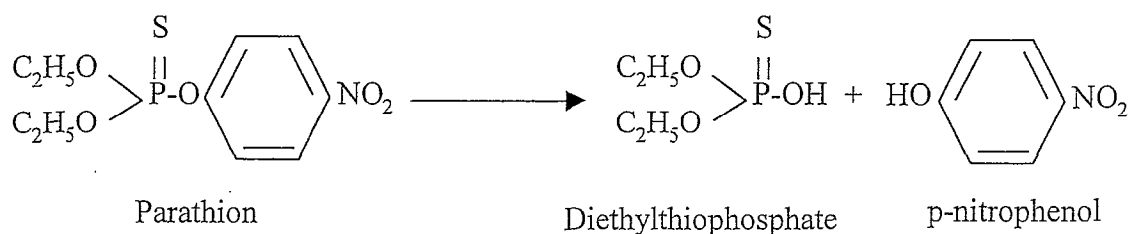
The synthetic pyrethroids are a class of lipophilic insecticides which have lower mammalian toxicity than the organophosphorus compounds but which are highly toxic to fish and aquatic invertebrates. They are degraded mainly by sunlight-initiated isomerisation processes involving the three membered ring but also by hydrolysis of the ester bond to the acid and alcohol moieties and by oxidation. The structure of the cypermethrin molecule is shown below as an example:
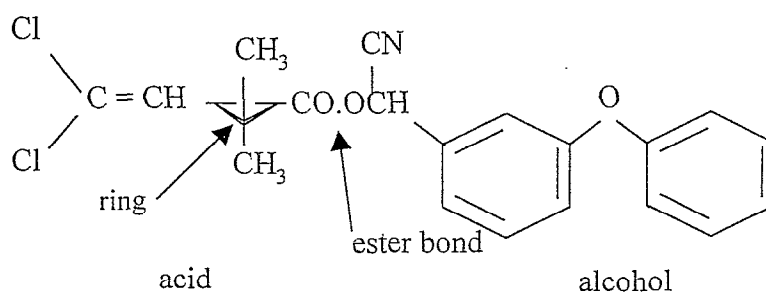
Cypermethrin

There have been several studies on the toxicities of the products of ester hydrolysis to aquatic organisms showing the major degradation products to be considerably more polar than the parent and much less toxic (Day 1991).

Nitrogen transformations

Nitrogen behaviour in the subsurface is controlled by a series of biologically mediated chemical transformations. Nitrogen in farm slurry or sewage sludge is present mainly as organic nitrogen. This is broken down in the soil or unsaturated zone to ammonia or ammonium compounds. Ammonium compounds are sorbed by the matrix and their migration is slow. Ammonium can be taken up and assimilated by plants and some may also be lost to the atmosphere by volatilisation. Under oxidising conditions ammonium is readily oxidised to nitrate. Nitrate is considered to be mobile in the subsurface. Where conditions remain oxic it is also persistent. Once nitrate has migrated beneath the root zone and is no longer available to growing plants the only mechanism for its removal from the subsurface is by transformation to nitrite and thence to nitrogen gas, a process known as denitrification. This reduction takes place in parts of the soil or aquifer where the redox potential is low because oxygen has been depleted, principally by reaction with dissolved organic carbon.
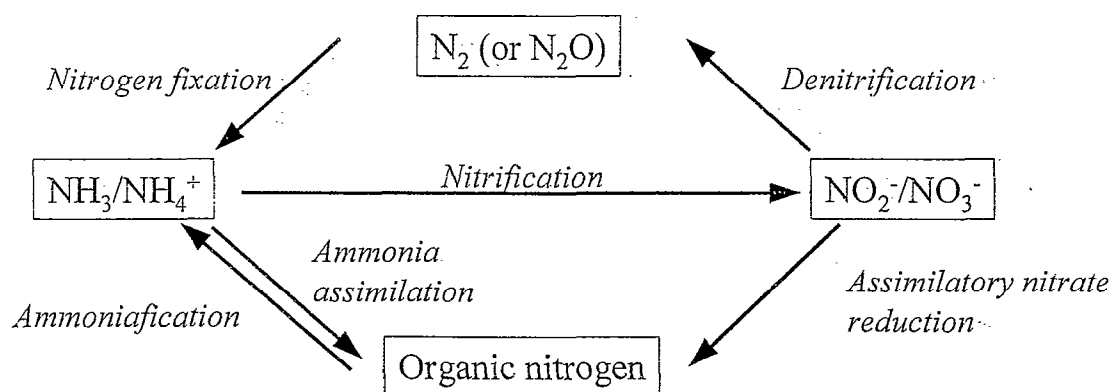
Transformations of nitrogen (after Jaffe 1992)

Diagram labels: N_2 (or N_2O); Nitrogen fixation; Denitrification; NH_3/NH_4^+; Nitrification; NO_2^-/NO_3^-; Ammonia assimilation; Ammoniafication; Assimilatory nitrate reduction; Organic nitrogen

2.3.5 Remobilisation

Contaminants present in the soil or the subsurface in an immobile form have the potential to be remobilised by a change in environmental conditions. Changes in pH or redox potential are likely to be the most significant. For example Alloway and Jackson (1991) point out that acidification of the soil as a result of acid rain from air pollution could remobilize metals which are retained in the soil.

Also in this category are processes involving dissolution of the source term, for example of petroleum hydrocarbons NAPL. The immiscible phase may be physically trapped in the unsaturated zone but act as a source of dissolved phase hydrocarbons to infiltrating water.

Metal leaching from sewage sludge

Smith (1996) has reviewed the environmental issues relating to the landspreading of sewage sludge in detail. The spreading of sewage sludge onto land can be very beneficial in terms of nutrient addition and soil condition, but can also introduce high levels of 'potentially toxic elements' (PTEs), such as heavy metals (Smith 1996). Values of mean concentrations of metals in sewage sludges spread upon agricultural land in 1990/91 are shown below. Further data regarding landspreading of sewage sludge are provided in the UK Sewage Sludge Survey (CESL1993).

The concentrations of metals in sewage sludge have declined over the past 30 years, and are predicted fall to lower levels still, although there will always be inputs from sources such as pipe corrosion (Smith 1996). The addition of PTEs to agricultural soils is controlled by the Sludge (Use in Agriculture) Regulations 1989, which sets out maximum acceptable levels of PTEs in the soil (not in the sludge).

The mobility of metals in sewage sludge-amended soils is determined by the same controls that affect metal transport in other soils, e.g. pH and organic matter content (Smith 1996). Sewage sludge is organic matter rich. The additional organic matter is relatively small in comparison to the native soil organic matter, but not when added repeatedly over many years. However, studies have shown that sewage sludge spreading does significantly increase the adsorption capacity of soils, and "in general, the presence of PTEs in sludge-treated soil is confined to the cultivation zone with very little movement below that depth" (Smith 1996). On the other hand, Lamy *et al.* (1993) found that in the pH range 5 to 7, soluble organic matter from liquid sewage sludge reduced cadmium sorption due to the formation of soluble complexes. This could be a mechanism for the transport of PTEs through soils.

Mean concentrations of potentially toxic elements in sewage sludge spread on agricultural land in 1990/91

Element	Mean concentration (mg/kg dry solids)
Zinc	903
Copper	552
Nickel	68
Cadmium	4.9
Lead	263
Mercury	3.5
Chromium	218
Molybdenum	8.4
Selenium	1.5
Arsenic	4.1
Fluoride	204

(from CESL 1993)

> **Metal leaching from sewage sludge continued**
>
> From his review of the literature, Smith (1996) concluded "environmental effects arising due to metal leaching from sludge-treated agricultural soils are unlikely". Smith (1996) did not find any reports of significant increases in levels of PTEs in groundwaters as a result of sewage sludge application to agricultural land. Nevertheless, McBride *et al.* (1997) report that several studies, including their own, have found that "large fractions of sludge-borne heavy metals cannot be accounted for several years after land application". Although there is no proven explanation for this observation, McBride *et al.* (1997) suggest that the discrepancy could result from the way in which metal migration is measured by analysing the concentration of extractable metals in the subsoil.
>
> A lack of increase in metals in the subsoil due to sludge application does not necessarily mean that metals are not being transported in solution; preferential flow through cracks, root channels and burrows could result in transportation of dissolved metals (McBride *et al.* 1997). Perhaps more important is the question of what happens to PTEs bound to the sludge organic matter when the organic matter oxidises, as it is likely to do over a period of years following application

2.4 Key processes and contaminant data requirements

2.4.1 Key processes

When considering List I substances it is apparent that if a rigorous conclusion is required all processes which delay the arrival of a contaminant but do not remove it from infiltrating water must be excluded from consideration. Degradation and sorption processes in the soil may be adequately effective but no unsaturated zone processes other than degradation can therefore be relied upon to prevent contaminant arrival at the water table. Unsaturated zone half-life for the contaminant and travel time to the water table are the essential data requirements.

When considering List II substances the decision process must be more complex since retardation and dilution may serve to reduce contaminant concentrations to below those considered to be acceptable. More information on the attenuating capacity of the unsaturated zone will be required, in terms of both physical properties and chemical properties such as organic carbon content. Jury et al. (1987) describe such an evaluation for a range of pesticides commonly used in the USA and Wilson et al. (1996) for organic contaminants in sewage sludges applied to agricultural soils. Data requirements for the soil and unsaturated zone are considered further in Chapter 4.

2.4.2 Contaminant data requirements

Significant attenuation processes for various classes of contaminant are summarised in Table 2.1. Information on the physical properties of contaminants can be found in a number of sources (for example in the on-line Aster Toxicity Index) and on environmental degradation

rates in compilations such as Howard et al. (1991). Examples of sorption coefficients and half-life data in soils and aquifers for selected pesticides and hydrocarbons are shown in Tables 2.2 and 2.3.

