

Methodology for the Derivation of Remedial Targets for Soil and Groundwater to Protect Water Resources

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Preface

Although this report has been produced by the Environment Agency, it also has the support of the Scottish Environment Protection Agency (SEPA), which has been represented on the Peer Review Group. Where reference is made to “the Agency” or “the Agencies” in the report, this can be taken as referring to both the Environment Agency and SEPA.

This report constitutes Environment Agency R&D Publication 20.

Note

This report adopts normal cartesian co-ordinates in all equations and formulae. This results in slightly different formulae from those given in Domenico (1987) (Ref 9) and in ConSim (Ref 15). Care should be exercised when comparing between referenced sources and standard texts.

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Statement of use

This R&D report integrates and supersedes the procedures presented in two earlier R&D Technical Reports P12 and P13. It describes a methodology for deriving remedial targets for contaminated soil and groundwater where this is necessary to protect water resources (controlled waters). It adopts a tiered risk-based approach to the assessment of the significance of such contamination in terms of the need for remediation to protect defined water receptors. It will be directly applicable to both Agency staff and others involved in the remediation of contaminated soil and groundwater and form the basis for agreeing remedial targets where the risks to controlled waters are unacceptable.

The methodology has potential application to the remediation of sites controlled under the Town & Country Planning system, sites regulated under Part IIA of EPA90 and sites where Works Notices under section 161 of WRA91 are served. However, users of this methodology should refer to relevant guidance under each regulatory regime in order to understand how this procedure should be applied in each context.

Research contractor

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FOREWORD

The Environment Agency of England and Wales has a duty to monitor and protect controlled waters. Increasing focus has been placed on the protection and remediation of land and groundwater in recent years. New legislation has been introduced to give the Agency powers to prevent future pollution of controlled waters, and the Agency anticipates further powers in relation to the identification and remediation of contaminated land.

The Environment Agency, in conjunction with the Scottish Environment Protection Agency, identified the need to develop a standardised, practical and reasonable approach to soil and groundwater remediation for the protection of the aquatic environment that can be applied on a site by site basis and is consistent with current UK legislation.

This methodology, which builds on previous Environment Agency R&D Technical Reports P12 and P13, provides a framework for determining the degree of soil and groundwater remediation that is necessary to protect water resources, and which can be applied under the current range of applicable legislative regimes. This document will be of use to owners of contaminated sites and their consultants, and will provide an accepted basis for discussion with the environment agencies. The Agency hopes that the publication of this methodology will provide a consistent framework for establishing remedial targets that are protective of controlled waters, and that it will facilitate discussion and allow improved decision making where soil and waters are contaminated.

A handwritten signature in dark ink, appearing to read 'R. J. Pentreath', written in a cursive style.

Dr R J Pentreath
Chief Scientist and Director of Environmental Strategy

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SUMMARY

The Environment Agency and the Scottish Environment Protection Agency have identified the need to develop a standardised, practical and reasonable approach to soil and groundwater remediation for the protection of water resources that can be applied on a site-by-site basis and is consistent with current legislation and guidance.

This report provides a methodology to derive the level of remediation required to protect groundwater and surface water and forms part of the overall process to evaluate the health and environmental risk that contaminated soil and groundwater represent. The methodology is based on a *risk assessment* approach incorporating a *source-pathway-receptor* analysis, that leads to the derivation of site-specific remediation criteria based on an assessment of the potential impact at the identified receptor.

Consistent with the Agencies' approach to risk assessment, the overall methodology is based on a tiered approach to determine risk-based remedial targets for soil and groundwater, involving structured decision-making, cost-benefit considerations and progressive data collection and analysis. At each tier a remedial target is derived, but this is likely to be less onerous at the next tier as additional processes (such as dilution and attenuation) that affect contaminant concentrations along its pathway to the receptor are taken into account. With successive tiers, the data requirements and the sophistication of the analysis increase, and the confidence in the predicted impact also increases. Consequently the source-pathway-receptor relationship is better defined, and remedial requirements are likely to be less onerous, if the risk assessment is favourable. The tiered approach enables low-risk sites to be screened out and attention to be focused on those sites where the risks are greatest.

The procedure for determining site-specific remedial targets is summarised below:

- 1) Determine a **target concentration** at the **receptor** or **compliance point** in relation to its use.
- 2) Undertake the **tier assessment** to determine whether the contaminant source would result in the target concentration being exceeded at the receptor or compliance point. At each tier, a **remedial target** is determined.
- 3) If the contaminant concentrations on-site exceed the remedial target, then the decision whether it is appropriate to upgrade the tier analysis is based on:
 - timescale - the decision to proceed to the next tier analysis should only be made if any risk involved in delaying the decision to implement the remedial action is acceptable;
 - what additional information is required and can be obtained;
 - cost-benefit analysis, i.e. the cost of tier upgrade in relation to the potential reduction in the cost of the remedial solution.

Four assessment tiers are proposed for the assessment of **contaminated soil** to protect water resources:

Tier 1 considers whether contaminant concentrations in “pore water” in contaminated soil are sufficient to impact on the receptor, ignoring dilution, dispersion and attenuation along the pathway. The “pore water” concentration is determined from:

- i) measured “pore water” concentrations or perched water quality;

- ii) soil leaching tests;
- iii) theoretical calculations based on soil/water partitioning equations.

Tier 2 considers **dilution** by the receiving groundwater or surface water body and whether this is sufficient to reduce contaminant concentrations to acceptable levels. The remedial target is defined as the target concentration multiplied by a dilution factor (DF).

Tiers 3 and 4 consider whether natural **attenuation** (including dispersion, retardation and degradation) of the contaminant as it moves through the unsaturated and saturated zones to the receptor are sufficient to reduce contaminant concentrations to acceptable levels. The remedial target is defined as target concentration multiplied by a dilution factor (DF) and attenuation factor (AF). In Tier 3 simple analytical models are used to calculate the significance of attenuation, whereas in Tier 4 more sophisticated numerical models are used.

For each tier, the “pore water” concentration determined for the soil zone is compared to the remedial target to determine the need for remedial action.

The assessment in relation to **contaminated groundwater** commences at Tier 2 as the contaminants have already moved through the soil zone, so that the only processes of significance are attenuation, dispersion and further dilution of this groundwater as it moves from the source towards the receptor. Thus the assessment tiers for contaminated groundwater are:

Tier 2 - the observed contaminant concentration in groundwater below the site is compared directly to the target concentration.

Tiers 3 and 4 - the observed groundwater concentration below the site is compared directly to the target concentration multiplied by an attenuation factor (AF); as with the soil tiered assessment, Tiers 3 and 4 are distinguished by the sophistication of the modelling and prediction processes.

It is recommended that sensitivity/uncertainty analysis is incorporated into each stage of the tier assessment.

The procedures for setting compliance points and for siting monitoring boreholes are reviewed in the report.

It is stressed that the assessment should be subject to a final review to check that the objectives and practicalities of the remedial action have been fully considered prior to implementation.

Key to parameters and units

A	=	area of contaminant source (m^2)
AF	=	attenuation factor (dimensionless)
a_x, a_y, a_z	=	dispersion coefficient in three dimensions (m)
C	=	concentration of contaminant at point x (mg/l)
C_s	=	soil concentration (mg/kg)
C_c	=	concentration of contaminant in contaminated water (mg/l)
C_{ED}	=	simulated compliance point concentration (mg/l)
C_0	=	initial concentration of contaminant (mg/l)
C_T	=	target concentration for water (mg/l)
C_U	=	background concentration of contaminant (mg/l)
d_a	=	aquifer thickness (m)
DF	=	dilution factor (dimensionless)
f_{oc}	=	fraction of organic carbon (fraction)
H	=	Henry's law constant (dimensionless)
i	=	hydraulic gradient
Inf	=	infiltration (m/d)
k	=	hydraulic conductivity (m/d)
K_d	=	soil/water partition coefficient (l/kg)
K_{oc}	=	organic carbon partition coefficient (l/kg)
$K_{oc,n}$	=	sorption coefficient for related species (l/kg)
$K_{oc,i}$	=	sorption coefficient for ionised species (l/kg)
L	=	length of site in direction of groundwater flow (m)
LTC	=	"pore water" remedial target concentration for in-situ soils (mg/l)
Mz	=	mixing zone thickness (m)
n	=	effective porosity (as a fraction)
pH	=	pH value
pK_a	=	acid dissociation constant
Q	=	abstraction rate (m^3/d)
Q_U	=	surface water flow upstream of discharge point (m^3/d)
Q_C	=	inflow of contaminated water (m^3/d)
R_c	=	retardation factor
STC	=	soil remedial target concentration for in-situ soils (mg/kg)
S_z, S_y	=	width and thickness of contaminant plume at source (m)
t	=	time (d)
w	=	width of site (m)
θ_a	=	air filled soil porosity (fraction)
θ_w	=	water-filled soil porosity (fraction)
ρ	=	bulk density (g/cm^3)
λ	=	decay constant (0.693/half life of contaminant in days)

1. INTRODUCTION

1.1 General

The Environment Agency has duties under the Water Resources Act 1991 to monitor and protect water resources. The Scottish Environment Protection Agency (SEPA) has similar duties under the Control of Pollution Act 1974 (as amended). The Agencies have identified the need to develop a standardised, practical and reasonable approach to soil and groundwater remediation for the protection of water resources that can be applied on a site-by-site basis and is consistent with current legislation and guidance. With this purpose, the Environment Agency commissioned the following research and development projects to derive **remedial targets**:

- 1) *A Methodology to Derive Groundwater Clean-Up Standards* (R&D Technical Report P12), undertaken by the Water Research Centre (Ref 1).
- 2) *Methodology to Determine the Degree of Soils Clean-Up Required to Protect Water Resources* (R&D Technical Report P13), undertaken by Dames and Moore (Ref 2).

The methodology outlined in the present report integrates these two studies, to provide a consistent methodology that meets the objectives noted above. It is based on a *risk assessment* approach incorporating a *source-pathway-receptor* analysis, that leads to the derivation of on-site remediation criteria based on an assessment of the potential impact at the identified receptor. In their general approach the procedures in this report are similar to those described in the ASTM *Risk-Based Corrective Action* procedure (Ref 3). However, the present report is focused on the protection of water resources and specifically recognises the statutory responsibilities of the Environment Agency and the Scottish Environment Protection Agency (SEPA) in England, Wales and Scotland.

The principal objectives of the methodology are to determine which of the following are required:

- no remedial action, that is, the level of contamination does not or is not likely to cause pollution of surface water or groundwater;
- remedial action to protect an identified groundwater or surface water receptor;
- further analysis and data collection to quantify the degree of risk to the receptor.

The overall methodology is based on a tiered approach to determine risk-based remedial targets for soil and groundwater, involving structured decision-making, cost-benefit considerations and progressive data collection and analysis. At each tier, a remedial target is derived, but this is likely to be less onerous at the next tier as additional processes (such as dilution and attenuation) that affect contaminant concentrations along its pathway to the receptor are taken into account. With successive tiers, the data requirements and the sophistication of the analysis increase, but the confidence in the predicted impact also increases, thereby potentially allowing a relaxation of the remediation requirements, if the risk assessment is favourable. In accordance with best practice, the tiered approach enables low-risk sites to be rapidly screened out and attention to be focused on those sites where the risks, and in consequence the information needs, are greatest.

This tiered approach was originally described in R&D Technical Report P13 (Ref 2) in relation to clean-up guidelines for soil. It has been developed in this document and a similar approach incorporated for groundwater. It is consistent with the broader framework of risk assessment in the Agencies.

This document sets out a methodology to derive the level of remediation required to protect groundwater and surface water receptors. It is one of the working tools that can be used in the overall process of evaluating the health and environmental risk that contaminated soil and groundwater represent, as illustrated by Figure 1.1. A separate approach, *The Contaminated Land Exposure Assessment Model* (CLEA, Ref 4), has been developed by the DETR/Agency to derive risk-based soil assessment criteria that are protective of human health, whilst the software package ConSim (Ref 15) has been produced for the Environment Agency to assist in the assessment of risks to controlled waters from land contamination, and can be used in conjunction with this report.

This methodology provides guidance for the assessment and management of risks specifically to the quality of controlled waters from land and groundwater contamination. Further guidance on the principles associated with assessing and managing risks from land contamination can be found in Contaminated Land Research Report CLR 11, *Handbook of Model Procedures for the Management of Contaminated Land* (Ref 5), which should be read prior to undertaking any detailed risk assessment on a potentially contaminated site. The model procedures detail the principles and processes that may be adopted for assessment and management of risks associated with land contamination.

It is important to recognise that the level of remediation required to protect other receptors may differ from those derived for the protection of water resources. Human health is generally perceived as the most important, but the persistence of some substances in groundwater and low concentrations of many environmental standards mean that this latter receptor is often (but not invariably) the most sensitive.

The methodology set out in this document can be used both for assessing risks to water quality from land contamination (i.e. is there a problem?) and in managing those risks that are considered unacceptable (i.e. what should be done about it?). It should be noted, however, that the methodology assumes that remedial action will take the form of contaminant concentration reduction, by either treatment or removal (i.e. treating the source of contamination). This is a narrower range of risk management actions than are covered by the definition of 'remediation' in the draft statutory guidance for Part IIA of the Environmental Protection Act 1990, which covers methods of managing those risks of pollution at any point on the source-pathway-receptor (pollutant) linkage. Other forms of "remedial" action may be appropriate and more cost-effective on specific sites (e.g. engineered containment, reactive barrier walls, hydraulic control) and this methodology does not preclude the use of alternative appropriate techniques for managing risks to controlled waters from land contamination.

1.2 How to use this document

The assessment framework and the basic approach for determining remedial targets for contaminated soil or groundwater are set out in Chapter 2. Detailed discussion of the methodology is then contained in Chapters 3 - 6 as follows:

- Initial assessment of source/pathway/receptor and remedial action(s) Section 3.1.

- Derivation of target concentration at receptor/compliance point Section 3.2

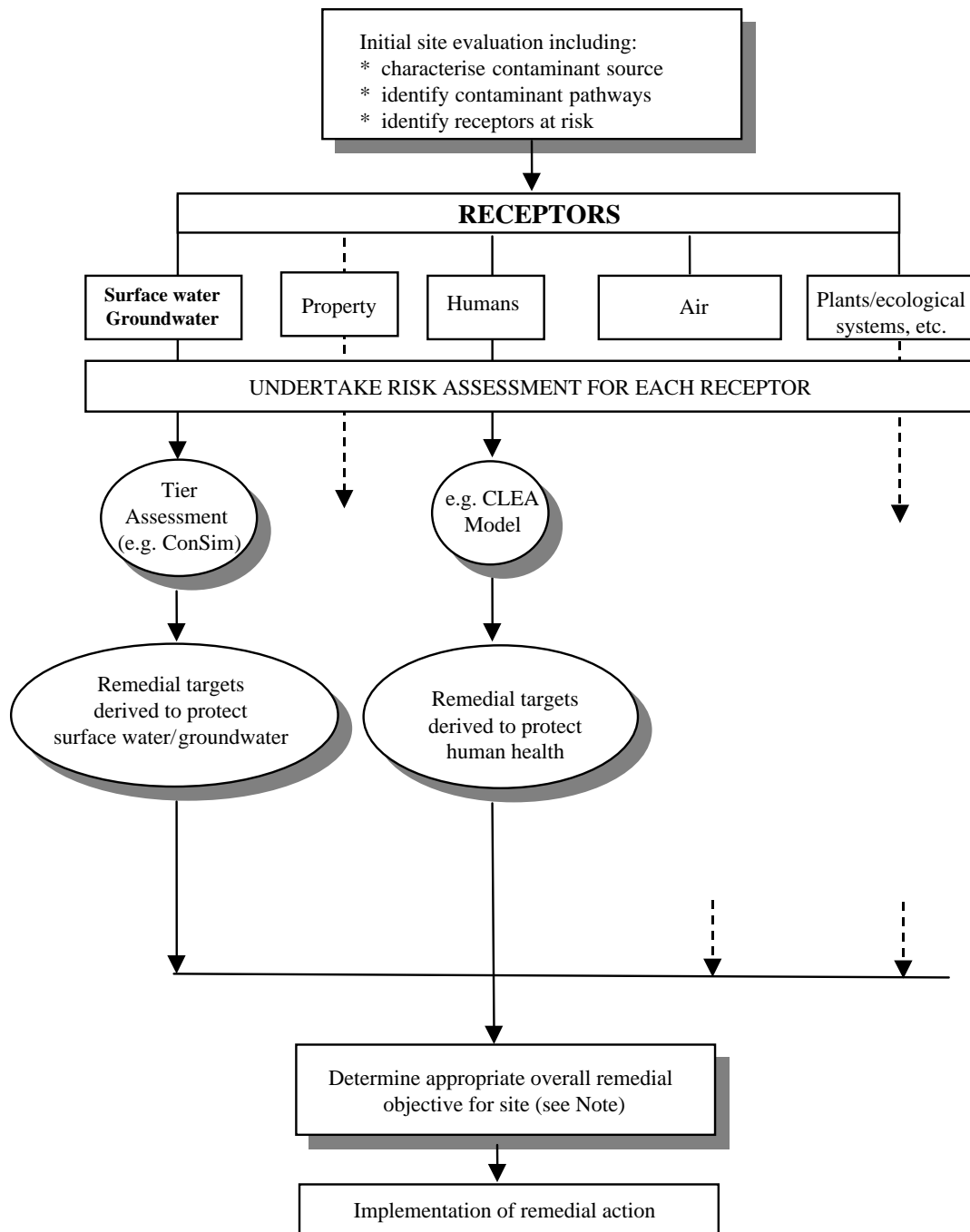
- Identification and selection of compliance point Section 3.3

- Determination of remedial target concentration for:
 - Contaminated soil Chapter 4
 - Contaminated groundwater Chapter 5
 - Contaminated soil and groundwater Chapter 6
 - Free product Section 5.4

A slightly different procedure is used depending on whether the source of contamination is soil or groundwater. For soils, the procedure assumes that there is the potential for pollution of surface water or groundwater, and a conservative approach should be adopted to ensure protection of these receptors. For groundwater, contamination will already have occurred. In this case the methodology recognises that complete clean-up of groundwater is not always achievable or cost-beneficial. For many sites, the assessment will need to consider both soil and groundwater contamination (Chapter 6).

Owing to the variability of soil and groundwater systems, this document is not intended to provide a prescriptive approach, but rather identifies the key decision factors in determining remedial targets. This decision process will generally require a high level of technical expertise, particularly for the application of the higher tiers of assessment (Tiers 3 and 4) and will require a detailed appreciation of both hydrogeological and geochemical processes, together with expertise in the application of models.

Figure 1.1 The context of the risk assessment



NOTE: The remedial targets required to protect different receptors will vary.

1.3 Legislative context

The Environment Agency has duties under the Water Resources Act 1991 to monitor and protect controlled waters (Ref 6A). Section 85 of the Water Resources Act provides powers of prosecution should pollution of controlled waters be caused or knowingly permitted. SEPA has similar powers under the Control of Pollution Act 1974 (as amended) (Ref 6B).

Under the EC Groundwater Directive (80/68/EEC) Member States are obliged to take specific measures to prevent List I substances from entering groundwater and to restrict the entry of List II substances so as to prevent pollution. It is important to note that the main focus of the Groundwater Directive is to prevent or restrict discharges, and its implementation in the UK is primarily via the Groundwater Regulations 1998 and the Waste Management Licensing Regulations 1994.

Under the Groundwater Directive there is a need to undertake “prior investigation” before Authorisations to release List I and II substances to ground are granted, and there should also be “requisite surveillance” of groundwater to assess the impact of Authorised discharges. The data obtained via these requirements may be useful in any assessments conducted under the methodology described in this report.

Until recently there has been little legislation that has specifically dealt with soil and groundwater contamination arising from historic activities, though Section 161 of the Water Resources Act 1991 gives the Environment Agency powers to remedy or forestall pollution of controlled waters and reclaim the costs of so doing from the person(s) causing or knowingly permitting the pollution to occur. Thus the Environment Agency may enter any land or carry out remedial works where that is deemed necessary and appropriate. In Scotland, these powers are provided by Sections 46A-D of the Control of Pollution Act 1974 (as amended).

Note: “Pollution” and “Controlled waters” are defined in the glossary.

The Environment Act 1995 introduced specific legislation into the UK for the first time to deal with the remediation of contaminated land and also proper provisions for the regulation of historical groundwater pollution. Part IIA of the Environmental Protection Act 1990 (EPA 1990), which is added by Section 57 of the Environment Act 1995, is due to be implemented in 2000. This requires local authorities to identify land within their boundaries that falls within the statutory definition of contaminated land and gives them powers to serve Remediation Notices on “appropriate persons” (that is, those who caused the pollution and/or the owner of the site identified as contaminated land). Land may be classed as contaminated land by virtue of actual or likely pollution of controlled waters caused by materials on or in the land. Where pollution of controlled waters is an issue, then the Agency must be consulted and its views taken into account. For particular categories of sites, known as “Special Sites”, the Agency takes over regulatory responsibilities. Special Sites include those where groundwaters in certain aquifers are contaminated by compounds defined in List I of the EC Groundwater Directive, where potable water abstractions are threatened, or where watercourses would fail criteria for classification under the Surface Waters Regulations.

In other situations where there is no existing pollutant linkage (because of natural circumstances or human intervention to remove the source or cut the pathway), a modification to Section 161 of the Water Resources Act 1991 can be used which allows Works Notices to be served on the person or persons who caused or knowingly permitted the pollution to arise, in order that it can be remedied or forestalled. This legislation was implemented in England

and Wales in 1999. Therefore, rather than undertake the work itself and face the difficulties of reclaiming the costs, the Agency can require those responsible for the pollution to undertake the requisite work. If such a person is unable to be found or identified and if remediation is required, the Environment Agency may decide to undertake the work itself.

The main focus of the current report is in assessing the remedial targets that should be applied to residual (usually historic) contamination. Thus its main use will be in relation to the application of Part IIA of the EPA 1990 and Works Notices, as described above, and to the redevelopment of contaminated land through the planning process.

It should be noted that some of the remediation activities that follow on from the assessment procedures noted in this report may in themselves constitute activities that could pose a risk to groundwater. These would come under the requirements of the Groundwater Directive and the appropriate means of implementation in the UK described above.

2. FRAMEWORK

2.1 Basic Steps

The basic steps in determining remedial targets and the need for remedial action to protect surface water or groundwater receptors are summarised in Figure 2.1 and are as follows:

2.1.1 Identification of potential risk

- 1) Identification and characterisation of the source, including preliminary assessment of the contaminant spatial distributions and concentrations, together with their physical and chemical properties.
- 2) Identification and characterisation of the potential environmental receptor(s).
- 3) Identification of the transport and exposure pathways of contaminants to a potential environmental (water-based) receptor.

This will largely be a desk-based exercise, supplemented by the results of an initial site investigation. If no receptor or pathway is identified, then no further action is required.

2.1.2 Assessment of Risk

- 4) Preliminary assessment (described in Chapter 3) includes an assessment of the timescale for undertaking a more detailed risk assessment and the need for interim corrective action where the source has already affected water quality or where the source is in close proximity (a short travel time) to the receptor, for example, within a groundwater Source Protection Zone (Ref 6A).
- 5) Determination of remedial targets for soil and groundwater to protect identified receptor(s) based on a risk assessment approach (a tiered approach to undertaking this assessment is set out in Chapters 4, 5 and 6).
- 6) Comparison of soil or groundwater contaminant concentrations with the remedial targets to determine which of the following actions are appropriate:
 - no action is required, as the observed concentrations do not represent a risk to water quality at the receptor;
 - upgrade tier assessment, including further data collection and analysis;
 - undertake remedial action to protect the receptor.

2.1.3 Implementation

In the event that remedial action is required, the following will be needed:

- 7) Design remedial actions to prevent or minimise the impact on the identified receptor. The overall scheme design should also take account of environmental benefit and cost.
- 8) Construction and operation of the remedial scheme(s).
- 9) Environmental monitoring to verify the effectiveness of remediation.
- 10) Decommissioning of the scheme(s) once remediation is effectively completed (it has been agreed that remedial objectives have been achieved).