Table 2.1 Dominant attenuation processes for various types of contaminant

Contaminant type	Examples	Dominant attenuation process	Significant factors involved
Major inorganics	Ca, Mg, Si	Precipitation	Solubility
		Cation exchange	Clay/organic content
	Cl	None	
Heavy metals – cationic	Hg, Cd, Zn	Sorption to oxides	High pH
		Binding to natural organics	pH, metal loading
Heavy metals – anionic	CrO_4, SO_4, AsO_4, AsO_3	Sorption to oxides	Low pH
Anions	PO_4, BO_3	Precipitation	pH
		Sorption to oxides	Solubility
	NO_3	Biotransformation	Redox
Gases	Organic vapour	Sorption	Hydrophobic K_d
	Methane	Dispersion	Aquifer characteristics
		Diffusion	Unsaturated zone porosity
Trace organics	Pesticides, PAH	Sorption	Hydrophobic K_d
		Degradation,	Half life
		Preferential flow	Aquifer characteristics
Hydrocarbons	Trichloroethene	Volatilisation	Henry's Law Constant
	Tetrachloroethene	Sorption	Hydrophobic K_d
	Benzene	Vapour diffusion	Unsaturated zone porosity
		Biodegradation of aqueous phase	Half life, redox potential

Table 2.2 Examples of sorption coefficients, Henry's Law constants and half-life data for commonly used classes of pesticide

Pesticide type	Example	Log K_{oc}	Log K_{ow}	K_H (atm.m^3/mol)	$t_{1/2}$ (soil) (days)	$t_{1/2}$ (aquifer) (days)
Chlorinated	Lindane	2.81-3.52	2.8	1.22×10^{-4}	14-266	6-240
Organophosphate	Malathion	3.25	2.36		1-7	5-100
	Diazinon	1.92	3.02		3-30	
Pyrethroid	Cypermethrin		6.6		50	
	Fenvalerate		3.08		75-80	
Triazine	Simazine	2.14		1.39×10^{-6}	75	
Phenyl urea	Isoproturon		2.24		20-50	4,200
	Diuron	2.57	2.81	2.21×10^{-6}	320	
Phenoxyacid	Mecoprop				10-20	>60, 200
	2,4-D	1.3	2.64	0.254	<7	800
Cationic	Paraquat	4.3	-		>2000	

Aquifer half-life estimated under aerobic conditions unless otherwise specified

Data from Agertved et al. (1992), Cavalier et al. (1991), Chilton et al. (1995), Chapman and Cole (1982), Guth et al. (1976), Heron and Christensen (1992), Jury et al. (1987), Howard et al. (1991), Montgomery and Welkom (1990)

Table 2.3 Examples of sorption coefficients, Henry's Law constants and half-life data for selected classes of hydrocarbons

Compound type	Example	Log K_{oc}	Log K_{ow}	K_H (atm.m^3/mol)	$T_{1/2}$ (soil) (days)	$T_{1/2}$ (aquifer) (days)
Chlorinated solvents	Tetrachloroethene	2.5-2.6	2.10-2.88	2.87×10^{-3}	180-360	360-700
	Trichloroethene	1.81-2.1	2.29-3.3	1.17×10^{-3}	180-360	320-1600
PCB	Arachlor 1221	2.44	2.8	3.24×10^{-4}		
Petroleum compounds	MTBE		0.94-1.30	4.5×10^{-4}	30-180	>180
	Benzene	1.69-2.00	1.56-2.13	5.48×10^{-3}	5-16	10oxic->800 anoxic
	Xylenes	2.11	2.77-3.16	5×10^{-3}	7-30	14oxic-360anoxic
	Fluoranthene	4.62	5.22	0.0169	140-440	280-1000
Diesel	Diesel					200 monoaromatics 500 weathered
Creosote	Phenol	1.3	1.47	2.7×10^{-7}	1-10	7-75
	4-methyl phenol	1.69	1.94	7.92×10^{-7}	0.04-0.7	1-150

Aquifer half-life estimated under aerobic conditions unless otherwise specified

Data from Bregnard et al. (1996), Davis et al. (1994), Howard et al. (1991), Hyett (1994) Montgomery and Welkom (1990), Thierrin et al. (1993), Zoeteman et al. (1981).

3. DESK STUDY INFORMATION SOURCES

3.1 Source Information

A variety of information sources area available which provide guidance towards the assessment of groundwater vulnerability. These may have been designed as decision support tools with specific regard to groundwater resource (groundwater vulnerability maps) or groundwater source vulnerability (source protection zones), or they may be generic information such as that contained in Ordnance Survey maps, geological and soil maps, and land use maps.

Groundwater vulnerability maps - These are available for the whole of England and Wales at a scale of 1: 100 000. They are a synthesis of geological and soil information relevant to the assessment of groundwater resource vulnerability. The geological types are divided into three broad groups based on the saturated aquifer permeability:

- Major Aquifers, which are highly permeable
- Minor Aquifers, which are moderately permeable
- Non-Aquifers, which are weakly permeable.

The soil classes are based on the leaching potential of the soil:

- High potential
- Intermediate potential
- Low potential

Vulnerability is greatest over the more permeable strata, and least over the weakly permeable strata due to the relative transport opportunities for surface pollutants to gain access to the water table. The soil type also influences pollutant movement through its texture or particle size distribution, depth and duration of waterlogging, its material type and depth, and its organic matter content.

Juxtaposition of the soil and geological classes provides three categories of Major Aquifer, three categories of Minor Aquifer, plus Non-Aquifer, for which no soil classes are applied. The presence or otherwise of greater than 5 m thickness of low permeability superficial material (e.g. till or Clay-with-Flints) is depicted on the maps by a grey stipple. Where present, this provides additional protection to the underlying groundwater resource.

Hydrogeological maps - Hydrogeological maps are a synthesis of the available hydrogeological data for selected area (Table 3.1). They provide hydrogeological information on top of the basic geological framework relevant to the unsaturated zone such as:

- type of aquifer - intergranular or fracture dominated transport
- depth to the water table

as well as information on :

- base of aquifer

Table 3.1 Features represented on hydrogeological maps and degree of their interpretation (after Struckmeier and Margat, 1995)

Features / Degree of interpretation	Hydrogeological	Groundwater	Anthropogenic
Basic data (results of measurements and observation)	Location of observation point (x,y,z); characteristics of outcropping strata; depth of top or base of aquifer; characteristics of aquifer.	Location of observation point (x,y,z); depth to groundwater; spring discharge; pH; conductivity; temperature; ion content.	Location of well, borehole, shaft (x,y,z); depth of well; discharge of well; drawdown.
Primary interpreted data (derived from simple treatment and interpolation)	Hydrogeological boundary; height of top or base of aquifer; isohypses (depth lines) and isopachytes (lines of equal thickness) of aquifer.	Equipotential line; groundwater fluctuation; mean spring discharge; boundary of particular aquifers; isobath of groundwater system; isolines of pH, temperature, specific ion contents, isotopes.	Potential of screen relative to datum level (mean sea level); mean well yield; mean abstraction or injection; mean drawdown.
Secondary interpreted data (derived from complex treatment and modelling)	Hydrogeological formation or aquifer parameters, e.g. porosity, permeability, transmissivity; grain size analysis; hydrogeological classification.	Boundaries of phreatic, confined, artesian groundwater; flow directions and velocities, groundwater divides; relation between groundwater system and river; fluxes of groundwater systems (recharge and discharge).	Specific yield; induced recharge; artificial drainage.
Tertiary interpretation for decision making (information)	Accessibility; risk of failure of drilling; possibilities of leakage; protectedness of aquifer.	Groundwater quality, suitability; vulnerability; protection areas.	Expected productivity; mean abstraction per unit area; injection possibilities; pollution.

- location of boreholes, wells, springs, surface water discharges, etc
- hydrometric area boundaries
- groundwater divides
- water quality.

Geological maps - Geological maps are available for much of England and Wales at scales of 1: 50 00 or 1: 63 360. In addition detailed geological mapping at 1: 10 000 scale is available for many areas. The data provided on these maps describes the geometry and lithological nature of both the drift and solid geological units occurring in a given area. They provide supporting evidence to the aquifer vulnerability map and are of particular value to assessing areas where no hydrogeological map is available.

Soil maps - These are available at a variety of scales for England and Wales. About 30% of the area is mapped at 1: 63 360 scale or greater whilst the remainder is available at only 1: 250 000 scale. The data presented in these maps have already been assimilated into the aquifer vulnerability maps but the soil maps provide additional information such as soil depth, clay mineralogy, soil texture and cementation.

Technical literature and borehole information (aquifer properties) - There are a variety of sources of basic local and regional information that are readily available. These include the British Geological Survey National Well Record Archive at Wallingford, the Environment Agency licensed abstraction and well record collection, the aquifer properties archive and CD-ROM (Allen et al., 1998), source protection zonation and supporting information sheets, technical reports and university theses, as well as published reports and papers.

Topographical maps - Available at scales up to 1: 10 000 topographic maps provide confirmation of site slope, proximity to water courses, and help evaluate depth to groundwater table. The maps are available both as hard copy maps and as digital compilations suitable for use in a GIS.

Meteorological information - Long term average rainfall and evaporation data (MORECS), as well as temporal data for gauged sites at monthly or daily intervals are available from the Meteorological Office. These data allow the effective infiltration to be estimated.

Run-off data - Catchment run-off statistics are available in the form of yearbooks and five year statistical compilations from the Institute of Hydrology (e.g. IH, 1998). These listings provide basic information on run-off, water loss (evaporation) and groundwater infiltration based on statistical analysis of hydrograph data on a catchment basis.

Field drains and land use maps - Land use data are compiled and presented in map form for a variety of purposes. These provide information on basic land use. A database of field drains is held for some areas by MAFF as a product of the field drain registration system.

3.2 Limitations of Sources

An important limitation of all mapped information is that of map scale and the resolution of the data the map portrays relative to the site. The broader scale information of a map may not equate to the site conditions due to some small-scale anomaly or some feature overlooked by the mapmakers. Care must, therefore, be maintained in using and interpreting mapped information.

Groundwater vulnerability maps - There are a number of limitations to the use of these maps (Palmer et al, 1995). These stem from data variability, including solid geology, but more particularly the integrity and depth of superficial deposits and the distribution of soil types for which maps are not available at a consistent scale. In addition the vulnerability maps make no allowance for potential by-pass flow, disregard the depth to water table as a key indicator of vulnerability, and make the assumption that permeability in the unsaturated zone is the same as that in the saturated aquifer.

The classes derived from the aquifer category and drift cover are shown in Table 3.2. The portrayal of sequential aquifer systems on these maps varies between regions, but is generally the uppermost solid geological unit which is zoned. It is therefore important that the maps are interpreted in conjunction with the soil and geological information of which they are based. For example, in cases where drift Minor Aquifers overlie solid Major or Minor Aquifers, the solid aquifer is the one represented on the map. If low permeability drift deposits occur between the zoned Major or Minor Aquifer and permeable drift deposit, these are not included in the classification and the vulnerability of the zoned aquifer may be overstated.

Table 3.2 Matrix of vulnerability classes derived from aquifer category and drift cover

Drift Solid	None	Permeable	Low permeability	Permeable over low permeability
Major Aquifer	Major	Major	Major with stipple*	Major[†]
Minor Aquifer	Minor	Minor	Minor with stipple	Minor
Non-aquifer	Non-Aquifer	Minor	Non-Aquifer	Minor
Minor Aquifer over Major Aquifer	Minor	Minor	Minor with stipple	Minor

* Where the low permeability drift contains more than 5 m of clay in parts of North-East Region, the major aquifer becomes Non-Aquifer

[†] Where the low permeability drift contains more than 5 m of clay in parts of North-East and North-West Regions, the Major Aquifer becomes a Minor Aquifer

However, the problem of dealing with the low permeability superficial strata is perhaps most acute. Existing mapping is, in some areas, inadequate to define the thickness and nature of these deposits. Strata mapped as till may range in lithology from clay or sand in a clayey matrix to sand and gravel lenses. Current research is addressing this problem using drift domain mapping, a technique which allows the geological history and provenance of a deposit to dictate its mapped form; however, the results of this work are not currently available for the assessment of site vulnerability.

Hydrogeological maps - Although these are not universally available, nor produced to a common scale they are a valuable source of hydrogeological data. However, the same limitations apply to all mapped data with regard to scale and to local features not presented on the map. These may include occurrence of perched aquifers, for example in superficial strata, local absence of protective till cover etc.

Geological maps - The main limitation is the scale of the map. Much of the data portrayed on these maps is synthesised within the aquifer vulnerability and hydrogeology maps.

Soil maps - The main limitation is the scale of the map. Much of the data portrayed on these maps are synthesised within the aquifer vulnerability and hydrogeology maps.

Technical literature and borehole information (aquifer properties) - Awareness of the data available in databases and in the literature is essential in assessing site vulnerability. However, the diverse sources and lack of indexing of much of these data make enquiry tedious and often unfruitful. However, as digitisation of data holdings progresses, more of the data will become accessible electronically, and GIS applications will become feasible. Coverage of information is patchy and may be project orientated or dependent on demand. Large areas of Central Wales, for example, are devoid of any significant data on borehole dimensions and the nature of the available groundwater. Data on unsuccessful or 'dry' and abandoned boreholes may be unrecorded providing a significantly positively biased data set.

Topographical maps - The basic limitation of scale is common to these data.

Meteorological information - The evaporation data are available as lumped means for $40 \times 40 \text{ km}^2$ areal blocks and data may relate poorly to regional trends across a block or to local or micro-climatic influences. Gauged site information may be remote from the site of interest and care must be taken in applying data remote sites.

Run-off data - There are some reservations with the low flow data quoted in the yearbooks relative to conventional water balance estimates. Nevertheless the data provide a first pass at establishing a catchment figure for run-off and infiltration.

Land use maps - Change in land use may not be recorded. Mapped categories may not be adequate for the purpose of site vulnerability assessment.

4. EXISTING GUIDANCE ON SITE CHARACTERISATION AND SITE MONITORING

This chapter describes existing guidance which can be used in support of decision-making based on the tiered assessments. The aims of the chapter are two-fold: firstly to identify sources of guidance and secondly to describe specific documents which may be of immediate use in the site assessment process. By directing the user to organisations which produce guidance, many of which can be accessed through websites, it is hoped that the user will be able to search for information on specific issues which may not be identified in this report, and will also be able to identify the most up to date guidance available. The documents described in this section mainly relate to frameworks for assessing sites or designing monitoring networks. These "codes of practice" give useful overviews of assessment process and may act as leads to guidance on particular technical issues.

4.1 Contaminated Land Research Reports (CLR)

A series of Contaminated Land Research Reports has been prepared for the Department of Environment which provides guidance on assessment, sampling and characterisation of contaminated land. **CLR Report No.1 "A framework for assessing the impact of contaminated land on groundwater and surface water"** provides a methodology for assessing the threat to water posed by contaminated land sites. The procedures outlined in the report describe both an initial qualitative assessment and a more detailed quantitative methodology. The report provides 11 guidance sheets relating to different aspects of the assessment, including nature of contaminant, rainfall/infiltration/runoff, soils, drift geology, hydrogeology and attenuation processes. Each guidance sheet consists of a description of why that factor is important, a checklist of data sources for that factor, and a flow diagram indicating the different elements to be considered, and their interrelationship. These guidance sheets provide a very useful source of information on what factors should be considered, why they are important and how they interact with each other. The report also provides a good background on how and why these assessments should be carried out, contains a useful glossary of terms, describes a number of simple calculations which may be used to predict impact, and reviews some of the available risk assessment tools such as DRASTIC and GOD. This latter section describes only a few of the tools now available however.

4.2 British Standards Institute (BSI)

The British Standards Institute has issued both guidance and codes of practice which provide technical information relevant to site-specific investigations. References to a number of relevant British Standards are given in Appendix 1. Information on currently available British Standards, their cost and how to order them can be obtained from their website at www.bsi.org.uk.

BS5930:1981 Code of practice for site investigations describes the data sources to be considered as part of a desk study as well as providing a comprehensive description of site investigation techniques such as drilling, soil sampling and hydraulic testing. Further information on soil and water sampling and monitoring is given in **BS 6068 Water Quality** and **BS 7755 Soil Quality**. Both of these British Standards consist of parts relating to terminology, sampling and chemical, biological and physical methods. The parts are divided

into sections or subsections describing particular methodologies e.g. **BS 7755: Section 5.1 : 1996 is Soil Quality Part 5: Physical methods Section 5.1 Determination of pore water pressure – Tensiometer method.** These sections and subsections may be identical to International Organisation for Standardisation (ISO) documents as BSI may have adopted ISO methods as British Standards.

DD175:1988 "Code of practice for the identification of potentially contaminated land and its investigation" was issued by the British Standards Institute as part of its Draft for Development series because of the insufficient experience in the UK of the type of guidance given in this code. A revised version titled **"Code of practice for investigation of potentially contaminated sites"** is currently issued as a draft for public comment with the aim of implementing it as a British Standard. This document recommends a minimum code of practice for the investigation design, field sampling, sample handling and analysis of samples. The code provides a good overview of the aims and philosophy of designing site investigation strategies, an overview of sampling methodologies for groundwater, soil and gases, a description of different analytical techniques and their applicability to different contaminants, and a very comprehensive bibliography of relevant papers and current guidance. The document however is aimed at contaminated land and thus focuses particularly on contaminants such as non-aqueous phase liquids and heavy metals.

4.3   International Organisation for Standardisation (ISO)

The International Organisation for Standardisation (ISO) publishes guidance on a wide range of activities including water quality, soil quality and hydrometric determinations. Full ISO standards are usually adopted by BSI as British Standard and thus much overlap exists between guidance from the two organisations. Details of available standards can be found at the ISO website at www.iso.ch. Relevant technical committees are TC 147 Water Quality, TC 190 Soil Quality and TC 113 Hydrometric determinations and copies of the ISO standards are available from the British Standards Institution.

4.4   American Society for Testing and Materials (ASTM)

The ASTM publishes a large number of standards relevant to all aspects site characterisation, from the development of initial conceptual models, through site investigation, sampling and monitoring. Details of available ASTM standards can be obtained by searching their website at www.astm.org. The ASTM has a European office based in the UK, more details of which can be found on their website at www.astmeuro.org.

The ASTM has produced a compilation document entitled "ASTM standards on ground water and vadose zone investigations", the second edition of which was published in 1994. The document consists of 46 individual standards relating to issues such as soil sampling and analysis, drilling, hydraulic testing and data requirements. Many of these standards correspond closely to guidance available as British Standards.

Three ASTM standards which define a framework for characterising sites are **D5979-96 Standard guide for conceptualization and characterization of ground-water systems, D5730-96 Standard guide for site characterization for environmental purposes with**

emphasis on soil, rock , the vadose zone and ground water, and D5717-95 Standard guide for design of ground-water monitoring systems in karst and fractured-rock aquifers.

Although these guides provide valuable checklists for the data to be considered and decisions to be made when characterising sites, many of the specific technical aspects are covered by reference to other guidance (particularly ASTM standards).

4.5 Construction Industry Research Information Association (CIRIA) publications

CIRIA have produced a series of volumes under the heading of Remedial treatment for contaminated land, Volume 3 of which deals with Site investigation and assessment. This document, published in 1996, contains chapters on planning and implementation of site investigations, sampling and testing, and a chapter on risk assessment. The report contains technical guidance on the applicability of different techniques, though the emphasis is from the contaminated land perspective. The 12 appendices provide comprehensive advice on issues such as guidance documents on site investigation, information sources for desk study and investigation techniques.

4.6 United States Environmental Protection Agency (USEPA)

The United States Environmental Protection Agency is a source of much reference material, including databases and software. Most of this is freely available through the National Environmental Publications Internet Site (NEPIS) which can be accessed through the publications section on the EPA website at www.epa.gov. NEPIS allows access to over 6000 documents which can be viewed and printed. These documents include full images of all the original pages.

5. DATA ASSESSMENT AND INVESTIGATION GUIDANCE FOR PHASE 2

Phase 2 attempts to quantify the processes acting at a particular site. Applications may pass on at this phase at the modelling stage using existing data or it may act as an indicator of deficiencies in the data available at the site, and may thus act as a lead into the specification of a site investigation programme to collect the basic data required. Phase 2 assessment needs to be carried out by someone who is competent in the technical issues required.

It is envisaged that Phase 2 assessments will be carried out by, or on behalf of, the applicant and submitted to the Environment Agency for review. This section describes specific guidance available to Environment Agency staff which will help them assess the applicability of the methodology used in a Phase 2 application. No prescriptive methodologies are given for this tier. The applicant must present a justifiable case that he has used a methodology appropriate to the site-specific conditions. This phase should involve consultation between the applicant and the Environment Agency early in the process in order to ensure that an acceptable approach is being taken towards satisfying the requirements of this phase.

5.1 Data assessment for modelling

It is necessary to understand the physical, chemical and biological processes which will control the rock/contaminant interaction at the site. The nature of the underlying geology will determine whether groundwater movement should be thought of as occurring in a porous medium or along fractures, and is used to assess likely hydraulic conductivities.

Depth to water table in any underlying unconfined aquifer - Where hydrogeological maps are available, contour maps of the minimum elevation of the water table are provided for most aquifers. Reference to the water borehole database (EA/BGS) should provide details of the depth to the water table at nearby boreholes. As a general rule, the depth is least beneath valleys and greatest upon the interfluves. Seasonal variation in the elevation of the water table may vary, from only a few metres in Permian and Triassic sandstones to some tens of metres beneath Chalk interfluves. Where data are provided, it is the highest level water table (winter/spring) that is pertinent to site vulnerability assessment.

Effective rainfall - Effective rainfall is available on a 40 x 40 km grid block basis for the whole of England and Wales through the Meteorological Office MORECS Database. Otherwise, generalised maps of effective rainfall distribution are available. It may sometimes be useful to compare effective rainfall with the generalised catchment run-off data published as statistical data listings by the Institute of Hydrology/British Geological Survey in order to verify the available data.

Water Balance - This provides an indication of the volume of water both infiltrating to the groundwater and going as runoff to surface water features. This information can be used to estimate both likely dilution effects and likely soil moisture contents. It represents a balance between rainfall, soil moisture content, evapotranspiration and runoff. Runoff will be increased by both steep slopes and the presence of low permeability surface deposits.

Determination of acceptable hydraulic load - In order to eliminate surface runoff to controlled waters the discharge rate and volume must not exceed the infiltration capacity and infiltration rate of the discharge site. Step 1 of any assessment will require calculation of these properties. The infiltration capacity of the site can be related to the soil moisture deficit, a parameter that can be purchased from the Meteorological Office. Data on infiltration rates may be available from the Soil Survey or may have to be measured at the site. The simplest method for measuring infiltration rates is the use of infiltrometer rings. These measure saturated infiltration rates, the maximum value for the soil. The use of infiltrometers is described both by Ballestro et al. (1996) and in ASTM standard D5126-90 and may be justified in the most complex assessment procedures.

More complex methods of determining the infiltration rate are described by the US EPA in a two-volume document on "Estimation of infiltration rate in the vadose zone" (USEPA), volume one of which is a compilation of simple mathematical models and volume 2 is the application of selected mathematical models. This can be downloaded from the US EPA website at www.epa.gov/ada/ninflmod.html. The aim of these two volumes is to compile relatively simple mathematical expressions which could be used in a spreadsheet to provide rational, quantitative results.

Volume 2 gives a conceptualised scenario for each infiltration model, describing assumptions, limitations and application, and also gives guidance on model selection for site-specific situations. The document also contains tables of input parameters relevant to models described and references data sources in the literature from which these data were obtained to allow the user to select appropriate parameters.

Soils - Soils consist of mineral and organic matter, together with living organisms and thus act as an active zone of attenuation and degradation of contaminants. Most soils are unsaturated and have both air and water filled pore spaces. Soils in the UK may be up to 2 m in depth. The permeability of soils can be enhanced by the presence of macropores which form by the binding of clay or organic matter, or due to animal activity. Cracking due to wetting and drying of clay-rich soils can also lead to faster migration of contaminants, which may therefore not be attenuated.