2.2 Underlying concepts

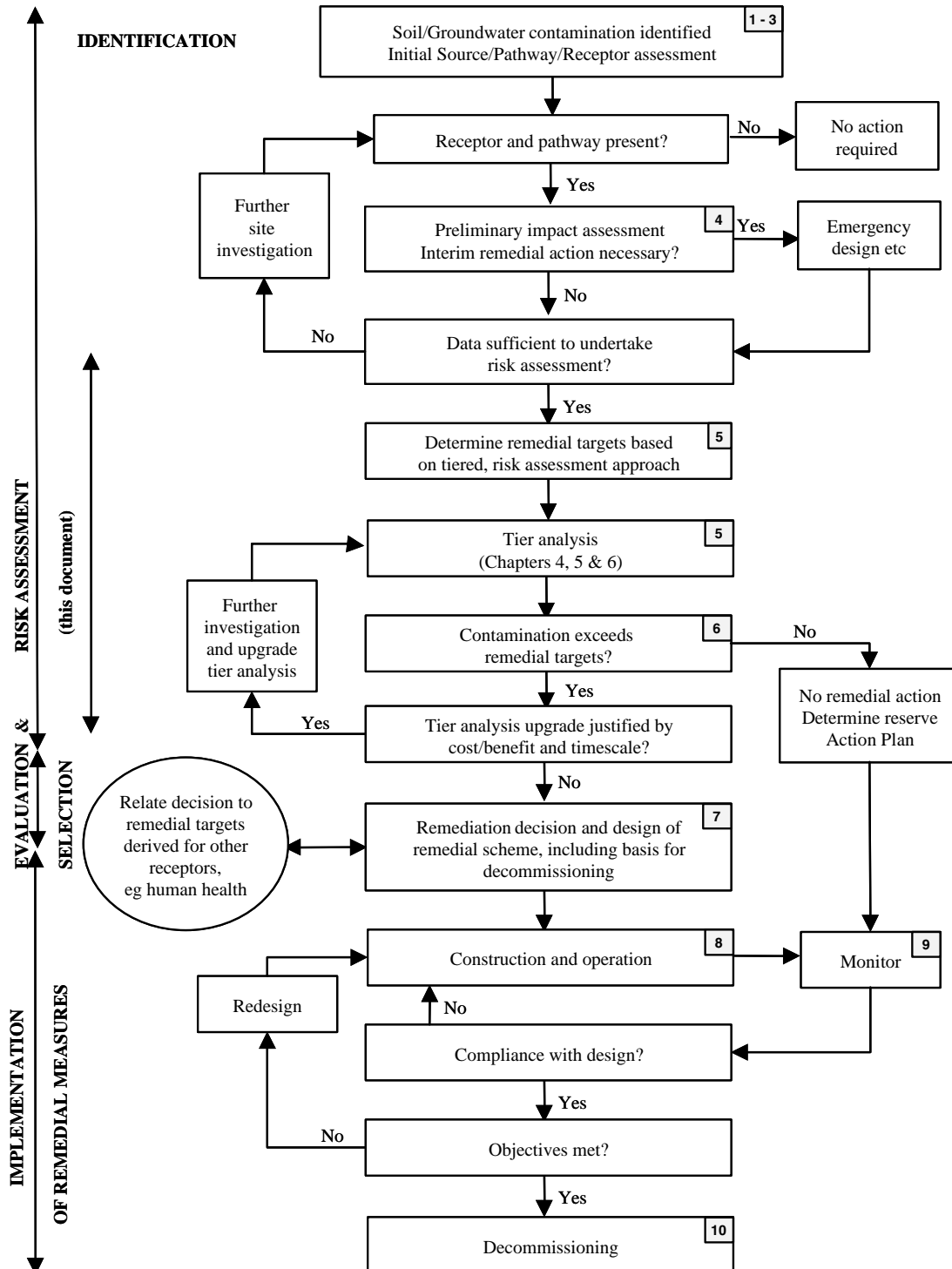
2.2.1 Conceptual model

It is essential that, at an early stage in the assessment, a conceptual model of the soil and groundwater system is drawn up based on all the physical, hydraulic and chemical data available and drawing on local knowledge of the site and the surrounding area. The physical and hydraulic components of the model will form the framework within which conclusions regarding the chemical data can be drawn. It is emphasised that the conceptual model is the key to risk assessment. If the basic physical and hydraulic data are substantially inadequate, conclusions drawn from the chemical data may be seriously in error. The conceptual model should also take account of any assumptions or simplifications made in the tier assessment process. For example, the application of analytical equations in Tiers 1 to 3 usually involves making a number of assumptions regarding the contaminant flow path.

The continuous refinement of the conceptual model and feedback into the investigatory process should provide a focus for the tier assessment process. The conceptual model forms a reference point for the risk assessment, and its sensitivity to uncertainty in the base data is the test of the robustness of the process. The ensuing decisions on the need for and extent of remedial measures should have regard to the uncertainties in the conceptual model.

Figure 2.1: Assessment Framework

(Box numbers refer to numbered steps in Section 2.1)



2.2.2 Sensitivity and timescale

The assessment and any course of action will need to take account of the sensitivity of the receptor, the timescale necessary for the assessment and the consequences of any impact (Figure 2.2).

The *sensitivity* of the site will be determined by its location in relation to:

- aquifer designation, e.g. Major, Minor or Non-Aquifer;
- actual use of groundwater resource, for example, developed for potable water supply;
- the groundwater protection status of the site, for example, within an Inner (50 day) or Outer (400 day) Source Protection Zone;
- aquifer vulnerability (for example, is there a thick cover of low permeability clays?);
- the proximity, type and degree of hydraulic continuity with surface water systems;
- existing surface water or groundwater quality.

The concepts of vulnerability and risk to groundwater are dealt with in further detail in Refs 6A and 6B.

In determining the course of action, *timescale* represents a key component in terms of both the time before an impact is observed at the receptor and the time to:

- undertake any further investigations and tier assessment;
- implement and complete remedial measures.

For example, for a contaminant source located within an Inner Source Protection Zone, and with a potentially severe impact, interim measures are likely to be needed as there will be insufficient time to complete the investigations and assessment necessary to refine the risk assessment at the higher assessment tiers. The assessment may need to take account of the fact that the source of contamination may have been known for some time, but without any clearly identified impact at the receptor.

2.2.3 Tiered analysis

The definitions of key terms are given in Table 2.1 and illustrated by Figures 2.3 and 2.4. The procedure for determining **remedial targets** is described in detail in Chapters 4 to 6 and summarised below:

- 1) Determine a **target concentration** at the receptor in relation to its use. This will normally be set as equivalent to a water quality standard or to background water quality.

Figure 2.2 Conceptual relationship of timescale, tiered assessment and remedial actions

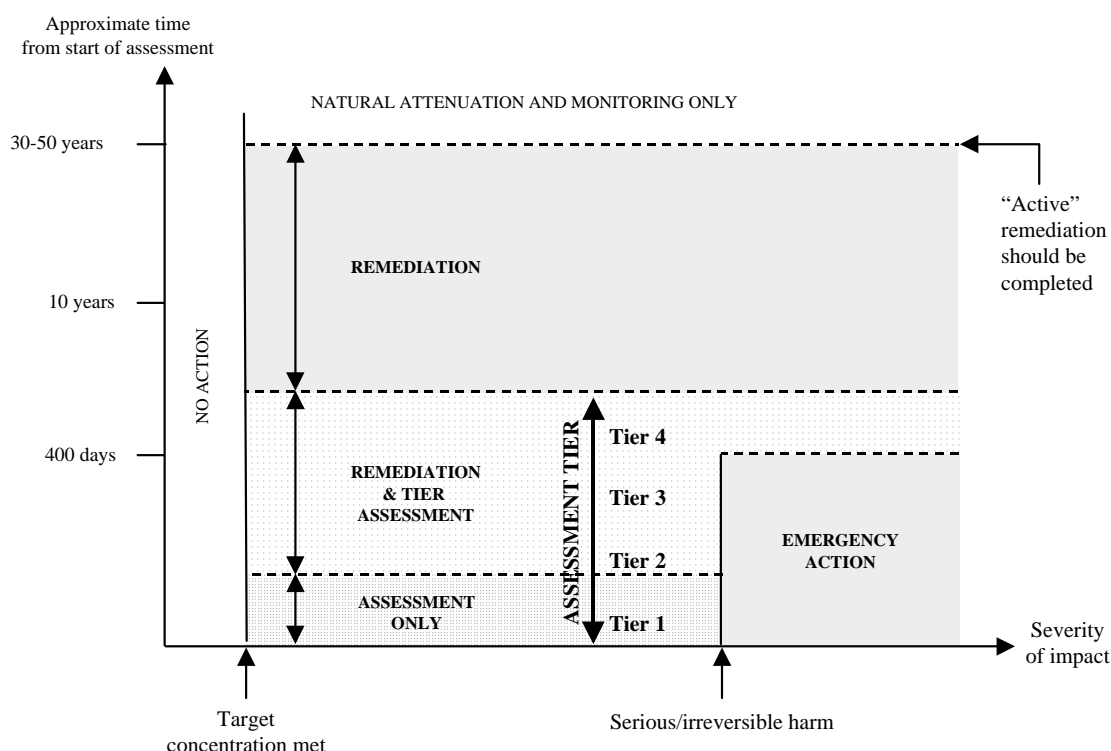


Table 2.1 Key Definitions

Target concentration

The concentration at the compliance point that should not be exceeded. This will normally be set as equivalent to a water quality standard or to background water quality. The target concentration remains constant during the assessment process.

Remedial target (remedial target concentration)

The derived soil or groundwater concentration from the tier analysis, above which remediation is required. This may be set as equivalent to the target concentration or to the target concentration multiplied by a dilution and attenuation factor, dependent on the level of the tier analysis. The remedial target concentration is site-specific and will change with each tier of assessment.

Compliance point

The point along the contaminant pathway where the target concentration should not be exceeded. This may be the receptor, such as an abstraction, the aquifer or even “pore water” in the soil zone. Its location will depend on the level of tier assessment.

Pore water

Throughout this report the term “pore water” will be used in a general sense to describe any free water (that is, not adsorbed within the matrix of a soil or rock and incapable of participating in contaminant movement) contained within the primary pore space or within fissures in either the unsaturated or the saturated zone.

Table 2.2 Summary of assessment tiers

SOIL

Tier 1 considers whether the concentrations in “pore water” in contaminated soil are sufficient to impact on the receptor, ignoring dilution, dispersion and attenuation along the pathway. The “pore water” concentration may be determined in a number of ways (note definition in Table 2.1), which in order of preference are:

- i) measured “pore water” concentrations or perched water quality;
- ii) soil leaching tests;
- iii) theoretical calculations based on soil/water partitioning equations.

Leaching tests will generally be the preferred method for determining potential soil “pore water” concentrations in the absence of direct data. The “pore water” concentration is compared with the target concentration derived for the receptor to determine the need for remedial action. The compliance point is taken as the soil zone (Figure 2.3).

Tier 2 considers dilution by the receiving groundwater or surface water body and whether this is sufficient to reduce contaminant concentrations to acceptable levels. The remedial target is defined as the target concentration multiplied by a dilution factor (DF). This factor will typically be calculated as the ratio between groundwater flow below the site (the source area) and infiltration through the contaminated soil. The compliance point is taken as groundwater beneath the source area (Figure 2.3).

Tiers 3 and 4 consider whether attenuation of the contaminant as it moves through the unsaturated and saturated zones to the receptor is sufficient to reduce contaminant concentrations to acceptable levels. The remedial target is defined as target concentration multiplied by a dilution factor (DF) and attenuation factor (AF). It is implicit in Tiers 3 and 4 that there is the possibility of an impact on groundwater quality between the source of contamination and the receptor. In Tier 3 simple analytical models are used to calculate the significance of attenuation whereas in Tier 4 more sophisticated numerical models are used. The compliance point is taken as a point down hydraulic gradient of the site. This may be an abstraction or at an agreed point between the source and the abstraction (Figure 2.3).

For each tier, the “pore water” concentration determined for the soil zone is compared to the remedial target to determine the need for remedial action.

GROUNDWATER

The assessment for contaminated groundwater commences at Tier 2 as the contaminants have already moved through the soil zone, so that the only processes of significance are degradation, retardation, dispersion and dilution of this contamination in the saturated zone as it moves from the source towards the receptor. For each tier, the observed contaminant concentration in groundwater is compared to the remedial target to determine the need for remedial action.

Tier 2 - the observed groundwater concentration below the site is compared directly to the target concentration. The compliance point is taken as groundwater below the site (Figure 2.4).

Tiers 3 and 4 - the observed groundwater concentration below the site is compared directly to the target concentration multiplied by an attenuation factor (AF). As with the soil tiered assessment, Tiers 3 and 4 are distinguished by the sophistication of the modelling and prediction processes.

In moving through from Tier 1 to Tier 4 the data requirements and resources required increase, but the degree of conservatism in the approach decreases and the cost-effectiveness of the final remedial solution is likely to improve.

- 2) Undertake the **tier assessment** (Table 2.2) to determine whether the contaminant source would result in the target concentration being exceeded at the receptor or **compliance point**. At each tier, a **remedial target** is determined, taking account of processes (such as dilution and attenuation) that may affect contaminant concentrations, above which the target concentration would be exceeded.
- 3) If the remedial target is exceeded, then the decision whether it is appropriate to upgrade the tier analysis is based on:
 - cost-benefit analysis, i.e. the cost of tier upgrade in relation to the potential reduction in cost of the remedial solution;
 - what additional information is required and can be obtained;
 - the timescale - the decision to proceed to the next tier analysis should only be made if any risk involved in delaying the decision to implement the remedial action is acceptable.

For most sites a number of contaminants will be present and the assessment will need to be carried out for each of these contaminants, along each feasible source-pathway-receptor (pollutant) linkage, in order to determine which is the most critical in relation to remediation.

The **remedial targets** that will drive the remedial actions should:

- be site-specific;
- relate to the actual or intended (planned) use of the most sensitive environmental receptor such as future land or groundwater use;
- be achievable within a reasonable (agreed) timescale;
- provide protection to the identified receptor(s);
- take account of the likelihood that they can be achieved and the cost of remediation to this target;
- take account of existing water quality.

The **remedial actions** that may be implemented should:

- prevent further contamination, including removal or treatment of the source;
- control or intercept the movement of contaminants away from the source (i.e. remove the pathway);
- implement treatment at the receptor.

Figure 2.3 Summary of Tier Assessment for Soils

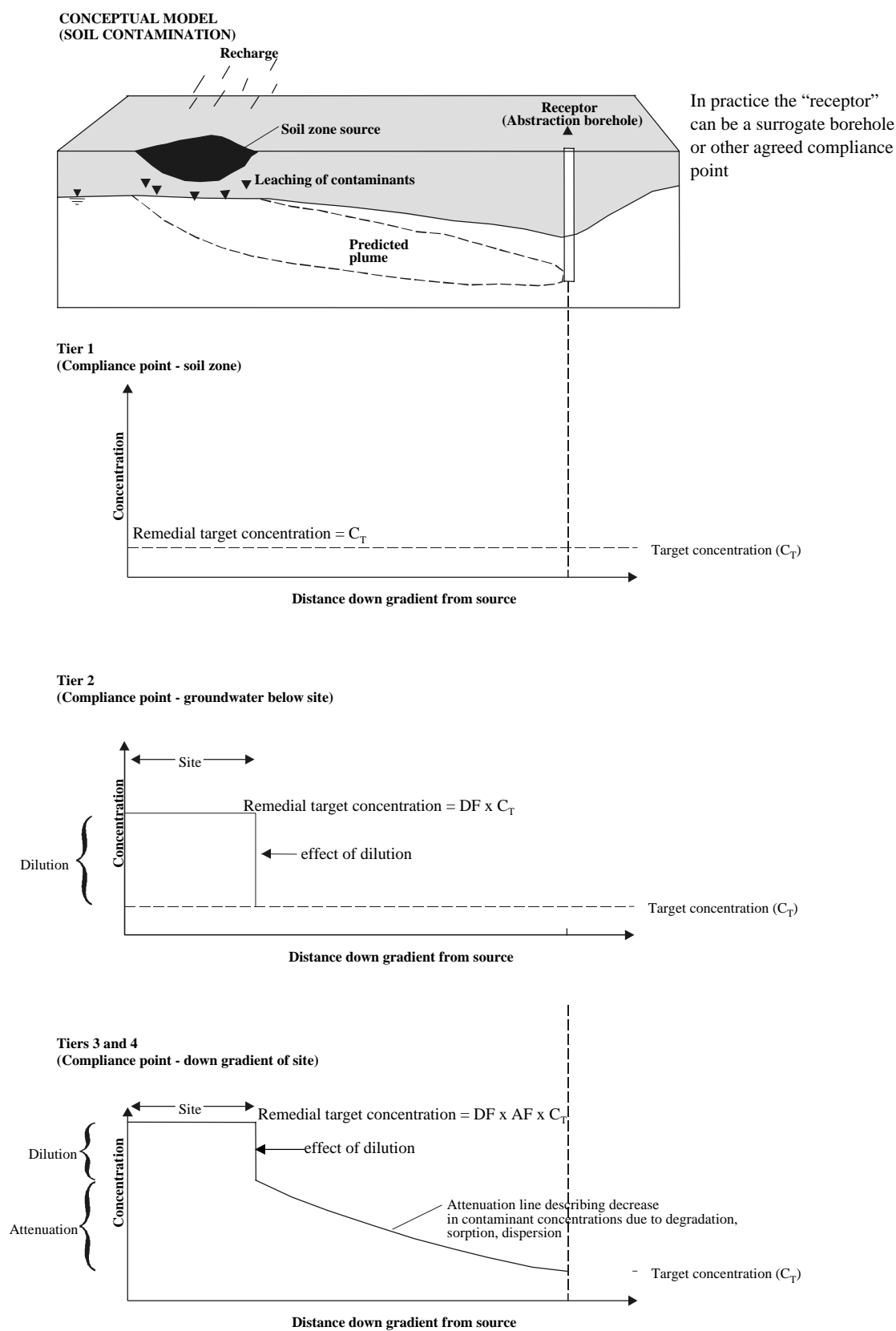
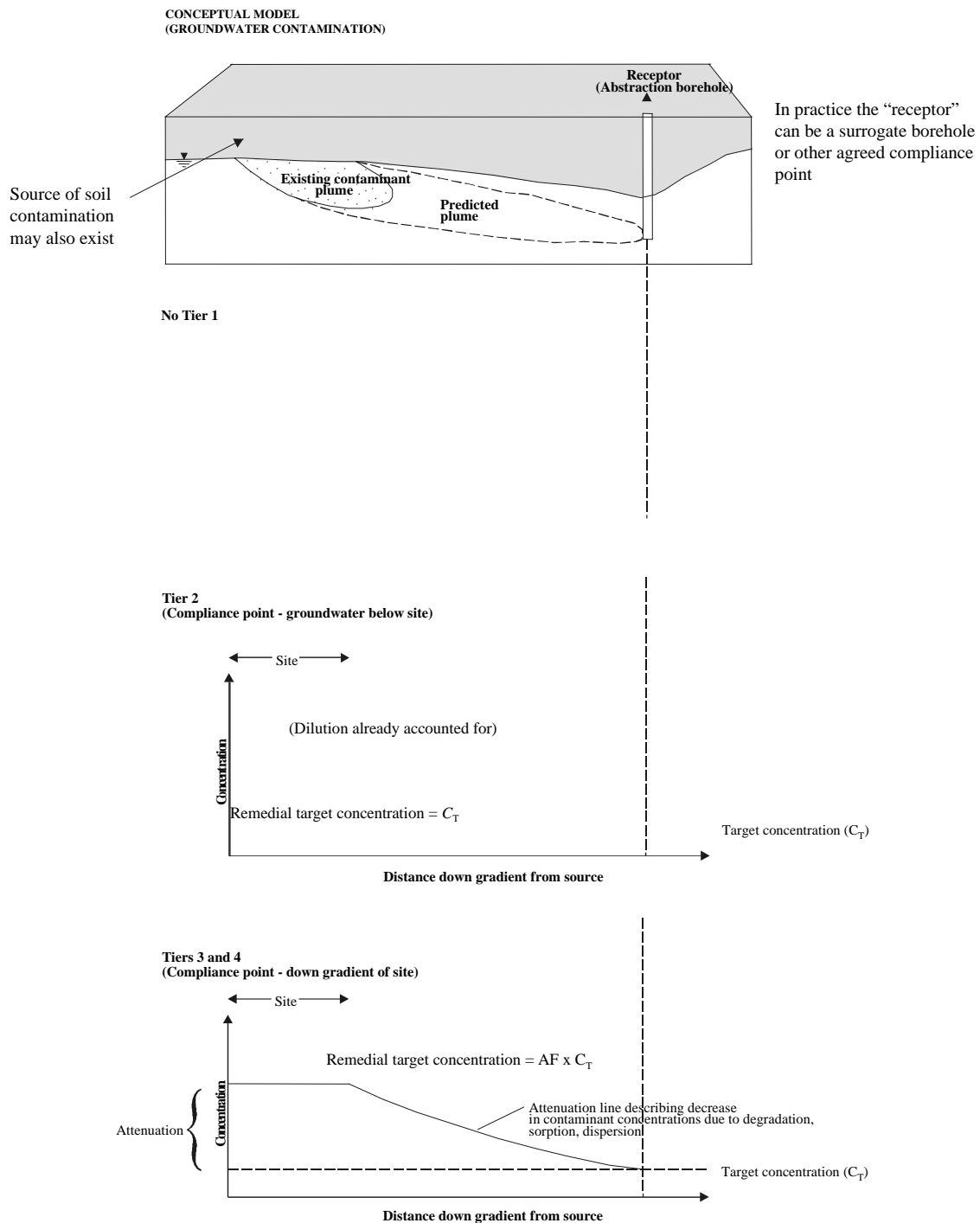


Figure 2.4 Summary of tier assessment for groundwater



3. ASSESSMENT

The procedures in this chapter are common to both soil and groundwater tiered analyses.

3.1 Source/pathway/receptor assessment

3.1.1 Source characterisation

The source of contamination should be defined in terms of:

a) Origin and extent

- primary
 - liquid (e.g. DNAPL) spillage/leak from containment or distribution system;
 - deposit of solid/sludge (waste) that contains leachable constituents (e.g. coal tar).
- secondary
 - historically contaminated soil (attached as a solid, or adsorbed onto soil grains);
 - vapour in unsaturated soil or aquifer pore space;
 - dissolved in groundwater (“pore water” or fissure water);
 - dissolved in surface water (effluent to groundwater).

b) Depth/location

- soil zone;
- unsaturated zone;
- perched horizons;
- saturated zone;
- free/dissolved/vapour phase;
- into natural ground or artificial structures/site services;
- vertical and lateral extent.

c) Physical and chemical properties

- density;
- mobility;
- solubility;
- volatility;
- toxicity;
- type of contaminant, inorganic, organic;
- degradability
- soil/water partitioning;
- persistence;
- present as free product or dissolved phase (single- or multi-phase flow);
- viscosity;
- leachability;
- material (contaminant)/water partitioning (for primary sources).

Table 3.1 Data requirements for the analysis

	Tier 1	Tier 2†	Tier 3†	Tier 4†
Likely data requirements (see also Appendix 1) for SOIL	<p>“Pore water” concentration, e.g. leaching test, direct measurement, etc. or if assessment based on theoretical calculation (Table 4.1), each of the following:</p> <p>Measured total soil concentration</p> <p>Water-filled soil porosity</p> <p>Air-filled soil porosity</p> <p>Henry’s law constant</p> <p>Soil bulk density</p> <p>Partition coefficient of contaminants.</p> <p>For organic contaminants, the partition coefficient can be calculated from the fraction of organic carbon and the organic carbon partition coefficient (Table 4.2)</p> <p>Soil pH value</p> <p>Contaminant properties, including solubility and density</p> <p>Not applicable</p>	<p><i>Infiltration</i></p> <p>Area of contaminated soil</p> <p>Effective rainfall</p> <p>Percentage run-off due to, for example, presence of hard standing</p> <p><i>Groundwater flow</i></p> <p>Hydraulic conductivity</p> <p>Hydraulic gradient</p> <p>Saturated aquifer/mixing zone thickness</p> <p>Source dimension relative to groundwater flow</p> <p><i>Other</i></p> <p>Flow in receiving watercourse</p> <p>Groundwater abstraction</p> <p>Background surface water or groundwater quality</p>	<p><i>As Tiers 1 and 2 plus</i></p> <p>Distance to compliance point</p> <p>Degradation characteristics of contaminant</p> <p>Effective porosity</p> <p>Dispersivity</p> <p>Partition coefficient - saturated zone</p> <p>Bulk density - saturated zone</p> <p><i>Unsaturated zone</i></p> <p>Depth of unsaturated zone</p> <p>Partition coefficient</p> <p>Bulk density</p> <p>Water-filled porosity (moisture content)</p> <p>Soil type</p> <p>Sorption characteristics</p>	<p><i>As Tiers 1, 2 and 3 plus</i></p> <p>Aquifer geometry</p> <p>Lateral and vertical variation of aquifer properties such as:</p> <ul style="list-style-type: none"> • effective porosity • storage • hydraulic conductivity <p>Groundwater head distribution (including changes with time)</p> <p>Aquifer inflows and outflows (including abstraction, effective recharge, spring discharges)</p> <p>Observed contaminant distribution (including changes with time)</p> <p>Field evidence of degradation</p>
Likely data requirements (see also Appendix 1) for GROUNDWATER		<p>Contaminant concentrations in groundwater within the plume</p> <p><i>Other</i></p> <p>Flow in receiving watercourse</p> <p>Groundwater abstraction</p> <p>Hydraulic conductivity</p> <p>Hydraulic gradient</p> <p>Saturated depth/mixing zone thickness</p> <p>Source dimension relative to groundwater flow</p>	<p><i>As Tiers 2 and 3 for soils and Tier2 for groundwater</i></p>	<p><i>As Tier 3 for groundwater and Tier 4 for soil</i></p>

† Data requirements in addition to those for previous tier. The amount and cost of obtaining data increases with each tier.

* Parameters which are likely to have a major affect on the Tier assessment due to both the sensitivity of the calculation and the fact that a large range in parameter values would be expected are highlighted in bold.

(For contaminants that will break-down by chemical or biodegradable processes it will be necessary to identify what the breakdown products are likely to be and whether these represent a secondary risk.)

3.1.2 Pathways

The potential contaminant pathways will need to be identified in terms of:

- pathway length (distance to the receptor);
- rate of contaminant movement and time to reach receptor;
- character of hydrogeological pathway;
- processes that will affect contaminant concentrations along the pathway, including:
 - diffusion/dispersion
 - dilution
 - attenuation, including volatilisation, sorption and degradation (chemical/biological);
- influence of artificial pathways and barriers, such as culverts, foundations, pipelines, etc;
- chemical environment (oxidising, reducing);
- groundwater/surface water interaction;
- microbiological environment;
- potential for transfer between environmental compartments, e.g. aqueous to sediment phases;
- background water quality;
- physical and chemical properties (particle size, organic carbon content, intergranular and/or fissure porosity);
- possible changes to the pathways through time (seasonal abstractions, rates of infiltration, flow conditions in culverts, etc.).

This information will be determined in increasing detail with each successive tier of assessment (refer to Table 3.1). At the initial assessment phase, a qualitative assessment only would have been made, based on existing data (geological maps, geological memoirs and borehole records), together with the site investigation results.

3.1.3 Receptors

The possible receptors include:

- groundwater abstractions;
- springs;
- groundwater within aquifers;
- estuaries and near-shore environments;
- surface watercourses;
- wetlands.

Information should be obtained in relation to:

- 1) importance of groundwater as a resource, e.g. aquifer classification (Major, Minor, Non-Aquifer);
- 2) aquifer vulnerability (both from maps and from a site-specific assessment);
- 3) proximity of source to, continuity with, and quality/classification of, surface water;
- 4) proximity of source to groundwater abstractions (licensed and unlicensed), including whether the site falls within a Source Protection Zone (SPZ I, II and III);
- 5) actual use of groundwater resource, e.g. developed for potable water supply;
- 6) designated ecologically sensitive sites, e.g. Sites of Special Scientific Interest (SSSIs), Environmental Sensitive Areas (ESAs) etc.;
- 7) historical, current and planned land use, land ownership, site security;
- 8) site services.

3.1.4 Assessment

Sufficient information should have been obtained as part of the above exercise to determine whether:

- no further action is required, as there is no receptor present or a pathway cannot be identified;
- the tiered assessment needs to be undertaken to derive remedial targets to determine the need for and design of the remedial action;
- interim or emergency action is required as the source has already resulted in contamination of the receptor or is in close proximity to the receptor (that is, in imminent danger of causing serious or irreversible harm).

This information should be used to determine the receptor(s) at potential risk and the urgency that may need to be attached to any remedial actions. Although this will need to be determined on a site-by-site basis, the general guidelines shown in Table 3.2 are likely to be appropriate to protect water resources.

Table 3.2 Guidelines for protection of water resources*

Location	Possible action (if risk is identified)
Site located with Inner (50 day) Source Protection Zone (Zone I), and/or close to small potable supply, and/or in hydraulic continuity with a watercourse.	Interim or emergency action.
Site located over major or minor aquifer. Travel time to identified receptor less than 400 days, e.g. within an Outer Source Protection Zone (Zone II).	Need for remedial action to be determined by tier assessment. Only Tiers 1 to 3 likely to be achievable within 400 day timescale.
Site located over major or minor aquifer. Travel time to identified receptor greater than 400 days.	Need for remedial action to be determined by tier assessment.
Site located over non-aquifer (no usable resource), and not in hydraulic continuity with local watercourse or other environmentally sensitive receptor.	No action.

* This table only refers to the action appropriate to protect water resources. Other receptors may still initiate remedial action, as noted in Chapter 1.

During the tiered assessment it will be necessary to determine both the target concentration and the compliance point at which this target will be set. Determination of these two factors must take account of:

- 1) Fundamental requirements to meet EU and UK legislation (e.g. compliance with the Groundwater Directive).
- 2) The background quality of water resources (the local groundwater and/or rivers), whether this be natural or the result of historical pollution not derived from the site-specific source.
- 3) Whether the identified receptor is a resource. In the case of groundwater, also whether the water is permanently unsuitable for use by virtue of quality or quantity (this links back to point 1).
- 4) Whether it is practically possible to give the desired degree of protection to the resource, given the site-specific circumstances.

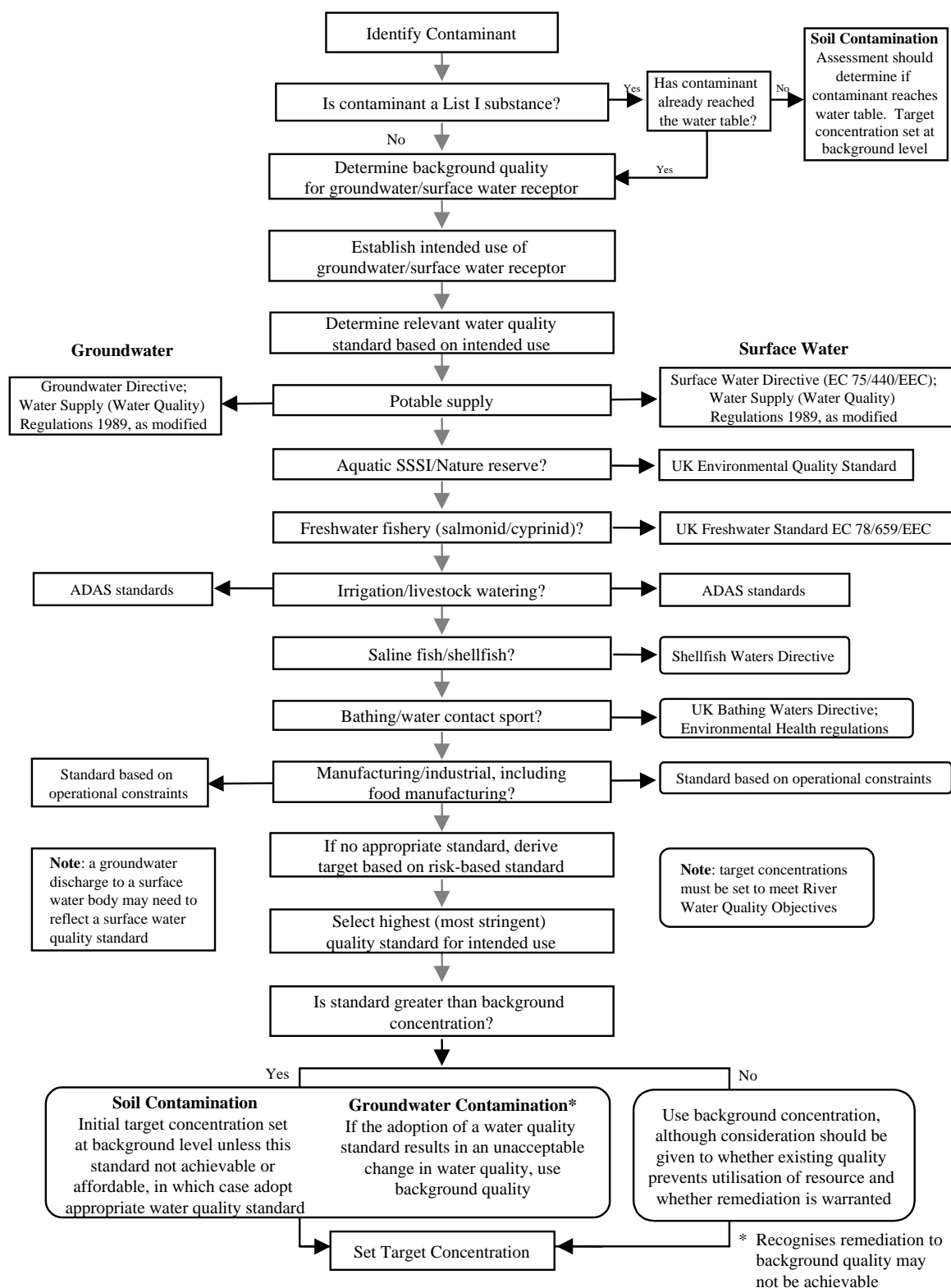
Ideally, the aim should be to protect natural groundwater quality and meet the requirements of all relevant legislation. However, in practice the legislation may not always be definitive and natural background quality may have been compromised by man's activities over generations, rendering remediation to original quality unattainable from a practical perspective. In such circumstances the Agency will seek to achieve the best environmental solution possible given site-specific circumstances, taking into consideration environmental costs and benefits (Ref 6A, Policy D6).

The following sections describe the approach to setting target concentrations and compliance points, with further elaboration in the succeeding chapters on tier analysis.

3.2 Derivation of target concentrations

The basis of this methodology is that a target concentration is set for the identified receptor or compliance point which should not be exceeded. This is then used in the Tier 1 to 4 calculations to derive a remedial target to which soil or groundwater concentrations are compared to determine the need for remedial action.

Figure 3.1 Derivation of target concentration



The choice of a target concentration is critical to the determination of a remedial target for soil or groundwater. The **ideal** remediation standard is natural background quality, namely, there should be no significant deterioration in the quality at the receptor (that is, it should not be detectable against natural background variations). It is recognised that this may not always be achievable or cost-effective. Experience of pump-and-treat groundwater remediation schemes in the USA and Netherlands has shown limited success in cleaning groundwater to background conditions in situations where the hydrogeological environment is complex and/or the type of contaminant is not amenable. Where the groundwater is currently not polluted and is usable as a resource, the objective should relate to the preservation of the existing water quality, rather than some remote target.

The general approach to setting a target concentration, noted in Figure 3.1, is that this target should relate to the present or intended use for groundwater, be it as strategic potable water resource or baseflow support to river flow or wetland habitats. However, at the outset there needs to be a basic understanding of the natural system in question, including the effects of any other anthropogenic activities on that system. Where groundwater contamination has been identified, the approach is to use a water quality standard (assuming the background quality is better than this) relevant to the current or intended use of the aquifer, on the basis that the clean-up to background quality is unlikely to be achievable. For soil contamination the target concentration should initially be set at background levels, but with the recognition that this may need to be changed to an appropriate water quality standard if remediation to background is not achievable or affordable. Other long term anthropogenic effects may need to be factored into this assessment.

The water quality standards that are likely to be applicable are given below:

- UK Water Supply (Water Quality) Regulations 1989;
- UK Private Water Supplies Regulations 1991;
- UK quality standards for water to be used for direct abstraction to potable supply, e.g. Surface Water (Abstraction for Drinking Water) (Classification) Regulations 1996;
- UK Environmental Quality Standards for the Protection of Aquatic Life;
- UK quality standards for saline water required to support fish and shellfish, e.g. Surface Waters (Fish Life) (Classification) Regulations 1997;
- UK quality standards for fresh and saline waters used for bathing and contact water sports, e.g. Bathing Waters (Classification) Regulations 1991;
- UK quality standards for freshwaters required to support fish;
- River Water Quality Objectives;
- EC Drinking Water Standards;
- EC Water Quality Standards.

Other possible relevant standards are:

- ADAS water quality standards for water used for irrigation and livestock watering;
- World Health Organisation (WHO) Guidelines for Drinking Water Quality;
- Environmental Health regulations.

Other legislation that is relevant includes:

- Groundwater Directive (80/68/EEC);
- Drinking Water Directive (80/778/EEC);
- Private Water Supplies Regulations (1991);
- Surface Waters Directive (75/440/EEC);
- Freshwater Fish Directive (78/659/EEC);
- Dangerous Substances Directive (76/464/EEC);
- Shellfish Waters Directive (79/923/EEC);
- Bathing Waters Directive (76/160/EEC).

For some contaminants no relevant standards may exist. In these cases separate toxicological or ecotoxicological risk-based assessments may need to be undertaken to derive an appropriate target. Where no existing Environmental Quality Standards (EQSs) have been formally set, predicted no-effect concentrations (PNECs) may be derived.

In general, the **target concentration** should be set to provide the **greatest level of protection to the receptor** and this will typically be the highest (most stringent) applicable water quality standard. The basis for taking a lower value could be:

- 1) background quality already exceeds the most stringent standard;
- 2) remediation to the most stringent standard can be demonstrated to be not achievable;
- 3) the standard is not relevant to the future intended use;
- 4) the system has been well defined from site investigations and a high level of certainty can be attached to any predicted impact;
- 5) the projected duration of contamination is very short and generally acceptable in the environment, i.e. transient presence/impact.

If by setting the target concentration as a quality standard (such as a drinking water standard) this is less onerous than achieving background quality, then a possible consequence of deriving the remedial target is that some deterioration in groundwater quality could occur. The acceptability of this should be assessed in relation to:

- whether higher standards of remediation (based on background quality) are achievable, reasonable and cost effective;
- the sensitivity of the receptor at risk;
- how conservative an approach has been used in deriving remedial targets, which will be a function of the assessment tier and the quality of data used.

For some contaminants, water quality standards are at very low concentrations (pesticides, for example) and their use ensures that there is unlikely to be any deterioration in background quality. For other contaminants, such as chloride, the standard (in this case the drinking water maximum acceptable concentration of 400 mg/l) may be significantly above background quality (often less than 50 mg/l). For such cases, consideration should be given to whether the

deterioration in background quality, that adoption of this standard would allow, is acceptable on a case by case basis.

In the case of soil contamination where the contaminant is a List I or List II substance but this has not reached the water table, the Groundwater Directive requires that (for all practical purposes) there should not be a direct discharge of List I substances to the water table and that any discharge of List II substances should not cause pollution. Therefore, the assessment should be directed at determining whether attenuation in the unsaturated zone is sufficient to prevent the contaminant reaching the water table, otherwise remediation will be required, and also whether the remediation itself could pose a risk to groundwater.

If the contaminant has already reached the water table, remediation may still be required, but in general the remedial target should be based on a water quality standard, on the basis that remediation to background levels is unlikely to be achievable and the Groundwater Directive is less applicable.

Background quality should be based on either monitoring up hydraulic gradient of the site or on regional water quality monitoring. It should be recognised that existing background quality may differ from natural background quality due to, for example, diffuse pollution from agricultural or industrial sources. In some instances existing water quality may be sufficiently poor to prevent its use, without significant treatment.

Other factors to be taken into account in deriving target concentrations include:

- 1) any changes in surface water quality should not cause a public nuisance;
- 2) the biological and ecological quality of water resources should not be adversely affected.

3.3 Selection of compliance points

3.3.1 Deterioration and precaution

In many instances the compliance point will be set at an individual, clearly identified receptor, for example, an abstraction borehole or a stream. However, this could imply that there could be deterioration in the quality of the groundwater between the contaminant source and the receptor, which may be judged unacceptable in terms of legislative requirements and/or the potential use of the resource.

At the other extreme, a precautionary approach would be to set the compliance point either directly beneath the contaminant source or at the site boundary. This is likely to result in a more stringent remedial target concentration. **However, where the groundwater is currently free from pollution by the overlying soils/land use, this may be a consequent requirement of the approach laid down in the EC Groundwater Directive.**

In view of the infinite variety of situations that could be encountered, it is not appropriate to lay down prescriptive procedures for all circumstances, however the compliance point should be located at a point at which it is possible to obtain samples of water and hence verify the effectiveness of remedial action or prediction on the fate of contaminants. In each case a site-specific assessment will be needed. However, some general guidelines can be set out and these are given below and in the tier analysis chapters.

3.3.2 Within the groundwater regime

Starting from the point where an identified receptor is selected as the compliance point, in Tier 2 assessments (where only dilution at the water table is used), movement of the compliance point towards the point of maximum dilution of the contaminant source in the aquifer has no effect on the remedial target concentration. This can be seen in Figure 2.4. However, this does assume that the receptor is directly down-gradient of the source and not on the lateral or vertical edge of a contaminant plume. At Tier 2, flow in three dimensions and other hydraulic processes such as dispersion are not considered.

In contrast in Tier 3, due to the effect of attenuation, the movement of the compliance point towards the source will have a major impact on the remedial target concentration as noted in Figures 2.4 and 4.1. This is described in more detail in Chapter 4.

In Tier 4 three-dimensional effects can be taken into consideration and potentially any movement of the compliance point in relation to its position with respect to the plume of contamination may result in a change in the remedial target concentration.

A special case arises where the contaminant source lies within the capture zone to a major potable abstraction and Source Protection Zones have been designated. Within the Inner (Zone I) and Outer (Zone II) Source Protection Zones (50 and 400 day travel times respectively), the compliance point would normally be set below and immediately down hydraulic gradient of the contaminant source, but after maximum dilution has taken place within the aquifer (often at the site boundary). Within the total Source Catchment (SPZ III) the compliance point would normally be set at the boundary with the Outer Source Protection Zone (SPZ II), thus ensuring a “safety zone” equivalent to 400 days groundwater travel time to the abstraction point and providing protection to the wider aquifer resource.

3.3.3 Surface waters

The interaction between groundwater and surface water and the additional factor of surface water quality standards produce a more complex situation with respect to the selection of the compliance point and associated target concentrations.

Different techniques can be adopted from Tiers 1 to 4 that reflect progressively less cautious approaches to the protection of surface water, dependent on the knowledge of the system.

In Tiers 2 and 3 the precautionary approach would be to set the compliance point within the groundwater body immediately up-gradient of the watercourse and fix the target groundwater concentration as being equal to the target concentrations that would be applied in the watercourse (for example, the relevant EQS). By this means, no matter what volume of groundwater enters the watercourse, the EQS cannot be compromised. A second iteration (if required) would then be to consider the potential interaction between the groundwater body and the watercourse and the dilution within the watercourse. Any assessment that considers dilution must consider background quality, low flow conditions and other potential pollutant inputs in the watercourse. However, to enable this to be assessed, more data are required, and unless an approach can be agreed with the regulatory agencies, based on empirical data and site-specific considerations, a Tier 4 assessment may be necessary. A major concern in the assessment would be the potential impact of multiple sources of contamination on the river, which may not be adequately accounted for in a basic Tier 2 analysis.

3.4 ConSim and other assessment tools

Many of the equations and calculations that are described in the succeeding chapters of this report are complex and quality assured methods should be used in their calculation. These methods could range from simple spreadsheets through to complex three-dimensional time-variant numerical computer models, depending on the tier and complexity of the situation.

The Environment Agency has promoted the development of a computer software package ConSim (Ref 15) to assist in the assessment of risks to water quality from land contamination. Other models are also available that can be adapted for use in the overall methodology presented in this report (Ref 3).

The ConSim model can be used to assist in Tier 1-3 type analysis, particularly for soils. However, it should be noted that there is a fundamental difference in approach between the **Tiers** presented in this report, which are basically driven by the amount and complexity of data required to undertake the assessment, and the **levels** used in ConSim. In the latter, the levels follow the potential contaminant pathway through the subsurface environment. The differences between the approaches are noted in Table 3.3.

ConSim calculates contaminant concentrations along the flow path based on a contaminant source concentration. This document describes the calculation of a remedial target at the source that would not exceed the target concentration at the receptor.

In practice, different elements of ConSim can be run to assist in the various assessment tiers and the varying approaches should not inhibit the assessment process.

The calculations within ConSim are performed using the same analytical solutions to groundwater flow and contaminant transport equations as noted in this report but, where appropriate, these are coupled with probabilistic Monte Carlo simulations. The output from ConSim is thus in the form of probabilistic plots, expressed as frequency or cumulative diagrams and/or tabular summaries.

It is stressed that ConSim and any other model or analytical package should be regarded as a tool in the assessment process and professional judgement will always be needed to integrate the results from such tools with other technical and professional guidance, cost-benefit considerations, and policy, planning and legislative requirements.

The selection of the remediation technique itself will need to take into account all of these factors, and as a consequence the final remedial target concentration that is applied at a site may not be the same as the output from the assessment tools described above.

Table 3.3 Comparison of ConSim “levels” and Assessment “tiers”

Tier/Level No.	ConSim (level)	This report (tier)
1	Comparison of contaminant source with receptor	As ConSim
2	Unsaturated zone travel time, transport processes, biodegradation and effects of dilution in the aquifer	Dilution in the receiving groundwater or surface water
3	Saturated zone transport, attenuation and retardation processes	Attenuation in the unsaturated and saturated zones; simple analytical models
4	Summary of level 1-3 results	As Tier 3 but more sophisticated numerical models

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4. TIER ANALYSIS - SOIL

4.1 Introduction

This chapter provides a description of each of the assessment tiers (refer to Tables 2.2, 4.1 and Figures 2.3 and 2.4) to derive soil remedial targets and is based on the approach used in R&D Technical Report P13 (Ref 2). Chapters 5 and 6 describe the approach to be adopted where contaminated groundwater represents a potential risk. The precise methodology to be adopted at each tier, particularly at Tiers 3 and 4, is not fixed and may need to be varied on a site-by-site basis. The methodology is illustrated by worked examples, which are included in this chapter.

The approach relies on the assessment of the contaminant concentration of water (“pore water”, as defined in Table 2.1) in contact with the contaminated soil (see Table 2.1). The “pore water” quality is then compared to the remedial target to establish the need for remediation to protect the identified receptor.

4.2 Tier 1

For this tier, the compliance point is taken as the soil zone and the remedial target is set as equivalent to the target concentration. No allowance is made for processes (such as dilution and attenuation) that may affect contaminant concentrations along the pathway between the soil and the identified receptor.

The “pore water” concentration (Table 2.1) is determined, in order of preference, from:

- 1) Analysis of “pore water” quality or perched water quality.
- 2) Results of leaching tests on the contaminated soil (see Table 4.2). For preference and where it is appropriate, the test should be undertaken according to the Environment Agency (NRA) R&D Note 301, Leaching Tests Assessment of Contaminated Land (Ref 7) to ensure consistency between sites. Adjustments for the weight of the sample and volume of leachate used may need to be made (Table 4.2). Other tests may be appropriate such as detailed in Ref 8.
- 3) Theoretical calculation of the “pore water” concentration that would be expected from contact with the soil or a discrete contaminant phase, based on the measured soil contaminant concentration and equations describing the partitioning of contaminants between water and the soil matrix or discrete contaminant phase (Table 4.3).

Each of these methods for deriving soil “pore water” quality has limitations as described below.