A three-fold classification of soils, based on the physical soil properties, was developed by the Soil Survey and Land Research Centre for the former National Rivers Authority. The scheme, which relates mainly to diffuse pollution, is described in "Policy and practice for the protection of groundwater".

Information on the availability of Soil Survey maps and reports can be obtained by contacting the Soil Survey and Land Research Centre, Cranfield University, Silsoe, Bedford, MK45 4DT, Tel. 01525 863242, Fax 01525 863252, email: soil.survey@cranfield.ac.uk or by visiting their website at www.cranfield.ac.uk/sslrc.

The US EPA has created a database of basic soil properties which may influence the hydraulic behaviour of soils. The database, called **UNsaturated SOil DAtabase (UNSODA),** can be downloaded free of charge from the EPA website at www.epa.gov/ ahaazvuc/unsoda.html. The database, which was compiled both from the open literature and through personal requests to scientists and engineers, contains information on hydraulic functions (water retention, hydraulic conductivity, soil water diffusivity) and other soil properties (particle size distribution, bulk density, organic matter content), soil classification,

and a description of measurement procedures. New data can also be added to the database. The data contained in UNSODA can be used in cases where insufficient **site-specific** data is available, by the selection of data for soils with similar texture and structure. Care should be exercised to assume data from this US =database is relevant to UK conditions.

The unsaturated zone - The depth to the water table will define the thickness of unsaturated zone beneath the site, and thus both seasonal and long-term trends in water table movement should be understood. The hydraulic conductivity in the unsaturated zone varies with moisture content and groundwater movement in the unsaturated zone is slower than in saturated parts of the same rock type. Chemical conditions in the unsaturated zone are normally aerobic and frequently alkaline. This means that heavy metals may precipitate, sorb or undergo cation exchange, while sorption, biodegradation or elimination of organic compounds, bacteria and viruses may also take place.

Quantification of contaminant transport through the unsaturated zone - Once the maximum allowable discharge rate has been calculated the fate of the contaminants as they move through the unsaturated zone must be modelled. Numerous models are available for use by applicants and the selection of the model should be based on its appropriateness to the site-specific conditions. These models are based upon equations describing the processes detailed in Chapter 2. The US EPA has published a review of vadose zone models entitled "Identification and compilation of unsaturated/vadose zone models" which can be downloaded from the EPA website www.epa.gov . The report reviews approximately 100 flow and transport models which could be used to simulate flow and transport processes in the unsaturated zone. Each model is described in a uniform way which includes assessments of input requirements and the models applicability. The report aimed to select models that were known for their use in a regulatory or enforcement environment or that were considered "typical" of a certain type of model.

Identification of need for site-specific data - The development of a conceptual model will identify the site-specific data which are available. The adequacy of these data must be assessed in terms of the sensitivity of the model output to each parameter. A need for site-specific data may be identified. A clear understanding of their impact on the model output must support the use of default values, particularly if the model is a deterministic one, and by evidence of how representative the default data are.

5.2   Collection of site-specific data

Planning of site investigation - A number of guidance documents on the planning and implementation of site investigations have been written in the UK e.g. BS 5930 Code of practice for site investigations, CIRIA Special Publication 103 Remedial treatment for contaminated land Volume 3 – Site investigation and assessment, and the BSI Draft for Public Comment of the "Code of practice for investigation of potentially contaminated sites". These documents provide overviews on sampling and testing methodologies.

The American Society for Testing and Materials publishes much guidance that is of relevance. D 5730-96 Standard guide for site characterisation for environmental purposes with emphasis on soil, rock, the vadose zone and groundwater, and D5717-95 Standard guide for design of groundwater monitoring systems in karst and fractured rock aquifers are useful protocols on the factors to be considered and the methods to be employed when

investigating sites. Many of the ASTM standards relating to specific methods e.g. the determination of hydraulic conductivity in the unsaturated zone are contained in a special volume entitled "ASTM standards on groundwater and vadose zone investigations"(ASTM 1992).

Measurement of unsaturated zone hydrogeological properties - A succinct review of both flow in the unsaturated zone and methods for determining storage, hydraulic conductivity and water quality is provided by the chapter on "Monitoring and sampling the vadose zone" in the volume Practical handbook of ground-water monitoring edited by David M.Nielsen.

Central to any quantification of contaminant transport processes in the unsaturated zone is the determination of the pathway hydraulic conductivity. Darcy=s law can be used in the unsaturated zone, but it must be remembered that the hydraulic conductivity is dependent on moisture content. No direct in situ methods exist for measuring the unsaturated hydraulic conductivity, instead measurements of flux are made, however it must be remembered that large variations in these parameters can occur because of soil heterogeneities.

Infiltrometer rings are used to get steady-state infiltrability which is equivalent to saturated hydraulic conductivity. This gives an upper limit and therefore conservative estimate of travel time. Hydraulic conductivity can be calculated from those data using either Darcy=s Law or the Green-Ampt approximation. The latter assumes a sharp wetting front, a constant matric potential at this front and requires knowledge of the depth to the wetting front.

The average linear velocity can be solved using Darcy=s Law

$$V_x = Q/(n_e A)$$

where Q/A is the measured steady state infiltration rate per unit area and n_e is the effective porosity. The Green-Ampt wetting front model gives travel times if moisture contents, depth to wetting front and moisture potential below the wetting front are known.

A brief description of some of the main techniques used for determining the properties of the unsaturated zone are described below:

Tensiometers measure soil matric potential by measuring pressure changes related to movement of water in or out of a porous cup installed in the unsaturated zone. Tensiometers should be installed with as little disturbance to the soil as possible and insuring that a good hydraulic connection is made between the porous cup and the surrounding strata. Detailed guidance on the installation of tensiometers is given in British Standard 7755 Part 5 Section 5.1.

Electrical Resistance Blocks are an inexpensive method for measuring either moisture content or soil-water pressure. They consist of two metal plates set in a block of porous material, usually gypsum. The electrical resistance between the two plates is measured and related to variations in moisture content of the surrounding soil. The blocks must be calibrated in the laboratory prior to use, using material collected from the site at which they are to be used. Problems associated with their use include temperature sensitivity and the independent effect of salinity on electrical resistance. Thus resistance blocks are mainly used for suctions of greater than 0.8 atm, which is the upper limit for the use of tensiometers.

Neutron Probes are used to determine moisture content, and involve lowering a probe into a borehole, which is normally cased with steel or aluminium. This method is expensive and is not very accurate for detecting small changes in water content. Detailed guidance on the use of this method is given in British Standard 7755 Part 5 Section 5.2.

Infiltrometers are a method of measuring infiltration into permeable materials. Steady state infiltration is the same as saturated hydraulic conductivity. Saturated hydraulic conductivity gives a conservative estimate of travel times in the unsaturated zone. The best design of infiltrometer is the double-ring, in which a head is maintained between an inner and outer set of rings. Both rings are sealed in the ground to prevent leakage and the outer ring minimises lateral flow from the inner ring. The volume of water added to the inner ring therefore is equal to the water infiltrating the soil. Hydraulic conductivity can be calculated using either Darcy's Law or the Green-Ampt approximation. The former requires an hydraulic gradient to be determined using tensiometer data and gives a saturated hydraulic conductivity, while the latter assumes that the wetting front is sharp, uniformly wetted and has a constant hydraulic conductivity and matric potential. For conservative estimates the matric potential can be assumed to be zero.

Monitoring water quality in the unsaturated zone -
Surface geophysical techniques, measuring electrical resistivity and conductance, can be used to delineate contaminant plumes where a contrast exists between the conductivity of the plume and the natural water. In situ measurements can be made using the electrical resistance blocks described in Section 5.2.5, if they have been calibrated to measure salinity. These measurements must also take account of the soil water temperature.

Suction lysimeters allow the in situ collection of soil water. They consist of a porous cup attached to a collection chamber and two access tubes connected to the surface. The sample tube ends at the bottom of the lysimeter while the air tube ends at the top of the collection chamber. Suction is induced in the cup by removing air via the air tube. This induces flow into the lysimeter from a zone a few centimetres around the cup. Reversing the pressure on the air tube then forces the collected sample up the sampling tube. A number of studies have shown that suction lysimeters can alter the chemistry of the collected samples when the sample waters have a total dissolved solids concentration of less than 500 mg/l. Trace metal concentrations can be altered even above this concentration. Volatile organics can be sampled where equilibrium suction is established and maintained.

Soil gas monitoring of volatile organic compounds can be used to delineate the presence of these compounds at deeper levels in the unsaturated or the saturated zone. The samples are taken by driving a hollow steel probe into the ground and drawing a sample using a vacuum pump. Samples may be analysed in the field using portable gas chromatographs (GCs) or detectors, or in the laboratory using GC. Detectors which may be used include electron capture detector (ECD), flame ionisation detector (FID), photoionisation detector (PID) and Hall electrolytic conductivity detector. Care must be taken that the appropriate detector is used, with the ECD working best for halocarbons, the FID for hydrocarbon compounds and the PID for vinyl chloride. The Hall detector works for both halocarbons and vinyl chloride but is less sensitive than the ECD.

6. PROTOCOL

6.1 Phase 1

Phase 1 is intended principally to evaluate the land disposal of agricultural fluids. Phase 1a evaluates the hazard to surface water and considers disposal to areas classed as being on a Non-Aquifer by the Groundwater Vulnerability maps. Disposal over Major or Minor Aquifers is considered in Phase 1b, where aquifer type and protection by clay cover are evaluated. Disposal of agricultural fluids, be they spent sheep dip, farm slurry or unwanted pesticide, is also subject to recommendations within the exiting Codes of Practice for disposal of agricultural materials with particular regard to dilution. Disposal to soakaway and of all other materials is referred to Phase 2 for consideration of additional information.

6.1.1 Phase 1a assessment using application form and vulnerability map

Phase 1a assessment can be made using two information sources only: the application form, and the groundwater vulnerability map. It enables a three-way decision to be made as follows (Figure 6.1):

either application approved either because there is no receptor (surface or groundwater) or no pathway to the receptor (surface water only);

or application refused because there is a clear risk to surface water

or application referral for further scrutiny in Phase 1b (aquifer present).

The Phase 1a assessment process works via a tick list/flowchart for which acceptance criteria are identified in Table 6.1. The tick list is shown in Figure 6.2. This information will be largely supplied by the applicant, although groundwater vulnerability and proximity to boreholes may be more easily supplied by the Environment Agency.

If the groundwater vulnerability map indicates that an aquifer is present then this must be assessed in Phase 1b, even where a Major Aquifer with no clay cover is indicated, since there may be circumstances where the groundwater vulnerability map alone could be misleading (see Section 3.2). If an area of Non-Aquifer is indicated then the site must be at least 200 m from the mapped boundary. This is both to ensure that sites on the feather edges of Non-Aquifers overlying a Major or Minor Aquifer have at least 5 m of impermeable cover and to allow for boundary uncertainty arising from scaling errors in information used to compile the vulnerability maps. If this is not the case referral to Phase 1b is appropriate.

Where basic information not available from the application form the assessment process can be supplemented by additional information available to the EA, such as that described in Chapter 3. This is presently available from a variety of diverse sources but a logical development would be to bring these sources together within a GIS so that they can be interrogated collectively. Suggested additional data relevant to Phase 1a that are available are listed below:

1) Soil maps   4) Borehole database
2) Topographic maps   5) Run-off data
3) Field drain register

Some of these data may also be carried forward to any Phase 2 assessment.

Table 6.1 Phase 1a criteria for disposal to land

Information type	Acceptable	Referral	Not acceptable
Aquifer vulnerability	All area designated Non-Aquifer and more than 200 m from the area boundary.	Areas of Major and Minor Aquifer (to Phase 1b) Areas of Non-Aquifer less than 200 m from an aquifer boundary (to Phase 1b)	
Substance to be disposed	Some List II substances conditional on dilution and prevailing conditions	All List I substances (to Phase 2) Other List II (to Phase 2)	
Land use	Grassland and stubble conditional on there being no animal access for grazing for a period of one month after disposal		Set-aside, conservation and amenity land
Surface water courses and standing water	>10 m distant		<10 m distant; areas liable to flooding
Groundwater sources (springs, wells and boreholes)	>50 m distant; but >500 m distant if source used for drinking water supply		<50 m distant; but <500 m distant if source used for drinking water supply
Topography	<1 in 5		>1 in 5; or undulating areas where ponding of disposal fluid may occur
Ground conditions	Well vegetated and naturally drained ground		Bare or compacted soil; sparsely vegetated; surface baked hard, frozen or waterlogged.

Information type	Acceptable	Referral	Not acceptable
Soil type*	Loamy, peaty		Gravel, sand, loamy sand
Soil drainage	Free or moderate		Poor
Soil thickness	>0.6 m		<0.6 m
Field drains	Absent; drainage pipes covered by >0.6 m of loamy or peaty soil		Areas of ridge and furrow; areas with shallow stone drains or shallow drains with permeable backfill; also land recently mole drained or subsoiled.
Land area	>0.2 ha per 4 000 l of discharge at prescribed dilution ie < 20 m^3/d/ha		
Previous disposal	Land not used in the previous 4 weeks for disposal		

[+]where insufficient data are supplied to identify criteria the application is automatically referred to Phase 2.
*soil pH should lie in the range 5.0 to 7.5, but not all applicants will be able to provide this information
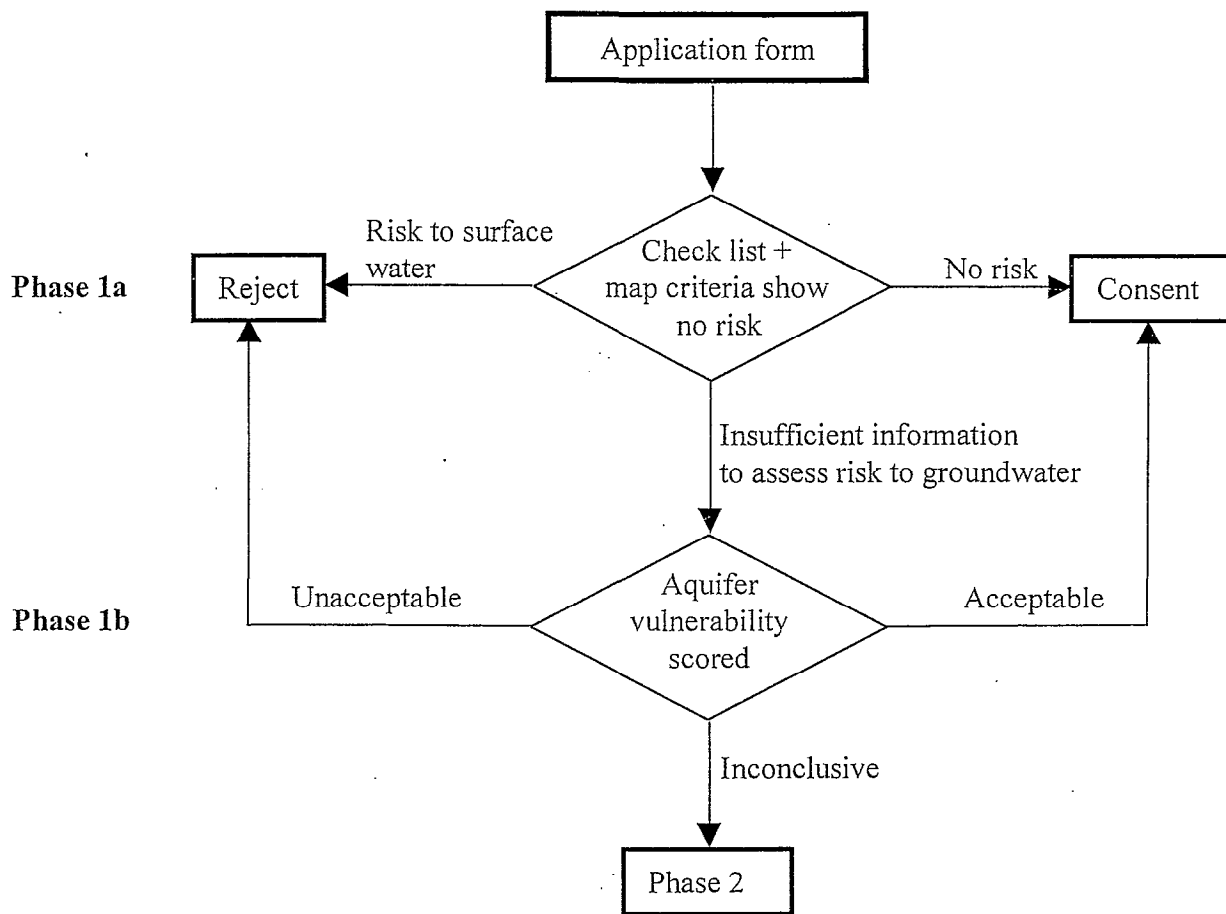
Figure 6.1 Flowchart for Phase 1 assessment

6.1.2 Phase 1b assessment of groundwater vulnerability

Applicants are referred to Phase 1b where there is insufficient information to assess the risk to groundwater. This could be due to a lack of information on the nature and thickness of the drift cover over the aquifer or uncertainty in cases where the site is on a Non-Aquifer but is close to the boundary of an aquifer (due to the coarse scale of the information used to construct the vulnerability map in some areas). For these latter cases information from the geological map and BGS well records can be used to ascertain whether an aquifer is present. Where there is no aquifer the application can be accepted without further vulnerability assessment.

The following methodology is suggested for assessing vulnerability information. The information is collated into an additive scoring system which is shown in Table 6.2. This assesses the information on the following basis: a) Major or Minor Aquifer type; b) fissured or flow system; c) thickness and nature of drift cover.

Aquifer type - The groundwater vulnerability map defines whether the aquifer is considered as Major, Minor or Non-Aquifer in the area being assessed in the geological classification notes, but it is important to understand how sequential systems are classified (see data limitations in Section 3.2). Reference to the geological map will provide information on what strata are present.

AQUIFER VULNERABILITY MAP

Major Aquifer	❏	go to Phase 1b	⇒
Minor Aquifer	❏	go to Phase 1b	⇒
Non-Aquifer (< 200 m from boundary)	❏	go to Phase 1b	⇒
Non-Aquifer (> 200 m from boundary)	❏	☺	ξ

SUBSTANCE TO BE DISPOSED

List I	❏	go to Phase 2	⇒
List II	❏	☺	ξ

LAND USE

Fallow land, set-aside	❏	rejection	☹
Conservation and amenity land	❏	rejection	☹
Grassland and stubble	❏	☺	ξ

SURFACE WATERS

<10 m distant or liable to flooding	❏	rejection	☹
>10 m distant	❏	☺	ξ

GROUNDWATER SOURCES

<50 m distant, but <500 m distant if used for drinking water	❏	rejection	☹
>50 m distant, or >500 m if source used for drinking water	❏	☺	ξ

TOPOGRAPHY AND SLOPE

Slope > 1: 5, or undulating land	❏	rejection	☹
Slope < 1: 5	❏	☺	ξ

Figure 6.2 Phase 1a prior investigation tick list

GROUND SURFACE CONDITIONS

Bare and compacted soil, hard baked,
frozen or waterlogged ❑ rejection ☹

Well vegetated and naturally drained soil ❑ ☺ ξ

SOIL DRAINAGE

Gravel, sand, loamy sand ❑ rejection ☹

Free or moderately free ❑ ☺ ξ

SOIL THICKNESS

<0.6 m ❑ rejection ☹

> 0.6 m ❑ ☺ ξ

PRESENCE OF FIELD DRAINS

ridge and furrow, shallow stone drains,
permeable backfill drains and land
recently mole drained or subsoiled ❑ rejection ☹

no field drains or pipes covered by
0.6 m loamy or peaty soil ❑ ☺ ξ

LAND AREA AVAILABLE FOR DISPOSAL

in accordance with codes of practice ❑ ☺ ξ

PREVIOUS DISPOSAL

not less than 4 months previously ❑ ☺ ξ

Table 6.2 Scoring system for Phase 1b groundwater vulnerability

Aquifer type	Major	0	Minor	1				
Flow system	Intergranular	2	Mixed	1	Fractured	0		
Clay cover (m)	>10	6	6-10	4	2-5	2	<2	0
Score								

Notes:

1) One category from each row is selected. For a score of 6 up to 9, the site is acceptable for disposal of farm derived substances at prescribed intervals and dilution; for a score 3 or less the site is not acceptable; for a score of 4 or 5 the application is referred to Phase 2;

2) Where scores are obtained from Table 6.3 these give a combined score for aquifer type and flow system.

Flow system - It is also valuable to know whether the aquifer transmits water through its pore spaces (intergranular aquifer) or whether it principally transmits water through cracks and joints (fractured aquifer). Reference to the hydrogeological map (where available) will provide this information, otherwise the generic listing in Table 6.3 will assist.

Clay cover - **Although** the groundwater vulnerability maps show by means of a stipple where it is believed that >5 m thickness of clayey till is present, reference to more detailed information will often be useful in areas that are peripheral to the stippled zone or where there is some doubt as to the integrity of the till, e.g. has the till been locally removed by engineering work, could the till be largely sandy in this particular area? Inspection of the BGS 1: 50 000 or older series 1: 63 360 scale drift or solid and drift maps may provide detail as to the thickness and integrity of the drift. The borehole database may also provide a local description and thickness log for the drift and bedrock.

Scoring system - The scoring system is designed to enable a three-way decision to be made (Figure 6.1):

either to identify all areas of Major and Minor Aquifer outcrop where clay cover is considered insufficient to attenuate contaminants and to reject the application without further consideration;

or to identify areas of less vulnerable aquifers where clay cover exceeds 10 m in thickness and to accept these without further assessment;

or to refer all other cases to Phase 2 for more detailed assessment, including those where there is insufficient information to enable a decision in Phase 1.