In Tier 1, the soil remedial target is set as either (Table 4.1):

- 1) a ***pore water remedial target concentration*** (if leaching tests or “pore water” data are available) equal to the target concentration for the identified receptor; or
- 2) a ***soil remedial target concentration*** equal to a calculated soil concentration (if soil analysis data only are available) using empirical equations (Table 4.3) that describe soil-water partitioning.

The data required for a Tier 1 assessment are summarised in Table 3.1, and should be obtained as part of an initial intrusive investigation and desk study.

Although a direct comparison between “pore water”/leaching test data and the target concentration at the receptor requires little data, in practice there can be wide variations between the results of leaching tests, direct “pore water” analysis and calculated concentrations. It is preferable, therefore, for more than one method of assessment described above to be used and the results compared, in an attempt to gain an understanding of the potential and actual contaminant mobility in the environment and to improve the quality of the assessment.

If total soil concentrations are used for the assessment, more data are required (Table 3.1), so that partitioning relationships can be used to calculate leachate concentrations. All analyses must be conducted by accredited laboratories using validated standard methods.

Table 4.1 Calculation of remedial target concentrations

Pore water remedial target concentration	Soil remedial target concentration
<i>The “pore water” concentration (Table 2.1) should not exceed the remedial target concentration LTC defined below:</i>	<i>The total measured soil concentration should not exceed the soil remedial target concentration STC defined below:</i>
Tier 1	
$LTC_1 = C_T$	$STC_1 = C_S = C_T \left(K_d + \frac{\theta_w + \theta_a H}{\rho} \right)$
Tier 2	
$LTC_2 = C_T \times DF$	$STC_2 = C_S \times DF$
Tiers 3 and 4	
$LTC_3 = C_T \times DF \times AF$	$STC_3 = C_S \times DF \times AF$
Definitions	
LTC_1 = Tier 1 “pore water” remedial target concentration for in-situ soils (mg/l)	STC_1 = Tier 1 soil remedial target concentration for in-situ soils (mg/kg)
C_T = target concentration for water (mg/l)	C_S = calculated total soil concentration (mg/kg)
LTC_2 = Tier 2 “pore water” remedial target concentration for in-situ soils (mg/l)	K_d = soil/water partition coefficient (l/kg)
LTC_3 = Tier 3 “pore water” remedial target concentration for in-situ soils (mg/l)	θ_w = water filled soil porosity (fraction)
	θ_a = air filled soil porosity (fraction)
	H = Henry’s law constant (dimensionless)*
	ρ = bulk density (g/cm ³)
AF = attenuation factor (dimensionless)	STC_2 = Tier 2 soil remedial target concentration for in-situ soils (mg/kg)
DF = dilution factor (dimensionless)	STC_3 = Tier 3 soil remedial target concentration for in-situ soils (mg/kg)

* The dimensionless Henry’s law constant (H) may be converted from the Henry’s law constant in atm - m³/mol by multiplying by 42.3 (unit conversion for 15°C).

Table 4.2 Soil leaching test

Soil leaching tests essentially consist of agitating a mass of contaminated soil with a volume of water (eluate) and measuring the concentration of contaminants in the eluate. Tests may vary in terms of the mass of soil, the volume of eluate, the period of agitation, preparation (crushing) of the soil and environmental controls (pH, temperature). For further information refer to Ref 7.

Soil leaching test results are typically expressed as either:

- mg of contaminants per litre of leachate, or
- mg of contaminant leached per kg of soil at natural moisture content.

The first case is directly applicable to the Tier 1 assessment. The second case is useful for the direct comparison of leaching test results derived from different tests, as an allowance is made for the weight of the sample and the volume of leachate used, as follows:

Conversion to mg/kg leached contaminant

mg/kg leached contaminant

$$= \text{leachate concentration (mg/l)} \quad \times \quad \frac{1000 \text{ (g)}}{\text{sample weight (g)}} \quad \times \quad \frac{\text{eluant volume (ml)}}{1000 \text{ (ml)}}$$

The tier assessment outlined in this section assumes contaminants will continue to be leached from the soil at the same concentration as determined from the leaching test. In reality the concentration will reduce with time as the contaminant is removed from the soil (i.e. the assessment assumes an infinite contaminant source or that the soil concentration greatly exceeds the leachate concentration). The alternative is to undertake repeated leaching tests on the same sample to determine the rate of source depletion.

With all such tests, direct comparison of analytical results from different test methods should only be undertaken with extreme caution and with an understanding of the differences between techniques. It is preferable not to compare results obtained under different test methods.

The soil porosity and bulk density should preferably be measured on a site-specific basis but can be estimated from published values for different soil types. The partition coefficient can be taken from published values (although these will generally be dependent on soil pH) or calculated based on soil pH, clay content and organic carbon content of the soil (Tables 4.2 and 4.3). Where literature values are used to determine partition coefficients, it should be noted that values can potentially range by several orders of magnitude; for example, for metals and ionisable organics this variation can be a function of the soil pH.

4.2.1 Assumptions/limitations

As subsequent tier analysis relies on the value(s) determined for “pore water” quality, it is clearly important that these data are selected with care.

It is important to note that the behaviour of contaminants in partitioning between the soil and water is difficult to predict. Equations describing this behaviour tend to be conservative and are sensitive to the soil/water partition coefficient, as noted above. Care needs to be exercised in choosing appropriate parameter values for these calculations.

In assessing the results of leaching tests, the following points need to be considered:

- breaking up of the soil and increasing the surface area in contact with “pore water”, together with agitation of the soil column, may result in additional, potentially unrepresentative, leaching of contaminants;
- leaching tests are primarily designed to assess inorganic contaminants - volatiles may be lost as part of the test, unless the test apparatus is specifically designed to prevent this;
- the distribution of a contaminant between soil and water is sensitive to pH and this parameter is difficult to control during the test.

Where more than one method of determining “pore water” quality is employed, the results should be compared to understand the reasons for any differences between them and which may be more appropriate for a particular contaminant. For most contaminants, leaching tests are likely to provide an appropriate method of determining soil “pore water” quality. For many site assessments, “pore water” quality may have been initially determined from total soil concentrations. Since this method would be expected to overestimate the soil “pore water” concentrations, it may be appropriate, where the remedial target is exceeded, to undertake soil leaching tests if these are likely to provide a better measure of “pore water” quality.

In assessing soil contaminant concentrations, consideration should be given as to whether the contaminant has by-passed the soil zone by flow along preferential pathways (e.g. fissures) and the main contamination is at or below the water table.

The assessment will also need to consider whether hot spots of contamination are significant with respect to water resources. This will generally involve calculation of the mass loading of contaminant(s) at the water table (Tier 2 assessment).

Table 4.3 Basic equations for Tier 1 assessment

Standard analytical equations (Ref 9) that can be used in Tier 1 are given below. This is not intended to be a definitive list.

Calculation of total soil concentration

$$C_s = C_T \left[K_d + \frac{(\theta_w + \theta_a H)}{\rho} \right]$$

Partition coefficient for non-polar organic chemicals (for example, aromatic hydrocarbons such as benzene, toluene):

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

Partition coefficient for ionic organic chemicals (for example, phenol)

$$K_d = K_{oc,n} (1 + 10^{pH-pK_a})^{-1} + K_{oc,i} [1 - (1 + 10^{pH-pK_a})^{-1}]$$

where

C_s	=	soil concentration (mg/kg)
C_T	=	target concentration (mg/l)
K_d	=	soil/water partition coefficient (l/kg)
K_{oc}	=	organic carbon partition coefficient (l/kg)
f_{oc}	=	fraction of organic carbon (fraction)
θ_w	=	water-filled soil porosity (fraction)
θ_a	=	air-filled soil porosity (fraction)
ρ	=	bulk density (g/cm ³)
H	=	Henry's law constant (dimensionless)
$K_{oc,n}$	=	sorption coefficient for related species (l/kg)
$K_{oc,i}$	=	sorption coefficient for ionised species (l/kg)
pH	=	pH value
pK _a	=	acid dissociation constant

Table 4.4 Tier 1 assessment - worked example

Soil contamination was identified at a former industrial site. Soil samples were obtained from 10 trial pits, analysis of which identified elevated copper and zinc concentrations as follows:

Contaminant	Soil concentration (mg/kg)		
	Average	Minimum	Maximum
Copper	160	40	280
Zinc	24	5	35

The Environment Agency indicated that the site was located directly over an aquifer and within the Outer Source Protection Zone to a potable groundwater abstraction. In view of the potential risk to this source, a Tier 1 assessment was undertaken.

Target concentrations based on the maximum admissible drinking water concentrations were agreed with the Environment Agency, as given in the table below. No leaching tests were carried out and the remedial targets were calculated using a theoretical equation describing soil/water partitioning (Table 4.3). The parameter values used to calculate the Tier 1 remedial targets are also given in the table below.

Parameter			Copper	Zinc	Source
Target concentration	C_T	mg/l	3	5	Drinking water standard
Bulk density	ρ	g/cm ³	1.65	1.65	Soil measurement
Porosity - air filled	θ _a	Fraction	0.18	0.18	Based on particle size analysis
Porosity - water filled	θ _w	Fraction	0.05	0.05	Based on particle size analysis
Soil pH value			7.0	7.0	Soil measurement
Henry's Law Constant	H		N/A*	N/A	
Partition coefficient	K _d	l/kg	4000	420	Literature value, selected on soil pH

* N/A Not applicable.

Example calculations to determine remedial targets (Table 4.3):

$$\text{Remedial target concentration (STC}_1) = C_T \left[K_d + \frac{(\theta_w + \theta_a H)}{\rho} \right]$$

$$\text{STC}_1 (\text{copper}) = 3 \times \left(4000 + \frac{(0.05 + 0.18 \times 0)}{1.65} \right) = \mathbf{12,000 \text{ mg/kg}}$$

$$\text{STC}_1 (\text{zinc}) = 5 \times \left(420 + \frac{(0.05 + 0.18 \times 0)}{1.65} \right) = \mathbf{2100 \text{ mg/kg}}$$

Summary

The measured soil concentrations for copper (40 to 280 mg/kg) and zinc (5 to 35 mg/kg) are all below their calculated remedial target concentrations of 12,000 mg/kg and 2100 mg/kg respectively. No further action was considered necessary.

4.3 Tier 2

In Tier 2 the analysis allows for the potential dilution of contaminants leached from the soil by groundwater flowing below the site (Figure 2.3). This provides a remedial target for the soil which is less conservative than that derived at Tier 1. **The remedial target is determined by multiplying the receptor target concentration by a dilution factor (DF).** The dilution factor is defined as the ratio of infiltration through the contaminated soil to groundwater flow. The compliance point is taken as groundwater beneath the source area or immediately adjacent to it, after full mixing has occurred. Examples of the equations that can be used to calculate the dilution factor (DF) are given in Table 4.5.

No account is taken of the attenuation processes that occur as contaminants move away from the site.

The selection of compliance points has been discussed in Section 3.3 above. Ideally at Tier 2 the groundwater flow regime beneath the site should be defined so that dilution at this point can be calculated.

For sites where limited data are available to define the groundwater system below the site, a secondary approach is to consider dilution at the receptor, whether this is an abstraction, a spring or surface watercourse. This assumes that the receptor intercepts or receives all of the groundwater flow below the site. The dilution factor is determined by the ratio of infiltration through the contaminated soil to either the groundwater abstraction or the stream flow (Table 4.5). This approach provides a less conservative remedial target, particularly for a large abstraction or a high stream flow. The approach should only be used as an initial screening exercise, in that, if contaminant concentrations exceed this remedial target, this points to the need for remedial action or an upgrade in the tier assessment and collation of site-specific data. Where concentrations are below the remedial target, then a decision is required on the need to collect site-specific data based on the sensitivity of the receptor and in discussion with the Agency.

The above approach allows the potential impact on the receptor to be examined, but takes no account of the impact on the aquifer below the site. Therefore it must be used with caution, taking into account the factors noted in Chapter 3.

A simple check that should be undertaken is that the calculated remedial target does not exceed the solubility limit for the contaminant. In this case remediation of the soil would be unnecessary to protect water resources, although free product may still represent a risk of forming explosive vapours or unacceptable human exposure (refer to Section 5.4).

Where the assessment shows that the remedial target is only exceeded by contaminant hot spots within the site, the risk analysis should be extended to determine if the total contaminant loading from the site would be sufficient to impact on the identified receptor. This analysis may identify that action is not necessary to protect the water resource.

The data requirements for a Tier 2 analysis are summarised in Table 3.1. These are primarily the volume of water infiltrating through the contaminated soil to the water table and groundwater flow below the site. Flow in the receiving watercourse or rate of groundwater abstraction should be obtained if dilution at the receptor is to be considered (Section 3.3). Background groundwater (Section 3.2) and/or surface water quality should also be determined.

In some cases, more than one source of contamination may exist, both inside and outside of the site, such as in an industrial complex. Groundwater flowing below the site may already have been contaminated. In these cases, the assessment should take account of the different sources of contamination as well as the quality of groundwater up hydraulic gradient of the site. This is likely to result in a lower (more stringent) remedial target concentration being set for the site, as the calculated dilution factor will be lower where background quality and/or multiple contaminant sources are taken into account.

In many cases a decision will need to be taken between the appropriate parties and the Agency as to whether it is reasonable to require remediation at this site in isolation of the other sources. For example, the site under consideration may only represent a small potential impact on the identified receptor compared with other contaminant sources.

4.3.1 Assumptions/limitations

A “do-nothing” outcome from a Tier 2 assessment implies that dilution of contaminants in the environment is sufficient for the mitigation of adverse effects. This is not necessarily applicable in all cases, since certain substances may accumulate in sediments and biota (or aquifer-based particles), forming a sink for future contaminant leaching and possibly adverse ecological or human health effects due to biomagnification. This must be assessed on a case-by-case basis, for example, by reference to bioaccumulative potential.

Table 4.5 Basic equations for Tier 2 assessment

Standard analytical equations that can be used in Tier 2 are given below. This is not intended to be a definitive list, as other equations are available may be more appropriate to a given situation.

Groundwater flow below site.

$$\text{Dilution factor (DF)} = \frac{(k i.Mz + L.Inf) C_c}{k i.Mz.C_u + L.Inf.C_c} \quad \text{or} \quad \frac{(k i.Mz + L.Inf) C_T - k i.Mz.C_u}{L.Inf.C_u}$$

$$\text{Dilution factor (DF)} = 1 + (k i.Mz/L.Inf) \quad \text{or} \quad 1 + (k i.Mz.w/A.Inf)$$

(no allowance for background concentration)

Receiving stream

$$\text{Dilution factor (DF)} = \frac{(Q_c + Q_u C_c)}{Q_c C_c + Q_u C_u} \quad \text{or} \quad \frac{C_T (Q_c + Q_u - Q_u C_u)}{Q_c C_T}$$

$$\text{Dilution factor (DF) (no allowance for background concentration)} = \frac{Q_c + Q_u}{Q_c}$$

Groundwater abstraction

$$\text{Dilution factor (DF)} = \frac{Q C_c}{Inf.A C_c + (Q - Inf.A) C_u} \quad \text{or} \quad \frac{Q C_T - (Q - Inf.A) C_u}{Inf.A C_T}$$

$$\text{Dilution factor (DF) (no allowance for background concentration)} = \frac{(Q - Inf.A)}{Inf.A}$$

Note

For a thin aquifer (typically less than 20 m), the mixing zone thickness can be taken as the aquifer thickness. This may be an unrealistic assumption for thick aquifers, and the mixing depth may need to be based on field investigations, experience of similar sites or estimated from the following expression (Ref 16):

$$\text{Mixing zone depth (Mz)} = (0.0112L^2)^{0.5} + d_a (1 - \exp[(-L.Inf / k I d_a)])$$

(Note if $Mz > d_a$, then $Mz = d_a$)

where

Mz = mixing zone thickness (m)

L = length of contaminant source in direction of groundwater flow (m)

d_a = aquifer thickness (m)

Inf = infiltration (m/d)

k = hydraulic conductivity (m/d)

i = hydraulic gradient

Q = abstraction rate (m³/d)

A = area of contaminant source (m²)

Q_u = surface water flow upstream of discharge point under low flow conditions (m³/d)

Q_c = inflow of contaminated water (m³/d)

C_c = concentration of contaminant in contaminated discharge (mg/l)

C_T = target concentration (mg/l)

C_u = background concentration of contaminant in receiving water (mg/l)

w = width of site (m)

Table 4.6 Tier 2 assessment - worked example

Soil contamination was encountered at a former chemical works. Analyses of soil samples found elevated concentrations of the chlorinated solvent tetrachloroethene (PCE) on part of the site. Soil leaching tests were undertaken on five soil samples, giving contaminant concentrations of 0.1, 1.2, 0.3, 0.4 and 0.2 mg/l respectively.

The site is underlain by river gravel deposits. There were no nearby licensed groundwater abstractions, but a good quality river was located about 80 m from the site. It was agreed with the Agency that this river was at possible risk due to the leaching of PCE by water infiltrating through the soil down to the water table.

Tier 1 assessment

A target concentration of 0.01mg/l (the Environment Quality Standard, EQS, for tetrachloroethene) was selected for the Tier 1 assessment. All of the leaching tests exceeded this target concentration, so there was a need either to upgrade the Tier analysis or to implement remedial action. The estimated cost of remediation was significantly higher than the cost of further investigations and therefore a Tier 2 assessment was undertaken.

Tier 2 assessment

Further investigations were undertaken to provide the necessary information to calculate groundwater dilution and also to determine if any groundwater contamination had occurred. Five monitoring boreholes were drilled in and around the site. No evidence of groundwater contamination was identified. Aquifer parameters determined from the further investigations are given below. The effective rainfall for the site was obtained from the Met Office. Approximately 25% of the site is covered by hardstanding, with run-off routed to foul drains. The site drains were assumed to be 80% efficient at preventing leakage, and therefore the infiltration factor was taken as 80% (i.e. 75% and 20% of 25%).

Parameter		Unit	Value	Source
Target concentration	C_T	mg/l	0.01	EQS
Saturated aquifer (mixing zone) thickness	M_z	m	6	Field measurement
Hydraulic conductivity	k	m/d	140	Field measurement
Hydraulic gradient	i		0.005	Field measurement
Effective rainfall		m/d	0.0006	Met Office
Infiltration factor			80%	Field data
Infiltration rate	Inf	m/d	0.00048	Calculated
Length of contaminated site, parallel to direction of groundwater flow	L	m	60	Field measurement

Example calculation

$$\text{Dilution factor (DF)} = 1 + \frac{k \cdot i \cdot M_z}{Inf \cdot L} = \frac{140 \times 0.005 \times 6}{0.00048 \times 60} = 147$$

$$\text{Remedial target (LTC}_2\text{)} = DF \cdot C_T = 147 \times 0.01 = \mathbf{1.5 \text{ mg/l}}$$

Summary

The dilution factor was calculated as 147, giving a Tier 2 remedial target of 1.5 mg/l. All of the leaching tests results fell below this target. Although this analysis indicated that no remedial action was necessary to protect the river, there is still a potential for groundwater below the site to be contaminated. As chlorinated solvents are classified as List I substances, continued monitoring is considered necessary to confirm that no deterioration in groundwater quality occurs, with the provision to implement remedial measures, if required.

4.4 Tier 3

4.4.1 The role of attenuation

Tier 3 and Tier 4 take account of the potential attenuation as contaminants move off-site to the receptor (refer to Figure 2.3). In Tier 3, analytical contaminant transport models are used to predict contaminant concentrations down-gradient of the site as a result of attenuation, including:

- degradation of contaminants, for example, biological breakdown of organic substances;
- sorption of contaminants onto the aquifer matrix and soil particles in the unsaturated zone;
- ion exchange;
- precipitation of inorganic compounds due to a change in the chemical environment;
- volatilisation of semi-volatile or volatile contaminants;
- dispersion of contaminants as they move through the aquifer - dispersion due to mechanical dispersion and molecular diffusion will not affect the total mass of the contaminant, but is likely to reduce maximum concentrations.

The effect of these processes is to reduce contaminant concentrations along the pathway. In some cases, natural attenuation may be sufficient to protect the identified receptor without need for any remedial action.

The proposed Tier 3 remedial target for soil is derived by multiplying the target concentration at the receptor or compliance point by the dilution (DF) and attenuation (AF) factors. The attenuation factor is defined as the ratio of the contaminant concentration in groundwater below the source to the calculated concentration at a point down hydraulic gradient of the site (Figure 4.1), as follows:

$$AF = C_0/C_T \text{ or } C_0/C_{ED}$$

where

C_0 = contaminant concentration in groundwater below the source (mg/l)

C_T = contaminant concentration at target (receptor) (mg/l)

C_{ED} = simulated compliance point concentration (mg/l)

The choice of whether to apply the target concentration at the receptor or a different (nearer) compliance point has been discussed in Chapter 3.

The **attenuation factor** can be derived using an analytical solution, such as the Domenico equation (Table 4.7 and Ref 9), although other analytical solutions may be equally, or more, valid for certain hydrogeological situations (Refs 3, 5 and 10).

The initial contaminant concentration, C_0 , can be taken as the observed concentration in groundwater below the site or can be calculated by dividing the soil “pore water” concentration (derived from the Tier 1 assessment) by the dilution factor (DF). This value is substituted in the Domenico equation (Table 4.7a) and the concentration at the compliance point calculated. Alternatively the attenuation factor can be calculated assuming an initial unit contaminant concentration. This is because the analytical equations describing steady-state contaminant transport are linear with respect to the starting concentration. Thus, for a given set of parameter values, the same attenuation factor would be calculated (from the Domenico equation in Table 4.7a) independently of whether a starting concentration of 1 mg/l, 10 mg/l or even 300 mg/l was used.

By introducing attenuation into the assessment, a Tier 3 or Tier 4 evaluation implies that groundwater quality down hydraulic gradient of the site can deteriorate, as illustrated by Figure 4.1b. An example is that whilst there may be no effect at the identified receptor, which may be a groundwater abstraction, groundwater quality for some distance down-gradient of the site may be affected. The acceptability of this will need to be assessed in relation to the cost and achievability of remediation against environmental protection. The selection of a compliance point between the receptor and the source can provide a realistic solution in terms of providing a balance between protecting the water resource and making use of natural attenuation processes.

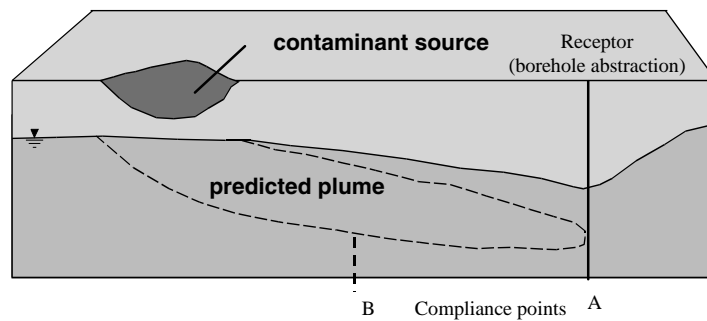
4.4.2 Compliance points and remedial targets

The location of the **compliance point** has an important control in the derivation of the attenuation factor and the remedial target concentration (Figure 4.1c). The further the compliance point is set from the site, the greater the attenuation factor and hence the higher the remedial target. This is also illustrated by Figure 4.2, which shows the different remedial target concentrations that would be derived for a compliance point at 100 m and 600 m down-gradient of the contaminant source. For the example given in Figure 4.2 and taking a degradation half-life of 365 days, the remedial target, calculated for a compliance point set at 100 m, is 1.0 mg/l, compared to 275 mg/l for a compliance point set at 600 m. For the same set of parameters, but with no degradation, the remedial targets determined for compliance points at 100 m and 600 m, are 0.4 mg/l and 2.1 mg/l respectively. This example also serves to illustrate the significance of degradation; where this process can be demonstrated, higher remedial targets can be derived.

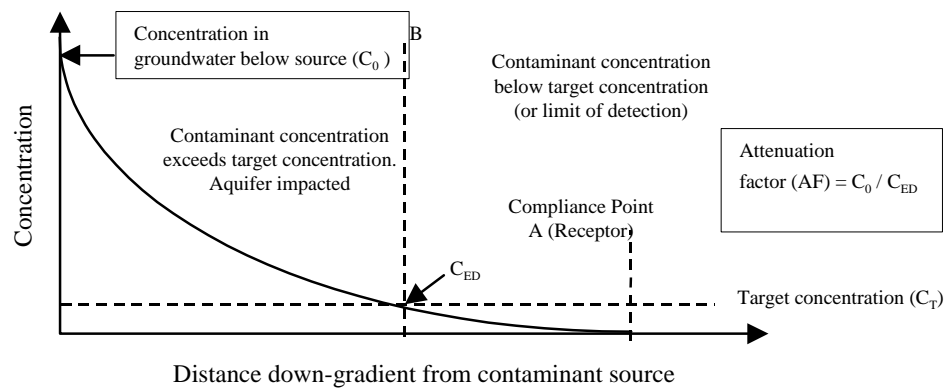
The recommended approach is to calculate contaminant concentrations at various locations down-gradient of the source, for different assumed positions of the compliance point. This information can be used to determine the influence of variations in the position of the compliance point on the remedial target and the potential contaminant concentrations in the aquifer. The results can then be used to agree a compliance point location, based on a balance between protecting the resource and setting a target that can be realistically achieved (as discussed in Chapter 3). In practice, the position of the compliance point will normally be at a distance of between 50 and 500 m down hydraulic gradient of the site.

Figure 4.1 Influence of natural attenuation on contaminant concentrations

(a) Conceptual model



(b) Contaminant concentrations decrease with distance due to natural attenuation (degradation)



(c) Influence of changing position of compliance point on remedial target concentration

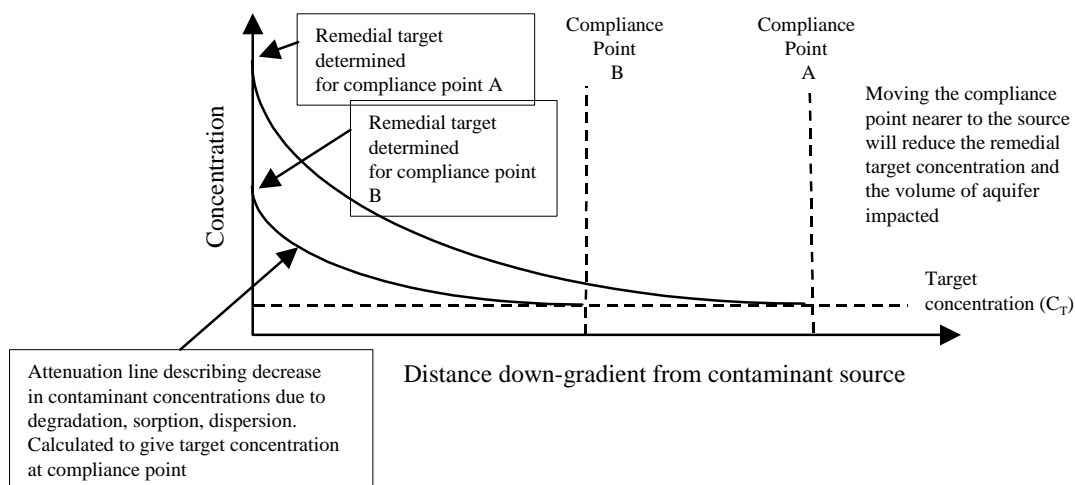
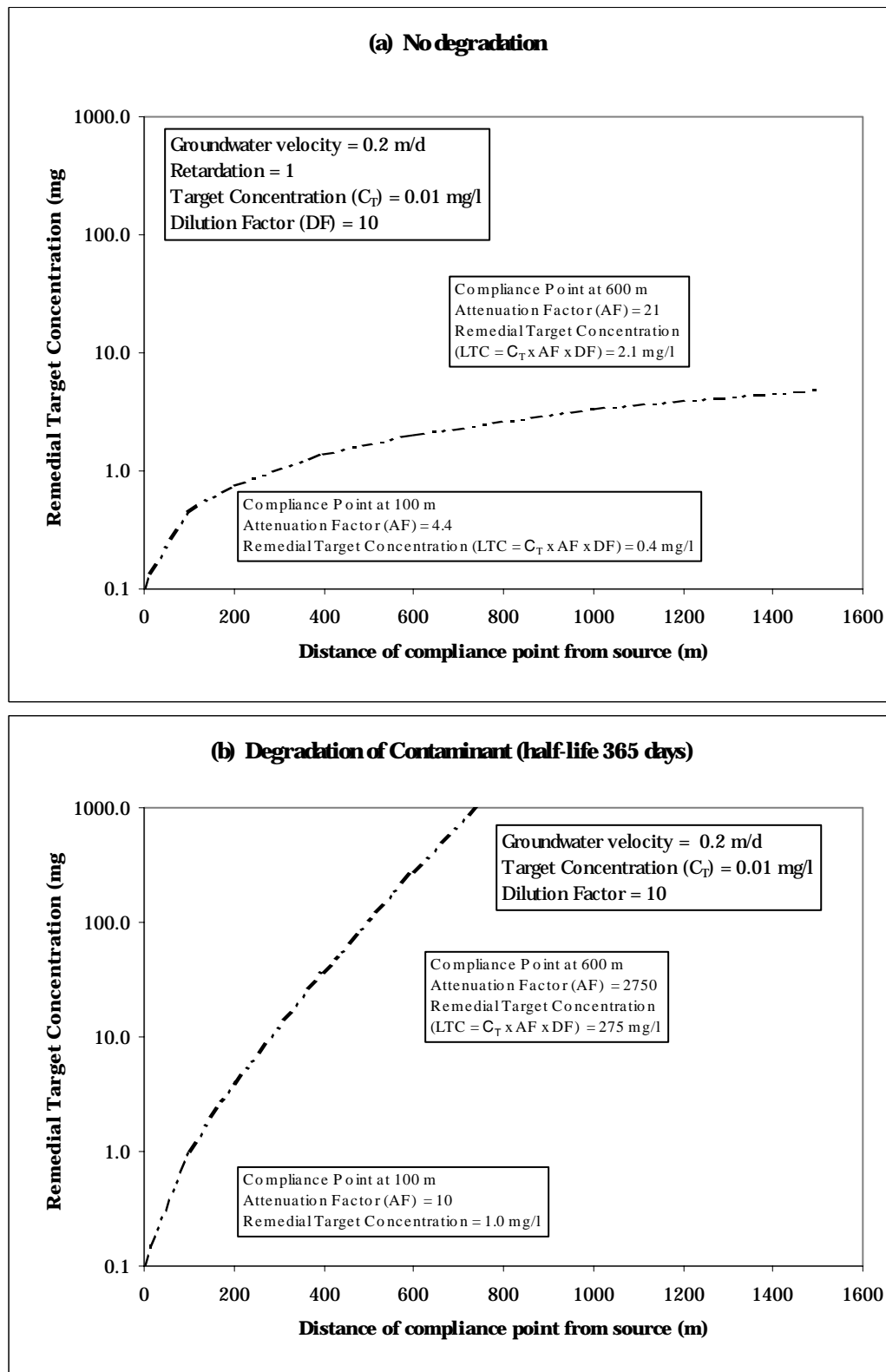


Figure 4.2 Tiers 3 and 4 – influence of the rate of degradation and the distance of the compliance point from the source on the calculated remedial target concentration (steady-state groundwater flow)



4.4.3 Source depletion

Other processes that can be included in Tier 3 are changes to the contaminant source and attenuation processes in the unsaturated zone. Changes to the source term may result from:

- depletion in the source term with time, for example, once the source of contamination is removed (such as a leaking storage tank), then the concentration of the contaminant in the soil zone will reduce with each successive flushing by rain water infiltrating through the soil;
- physical removal of the source term;
- degradation of the source;
- change in the volume of water infiltrating through the soil, for example, due to placement of a low-permeability layer over the area of contamination.

Repeated soil leaching tests may demonstrate a decline in the contaminant source with each flushing and it may be appropriate to include this in the assessment.

The equations described in Tables 4.5 and 4.7 assume a **constant source term** for the contaminant (Figure 5.1a). Some analytical techniques (Ref 11) and most numerical models (Tier 4) allow for changes in the source term to be taken into account.

For a **declining source term** (Figure 5.1b), the recommended approach is to calculate the variation in contaminant concentration with time at the compliance point. This would be expected to increase to a maximum value before declining. If calculated concentrations at the compliance point do not exceed the target concentration, no action is required. If the target concentration is exceeded, then action is likely to be required. The remedial target concentration can be determined by adjusting the source concentration until the maximum calculated concentration at the compliance point equals the target concentration. This is an interactive process and is summarised below:

- 1) Calculate the contaminant concentration at the compliance point using an assumed source concentration.
- 2) Compare the predicted concentration at the compliance point with the target concentration.
- 3) If the predicted concentration exceeds the target concentration, lower the source concentration and repeat steps 1 and 2. The remedial target is the concentration that gives a predicted concentration at the receptor equal to the target concentration.

4.4.4 The unsaturated zone

Attenuation processes (retardation, biodegradation, etc.) may also affect the contaminant as it migrates down through **the unsaturated zone** to the water table. In this case the remedial target is calculated as follows:

$$LTC_3 = AF_u \times DF \times AF_s \times C_T$$

where

DF = dilution factor;

AF_u = attenuation factor (unsaturated zone);

AF_s = attenuation factor (saturated zone);

C_T = target concentration.

The unsaturated zone attenuation factor is calculated by dividing the “pore water” contaminant concentration by the predicted concentration in water at the bottom of the unsaturated zone as a result of degradation, retardation and dispersion.

The travel time for a contaminant to move down through the unsaturated zone can be significant, particularly for low infiltration rates and a thick unsaturated zone. For contaminants that are readily sorbed onto the soil matrix, travel times can be of the order of hundreds or even thousands of years, and for degradable contaminants, biodegradation may prevent any impact at the water table.

The ConSim model (Ref 15) takes account of contaminant movement through the unsaturated zone, including the travel time for contaminants to move down through the unsaturated zone to the water table and biodegradation of contaminants.

Dilution by groundwater flow and soil leaching may also be reassessed as part of the Tier 3 assessment as additional site-specific data are likely to be available.

The Tier 3 assessment assumes that the plume has reached a steady-state or equilibrium condition. The analysis should also consider the rate at which contaminants move through the aquifer system to determine the time before the contaminant reaches the receptor as well as the time before steady-state conditions are established (Table 5.2 details the Domenico equation for time-variant conditions). For example, for flow systems where rates of movement are slow (metres per year), steady-state conditions may only be established after tens or even hundreds of years. This is important in designing the compliance monitoring for the site and in defining the period over which monitoring needs to be undertaken.

The data requirements for a Tier 3 assessment are summarised in Table 3.1.

4.4.5 Assumptions/limitations

The main assumptions in undertaking a Tier 3 analysis relate mainly to application of an analytical model and are:

- the aquifer system can be represented by relatively simple analytical models;
- the aquifer is intergranular, homogeneous and isotropic;
- steady-state groundwater flow;
- adsorption is linear, instantaneous and reversible;
- decay is governed by first-order kinetics.

Additional assumptions may apply according to the analytical model used. As in practice very few of the above assumptions will be strictly correct, it is important that some form of sensitivity/uncertainty analysis is undertaken, as described in Chapter 7.

The Tier 3 assessment uses analytical models to calculate an attenuation factor. This factor will be dependent on parameter values for dispersion, retardation and degradation. The calculation of an attenuation factor is sensitive to the assumed rate of biodegradation, and it is essential that a realistic or conservative value is used and, where possible, this is based on

field data. Limited data are available on *in-situ* rates of biodegradation and many of these relate to shallow groundwater systems and may not be applicable to deeper systems. Where a literature-based decay rate is used, the rate should be based upon a field observation from a natural system similar to the one in question and should be reviewed and agreed upon by the appropriate parties. This is to safeguard against the use of too rapid a rate of biodegradation, which may result in overestimated remedial target concentrations and hence insufficient aquifer protection. For example, published values may relate to degradation under aerobic aquifer conditions or in the soil zone, whereas the aquifer environment may be anaerobic, such that a different set of organisms are likely to be active and different degradation rates apply. In some cases, contaminant concentrations or the environment may inhibit the degradation process. In the absence of approved degradation rates, the Domenico equation should be used to calculate AF, without decay.

Values for dispersion are difficult to derive in the field and tend to be scale-dependent. Empirical models are generally used to determine a value for dispersion, the most common being that longitudinal dispersion is one tenth of the pathway length.

Parameters must be set to be the most conservative (but realistic) values that exist in the body of the aquifer anywhere between site and receptor, that is, the highest or lowest observed, and reliable parameter values that will give the lowest realistic AF. This is to ensure that the impact on the aquifer between the site and the compliance point is minimal (Section 7.1).

The assessment should also consider any substances that may result from chemical or biological processes that break down the contaminant.

Figure 4.3 Basic steps in constructing a numerical model

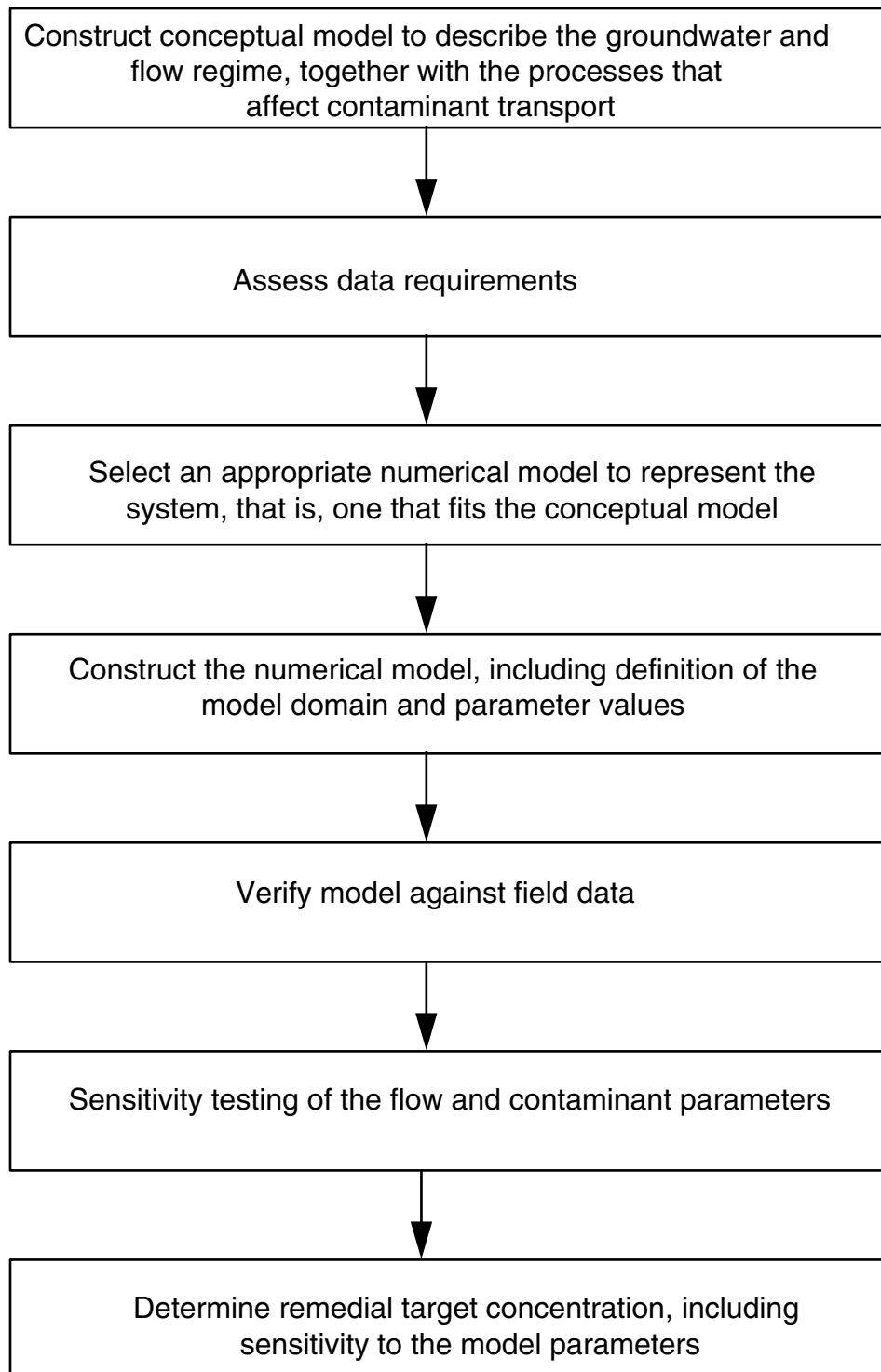


Table 4.7 Basic equations for Tier 3 assessment

Standard analytical equations (Refs 2 and 9) that can be used in Tier 3 are given below. This is not intended to be a definitive list.

(a) Domenico equation

Calculation of concentrations down-gradient of the site (steady-state) using the Domenico equation (this is a simplified version of the Ogata-Banks equation, which is given in the second part of this table).

$$C_{ED} = C_0 \exp \left\{ \frac{x}{2a_x} \left[1 - \sqrt{1 + \frac{4\lambda a_x}{u}} \right] \right\} \operatorname{erf} \left(\frac{S_y}{4\sqrt{a_y x}} \right) \operatorname{erf} \left(\frac{S_z}{4\sqrt{a_z x}} \right)$$

Rate of groundwater flow $v = \frac{ki}{n}$

Retardation factor $R_c = \left(1 + \frac{K_d \rho}{n} \right)$

Rate of contaminant movement due to retardation $u = \frac{ki}{n R_c} = \frac{ki}{n + K_d \rho}$

where

C_{ED}	= concentration of contaminant at distance x (mg/l)
C_0	= initial contaminant concentration in groundwater (mg/l)
λ	= decay constant = 0.693/half-life for degradation of contaminant in days
a_x, a_y, a_z	= dispersion coefficient in three dimensions (m)
S_z, S_y	= width and thickness of plume at source (in the saturated zone) (m)
R_c	= retardation factor
K_d	= partition coefficient (l/kg)
ρ	= bulk density (g/cm ³)
n	= effective porosity
i	= hydraulic gradient
k	= hydraulic conductivity (m/d)
x	= distance to compliance point (m)
erf	= error function
\exp	= exponential

Note: For certain cases or choices of parameter value, the Domenico equation can give slightly different calculated values to the Ogata-Banks equation. This will be a function of the simplifications made in the Domenico solution. The ConSim model uses the Ogata-Banks equation.

Plume thickness at source, S_y , is equal to mixing zone thickness derived at Tier 2.

Table 4.7 continued

(b) Ogata-Banks equation

Calculation of concentrations down-gradient of the site (time variant) using the Ogata-Banks equation (the first part of this table gives the steady-state solution of this equation and Table 5.2 gives the simplified Domenico time-variant version of this equation).

$$C_{ED} = 0.125 C_0 \left[\exp \left\{ \frac{x}{2a_x} \left[1 - \sqrt{1 + \frac{4\lambda a_x}{u}} \right] \right\} \operatorname{erfc} \left\{ \frac{1}{2\sqrt{a_x u t}} \left[x - u t \sqrt{1 + \frac{4\lambda a_x}{u}} \right] \right\} \right. \\ \left. + \exp \left\{ \frac{x}{2a_x} \left[1 + \sqrt{1 + \frac{4\lambda a_x}{u}} \right] \right\} \operatorname{erfc} \left\{ \frac{1}{2\sqrt{a_x u t}} \left[x + u t \sqrt{1 + \frac{4\lambda a_x}{u}} \right] \right\} \right] \\ \operatorname{erf} \left(\frac{S_y}{4\sqrt{a_y x}} \right) \operatorname{erf} \left(\frac{S_z}{4\sqrt{a_z x}} \right)$$

$$\text{Rate of contaminant movement due to retardation } u = \frac{k i}{n R_c} = \frac{k i}{n + K_d \rho}$$

where

C_{ED}	= concentration of contaminant at distance x (mg/l)
C_0	= initial contaminant concentration in groundwater (mg/l)
λ	= decay constant = 0.693/half life for degradation of contaminant in days
a_x, a_y, a_z	= dispersion coefficient in three dimensions (m)
S_z, S_y	= width and thickness of plume at source (in the saturated zone) (m)
R_c	= retardation factor
K_d	= partition coefficient (l/kg)
ρ	= bulk density (g/cm ³)
n	= effective porosity
i	= hydraulic gradient
k	= hydraulic conductivity (m/d)
x	= distance to compliance point (m)
z	= distance (lateral) to compliance point perpendicular to flow direction (m)
y	= distance (depth) to compliance point perpendicular to flow direction (m)
erf	= error function
\exp	= exponential
erfc	= complementary error function
t	= time (in days) since contaminant entered groundwater

Note: Plume thickness at source, S_y , is equal to mixing zone thickness derived at Tier 2.

Table 4.8a Tier 3 assessment - worked example

Organic liquor had previously been stored in two unlined storage lagoons covering an area of 5000 m². This practice was discontinued and the lagoons drained. Sampling of soils below these lagoons found high levels of contamination by benzene, with soil concentrations ranging from 400 mg/kg to 3200 mg/kg. The lagoons are located over a sand and gravel aquifer with regional groundwater flow to a good quality river located 100 m from the site.

Tier 1 assessment

Soil leaching tests were undertaken on 12 samples, with toluene concentrations in the leachate ranging from 5 to 65 mg/l (average concentration 30 mg/l). The Environmental Quality Standard for benzene is 0.03 mg/l and this was set as the target concentration. The leaching test results all exceeded this value. It was agreed with the Environment Agency that dilution and attenuation would potentially be significant processes in reducing contaminant concentrations as groundwater moves from the site towards the river. Therefore the assessment was upgraded to include both Tiers 2 and 3.

Tier 2/3 assessment

Further site investigations (including construction of monitoring boreholes) were undertaken to determine the direction of groundwater flow, the hydraulic gradient, the saturated thickness and hydraulic conductivity of the sand and gravel aquifer. Sampling of the monitoring boreholes indicated that some groundwater contamination had occurred. The remedial target concentration was derived taking account of attenuation and dilution as described in the example calculations given below. The parameter values used to derive the dilution factor (DF) and the attenuation factor (AF) are given below:

Parameter		Unit	Value	Source
Target concentration	C_T	mg/l	0.03	Environmental Quality Standard
Source length	L	m	40	Field measurement
Source width	S _z	m	125	Field measurement
Infiltration	Inf	m/d	0.003	Met. Office
Mixing zone / initial plume thickness	Mz	m	5	Field measurement
(S _y)				
Hydraulic conductivity	k	m/d	25	Field measurement
Hydraulic gradient	I		0.01	Field measurement
Porosity	n		0.15	Estimated
Bulk density	ρ	g/cm ³	1.65	Laboratory measurement
Decay constant	λ		0.0019	Literature value for half-life of 365 days
Distance to compliance point	x	m	100	Field measurement
Dispersivity (longitudinal)	a _x	m	10	Assumed
Dispersivity (transverse)	a _z	m	1	Assumed
Dispersivity (vertical)	a _y	m	0.0001	Set as small value as thin aquifer
Partition coefficient	K _d	l/kg	5.7	Literature
Input concentration	C ₀	mg/l		See example calculation below
Attenuation factor (C₀/C_{ED})	AF			Calculated (see example below)

Table 4.8 continued

Example calculation

Tier 2 (refer to Table 4.5)

$$\text{Dilution factor (DF)} = 1 + \frac{k_i M_z}{\text{Inf.L}} = 1 + \frac{25 \times 0.01 \times 5}{0.003 \times 40} = 11.4$$

$$\text{Tier 2 Remedial target} = \text{DF} \cdot C_T = 11.4 \times 0.03 = 0.34 \text{ mg/l}$$

Concentrations of benzene derived from the soil leaching tests (5 to 65 mg/l) exceed this remedial target so the assessment proceeded to Tier 3.