Table 6.3   Nature of principal aquifers in England and Wales and appropriate generic score

Aquifer	Type	Score
MAJOR AQUIFERS (highly permeable)		
river gravels (Middle Thames valley)	intergranular	2
Chalk	fractured	0
Red Chalk/Hunstanton Formation	fractured	0
Upper Greensand (except east of Hog's Back)	intergranular	2
Carstone (Norfolk)	intergranular	2
Lower Greensand (undifferentiated and Folkestone and Hythe Beds)	intergranular	2
Dersingham Formation (sands)	intergranular	2
Spilsby Sandstone	mixed	1
Sandringham Formation	intergranular	2
Portland Stone	fractured	0
Corallian/Brantingham Formation (Yorkshire) and Osmington Oolite	fractured	0
Cornbrash Formation (if in hydraulic contact with underlying limestones)	fractured	0
Forest Marble and Great Oolite limestones (south of Oxford)	fractured	0
Inferior Oolite/Lincolnshire Limestone	fractured	0
Upper Lias (Cotteswold, Midford, Yeovil sands)	intergranular	2
Dolomitic Conglomerate	fractured	0
Sherwood Sandstone Group	mixed	1
Permian Sandstones (including Dawlish Sandstone, Collyhurst Sandstone,	mixed	1
Bridgnorth Sandstone, St Bees Sandstone, Penrith Sandstone)	mixed	1
Upper Magnesian Limestone/Brotherton and Seaham Formations	fractured	0
Middle Magnesian Limestone/Ford Formation	fractured	0
Lower Magnesian Limestone/Cadeby and Raisby Formations	fractured	0
Carboniferous Limestone (except in Northern England)	fractured	0
MINOR AQUIFERS (variably permeable)		
granular superficial deposits	intergranular	3
disturbed Blackheath Beds	intergranular	3
Crag (Norwich, Red and Coralline Crags)	intergranular	3
Pliocene gravels	intergranular	3
Bembridge Limestone	fractured	1
Bovey Formation	intergranular	3
Barton Group (sands)	intergranular	3
Bracklesham Group (sands)	intergranular	3
Bagshot Formation	intergranular	3
London Clay Formation (sands)	intergranular	3
Claygate Member	intergranular	3
Blackheath and Oldhaven beds/Harwich Formation	intergranular	3
Woolwich Formation and Reading Formation/Lambeth Group	intergranular	3
Thanet Sand Formation	intergranular	3
Haldon Gravels	intergranular	3
Upper Greensand (east of Hog's back)	intergranular	3
Carstone (except Norfolk)	intergranular	3
Whitchurch Sands Formation	intergranular	3
Sandgate Beds	intergranular	3

Aquifer	Type	Score
MINOR AQUIFERS continued		
Weald Clay (sandstones and limestones)	mixed	2
Tealby Limestone	fractured	1
Claxby Formation	fractured	1
Tunbridge Wells Sands	intergranular	3
Wealden Beds (sands)	intergranular	3
Wadhurst Clay Formation (sands)	intergranular	3
Ashdown Beds (except clay)	intergranular	3
Purbeck (sands)	intergranular	3
Portland Sands	intergranular	3
Corallian Group (except Yorkshire and Osmington Oolite)	fractured	1
West Walton Formation (limestone)	fractured	1
Kellaways Sand/Osgodby Formation	intergranular	3
Cornbrash Formation	fractured	1
Ravenscar Group	mixed	2
Blisworth Limestone	fractured	1
Glentham Formation (limestones)	fractured	1
Fuller's Earth Rock	fractured	1
Northampton Sand	intergranular	3
Upper Lias (Yeovil/Bridport Sands)	intergranular	3
Junction Bed	fractured	1
Marlstone Rock Formation	fractured	1
Dyrham Formation	intergranular	3
Lower Lias (limestones)	fractured	1
Blue Lias	fractured	1
White Lias/Langport Member	fractured	1
Sandstones in Mercia Mudstone Group	fractured	1
Permian breccias and conglomerates (south-west England)	mixed	2
Basal Permian Sands	mixed	2
Coal Measures (including Barren Measures)	fractured	1
Millstone Grit	fractured	1
Culm	fractured	1
Carboniferous Limestone (limestones in northern England, Yoredales, Limestone Shales)	fractured	1
Devonian sandstones	fractured	1
Silurian limestones	fractured	1
volcanic rocks	fractured	1

6.2 Phase 2

Whilst it is anticipated that a decision on many lower risk applications can be made at Phase 1, applications will need to be referred to Phase 2 for a more detailed assessment where:

- the disposal site has been identified in Phase 1b as situated over a Major or Minor Aquifer with potentially inadequate drift cover

- inadequate data were available to make an assessment at Phase 1;

In addition the proposal will automatically be referred to Phase 2 where:

- the disposal substance is List I;

- a method other than land spreading is planned (for example soakaway drainage).

The Phase 2 assessment requires quantification of the transport processes operating between the discharge point and receiving water table. It is assumed that an application directly at this level would be sufficiently significant to involve a contracted expert to prepare the technical simulation or that it would be carried out by experts in the employment of the applicant. The onus is on the applicant to demonstrate, through the use of appropriate quantitative methods, that the impact on receiving groundwater of any discharge complies with the Groundwater Regulations.

Phase 2 is subdivided into consideration of attenuation in the soil (Phase 2a) and the unsaturated zone beneath the soil layer (Phase 2b), where the properties of the contaminant, the method of disposal and the properties of the subsurface are all taken into account. A flow diagram is shown in Figure 6.3.

A suitable contaminant transport model, such as ConSim, is used to calculate the concentration of contaminants leaving the base of the soil (Phase 2a) or the unsaturated zone (Phase 2b). These are termed the 'modelled concentrations' in this report. This calculated impact is then compared to criteria specified by the EA. It assumes that discharge is maintained at a level at which the unsaturated zone remains unsaturated.

6.2.1 Modelling using generic data

Sources of generic data are for contaminant properties are described in Chapter 2 and for other data required in Chapter 5. As an example, the ConSim model data requirements for an assessment of leaching through the unsaturated zone from an area of contaminated soil are shown in Table 6.4.
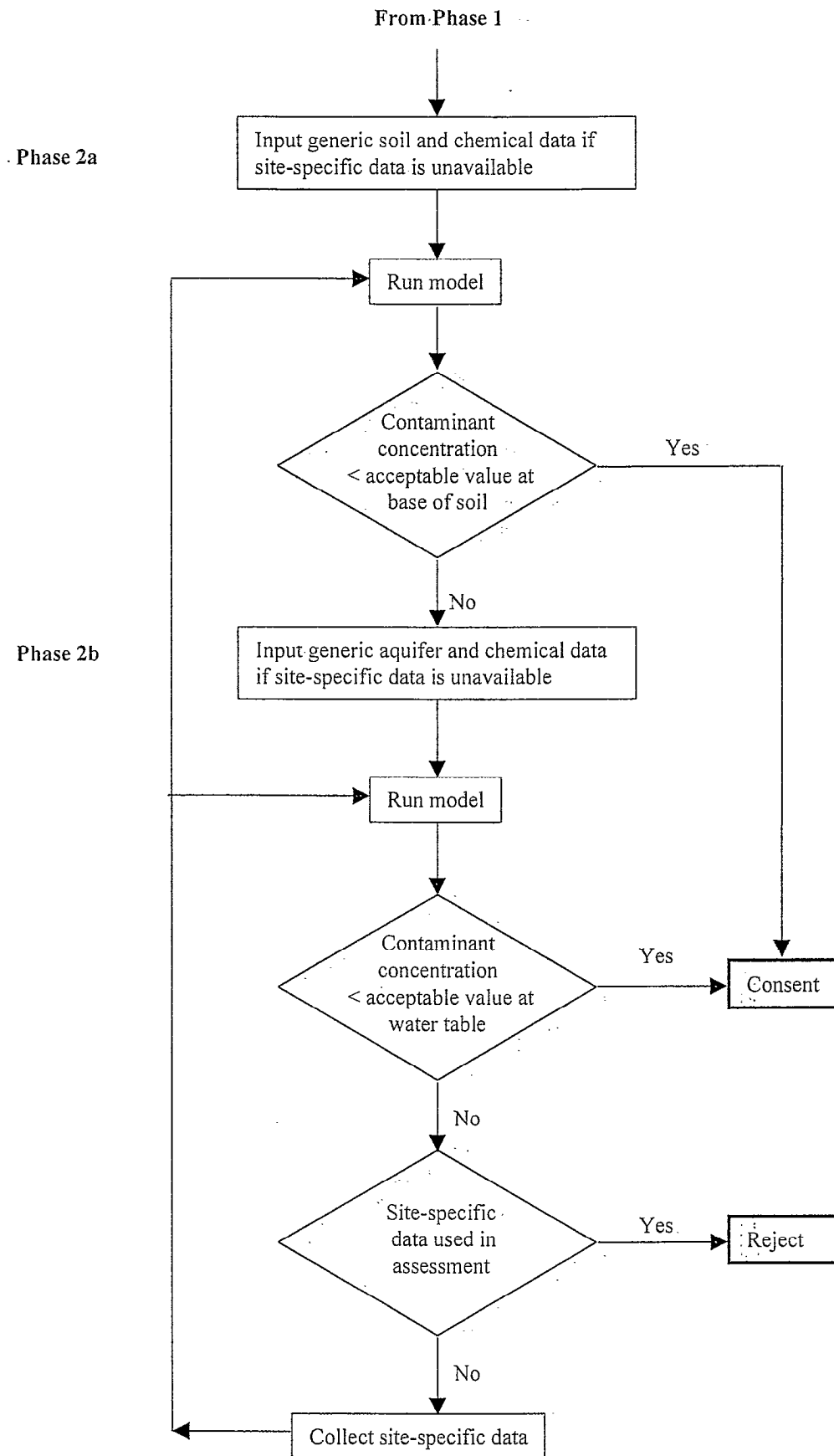
From Phase 1

Phase 2a

```
Input generic soil and chemical data if
site-specific data is unavailable
```

Run model

Contaminant
concentration
< acceptable value at
base of soil

Yes

No

Phase 2b

```
Input generic aquifer and chemical data
if site-specific data is unavailable
```

Run model

Contaminant
concentration
< acceptable value at
water table

Yes → Consent

No

Site-specific
data used in
assessment

Yes → Reject

No

Collect site-specific data

Figure 6.3 Flow chart for Phase 2 assessment

Table 6.4 ConSim model data requirements for leaching from soil

	Data requirement
Contaminant properties	Hydrophobic sorption coefficient K_d, Half-life (unsaturated zone) $T_{1/2}$
Source dimensions	Contaminant concentration, Area of application, Infiltration rate to unsaturated zone, Soil thickness
Unsaturated zone properties	Effective porosity, Fissure porosity, Hydraulic conductivity, Dry bulk density
Unsaturated zone dimensions	Thickness

Since data inadequacy is covered by a range of model default values or other generic data, the model results will inevitably comprise ranges rather than hard and fast values. It is important to take into account this element of uncertainty in any assessment and one way to build in a safeguard would be to set an 'acceptable concentration' at a value less than the permitted concentration. That is if the modelled concentration is lower than the acceptable concentration for either phase the application can be passed. It is appropriate for different criteria to apply to List 1 and List II compounds. For List I compounds the EC Directive requirement is zero and we suggest the detection limit should be used as the permitted concentration. We also suggest that for List 1 compounds the acceptable concentration should be two orders of magnitude less than the permitted concentration. For List II one order of magnitude less may be appropriate.

Where the soil is of a fissured clay type, attenuation in the soil zone cannot be assumed. Where the modelled concentration at the base of the unsaturated zone does not meet the criteria following modelling both the soil and unsaturated zones, then the application will not be accepted.

It is assumed that an application at this level would involve an expert to prepare the technical simulation.