Tier 3 (refer to Table 4.7a)

The calculation steps are as follows:

$$\text{Retardation factor} \quad R_c = \left(1 + \frac{K_d \rho}{n} \right) = 1 + \frac{5.7 \times 1.65}{0.15} = 63.7$$

$$\text{Rate of contaminant movement} \quad u = \frac{k_i}{n R_c} = \frac{25 \times 0.01}{0.15 \times 63.7} = 0.026 \text{ m/d}$$

Calculated concentration (C_{ED}) at compliance point using the Domenico equation:

$$C_{ED} = C_0 \exp \left\{ \frac{x}{2a_x} \left[1 - \sqrt{1 + \frac{4\lambda a_x}{u}} \right] \right\} \text{erf} \left(\frac{S_y}{4\sqrt{a_y x}} \right) \text{erf} \left(\frac{S_z}{4\sqrt{a_z x}} \right)$$

$$C_{ED} = C_0 \exp \left\{ \frac{100}{2 \times 10} \left[1 - \sqrt{1 + \frac{4 \times 0.0019 \times 10}{0.026}} \right] \right\} \text{erf} \left(\frac{5}{4\sqrt{0.0001 \times 100}} \right) \text{erf} \left(\frac{125}{4\sqrt{1 \times 100}} \right) = 0.0076 C_0 \text{ mg/l}$$

$$\begin{aligned} \text{Since} \quad \text{Attenuation Factor (AF)} &= C_0 / C_{ED} \\ &= C_0 / (0.0076 \times C_0) \text{ (substituting for } C_{ED} \text{ from the} \\ &\quad \text{above Domenico equation)} \end{aligned}$$

$$\text{AF} = 131$$

The Tier 3 remedial target (LTC_3) was calculated as follows:

$$\begin{aligned} \text{LTC}_3 &= \text{AF} \times \text{DF} \times C_T \\ &= 131 \times 11.4 \times 0.03 = \mathbf{44.8 \text{ mg/l}} \end{aligned}$$

Summary

The remedial target value of 45 mg/l (leachable benzene in soils) lies within the observed range of benzene concentrations from leaching tests (5 to 65 mg/l). Consequently remedial action was considered necessary to treat the most contaminated areas of the site, and a groundwater monitoring scheme was implemented to provide confirmation that residual contamination in groundwater would not pose an unacceptable risk to the river. This was considered more cost-effective than undertaking further detailed investigation and assessment at Tier 4.

4.5 Tier 4

Tier 4 is comparable to Tier 3 in that the **remedial target is derived by multiplying the target concentration at the receptor or compliance point by the dilution (DF) and attenuation (AF) factors.** For Tier 4, a more complex analysis using numerical models is undertaken to provide a more detailed representation of groundwater flow and contaminant transport to the compliance point or receptor.

The Tier 4 model would be expected to provide the most reliable means of assessing the impact on the receptor, particularly where the model can be verified against field data. There should be more confidence in the remedial target values. Even so, the remedial target values need to be reviewed in the context of:

- the assumptions made in constructing the model;
- the reliability of the data;
- the accuracy with which the model represents observed conditions - is it well calibrated with respect to both flow and quality?

A Tier 4 assessment requires:

- specialist and detailed hydrogeological investigations to define the flow regime and contaminant transport processes;
- technical expertise in groundwater and contaminant movement;
- detailed understanding of the flow regime and the processes that influence contaminant transport;
- time to collect adequate monitoring/calibration data.

This information and analysis has cost and time implications, such that this assessment may only be appropriate when one or more of the following factors apply:

- the hydrogeological regime is complex;
- more detailed assessment is likely to demonstrate that a more economic remedial option is appropriate;
- it is necessary to undertake a detailed assessment (verification) of the impact of the remedial scheme;
- there is no immediate risk to the identified receptor, a Tier 4 assessment may take several months to complete;
- the contamination is large-scale or severe in terms of impact.

Within Tier 4, the methodology may differ from site to site and may also include a phased approach to modelling, starting with a relatively simple one-dimensional numerical transport model and ending with a three-dimensional transport model, if the problem merits this. It is essential that, as part of the Tier 4 assessment, a robust conceptual model of the problem should be formulated and clear objectives for the assessment defined.

The data requirements at Tier 4 are greater than those at Tiers 1, 2 and 3. The information that is likely to be required (in addition to that required for Tiers 1, 2 and 3) is summarised in

Table 3.1. The amount of data required will be a function of the complexity of the problem. A key part in developing a robust model that can be used with confidence is the ability of the model to simulate observed conditions. For some sites it may be appropriate to calibrate the model assuming steady-state conditions. For other more complex sites it may be necessary to simulate variations in groundwater heads and contaminant concentrations with time to provide sufficient confidence that field processes are adequately represented by the model. An example, is where degradation of the contaminant plume is suspected, and the model will need to demonstrate that observed changes in contaminant concentrations with time can be simulated.

The basic steps in undertaking a Tier 4 (numerical modelling exercise) are summarised in Figure 4.3.

It is not intended to provide details of how to undertake a Tier 4 modelling assessment in this document and reference should be made to other references, including Refs 12 and 13.

4.5.1 Assumptions/limitations

The major limitations of Tier 4 modelling are:

- availability of data - for most sites there will be insufficient information for a Tier 4 assessment and additional and often costly investigations will be necessary;
- availability of resources, in terms of expertise and time available to undertake the analysis.

In addition, a number of assumptions will be needed for the assessment, including how the characteristics of the site may change in the future, such that there may be some uncertainty attached to the assessment.

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5. TIER ANALYSIS - GROUNDWATER

5.1 Introduction

This chapter provides a description of each of the assessment tiers to derive remedial targets for contaminated groundwater to protect the identified groundwater or surface water receptor. In this chapter it is assumed that the soil does not present a problem, namely the contaminant has by-passed the soil zone or the original soil contamination has been removed. A tiered approach, similar to that described in Chapter 4 for soils, is recommended with the exception that the assessment commences at Tier 2, as the contaminants have already moved through the soil zone. Thus the only processes of significance are attenuation, dispersion and dilution in the saturated zone between the identified source of contaminated groundwater and the receptor. This chapter repeats some of the steps described in the previous chapter on the tier assessment for soils and so they are not described in detail other than to reference the relevant parts of Chapter 4. In Chapter 6 the approach to dealing with both contaminated soil and groundwater is outlined.

The approach relies on comparison of contaminant concentrations in groundwater with the remedial target to establish the need for remediation (Figure 2.4).

In setting a remedial target for groundwater, it is important that account should be taken of whether remediation to this standard is achievable or cost-beneficial. Experience of pump-and-treat systems has shown that generally it has not been possible to return groundwater to background quality. For this reason, the target concentration will generally be set at a water quality standard appropriate to the intended use of the aquifer rather than as background quality (see Section 3.2, Figure 3.1). In deriving a remedial target for groundwater, the assessment may need to consider a decline in the source term (i.e. removal of the contaminant source) at Tier 3/4.

5.2 Tier 2

At Tier 2 the remedial target is set as the target concentration at the receptor (Figure 2.4). Observed contaminant concentrations within the plume of contaminated groundwater are compared to this target concentration to determine the need for further action. The data requirements are given in Table 3.1, the main requirement being information on contaminant concentrations in groundwater.

Definition of the contaminant plume forms an important part of the assessment in determining maximum contaminant concentrations. This will be a function of:

- the number, location and construction of the monitoring boreholes;
- the complexity of the hydrogeological regime (the plume may be diving, such that the boreholes may miss the centre of the plume);
- the nature and distribution of the contaminant (for example, if the contaminant is LNAPL, are the boreholes screened at the water table and is the risk mainly associated with movement of the free product or due to dissolution and migration by groundwater?);

- the history of contamination and contaminant movement (for example, the plume may have already moved beyond the site boundary or a number of separate contaminant pollution releases may have occurred).

It should be stressed that the geometry of contaminant plumes can be complex and for most sites typically there will be insufficient boreholes to define the contaminant plume with certainty, particularly when the borehole locations may be constrained by existing buildings and services.

It is essential that the observation borehole network provides sufficient confidence that the geometry of the contaminant plume is defined and the maximum contaminant concentration relates to a point in the centre rather than the perimeter of the plume. Otherwise further monitoring boreholes are required and in addition a more detailed assessment involving analytical or numerical modelling, to establish whether the observed concentrations can be simulated and that the system is understood and defined.

In general, the maximum observed groundwater concentration in the plume should be compared to the remedial target. If this exceeds the target, remedial action or an upgrade in the tier assessment (probably including further site investigation) will be required. If the concentration is below the target, further monitoring will be necessary to show that this is not exceeded in the future and/or that this is representative of the contaminant source. The next stage in this assessment is to determine what proportion of the plume exceeds the remedial target so that the volume of groundwater that requires treatment can be assessed. The Tier 3 and 4 assessments consider the reduction in this concentration as the plume moves away from the source.

The assessment requires a high level of technical expertise in interpreting the field data, deciding if further information is required and determining a realistic maximum contaminant concentration for comparison with the target concentration.

The compliance point will typically be groundwater below the site, but in some cases the plume of contaminated groundwater will have migrated beyond the site boundary and this needs to be considered in the assessment, particularly if higher contaminant concentrations are suspected in the off-site plume.

Where the receptor is a stream or a groundwater abstraction, dilution at this point might be considered. This assumes that the receptor intercepts or receives all of the contaminated groundwater flow. In this case, the dilution factor (Table 5.1) is defined as the ratio of the stream flow or the groundwater abstraction to the flow of contaminated groundwater through the centre of the plume. This approach allows the actual impact on the receptor to be examined, but takes no account of the acceptability of the impact on groundwater. It provides less conservative **remedial targets** and the assessment should consider whether the observed groundwater concentrations are acceptable (as described in Chapter 3).

5.3 Tiers 3 and 4

Tier 3 and Tier 4 take account of the potential attenuation as contaminated groundwater moves off-site to the receptor. **The Tier 3 and Tier 4 remedial target concentration for groundwater is derived by multiplying the target concentration at the receptor or compliance point by the attenuation factor (AF) (Figure 4.1b).** Observed contaminant

concentrations within the plume of contaminated groundwater are compared to this remedial target. This approach also gives contaminant concentrations down-gradient of the source. The attenuation factor is defined as the ratio of the contaminant concentration in groundwater to the calculated concentration at a point down hydraulic gradient of the source, as follows:

$$AF = C_0/C_{ED}$$

where:

C_0 = contaminant concentration in groundwater below the source (mg/l)

C_{ED} = simulated compliance point concentration (mg/l)

The compliance point is located down hydraulic gradient of the source. This may be an identified receptor (for example, a groundwater abstraction) or an actual or surrogate borehole located between the source and the receptor.

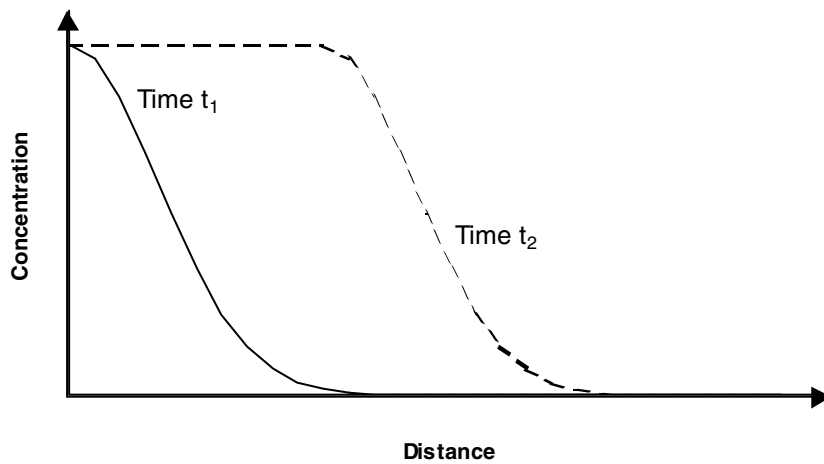
The general approach to calculating the attenuation factor and setting the compliance point is set out in Chapter 4. In **Tier 3**, analytical contaminant transport models (see Tables 4.7 and 5.2) are used to predict contaminant concentrations down-gradient of the source as a result of dispersion, retardation and degradation. The analysis may need to consider the use of alternative analytical expressions, for example, where the source of contamination is due to a single spillage rather than a continuous source of contamination (Ref 10). This reflects, that as a plume moves through the aquifer, concentrations will reduce due to dispersion and degradation, as illustrated in Figure 5.1.

For **Tier 4**, a more complex analysis using numerical modelling is undertaken, to provide a more detailed representation of groundwater flow and contaminant transport to the compliance point or receptor (Chapter 4). By this means it is possible to establish what level of contamination would result in an unacceptable impact at the receptor.

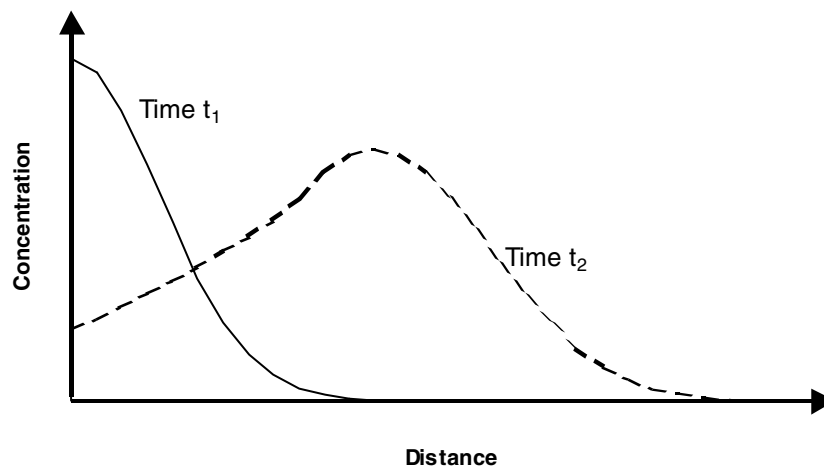
By introducing attenuation into the assessment, a Tier 3 or 4 evaluation implies that groundwater quality down hydraulic gradient of the site can deteriorate. The acceptability of this will need to be assessed in relation to the cost and achievability of remediation against the requirements for environmental protection. Sections 3.3 and 4.4 set out the approach to determining the position of the compliance point used in the calculation of the attenuation factor.

Figure 5.1 Movement of contaminant plume for differential source terms

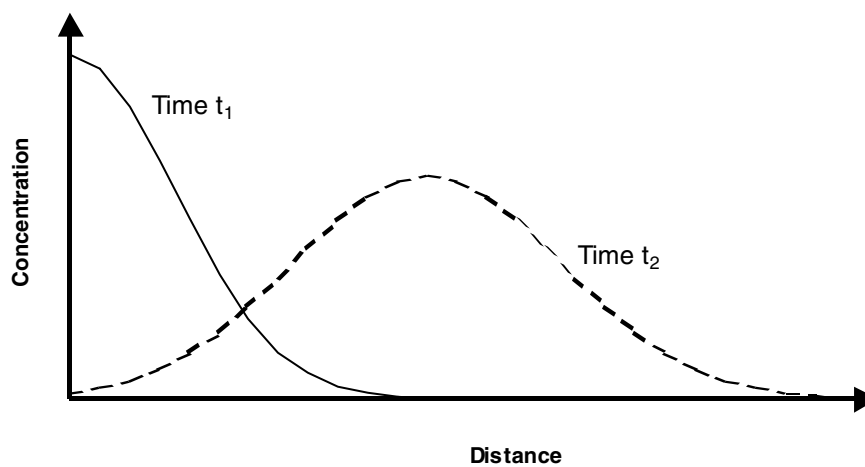
(a) Constant Source Term



(b) Declining Source Term



(c) Single Spill



As part of the Tier 3 and 4 assessment, contaminant concentrations in groundwater down-gradient of the site should be compared with observed concentrations to provide verification of the analysis. Predicted concentrations will generally need to be determined using time-variant equations, such as given in Table 5.2. Where necessary, parameter values should be varied to provide the closest fit with the observed data, before deriving the remedial target. This type of analysis is important for degradable organic contaminants to provide field confirmation of the rate of degradation used in the assessment. If the monitoring network is adequate and variations in contaminant concentration with time have been measured, the significance of degradation can be assessed as follows:

- 1) *Shrinking plume* where contaminant concentrations in monitoring boreholes decrease with time. In this case the rate of contaminant movement is exceeded by the rate of degradation, and indicates depletion in the contaminant source.
- 2) *Steady-state plume* where contaminant concentrations in monitoring boreholes do not change with time. In this case the rate of contaminant movement is balanced by the rate of degradation.
- 3) *Migrating Plume* where contaminant concentrations in monitoring boreholes increase with time. Rate of contaminant movement exceeds rate of degradation with plume likely to represent a risk to the receptor.

Groundwater contamination problems are more likely to involve a Tier 3 or Tier 4 assessment, coupled with detailed site investigation to define aquifer properties and the extent and degree of contamination. The investigations undertaken will be important in providing field data to verify the risk assessment, particularly where degradation may be a factor. The assessment will need to be undertaken by suitably qualified staff, particularly where the hydrogeological regime is complex. The decision to undertake any remediation will need to balance the need to protect water resources, the role of natural attenuation (notably degradation), the practicality of any remediation scheme in improving water quality, the timescale to implement any measures, and the cost of remediation.

5.4 Free product or non-aqueous phase liquid (NAPL)

A common problem that may need to be assessed is where the source of contamination is either free product floating on the water table (LNAPL) or more dense material present below the water table (DNAPL). The free product may represent a direct risk to the receptor via its movement through the saturated zone, or an indirect risk due to its solution and subsequent transport (dissolved phase) to the receptor. The assessment will need to consider both cases. If free product is considered to represent a direct risk to an identified receptor, then remedial action will generally be required. Where solution and transport by groundwater needs to be assessed, then the remedial target is determined for groundwater in direct contact with the free product. The dissolved concentration in groundwater is either the:

- observed concentration in groundwater immediately down-gradient of the free product (representative sampling of groundwater through a layer of free product is difficult); or
- calculated concentration based on the solubility of individual constituent organics, or less conservatively using the following equation (Raoult's law):

$$C_d = SX$$

where

- C_d = dissolved phase concentration in groundwater (mg/l)
- S = pure phase (liquid) solubility of organic compound (mg/l) (usually obtained from literature sources)
- X = molar fraction of organic contaminant in free product (obtained from laboratory analysis of free product)

At Tier 2, the dissolved contaminant concentrations, determined above, are compared with the target concentration. At Tier 3, attenuation of the dissolved phase is taken into account (degradation is likely to be a significant factor for organic contaminants) and the attenuation factor calculated as described in Chapter 4. The Tier 3 assessment should also consider depletion of the source, i.e. if the source of the free product has been removed (leaking oil tank), then the volume of free product would be expected to reduce with time due to solution by groundwater, although for large spills this may take years to occur and other processes such as degradation and volatilisation of the free product are probably more significant. For substances such as coal tar, source depletion will take years and other processes may be negligible.

Particular care should be taken in interpreting data relating to the presence of free product, due to the difficulties associated with:

- representative sampling;
- non-equilibrium conditions between the free product and water phases;
- the presence of co-solutes;
- sample extraction techniques.

Close liaison between those undertaking sampling, analysis and the assessment itself is particularly important where free product is involved.

Table 5.1 Basic equations for Tier 2 groundwater assessment

Standard analytical equations that can be used in Tier 2 are given below. This is not intended to be a definitive list, as other equations are available that may be more appropriate to a given situation.

Groundwater flow below site $(Q_c) = k I w.Mz$

Receiving stream

$$\text{Dilution factor (DF)} = \frac{(Q_c + Q_u) C_c}{Q_c C_c + Q_u C_u} \quad \text{or} \quad \frac{C_T (Q_c + Q_u - Q_u C_u)}{Q_c C_T}$$

$$\text{Dilution factor (DF) (no allowance for background concentration)} = \frac{Q_c + Q_u}{Q_c}$$

Groundwater abstraction

$$\text{Dilution factor (DF)} = \frac{Q C_c}{\text{Inf}.A C_c + (Q - \text{Inf}.A) C_u} \quad \text{or} \quad \frac{Q C_T (Q - \text{Inf}.A) C_u}{\text{Inf}.A C_T}$$

$$\text{Dilution factor (DF) (no allowance for background concentration)} = \frac{(Q - \text{Inf}.A)}{\text{Inf}.A}$$

where

- Mz = mixing zone thickness (m)
- w = width of contaminated zone (plume) at right angles to groundwater flow (m)
- k = hydraulic conductivity (m/d)
- i = hydraulic gradient
- Q = abstraction rate (m³/d)
- Q_u = surface water flow upstream of discharge point (m³/d)
- Q_c = groundwater flow below site (m³/d)
- C_c = concentration of pollutant in contaminated groundwater (mg/l)
- C_u = background concentration of contaminant (mg/l)
- C_T = target concentration (mg/l)
- Inf = infiltration (m/d)
- A = area of contaminant source (m²)

Table 5.2 Domenico equation (time-variant conditions)

Calculation of concentration down-gradient of site using the **Domenico equation** (simplified version of the Ogata-Banks equation, refer to Table 4.7b).

$$\frac{C}{C_0} = 0.5 \exp \left\{ \frac{x}{2a_x} \left[1 - \sqrt{1 + \frac{4\lambda a_x}{u}} \right] \right\} \operatorname{erfc} \left\{ \frac{1}{2\sqrt{a_x u t}} \left[x - ut \sqrt{1 + \frac{4\lambda a_x}{u}} \right] \right\} \operatorname{erf} \left(\frac{S_y}{4\sqrt{a_y x}} \right) \operatorname{erf} \left(\frac{S_z}{4\sqrt{a_z x}} \right)$$

Rate of groundwater flow $v = \frac{ki}{n}$

Rate of contaminant movement due to retardation $u = \frac{ki}{n R_c}$

where

Retardation factor $R_c = \left(1 + \frac{K_d \rho}{n} \right)$

where

- C = concentration of contaminant at point x and time t (mg/l)
- C_0 = initial contaminant concentration in groundwater (mg/l)
- λ = decay constant = 0.693/half life for decay of contaminant in days
- a_x, a_y, a_z = dispersion coefficient in three dimensions (m)
- S_z, S_y = width and thickness of plume at source (in saturated zone) (m)
- R_c = retardation factor
- K_d = partition coefficient (l/kg)
- ρ = bulk density (g/cm³)
- n = effective porosity
- i = hydraulic gradient
- k = hydraulic conductivity (m/d)
- x = distance to compliance point (m)
- erfc = complementary error function
- erf = error function
- \exp = exponential
- t = time since contaminant entered groundwater (days)

6. SOIL AND GROUNDWATER ASSESSMENT

This chapter outlines the approach to be adopted where contamination of both soil and groundwater has been identified. The assessment should follow the approach detailed in Chapters 4 and 5 and set out in Figure 6.1, with the objective of:

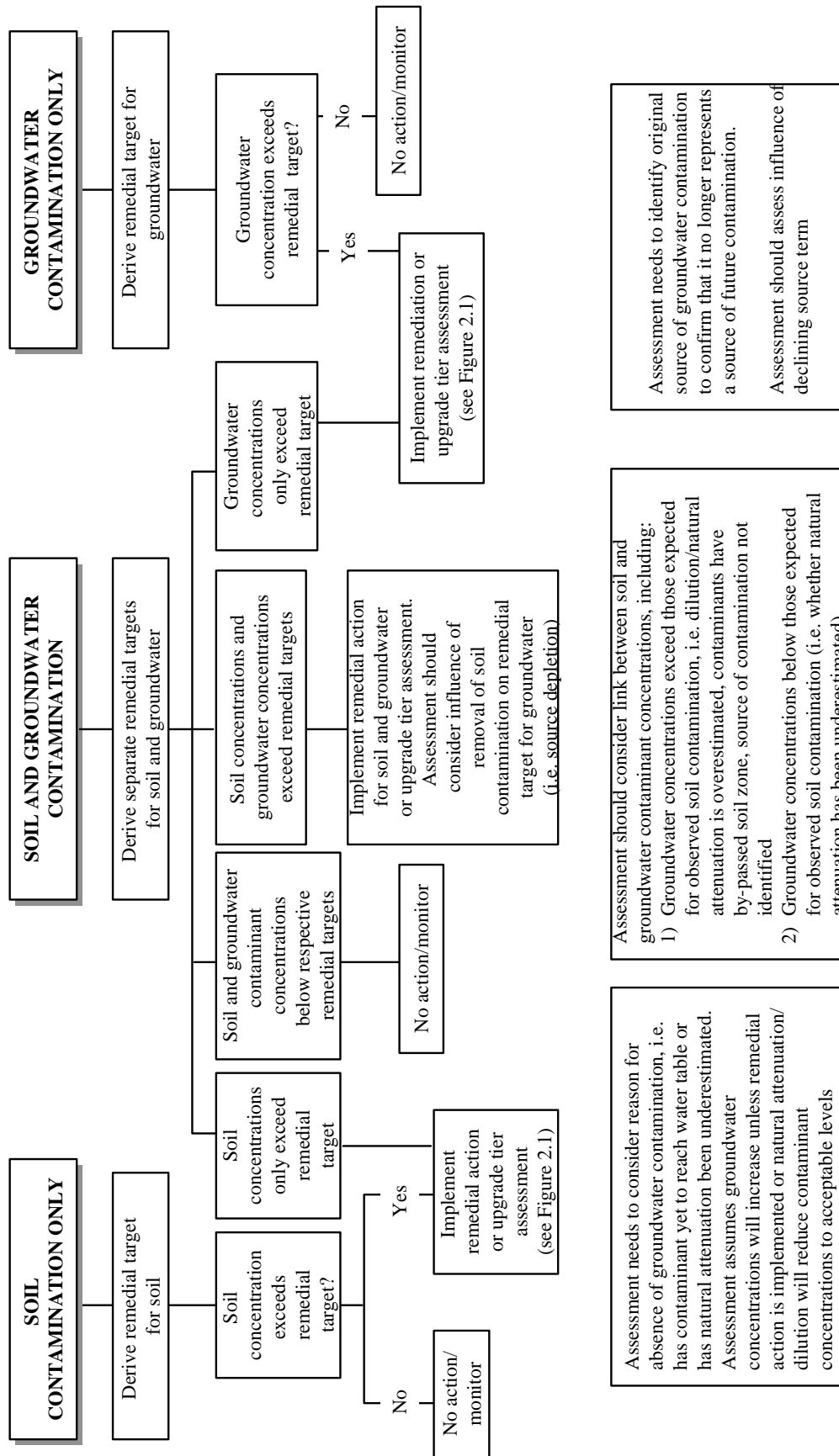
- determining remedial targets for both soil and groundwater (an example of this approach is given in Appendix 3);
- establishing if remedial action is required for soil and/or groundwater and which of the two should be given greater priority (refer to Figure 6.1);
- considering whether, after removal of the soil source of contamination, remedial action is still required for groundwater.