The applicant must satisfy the Environment Agency that the following issues have been appropriately addressed:

1. **Hydraulic load** will **not** exceed the infiltration capacity of the soil and the application rate will **not** exceed the infiltration rate.

2. Numerical models consistent with the conceptual models developed in the Phase 1 evaluation have been used.

3. That appropriate data have been used. If default values are being used in place of site specific data an analysis of the impact of this on the model output must be provided.

The onus is then on the applicant to demonstrate, to the satisfaction of the Environment Agency using site-specific data for soils, the aquifer and the contaminant that disposal would not produce unacceptable concentrations at the water table.

6.2.2 Modelling with site-specific data

This would require collecting primary data using standard methodologies such as those described in Chapter 4 and applying these to the model. It is probable that this would involve invasive site investigation, either to collect data for the assessment or as part of a monitoring programme stipulated as part of the consent to discharge.

All applications where site investigation is required should address the following issues:

1. Outline the aims of the site investigation in terms of what data will be collected and how these data will fit into the overall assessment

2. Define the methods that are going to be used. Methodologies should be described or reference made to standards which will be followed.

3. Aspects of the site investigation programme which should be detailed are:

- drilling techniques
- borehole completions
- sampling strategy
- sample collection (including methods and frequency)
- testing methologies

7. REFERENCES

Agertved J., Rügge K. and Barker J.F. (1992) Transformation of the herbicides MCPP and atrazine under natural aquifer conditions. *Ground Water*, 30, 4, 500-506.

Allen, H.E., Chen, Y-T., Li, Y., Huang, C.P. and Sanders, P.F. (1995) Soil partition coefficients for Cd by column desorption and comparison to batch adsorption measurements. *Environmental Science and Technology*, 29, No. 8, 1887-1891.

Aller, L., T. W. Bennett, et al. (1989) Handbook of suggested practices for the design and installation of ground-water monitoring wells. National Water Well Association.

Alloway, B.J. and Jackson, A.P. (1991) The behaviour of heavy-metals in sewage sludge-amended soils. *Science of the Total Environment*, 100, 151-176.

API (1996) *Estimation of Infiltration and Recharge for Environmental Site Assessment*, American Petroleum Institute.

Appelo, C.A.J. & Postma, D. (1993) *Geochemistry, Groundwater and Pollution.* Rotterdam: Balkema.

ASTM. (1988) *Ground Water and Vadose Zone Monitoring,* American Society for Testing and Materials

ASTM (1992) *ASTM standards on ground water and vadose zone investigations.* American Society for Testing and Materials, Committee D-18 on Soil and Rock.

Atlas R.L.(1981) Microbial degradation of petroleum hydrocarbons: an environmental perspective. *Microbiological Reviews*, 45, 1, 180-209.

Baedecker M.J., Cozzarelli I.M., Eganhouse R.P., Siegel D.I. and Bennett P.C. (1993) Crude oil in a shallow sand and gravel aquifer-III. Biochemical reactions and mass balance modeling in anoxic groundwater. *Applied Geochemistry*, 8, 569-586.

Ballestero, T., B. Herzog, et al. (1991) Monitoring and sampling the vadose zone. In *Practical Handbook of Groundwater Monitoring.* edited by D.M. Nielsen. Chelsea, Michigan: Lewis Publishers Inc.

Barbaro J.R., Barker J.F., Lemon L.A. and Mayfield C.I. (1992) Biotransformation of BTEX under anaerobic denitrifying conditions: field and laboratory observations. *Journal of Contaminant Hydrology*, 11, 245-272.

Barry, D.L. (1988) Safety during investigation and redevelopment works. In *Soil: the aggressive agent.* London: IBC Technical Services Ltd.

Bedient, P.B., Rifai, H.S. & Newell, C.J. (1994) *Ground Water Contamination: Transport and Remediation.* London: Prentice Hall.

Bitton, G. and Gerba C.P. (1984) *Groundwater Pollution Microbiology.* New York: John Wiley and Sons.

Board, P. (1993) Quality assurance principles in contaminated land analysis. *Land Contamination & Reclamation* 1, 4, 201-206.

Bregnard, T. P-A., Höhener P., Häner A. and Zeyer J. (1996) Degradation of weathered diesel fuel by microorganisms from a contaminated aquifer in aerobic and anaerobic microcosms. *Environmental Toxicology and Chemistry*, 15, 3, 299-307.

BSI (1981) *BS 5930 Code of Practice for Site Investigations* (formerly CP2001), British Standards Institution.

BSI (1988) *Code of Practice for the Identification of Potentially Contaminated Land and its Investigation.* DD175 Draft for development, British Standards Institution.

BSI (1993) *BS 6068 Water Quality* ,Part 6. Sampling Section 6.11 Guidance on sampling of groundwaters, British Standards Institution.

BSI (1993). *Glossary of Building and Civil Engineering Terms*. Oxford: Blackwell Scientific Publications.

BSI (1996). *BS 7755 Soil Quality* Part 5. Physical Methods Section 5.2 Determination of water content in the unsaturated zone. Neutron depth probe method, British Standards Institution.

BSI (1996). BS 7755 *Soil Quality* Part 5. Physical Methods Section 5.1 Determination of pore water pressure - Tensiometer method. British Standards Institution.

BSI (1997). *BS 7755 Soil Quality* Part 1. Section 1.1 Soil Quality. Terminology and classification.Terms and definitions relating to the protection and pollution of soil, British Standards Institution.

BSI (1998). *BS 7755 Soil Quality* Part 5. Physical Methods Section 5.3 Determination of particle density, British Standards Institution.

BSI (1998). *Code of Practice for Investigation of Potentially Contaminated Sites*, British Standards Institute.

BSI *BS 6068 Water Quality*, British Standards Institution.

BSI *BS 7755 Soil Quality*, British Standards Institution.

Cairney T. (1993) *Contaminated Land: Problems and Solutions*. London: Blackie Academic and Professional.

Carpenter, R.J., Goaman H.F. et al. (1985) Guidelines for site investigation of contaminated land. Greater London Council.

Cavalier T.C., Lavy T.L. and Mattice J.D. (1991) Persistence of selected pesticides in ground-water samples. *Ground Water*, 29, 2, 225-231.

CESL (1993) *UK Sewage Sludge Survey*. Final Report. Consultants in Environmental Sciences Limited, Gateshead.

Chapelle, F. H. (1993) *Ground-Water Microbiology and Geochemistry*, New York: John Wiley.

Chapman R.A. and Cole C.M. (1982) Observations on the influence of water and soil pH in the persistence of insecticides. *Journal of Environmental Science and Health*, B17, 5, 487-504.

Chilton P.J., Stuart M.E., Gooddy, D.C., Williams R.J and Williamson A.R. (1995) The occurrence in and the modelling of their transport to the Chalk aquifer beneath arable land in southern England. In *Pesticide Movement to Water*, BCPC Monograph 62, edited by A.Walker, R. Allen, S.W. Bailey, A.M. Blair, C.D. Brown, P. Günther, C.R. Leake and P.H. Nicholls, pp111-116, Farnham: British Crop Protection Council.

Clark, L. (1988). *The Field Guide to Water Wells and Boreholes*, Open University Press and Halsted Press (John Wiley and Sons).

Clark, L. (1992). *Methodology for Monitoring and Sampling Groundwater*, NRA.

Clayton, C. R. I., Simons N.E., Matthews M.C. (1982). *Site Investigation*, Granada.

Collins, C. H., Lyne P.M., Grange J.M. (1993) *Collins and Lyne's Microbiological methods*, Butterworth and Heinemann.

Conant, B.H., Gillham, R.W. and Mendoza, C.A. (1996) Vapour transport of trichloroethylene in the unsaturated zone: Field and numerical modelling investigations. *Water Resources Research*, 32, 9-22.

Council of the European Communities (1991) Council Directive of 21 May 1991 concerning urban waste water treatment (91/271/EEC). Official Journal of the European Communities, L135/40-52.

Crowhurst, D. and S.J. Manchester (1993) *The measurement of methane and other gases from the ground*. Construction Industry Research and Information Association.

Culshaw M.G., Editor. (1990) *Field Testing in Engineering Geology*. Geological Society Engineering Geology Special Publication No 6., London: The Geological Society.

Davis J.W., Klier N.L. and Carpenter C.L. (1994) Natural biological attenuation of benzene in groundwater beneath a manufacturing facility. *Ground Water*, 32, 2, 215-226.

Day K.E. (1991) Pesticide transformation products in surface waters. In *Pesticide Transformation Products: Fate and Significance in the Environment*, edited by L.Somasundaram and J.L. Coats, ACS Symposium Series 459, pp 217-241, Washington: American Chemical Society.

Devinny, J. S., Everett L.G., Lu J.C.S., Stollar R.L. (1989) *Subsurface Migration of Hazardous Wastes*. New York: Van Nostrand Reinhold.

DOE (1989). Water and the environment. The implementation of EC directives on pollution caused by certain dangerous substances discharged into the aquatic environment., Department of the Environment.

DOE (1990). EC directive on protection of groundwater against pollution caused by certain dangerous substances (80/68/EEC): classification of listed substances., Department of the Environment.

DOE (1994). A framework for assessing the impact of contaminated land on groundwater and surface water. CLR 1,Department of the Environment

DOE (1994). Documentary research on industrial sites. CLR 3, Department of the Environment

DOE (1994). Guidance on preliminary site inspection of contaminated land. CLR 2, Department of the Environment

DOE (1994). Sampling strategies for contaminated land. CLR 4, Department of the Environment

DT (1987). Specification and method of measurement for ground investigation., Department of Transport. Department of the Environment, Property Services Agency

Dunnivant, F.M., Jardine, P.M., Taylor, D.L. and McCarthy, J.F. (1992) Cotransport of cadmium and hexachlorobiphenyl by dissolved organic carbon through columns containing aquifer material. *Environmental Science and Technology*, 26, No. 2, 360-368.

Environment Agency (1998). Policy and practice for the protection of groundwater. Environment Agency, Bristol

Eganhouse R.P, Dorsey T.F., Phinney C.S. and Westcott A.M. (1996) Processes affecting the fate of monoaromatic hydrocarbons in an aquifer contaminated by crude oil. *Environmental Science and Technology*, 30, 3304-3312.

EPA (1993) Subsurface characterization and monitoring techniques: A desk reference guide. Volume 2: The vadose zone, field screening and analytical methods. Appendices C and D, United States Environmental Protection Agency.

Ferguson, C. and A. Abbachi (1993) Incorporating expert judgement into statistical sampling designs for contaminated sites. *Land Contamination & Reclamation*, 1, 3, 135-142.

Ferguson, C.C. (1992) The statistical basis for spatial sampling of contaminated land. *Ground Engineering*, 25, 5, 34-38.

Ferguson, C.C. (1993) *Designing sampling strategies for contaminated sites*. Site Investigations for Contaminated Sites, London: IBC.

Fetter C.W. (1993) *Contaminant Hydrogeology*. London; Prentice Hall .

Finnecy, E. E. and A. Parker (1985) The environmental assessment of contaminated land in the UK. The role of preliminary investigation. *Proceedings of the First International TNO Conference on Contaminated Soil*, Utrecht: Martinus Nijhoff.

Foster, S.S.D and Gomes D.C. (1989) Groundwater Quality Monitoring: an Appraisal of Practices and Costs. WHO-PAHO/HPE/CEPIS Technical manual, Lima, Peru

Gale, I. N. and Robins N.S. (1989) The sampling and monitoring of groundwater quality, BGS Technical Report WD/89/37.

Gerhardt, P. (1981) *Manual of methods for general bacteriology.*

Ghiorse W.C. and Wilson J.T. (1988) Microbial ecology of the terrestrial subsurface. *Advances in Applied Microbiology*, 33, 107-172.

Greenberg, A. E., Clesceri L. S. and Eaton A.D., Editors (1992). *Standard Methods for the Examination of Water and Wastewater*. Washington DC, American Public Health Association.

Guth J.A., Burkhard N. and Eberle D.O. (1976) Experimental models for studying the persistence of pesticides in soils. In *Persistence of Insecticides and Herbicides, Proceedings of BCPC Symposium* (1976), Farnham: British Crop Protection Council.

Hamer, K., von Luhrte, R. & Isenbeck-Schr $\overline{\text{t}}$ er, M. (1994) Transport of Cd and Cu in a zone of calcite dissolution: column experiments and modelling. In *Proceedings of the IAHR Symposium on Transport and Reactive Processes in Aquifers* (Zurich, 1994), edited by T.H. Dracos and F. Stauffer, 105-110. A. A. Balkema, Rotterdam.

Head, K. H. (1986). *Manual of Soil Laboratory Testing*, Pentech Press.

Heron G. and Christensen T.H. (1992) Degradation of the herbicide mecoprop in an aerobic aquifer determined by laboratory batch studies. *Chemosphere*, 24, 5, 547-557.

Higgo J.J.W., Nielsen P.H., Bannon M.P., Harrison I. and Christensen T.H. (1996) Effect of geochemical conditions on the fate of organic compounds in groundwater. *Environmental Geology*, 27, 335-346.

Hitchman, S. P. (1983) A guide to the field analysis of groundwater, BGS Technical Report FLPU 83-12..

Howard P.H., Boethling R.S., Jarvis W.F., Meylan W.M. and Michalenko E.M. (1991) *Handbook of Environmental Degradation Rates*, Chelsea, MI: Lewis.

Hvorslev, M. J. (1951) *Time lag and soil permeability in ground-water observations*, Waterways Experiment Station. Corps of Engineers, U. S. Army.

Hyett G.H. (1994) *TBME as a groundwater contaminant.* Project Record O1562/3/A, National Rivers Authority, Bristol.

Interdepartmental Committee on the Redevelopment of Contaminated Land (1987). 59/83 Guidance on the assessment and redevelopment of contaminated land.

IP (1993). *Code Of Practice for the Investigation and Mitigation of Possible Petroleum-Based Land Contamination,* Institute of Petroleum.

ISRM (1981). *Rock characterization testing and monitoring,* edited by E.T. Brown, International Society for Rock Mechanics.

Jaffe, D.A. (1992) The nitrogen cycle. In *Global Biochemical Cycles*, edited by S.S. Butcher, R.J.Charlson, G.H.Orians and G.V.Wolfe, 263-284, London: Academic Press.

Joyce, M. J. (1982). *Site Investigation Practice*.

Jury W.A., Focht D.D. and Farmer W.J. (1987) Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradation. *Journal of Environmental Quality*, 16, 4, 422-428.

Lamy, I., Bourgeois, S. and Bermond, A. (1993) Soil cadmium mobility as a consequence of sewage sludge disposal. *Journal of Environmental Quality*, 22, 731-737.

Langmuir D. (1997) *Aqueous Environmental Chemistry*, New Jersey: Prentice Hall.

Ledin, M., Pedersen, K. and Allard, B. (1997) Effects of pH and ionic strength on the adsorption of Cs, Sr, Eu, Zn, Cd and Hg by *Pseudomonas putida*. *Water, Air, and Soil Pollution*, 93, 367-381.

Leij, F.J., Alves W.J, Genuchten M.T. and Williams J.R. (1996). The UNSODA Unsaturated Soil Hydraulic Database. User's Manual Version 1.0, United States Environmental Protection Agency.

Lerner, D.N. and J. H. Tellam (1992). The protection of urban groundwater from pollution. *Journal of the Institution of Water & Environmental Management*, 6, 1, 28-37.

MAFF (1983). Field assessment of soil texture and drainage class, ADAS.

MAFF (1993) Solving the nitrate problem (ref. PB 1092). MAFF Publications, London.

MAFF (1998) Code of Good Agricultural Practice for the Protection of Water.

Mani S.V., Connell D.W. and Braddock R.D. (1991) Structure activity relationships for the prediction of biodegradability of environmental pollutants. *Critical Reviews in Environmental Control*, 21, 3, 4, 217-236.

McBride M.B. (1994) *Environmental Chemistry of Soils*, 308-341, New York, Oxford University Press.

McBride, M.B., Richards, B.K., Steenhuis, T., Russo, J.J. and Sauve, S. (1997) Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. *Soil Science*, 162, 7, 487-500.

McCarthy, J.F. and Zachara, J.M. (1989) Subsurface transport of contaminants. *Environmental Science and Technology*, 23, 496-502.

Meeusen J.C.L., Keizer M.G., Van Riemsdijk W.H. and De Haan F.A.M. (1994) Solubility of cyanide in contaminated soils. *Journal of Environmental Quality*, 23, 4, 785-792.

Montgomery J.H. and Welkom L.M. (1990) *Groundwater Chemicals Desk Reference*. Chelsea, Michigan: Lewis.

NRA (1991). Proposals for statutory water quality objectives., National Rivers Authority.

NRA (1992). The National Rivers Authority's response to the sixteenth report of the Royal Commission on Environmental Pollution on freshwater quality, National Rivers Authority.

Palmer, R.C., Holman, I.P., Robins, N.S. and Lewis, M.A. (1995) Guide to groundwater vulnerability mapping in England and Wales. London: HMSO.

Petts, J., Cairney T. and Smith M. (1997). *Risk-based Contaminated Land Investigation and Assessment*, John Wiley and Sons.

Pothuluri J.V., Moorman T.B., Obenhuber D.C. and Wauchope R.D. (1990) Aerobic and anaerobic degradation of alachlor in samples from a surface-to-groundwater profile. *Journal of Environmental Quality*, 19, 525-530.

Potter, K. J. (1992). An approach being developed in ICI for the assessment of soil and groundwater contamination. In *Contaminated Land Treatment Technologies*. edited by J.F.Rees, Elsevier Applied Science.

Puls, R.W. & Powell, R.M. (1992) Surface-charge repulsion effects on the mobility of inorganic colloids in subsurface systems. In *Transport and remediation of subsurface contaminants*, edited by Sabatini & Knox.

Ravi, V. and J.R. Williams (1998) Estimation of infiltration rate in the vadose zone: Compilation of simple mathematical models, Environmental Protection Agency.

RTDF (1997) *Natural attenuation of chlorinated solvents in groundwater: principles and practices*. Remediation Technologies Development Forum.

Schuster, E. (1991) The behaviour of mercury in the soil with special emphasis on complexation and adsorption processes - a review of the literature. *Water, Air, and Soil Pollution*, 56, 667-680.

Schwarzenbach, R.P. and Westall J. (1985) Sorption of hydrophobic trace organic compounds in groundwater systems. *Water Science and Technology*, 17, 39-55.

Shuter, E., Teasdale W.E. (1989) Application of drilling, coring, and sampling techniques to test holes and wells, Techniques of Water Resources Investigations, United States Geological Survey.

Site Investigation Steering Group (1993). 1. Without site investigation ground is a hazard, Site Investigation Steering Group.

Site Investigation Steering Group (1993). 2. Planning, procurement and quality management, Site Investigation Steering Group.

Site Investigation Steering Group (1993). 3. Specification for ground investigation, Site Investigation Steering Group.

Site Investigation Steering Group (1993). 4. Guidelines for the safe investigation by drilling of landfills and contaminated land, Site Investigation Steering Group.

Smith, M. A. (1988). Investigation of aggressive ground. In *Soil: the aggressive agent*, London: IBC Technical Services Ltd.

Smith, M. A. (1991) Identification, investigation and assessment of contaminated land. *Journal of the Institution of Water & Environmental Management*, 5, 6, 617-623.

Smith, S.R. (1996) *Agricultural Recycling of Sewage Sludge and the Environment.* Wallingford: CAB International.

Standing Committee of Analysts (1980). General Principles of Sampling and Accuracy of Results. Methods for Examination of Waters and Associated Materials.

Struckmeier, W.F. and Margat, J. (1995) Hydrogeological maps. A guide and a standard legend. *International Contributions to Hydrogeology* ,17.

Stuart, A. (1984). Borehole sampling techniques in groundwater pollution studies. BGS Technical Report

Stuart, M. E. (1993). Protocols used within hydrogeology group for determination of chlorinated solvents. BGS Unpublished report

Stumm, W. & Morgan, J.J. (1996) *Aqueous Chemistry: Chemical Equilibria and Rates in Natural Waters.* New York.:Wiley.

Suflita J.M. and Sewell G.W. (1991) *Anaerobic biotransformation of contaminants in the subsurface.* USA EPA Research and Development EPA/600/M-90/024.

Thierrin J., Davis G.B., Barber C., Patterson B.M., Pribac F., Power T.R. and Lambert M. (1993) Natural degradation rates of BTEX compounds and naphthalene in a sulphate reducing environment. *Hydrogeological Sciences*, 38, 8, 309-321.

Van de Heijde, P. K. M. (1994). Identification and compilation of unsaturated/vadose zone models, United States Environmental Protection Agency.

Vrba, J. & Zaporozec, A. (1994) Editors, *Guidebook on Mapping Groundwater Vulnerability.* Heise, Hanover: International Association of Hydrogeologists.

Weltman, A. J. and J. M. Head (1983) *Site Investigation Manual.* Construction Industry Research Information Association, Publication 25.

West, G. (1991) *The Field Description of Engineering Soils and Rocks*, Open University Press.

Williams, J. R., Ouyang Y., Chen J-S. and Ravi V. (1998) Estimation of infiltration rate in the vadose zone: Application of selected mathematical models, United States Environmental Protection Agency, EPA/600/R-97/128b.

Wilson S.C, Duarte-Davidson R and Jones K.C. (1996) Screening the environmental fate of organic contaminants in sewage sludges applied to agricultural soils: 1. The potential for downward movement to groundwaters. *The Science of the Total Environment*, 185, 45-57.

Wilson S.C., Burnett V., Waterhouse K.S. and Jones K.C. (1994) Volatile organic compounds in digested United Kingdom sewage sludges. *Environmental Science and Technology*, 28, 259-266.

Wood, W. W. (1976) Guidelines for collection and field analysis of ground-water samples for selected unstable constituents, Techniques for Water Resources Investigations, United States Geological Survey.

Yin, Y., Allen, H.E., Li, Y., Huang, C.P. and Sanders, P.F. (1996) Adsorption of mercury(II) by soil: effects of pH, chloride, and organic matter. *Journal of Environmental Quality*, 25, 837-844.

Zoeteman B.C.J, de Greef E. and Brinkman F.J.J. (1981) Persistency of organic contaminants in groundwater, lessons from soil pollution incidents in the Netherlands. In *Quality of Groundwater, Proceedings of an International Symposium* (Noordwijkerhout, Netherlands 1981), edited by W. van Duijvenbooden, P. Glasbergen and H. van Lelyveld, *Studies in Environmental Science*, 17, 465-478.