The assessment should consider the link between the observed soil and groundwater contamination by calculating the groundwater contaminant concentrations that would be expected from the observed soil contamination, and considering the following cases:

- *Predicted concentrations are lower than observed concentrations.* This could indicate that either there is an additional source of contamination, contaminants have by-passed the soil zone, and/or dilution and attenuation processes have been overestimated. The reason for the higher groundwater concentrations needs to be understood and if necessary the source of the contamination more accurately defined so that any remedial action can be appropriately targeted.
- *Observed concentrations are lower than those predicted.* This could indicate that either groundwater concentrations could increase in the future or the assessment has been too conservative and, for example, underestimated the significance of attenuation and, therefore, overestimated the remedial target. The reason for the lower predicted groundwater concentrations needs to be understood as, in the latter case, this may indicate that no remedial action is required.
- *Predicted and observed concentrations are similar.* This suggests that the conceptual model and analysis are correct and it provides verification of the remedial targets determined. Care needs to be exercised, however, as there may be more than one combination of parameter values that can be used to obtain a reasonable simulation of the observed groundwater concentrations, but could result in the determination of very different remedial targets.

It is important to recognise that in many site investigations only the soil zone may have been considered. Therefore, the assessment should be extended to consider whether contamination of groundwater would have occurred or could occur, with the need to extend the scope of the investigations. Moreover, it needs to be established that, if groundwater is remediated in isolation, it will not be recontaminated by contaminated soil or a discrete phase of contaminated material.

Figure 6.1



7. UNCERTAINTY, MONITORING AND FINAL REVIEW

7.1 Selection of parameter values and uncertainty analysis

In deriving remedial targets and determining the need for soil/groundwater remediation, consideration must be given to the degree of uncertainty with respect to:

- accuracy of the data and the range of possible parameter values;
- the assumptions made with respect to the flow regime (past, current and future);
- the deficiencies in knowledge with respect to contaminant pathways and processes;
- the assumptions made in deriving the target concentration, setting the compliance point, and calculating the remedial target concentration;
- the accuracy with which the analytical or numerical model represents the site.

It is important to stress that, in deriving a remedial target concentration as part of the Tier 1 to 4 analysis, it is unlikely that the input parameters will be a single value but will comprise ranges of values. For example, field testing may have given a range of values for the hydraulic conductivity for the strata below the site. Dependent on the choice of parameter value, a range of remedial target concentrations could be derived. The previous worked examples have assumed single parameter values to illustrate the approach. In Appendix 3, a worked example using a range of parameter values is presented.

Several approaches are possible in selecting parameter values. The precautionary approach, of using conservative parameter values, will afford greatest protection to the receptor, but this could lead to combinations of unrealistic values with consequent implications for cost and achievability and could be challenged. A more practicable approach is to use realistic parameter values and to undertake a sensitivity analysis, particularly in assessing the significance of attenuation (Tiers 3 and 4). **It is preferable to select realistic values and then consider a safety margin based on the sensitivity analysis, rather than use an unrealistic combination of worst case values.**

For degradable contaminants, the rate of degradation used should be chosen conservatively, as the calculated attenuation factor is very sensitive to this parameter. As more data are collected as part of site investigations or monitoring, it may be possible to use less conservative parameter values. In Table 3.1, the most sensitive parameters in determining a remedial target concentration are identified.

The calculation of the remedial target should therefore take account of the uncertainty in the input parameter values. Two factors need to be considered in this:

- 1) the sensitivity of the calculation to a change in the parameter value; and
- 2) the range in the parameter value as determined from field and laboratory testing.

For example, in calculating the rate of contaminant groundwater movement using the following equation, the calculation is as sensitive to a change in the value of bulk density as it is to a change in the value of hydraulic conductivity:

$$\text{Contaminant velocity} = \left(\frac{k i}{n + K_d \rho} \right)$$

where

K_d	= partition coefficient (l/kg)
ρ	= bulk density (g/cm ³)
n	= effective porosity
i	= hydraulic gradient
k	= hydraulic conductivity (m/d)

However, the value of bulk density determined for a soil is only likely to vary from 1.6 to 2.0 g/cm³, whereas the value of hydraulic conductivity determined from field testing can often vary by more than an order of magnitude.

A recommended approach for a sensitivity analysis is to change each input parameter in turn by a given percentage, $\pm 20\%$ for example, to determine the most sensitive parameters. This may assist in focusing any investigations. The analysis can then be repeated by calculating the remedial target according to the observed range in the more sensitive parameters. The difficulty in this is deciding what values to use. For example, if values for hydraulic conductivity of 1.5, 17, 22 and 25 m/d had been derived from field testing, the remedial target derived using the lower value of 1.5 m/d would be an order of magnitude smaller than if the average value had been used. This will not present a problem where the observed concentrations are below the remedial target concentration, particularly as this involves a conservative use of the field data. It presents a potential difficulty where, for example, the observed concentrations exceed the remedial target calculated using the minimum value of hydraulic conductivity. In reality, the lower value is likely to be unrepresentative of the aquifer and should not be used in calculating the remedial target. This illustrates that the assessment needs to include an element of expert judgement in deciding what value should be used and whether further investigations are necessary.

The alternative is to use a stochastic approach, such as that adopted in ConSim (Ref 15 - described in Section 3.4), which in summary comprises:

- 1) Assigning a probability distribution to describe the observed variation in each of the input parameters.
- 2) Solving the appropriate equation(s) by randomly selecting a parameter from the probability distribution, recording the result, and repeating the calculation by selecting a new parameter value. This process is repeated hundreds to thousands of times.
- 3) Statistically analysing the results to derive a probability distribution to describe the uncertainty in the calculated result. Typically, the results are expressed in terms of the 50 percentile value and the 95 percentile value (often taken as a reasonable worst case value).

The following factors need to be considered in undertaking a stochastic analysis:

- 1) Are sufficient data available to define the variation in a parameter values?

- 2) Parameters may be dependent on each other and this relationship may need to be defined, i.e. a high value for hydraulic gradient would not be expected for high values of hydraulic conductivity.
- 3) Interpretation of the results, i.e.: which percentile value should be used to define the remedial target. This may be the 50 percentile or 95 percentile value, the latter often being taken as a “worst case”.

If the analysis indicates a high degree of uncertainty in the derived remedial targets, which has implications for the risk to the receptor and the cost of a scheme, then further consideration needs to be given to the selection of parameter values and the severity and consequences of the predicted impact. This may assist in the decision either to set more conservative remediation targets or to collect additional site information and upgrade the tier assessment. The uncertainty analysis will be important in determining the benefit of further site investigations.

When possible, the assessment should be checked by:

- verifying the predicted values against observed data;
- undertaking, where possible, independent calculations, for example groundwater flow could be estimated using the equation given in Table 5.1 ($Q_c = k_i w.Mz$) and this value checked against the flow expected from an estimate of effective rainfall over the groundwater catchment to the site - such an approach can help to rule out unrealistic parameter values.

It is important to understand that the remedial target concentrations derived are unlikely to be definitive and expert judgement is required in assessing an appropriate action.

7.2 Monitoring

A monitoring programme will be needed unless investigations have demonstrated that the observed contamination does not represent an unacceptable risk or that the proposed measures, such as removal of the source, will be effective in protecting the receptor(s). The objectives of compliance monitoring are to:

- establish the need to implement remedial action, if the remedial target levels are exceeded in the future;
- determine when remediation should cease, that is, when concentrations consistently fall below the remedial target;
- determine the effectiveness of the remediation scheme, with a view to implementing corrective action if the objective has not been met.

The monitoring programme should be related to the remedial target concentration defined at the compliance point. This will vary according to the assessment tier.

Where the assessment has been undertaken for soil contamination, any monitoring boreholes should be located at the edge of the source area to demonstrate that no significant contamination has occurred or to trigger further action.

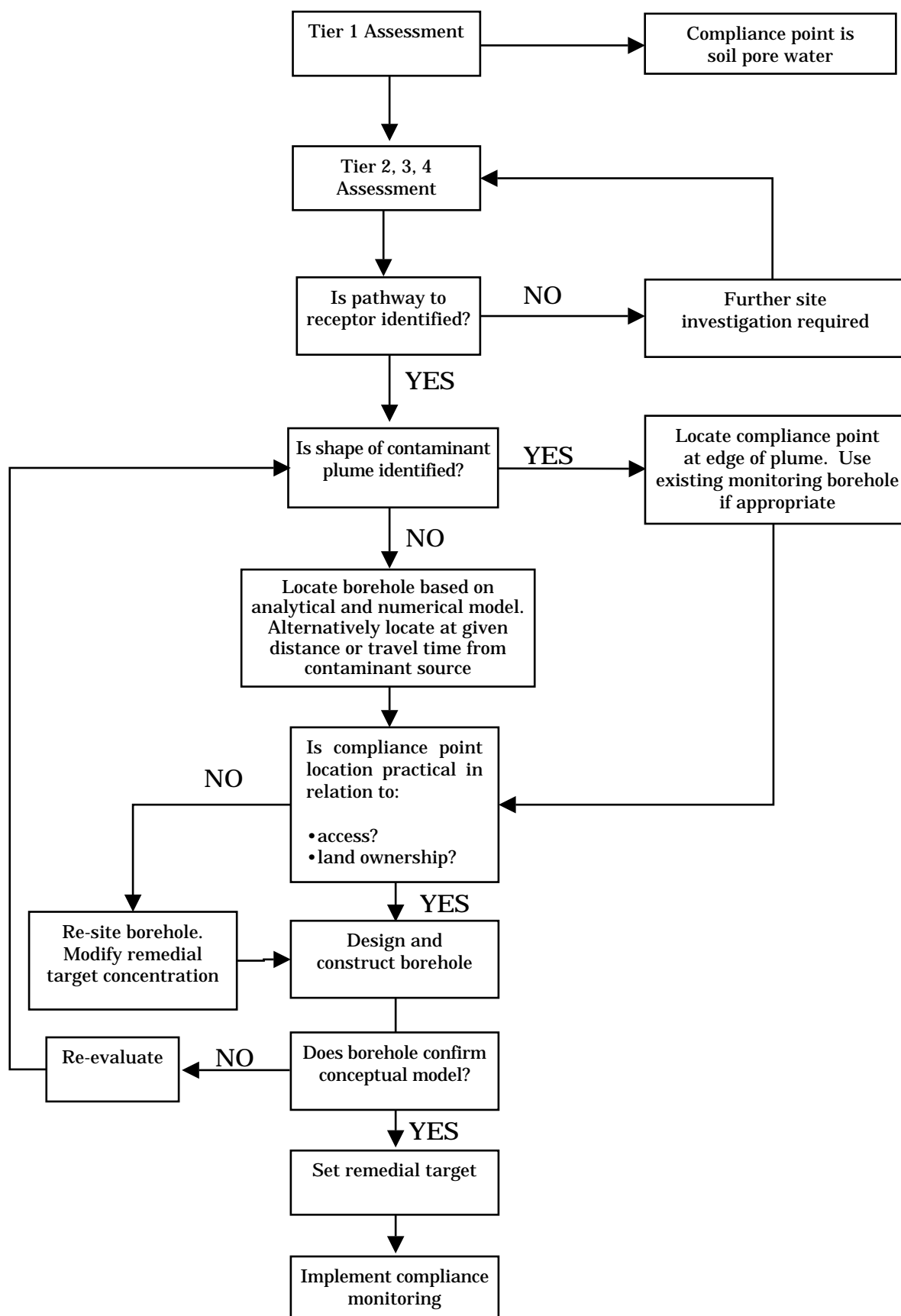
For contaminated groundwater problems, the boreholes will normally be located between the source and the identified receptor to provide confirmation that the predicted or assumed attenuation processes are effective. The decision factors to be adopted in determining the position of a compliance monitoring borehole are summarised in Figure 7.1.

The number, location and construction of monitoring boreholes required will normally be determined on a site-specific basis, but will be a function of:

- size of the contaminant source;
- type and distribution of contaminant (for example, if there is an LNAPL, then monitoring should include sampling at the water table);
- complexity of the hydrogeological regime and pathways;
- cost;
- access, including presence of existing buildings and services, together with land ownership and security of installation;
- sensitivity of the receptor at risk;
- analysis tier.

It is essential that the borehole locations should be agreed with a hydrogeologist.

Figure 7.1 Setting a compliance monitoring point



Generally, the **minimum** requirement for monitoring boreholes (Figure 7.2) will be as follows:

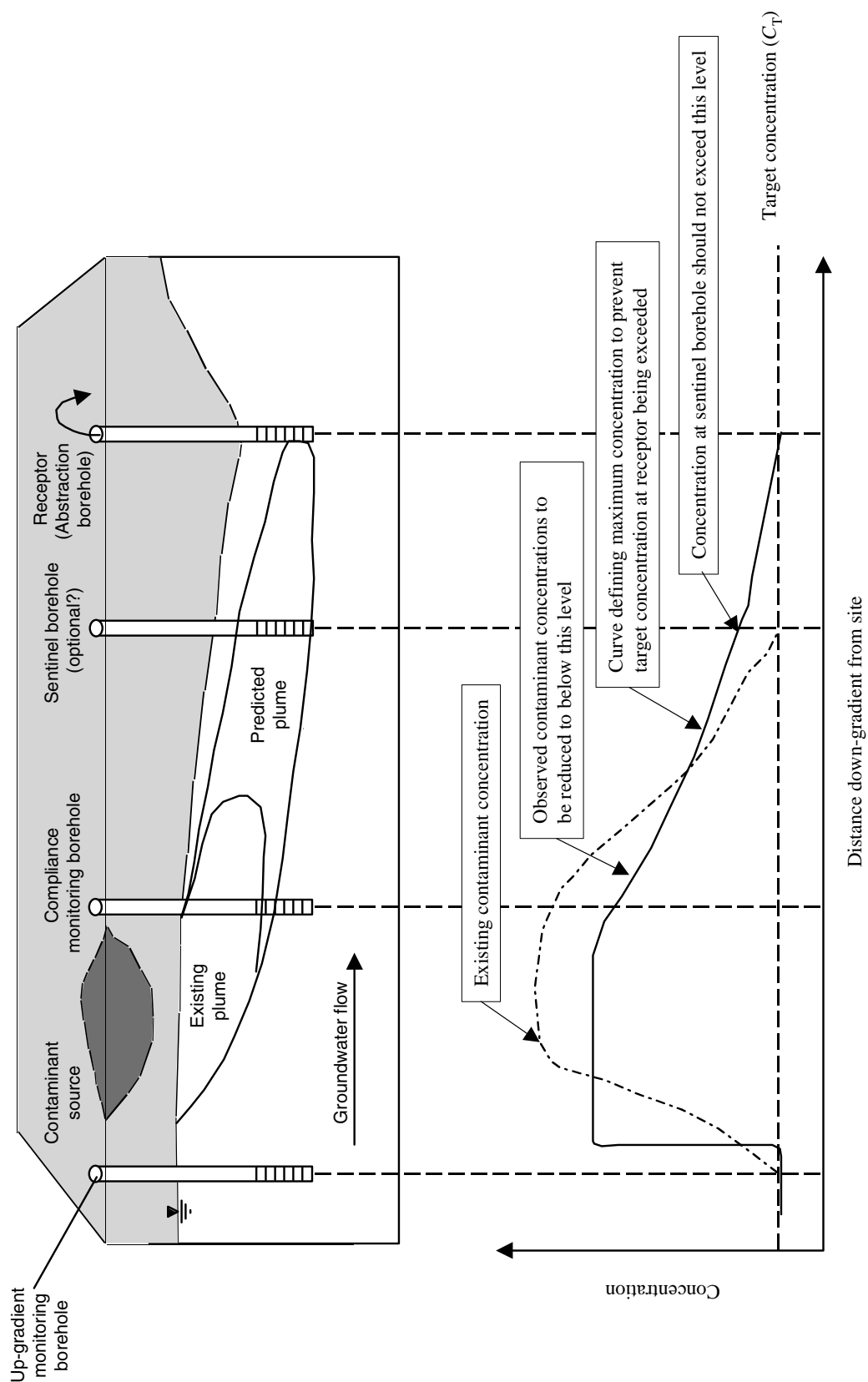
- One borehole should be located up hydraulic gradient of the contaminant source to determine background quality.
- At least two boreholes should be located at either the down-gradient edge of the contaminant source or the contaminant plume, with at least one of these being the compliance point. A single down-gradient borehole is not considered satisfactory due to the uncertainty in ensuring that this borehole is in the line of contaminant movement.
- At least one borehole should be located directly on the flow path between the source and the identified receptor to act as a sentinel or early warning borehole (Tiers 3 and 4 only). The Environment Agency Pollution Prevention Manual (Ref 14) recommends a distance of 200 m or a groundwater travel time of 400 days but these arbitrary limits may in practice not be suitable. Alternatively the analytical or numerical model that is used to determine the remedial target concentration (Tier 3 and Tier 4) provides a practical method of determining the location of the compliance monitoring point, as this should relate directly to the remedial target.
- Further boreholes should adequately define the direction of groundwater flow, if any existing and proposed boreholes noted above are insufficient for this purpose; there is a danger that the above boreholes will have a linear distribution, which will be inadequate for determining flow direction(s).

For boreholes located away from the contaminant source, it is essential that the borehole is correctly sited with consideration given to the fact that the contaminant plume may be moving via discrete pathways or diving. The certainty that the borehole is correctly sited will reduce with increasing distance from the plume, even though the size of any plume is likely to increase as a result of dispersion. The safest approach is to locate the compliance borehole at the edge of the known contaminant plume. This provides greatest certainty that monitoring is undertaken at the correct location.

A monitoring programme should be agreed with the Agency in terms of:

- the number, location and construction details of the boreholes;
- the methodology needed to obtain representative samples;
- the number and type of samples;
- range of determinands for analysis, which should include the key contaminants identified, appropriate analytical methods and their limits of detection, and breakdown products, where appropriate;
- the cost-effectiveness of the sampling/analytical strategy;
- frequency and duration of monitoring;

Figure 7.2 Compliance monitoring



- the basis for determining that measured concentrations exceed the trigger level, namely the mean or to a prescribed statistical threshold (e.g. 95 percentile), to account for likely variation in water quality as a function of sampling and analytical procedures.

7.3 Final review

It is important that the assessment should be subject to a final review. Key questions are:

- Is the target concentration appropriate?
- Where multiple contaminants are present, has the assessment been carried out for the key contaminant in terms of environmental sensitivity?
- Is the plume of contamination increasing or decreasing?
- If no remedial action is required, is monitoring required?
- In assessing soil contamination, have contaminants by-passed the soil zone?
- Are the proposed remedial measures achievable and cost-beneficial? For example, remediation of groundwater to background levels may not always be achievable either technically or cost effectively, as demonstrated by some pump-and-treat systems.
- What are the uncertainties in determining the proposed action, and is further investigation required?
- Are the timescales for implementation of the remediation scheme defensible in terms of the capabilities of those undertaking the remediation, the principle of sustainable development and the risk of further contamination of water resources whilst the scheme is being prepared and implemented?
- Is the receptor adequately protected?
- Have other sources of contamination been considered?
- Will the remediation scheme result in additional environment impacts? For example, a pump-and-treat system may result in derogation of existing water resources or any consequent discharge may have an impact on the receiving water.
- Is the level of monitoring warranted or satisfactory?

In evaluating the target and remedial target concentrations, together with any remedial measure, consideration should be given to whether there will be a short- or medium-term increase in the volume of groundwater contamination between the source of contamination and the receptor. The acceptability of this will be a balance between protection of the environmental target and the cost and practicality of doing so. In exceptional circumstances, if the predicted duration of the impact at the receptor is very short, it may be more effective to treat or isolate the receptor, then to remediate groundwater *per se*.

7.4 Liaison and communication

This document has focused on the technical basis for deriving remedial targets to protect water resources. Throughout this process it is essential that the appropriate regulatory bodies, and in this instance particularly the Agency, are closely involved in the assessment process.

The setting of target concentrations and remedial targets must be agreed with the Agency prior to the implementation of remedial measures. In most cases statutory Consents will be required from the Agency (and possibly the planning authority for certain activities) and a formal liaison process will take place. However, less formal liaison is desirable at all stages.

It is important to recognise that the assessment processes discussed in this document are complex and may be unfamiliar to many third parties (adjacent land owners, general public) who may be affected by or concerned about soil and groundwater contamination and the consequent remedial activities. Good communication with such parties is encouraged and will be essential where access to land not in the site owner's control is required, for example, in the siting of monitoring boreholes outside the source zone of contamination.

8. REFERENCES

1. Environment Agency, 1996. *A Methodology to Derive Groundwater Clean-Up Standards. R&D Technical Report P12*. Prepared by WRc.
2. Environment Agency, 1996. *Methodology to Determine the Degree of Soils Clean-Up Required to Protect Water Resources. R&D Technical Report P13*. Prepared by Dames & Moore.
3. American Society for Testing and Materials, 1995. *Risk-Based Corrective Action Applied at Petroleum Release Sites*. ASTM Standard Guide E1739-95.
4. Department of the Environment, 1995. *The Contaminated Land Exposure Assessment Model (CLEA): Technical Basis and Algorithms*. DoE, London. Draft.
5. DETR/Environment Agency, 1999. *Handbook of Model Procedures for the Management of Contaminated Land*. Contaminated Land Research Report CLR11. Draft.
6. (A) Environment Agency, 1998. *Policy and Practice for the Protection of Groundwater*. Second Edition. (B) SEPA, 1997. *Groundwater Protection Policy for Scotland (08/97)*.
7. National Rivers Authority, 1994. *Leaching Tests for Assessment of Contaminated Land*. Interim NRA Guidance. NRA R&D Note 301. Prepared by WRc.
8. United States Environment Protection Agency, 1989. *Performance Testing of Method 1312-QA Support for RCRA Testing*. EPA/600/4-89/022, June 1989.
9. Domenico, P. A., 1987. An analytical model for multidimensional transport of a decaying contaminant species. *J. Hydrology*, **91**, 49-58.
10. Domenico, P.A. and Schwartz, F.W., 1990. *Physical and Chemical Hydrogeology*. J. Wiley & Sons, Chichester.
11. Van Ommen, 1985. The “mixing cell” concept applied to transport of non-reactive and reactive components in soil and groundwater. *J. Hydrology*, **78**, 201-213.
12. Spitz, K. H. and Moreno, J. L., 1996. *A Practical Guide to Groundwater and Solute Transport Modelling*. J. Wiley & Sons, Chichester. 461pp.
13. Bear, J. and Verruijt, A., 1987. *Modelling Groundwater Flow and Pollution*. D. Reidel, Dordrecht, 414pp.
14. National Rivers Authority, 1994. *Pollution Prevention Manual*. Vol 026. Version 1 (09/95).
15. Environment Agency, 1999. *ConSim: Contamination Impacts on Groundwater: Simulation by Monte-Carlo Method*. Prepared by Golder Associates (UK) Ltd.
16. United States Environment Protection Agency, 1994. *Technical Background Document for Soil Screening Guidance*.

9. GLOSSARY

Absorption	The incorporation of a chemical within a solid or liquid.
Adsorption	The attachment of a chemical to the surface of a solid or liquid.
Advection	Mass transport caused by the bulk movement of flowing groundwater.
Aquifer	A permeable geological stratum or formation that is capable of both storing and transmitting water in significant amounts.
Attenuation	Reduction in contaminant concentration through biological, chemical and physical processes as it passes through a medium.
Biodegradation	The breakdown of a substance or chemical by living organisms, usually bacteria.
Compliance point	Negotiated location where the remedial target concentration must be achieved.
Conservative pollutants	Pollutants that can move readily through the aquifer with little reaction with the rock matrix and that are unaffected by biodegradation (e.g. chloride).
Controlled waters	(as defined by Water Resources Act 1991, Part III, Section 104.) All rivers, canals, lakes, groundwaters, estuaries and coastal waters to three nautical miles from the shore.
Dense non-aqueous phase liquid (DNAPL)	A liquid immiscible with water that has a density greater than water and so sinks in water.
Diffusion	Migration of substances by natural movement of their particles.
Dilution	Reduction in concentration brought about by the addition of water.
Dispersion	Irregular spreading of solutes due to aquifer heterogeneities at pore-grain scale (mechanical dispersion) or at field scale (macroscopic dispersion).
Effective rainfall	The amount of rain available for recharge to the aquifer after evapotranspiration (length units).
Eluate	A solution resulting from the mixing of soil and water in order to remove sorbed substances.
Equilibrium	No net transfer between two phases.

Free phase contamination	Product (e.g. gasoline, diesel) that is present in its original state and at a high saturation. May also include coal tars.
Groundwater	The mass of water in the ground below the water table (saturated zone) occupying the total pore space in the rock and moving slowly down the hydraulic gradient where permeability allows.
Groundwater Protection Zone (GPZ)	An area designated around a groundwater source, the maximum extent of which is the catchment area for the source and within which there are limits to the processes and activities that can occur within that area.
Henry's law constant	Coefficient that represents the equilibrium partitioning factor between a solute in the water and vapour phases.
Hydraulic conductivity	A coefficient of proportionality describing the rate at which water can move through a permeable medium. The density and kinematic viscosity of the water must be considered in determining hydraulic conductivity.
Hydraulic gradient	The change in total head with a change in distance in a given direction. The direction is that which yields a maximum rate of decrease in head.
Hydraulic head	The sum of the elevation head, the pressure head and the velocity head at a given point in the aquifer.
Intergranular	Occurring between the grains of a rock or soil.
Light non-aqueous phase liquid (LNAPL)	A liquid immiscible with water that has a density less than water and so floats on water.
Non-aqueous phase liquid (NAPL)	Liquids that are immiscible with water.
Non-polar molecule	A molecule not susceptible to permanent charge, usually without ionisable groups attached.
Partition coefficient	In a heterogeneous system of two or more phases in equilibrium, the ratio of the activities (or less accurately the concentrations) of the same molecular species in the phases is a constant at constant temperature. This constant is termed the partition coefficient.
Partitioning	The process by which a contaminant, released originally in one phase (e.g. adsorbed to soil grains), becomes distributed between other phases (i.e. vapour and dissolved phase).

Pathway	A route along which a particle of water, substance or contaminant moves through the environment.
Perched water	This is a layer of saturated soil formed above the main water table due to a layer of low permeability material intercepting water moving downwards through the unsaturated zone.
Permeability	Measure of the ability to transmit water. Defined as the volume of water passing through 1 m ² of aquifer under unit hydraulic gradient; units m ³ /m ² d or m/d.
Polar molecule	A charged molecule that is affected by changes in pH.
Pollution	(as defined by Environmental Protection Act 1990) Pollution of the environment due to the release (into any environmental medium) from any process of substances which are capable of causing harm to man or any other living organism supported by the environment.
Pollution	(of groundwater, as defined in Groundwater Directive) The discharge by man, directly or indirectly, of substances or energy into groundwater, the results of which are such as to endanger human health or water supplies, harm living resources and the aquatic ecosystem or interfere with other legitimate uses of water.
Pore water	Any free water (that is, not adsorbed within the matrix of a soil or rock and incapable of participating in contaminant movement) contained within the primary pore space or within fissures in either the unsaturated or the saturated zone.
Porosity	The ratio of the volume of void spaces in a rock or sediment to the total volume of the rock or sediment.
Receptor	An entity/organism or a controlled water that is being or could be harmed by a potential pollutant.
Recharge	The amount of water that reaches a water source such as an aquifer, which is calculated as rainfall less run-off, evapotranspiration and soil storage.
Remedial target	The goal of remedial activity set at the compliance point, in the form of a desired concentration in the soil or groundwater.
Retardation	A measure of the reduction in solute velocity relative to the velocity of the advecting groundwater caused by processes such as adsorption.
Saturated zone	The zone in which the voids of the rock or soil are filled with water at a pressure greater than atmospheric. The water table is the top of the saturated zone in an unconfined aquifer.

Sentinel borehole	A monitoring borehole up-gradient of a receptor.
Sorption	Absorption and adsorption considered jointly.
Surrogate borehole	A borehole located between the source and the receptor, at which a target concentration may be defined.
Target concentration	Derived chemical concentration at compliance point.
Total soil concentration	The total concentration of contaminants within the soil matrix, whether it be adsorbed, absorbed or in free phase.
Unsaturated zone	The zone between the land surface and the water table. It includes the root zone, intermediate zone and capillary fringe. The pore spaces contain water at less than atmospheric pressure, as well as air and other gases. Saturated bodies, such as perched groundwater, may exist in the unsaturated zone. Also called zone of aeration and vadose zone.
Volatilisation	The process by which the pure liquid phase turns to the gaseous phase, or boils.

Appendix 1 Sources of Information

Parameter	Data source	Comments
Tier 1 assessment		
Porosity	Laboratory measurement, Grain size, Literature	Important to differentiate between total and effective porosity. In soil and unsaturated zone only partial saturation. Water-filled porosity can be estimated from moisture content.
Henry's law constant	Literature	Volatile contaminants only
Bulk density	Laboratory measurement, Literature	
Clay content	Laboratory measurement	
Fraction of organic carbon	Laboratory measurement, Literature	
Sorption/partition coefficient	Literature, Tracers, Laboratory experiments	Lithology, bulk density, pH-dependent. Competition between different species, chemical reactions, solubility, polarity, changes in media properties
Tier 2 assessment		
Hydraulic conductivity	Rising/falling head tests, Packer tests, Pumping tests, Literature, Laboratory tests	Porous or fissured aquifer. Hydraulic conductivity may vary laterally and vertically (anisotropy). Unsaturated zone hydraulic conductivity dependent on saturation
Hydraulic gradient	Observation boreholes	Pressure gradient where density is a factor
Aquifer depth	Boreholes, Geophysical logging, Packer testing	Flow may be in discrete zones such that aquifer depth may differ from the total depth of the formation
Mixing depth	Monitoring results, Geophysical logging	Can be estimated using empirical equations
Direct recharge	Climatological data (rainfall, evaporation), land-use, soil type	Variable recharge due to low-permeability cover
Indirect recharge (leakage or discharge to sewers, drains, water mains)	Flow gauging	
Stream flow	Environment Agency, SEPA Stream gauging, Institute of Hydrology	
Abstraction	Environment Agency, SEPA Water utilities Environmental Health Departments	Actual abstraction may not equal the licensed abstraction rate

Parameter	Data Source	Comments
Tier 3 assessment		
Dispersion coefficient	Tracer studies, Literature, Laboratory experiments, Empirical values (one-tenth of distance plume has migrated)	The value of the dispersion coefficient is scale dependent. Values reported in field experiments are often several orders of magnitude greater than from laboratory experiments
Biodegradation	Literature	Breakdown products with different properties. Chemical environment. Typically represented as first- or second-order decay kinetic reaction. Alternatively may be linked to available electron acceptors (oxygen, nitrate, sulphate, ferrous iron)
Storage coefficient/aquifer porosity	Pumping tests, Grain size analysis, Laboratory tests, Literature	Pumping tests may not be of sufficient duration to define specific yield. Effective porosity may differ from total porosity. Model values may differ from field values. Delayed yield may be a factor
Tier 4 assessment		
Aquifer geometry	Geological maps, Boreholes, Geophysical survey	
Groundwater levels Spring/stream flows	Observation boreholes, Stream gauging, Topographic maps showing location and elevation of springs and streams	
Diffusion coefficient	Literature, Laboratory experiments	Fissure-“pore water” diffusion in dual porosity media
Specific gravity of contaminant	Literature, Ionic concentration (field investigation)	Temperature, pressure
Solubility/precipitation	Literature	Chemical environment (pH, E_h , temperature, concentration, carbon dioxide)
Ion exchange	Literature, Tracers, Laboratory experiments	Lithology, pH, chemical reactions, competition between different species, polarity, valency, changes in media properties
Immiscibility	Literature	Density, viscosity, soil capillarity, surface tension
Photolysis	Literature	Water clarity, depth
Hydrolysis	Literature	Bacterial chemical environment
Bioaccumulation	Literature	Population changes
Environmental factors (pH, E_h , dissolved oxygen, temperature)	Field measurement	Spatial variation

Appendix 2 Case example - soil

Soil contamination has been identified below a former chemical site, with the principal contaminants being cadmium, phenol and benzo[*a*]pyrene. The contamination is present within fill materials (a mixture of slag, clinker and gravel). The total area of the site is about 20,000 m². The observed concentrations of contaminants are as shown in Table A2.1.

Table A2.1 Observed contaminants

Contaminants	Concentration (mg/kg)	Description
Cadmium	5-10	Over most of site area, no clear cut distribution
Phenol	1-2	Over most of site
	10-20	Hot spots within site
Benzo[<i>a</i>]pyrene	5-30	Over most of site
	200-300	Hot spots within site

The site is underlain by Triassic Sandstone, classified as a Major Aquifer by the Environment Agency. A public water supply borehole, with a licensed abstraction of 2000 m³/d, is located about 1900 m from the site. The site falls within the catchment (Source Protection Zone III) of this abstraction borehole.

Assessment

The potential receptors are identified as:

- the Triassic Sandstone aquifer;
- the public water supply source.

The source of contamination is the soil zone. No information is available on the strata at depth, but it is assumed that any contaminants would migrate vertically down through the unsaturated zone to the saturated zone. A risk assessment is necessary to determine whether this site represents a risk to water resources.

Derivation of target concentrations

Information on background quality and environmental standards related to the intended use of the receptor was collated for each contaminant and is summarised in Table A2.2. This information has been used to determine target concentrations.

Table A2.2 Derivation of target concentrations

Contaminant	Background concentration (mg/l)	Environmental standard* (mg/l)	Target concentration† (mg/l)
Cadmium	<0.01	0.005	0.005
Phenol	<0.001	0.0005	0.0005
Benzo[a]pyrene	No data	0.00001	0.00001

* In this case the most sensitive receptor was taken as the public water supply borehole. For these contaminants, UK drinking water standards provide the most stringent environmental standard.

† Set as the Environmental Standard.

Tier 1 assessment

Information on soil “pore water” quality is available from leaching tests and summarised in Table A2.3.

The leaching test results all exceed the target concentrations, indicating the potential need for remediation. An initial analysis of costs indicates that the cost of remediation is an order of magnitude greater than undertaking a Tier 2 assessment. The decision, therefore, is to proceed with the next tier of analysis.

No immediate need for interim action is considered necessary whilst the Tier 2 assessment is undertaken, as:

- there is no evidence of any contamination at the public water supply source;
- the public water supply source is located 1.9 km from the source of contamination, and from discussion with the Environment Agency hydrogeologist, this source is not considered to be at immediate risk due to relatively slow rates of groundwater movement.

Table A2.3 Soil “pore water” quality*

Contaminant	Target concentrations at receptor (mg/l) (C_T)	Soil leaching test† (mg/l)
Cadmium	0.005	<i>0.01</i>
Phenol	0.0005	<i>0.2</i>
Benzo[a]pyrene	0.00001	<i>0.001</i>

* Values denoted in ***bold italics*** exceed the target concentrations.

† Based on maximum soil concentration.

Tier 2 assessment

Borehole drilling and testing were undertaken to determine aquifer thickness, hydraulic conductivity and hydraulic gradient. Information was also obtained from the Meteorological Office on the effective rainfall for the site. This information is required to calculate the Tier 2 dilution factor (DF).

The parameter values for and the calculation of the dilution factor are set out in Table A2.4.

Table A2.4 Tier 2 parameter values

Parameter	Unit	Range	Value used in Tier 2 assessment*	Source
Hydraulic conductivity	k m/d	5-12	5	Falling head tests
Hydraulic gradient	i	0.01	0.01	Water level measurement†
Depth of mixing	Mz m	Base of aquifer not penetrated	10	Evidence of high- permeability horizon from borehole logs
Length of site parallel to flow	L m	100	100	
Width of site parallel to flow	W m	200	200	
Infiltration	Inf m/d	0.0005‡	0.0005	Met. Office

* For this assessment, conservative values were selected. Further assessment may warrant undertaking a sensitivity analysis.

† Hydraulic gradient determined from water level measurement in six boreholes across the site.

‡ Infiltration derived from MORECS data.

Calculation of dilution factor (DF) - background concentration assumed to be zero:

$$DF = 1 + (k \cdot i \cdot Mz / Inf.L) = 1 + \frac{5 \times 0.01 \times 10}{0.0005 \times 100} = 11$$

The leaching test results are compared to the Tier 2 remedial target concentrations in Table A2.5.

Table A2.5 Determination of Tier 2 remedial targets

Parameter	Tier 2 remedial target* (mg/l)	Leaching test concentration (mg/l)
Cadmium	0.055	0.01
Phenol	0.0055	<i>0.2</i>
Benzo[a]pyrene	0.00011	<i>0.001</i>

* Values denoted in ***bold italics*** exceed the target concentrations.

† Remedial target concentration (LTC₂) = dilution factor (DF) x target concentration (Table A2.3). Dilution factor = 11.

Groundwater

Sampling of the monitoring boreholes down hydraulic gradient of the site identified elevated phenol concentrations, in the range 0.2 to 15 mg/l, compared to observed concentrations (less than 0.001 mg/l) in a borehole located up hydraulic gradient of the site. These concentrations are higher than would be expected from the observed soil concentrations and this is interpreted as indicating that phenol has by-passed the soil zone. Benzo[a]pyrene was not detected in any groundwater samples.

Discussion

The leaching test results show that phenol and benzo[a]pyrene exceed the soil remedial targets. In addition, the observed phenol concentration in groundwater exceeds the remedial target concentration of 0.01 mg/l, although benzo[a]pyrene was not detected. In view of these results the decision was made to proceed with Tier 3. In the case of phenol, as groundwater concentrations exceed those that would be expected from the observed soil concentration, groundwater rather than the soil represents the main risk to the identified receptors.

Tier 3 assessment

Additional information was obtained to determine the degree of attenuation of contaminants moving beyond the site boundary and towards the public water supply source. This included drilling of boreholes down hydraulic gradient of the site to obtain additional information on water quality and the hydraulic gradient and hydraulic conductivity of the aquifer.

For this assessment a compliance point was set at 200 m from the site boundary, in order to provide protection to the Triassic Sandstone aquifer itself, rather than to just the public water supply borehole.

The additional site information was used to recalculate the dilution factor. The attenuation factor was calculated using the Domenico analytical equation (assuming steady-state conditions) (Table A2.6). This attenuation factor is relevant to both the calculation of the Tier 3 remedial target for soil and groundwater.

Table A2.6 Parameter values and calculation of attenuation factor

Parameter		Unit	Values used in Tier 3 assessment			Source
Source width	$w (S_z)$	m	200	(4 to 20)		Falling head tests Water level measurement Literature
Source thickness	$S_y(Mz)$	m	10			
Hydraulic conductivity	k	m/d	8			
Hydraulic gradient	i		0.01			
Porosity	n	g/cm ³	0.15			Laboratory measurement Taken as one-tenth of the distance to the abstraction borehole
Bulk density	ρ		1.65			
Distance to compliance point	x	m	200			
Dispersivity (longitudinal)	a_x		20			
Dispersivity (transverse)	a_z		2			
Dispersivity (vertical)	a_y		0.2			
Dilution factor	DF		17			Calculated
Partition coefficient	K_d	l/kg	<i>Cadmium</i> 120	<i>Phenol</i> 0.18	<i>Benzof[a]pyrene</i> 7328	Literature Assumed unit concentration* Literature Calculated†
Input concentration	C_0	mg/l	1	1	1	
Half life		d	No decay	3 000	No decay	
Calculated concentration at compliance point	C_{ED}	mg/l	0.43	0.33	0.43	
Attenuation factor	(C_0/C_{ED})		2.3	3.0	2.3	Calculated

* Since the Domenico equation is linear with respect to the input concentration, assumed concentration can be used to calculate the attenuation factor.

† Calculated from Table 4.7a. Note that the use of the Domenico equation can in certain situations give slightly different values to the Ogata-Banks equation (Table 4.7b), as used in the ConSim model. The Ogata-Banks equation provides a more accurate solution.

Soil

The soil leaching test results are compared to the Tier 3 soil remedial target concentration in Table A2.7:

Table A2.7 Determination of the Tier 3 soil remedial target

	Attenuation Factor (AF) (Table A3.7)	Tier 3 remedial target* (mg/l)	Leaching test concentration (mg/l)
Cadmium	2.3	0.20	0.01
Phenol	3.0	0.025	0.02
Benzo[a]Pyrene	2.3	0.0004	0.001

* **Remedial target** = $AF \times DF \times \text{target concentration } (C_T)$ (Table A2.3). Dilution factor (DF) = 17.

Groundwater

The observed phenol and benzo[a]pyrene concentrations in groundwater are compared to the Tier 3 groundwater remedial target in Table A2.8.

Table A2.8 Determination of the Tier 3 groundwater remedial target

	Observed concentration (mg/l)	Tier 3 remedial target (mg/l)
Phenol*	0.2-15	0.0015
Benzo[a]pyrene	<0.00001	0.00003

* **Remedial target** = $AF \times \text{target concentration } (C_T)$.

For phenol attenuation factor (AF) = 3 and target concentration (C_T) = 0.0005.

Summary

The analysis has shown that for phenol the levels of soil concentration are close to the remedial target. A decision to implement remedial action on the basis of observed soil phenol concentrations is marginal, particularly when the results of the sensitivity analysis (see below) are taken into account. However, the observed phenol concentrations in groundwater are significantly above the remedial target for groundwater and, therefore, remedial action needs to be implemented in respect of contaminated groundwater. The observed concentrations in groundwater are interpreted as indicating that phenol has by-passed the soil zone, but it is also likely that the main source of contamination no longer exists and that phenol concentrations in groundwater would be expected to decrease with time. Leaching of the contaminated soil may give some additional loading but this is considered to be small compared to the original source. For benzo[a]pyrene, soil leaching concentrations exceed the remedial target, but no evidence for this contaminant has been identified in groundwater. Benzo[a]pyrene has a very

low mobility (high partition coefficient) and sorption in the unsaturated zone may explain its absence in groundwater. No action is required for cadmium.

Sensitivity Analysis

A sensitivity analysis was also carried out as part of the Tier 3 assessment. This examined the influence of changing the values of the least certain parameters on the calculated remedial target for phenol. These parameters are hydraulic conductivity, partition coefficient and the degradation rate. Each parameter value was varied by $\pm 25\%$ and the results are given in Table A2.9. The leaching test concentrations are below the calculated remedial targets, providing confirmation that the assessment for soils has been conservative. In addition, the remedial target was calculated using the range of values of hydraulic conductivity derived from field testing.

Table A2.9 Sensitivity analysis

Parameter	Percentage change in value (%)	Calculated remedial target for soil (mg/l)
Remedial target (Table A2.8)		0.025
Hydraulic conductivity (m/d)	+25	0.025
Hydraulic conductivity (m/d)	-25	0.028
Degradation rate (m/d)	+25	0.027
Degradation rate (m/d)	-25	0.025
Partition coefficient (l/kg)	+25	0.027
Partition coefficient (l/kg)	-25	0.025
All values changed by 25% to give minimum remediation target		0.022
Hydraulic conductivity minimum value = 4 m/d		0.054
maximum value = 20 m/d		0.017
Leaching test concentration (mg/l)		0.02

Appendix 3 Case example - groundwater

Groundwater investigations found that groundwater below a former chemical site was contaminated. Benzene was the main contaminant identified, with concentrations ranging from 1 to 10 mg/l. The site is located on a sand and gravel aquifer. This aquifer provides baseflow to a river located about 200 m from the site. The target concentration for benzene entering the river as baseflow has been set as equivalent to the Environmental Quality Standard of 0.03 mg/l.

Tier 2 assessment

Benzene concentrations observed in groundwater (1 to 10 mg/l) below the site exceed the Tier 2 target concentration (0.03 mg/l), with the requirement either to remediate groundwater or to undertake a Tier 3 assessment. The cost of Tier 3 in this case is significantly lower than remediation and the decision has been made to proceed with this assessment.

Tier 3 assessment

Information on the aquifer properties has been determined as part of an initial investigation, and is summarised in Table A3.1.

Table A3.1 Aquifer properties

Parameter		Unit	Value	Assessment of compliance point position	
Width of plume at source	S_z	m	60		
Thickness of plume at source	S_y (Mz)	m	10		
Hydraulic conductivity	k	m/d	20		
Hydraulic gradient	i		0.005		
Porosity	n		0.25		
Bulk density	ρ	g/cm ³	1.8		
Distance to compliance point	x	m	200	100	50
Dispersivity (longitudinal)	a_x		20		
Dispersivity (transverse)	a_z		2		
Dispersivity (vertical)	a_y		0.0002		
Partition coefficient	K_d	l/kg	0.83		
Input concentration	C_0	mg/l	100		
Half life		d	100		
Calculated concentration*	C_{ED}	mg/l	0.00086	0.30	5.7
Attenuation factor	(C_0/C_{ED})		117300	333	18

* Using the steady-state Domenico equation (Table 4.7a).

The observed groundwater concentrations below the site have been compared with the target concentration multiplied by the attenuation factor, as summarised in Table A3.2. Also included in this table are the remedial targets that would be applied if a surrogate borehole located at 50 and 100 m from the site had been used as the compliance point.

Table A3.2 Comparison of calculated remedial targets for groundwater for different compliance points

Target concentration (mg/l)	Distance to compliance point (m)	Attenuation factor	Tier 3 remedial target (mg/l)	Observed concentration (mg/l)
0.03	200 (distance to receptor)	117,300	3520	1-10
	100	333	10	
	50	18	0.5	
	200 (no degradation)	1*	0.03	

* Calculated using the above parameters but with an infinite half-life.

The observed benzene concentrations are below the remedial target calculated for a compliance point set at the receptor and, therefore, no action is considered necessary. However, the calculations also show that if the compliance point was set at a distance of less than 100 m from the site, there would be a need for remediation. There would also be a requirement for remediation if benzene did not degrade as considered in the above assessment. A monitoring programme, including routine sampling of boreholes drilled along the site boundary and at a distance of 50 m down hydraulic gradient of the site, has been implemented to provide confirmation of the above assessment.

