european oil industry guideline for risk-based assessment of contaminated sites (revised)

Prepared for the CONCAWE Water Quality Management Group by its Special Task Force (WQ/STF-27):

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ABSTRACT

This report proposes a three-tiered approach to assessing the nature and extent of the contamination of soil and groundwater at oil industry sites and implementing corrective action. Such sites range from complex refineries down to retail service stations. The nature and extent of contamination range from major to insignificant while the potential for exposure of own workers or third parties also varies enormously. The principle of the approach is to tailor corrective action to site-specific conditions and hazards (risk-based corrective action). This leads to more cost-effective solutions, and allows the greatest effort to be targeted to where it is most beneficial.

This report updates and expands CONCAWE report 2/97. In particular it includes appendices including a number of discussion papers on technical and policy issues which should be of interest and value to regulators and their technical staff developing or reviewing risk-based strategies for the remediation of contaminated land and water.

KEYWORDS

Clean-up, contaminated sites, contamination, corrective action, oil, oil industry, petroleum, RBCA, refineries, remediation, risk, risk based corrective action, screening, terminals, toxicity.

INTERNET

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SUMMARY

Industry, regulatory and public attention to contaminated land in Europe has escalated dramatically over recent years. Faced with a variety of local and national approaches to this problem, a process has been developed to assist the European oil industry in assessing the condition and corrective action requirements for sites ranging from complex refineries down to retail service stations. The nature and extent of contamination at such sites ranges from major to insignificant. The potential for soil and groundwater contamination to expose a neighbour, an on-site worker, or another potential receptor also varies enormously.

Some countries have set fixed numerical criteria to decide these issues based on generic assumptions on site conditions such as soil type, depth to groundwater, geology and hydrogeology and proximity to potential receptors (e.g. groundwater supply well, basement, surface water body). Such an approach ignores the fact that contaminated sites vary widely in terms of both complexity and the potential risk they may pose to either human health or the environment. As fixed numerical criteria are nearly always set at very low levels, their use leads to more clean-up of land than may be necessary. The result is wastage of resources (and ultimately added cost to the consumer) with clean-up costs incurred without an incremental reduction in risk to human health and the environment.

In recent years, the principles of Risk-Based Corrective Action (RBCA) have been applied. This follows a flexible approach to decision making whereby corrective action is appropriately tailored to site-specific conditions and hazards. This leads to more cost-effective solutions, and allows the greatest effort to be targeted to where it is most beneficial. In its broadest sense, risk assessment in relation to contaminated land can be defined as “an evaluation of whether there is a potential for adverse effects to occur, based on factual knowledge about a site, and scientific evidence concerning the environmental behaviour and toxicity of the chemicals present".

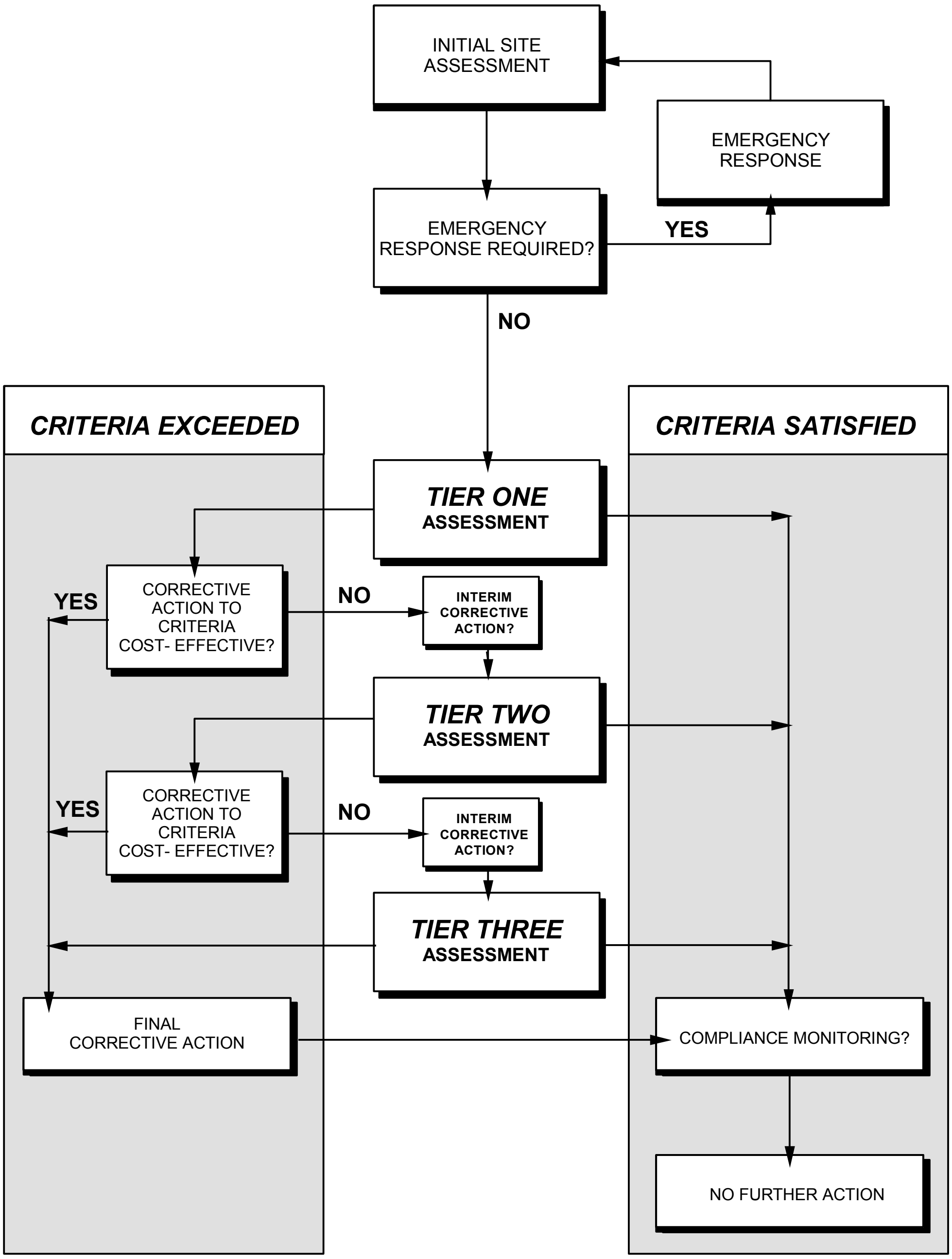
The risk-based approach to managing contaminated land has become widely adopted in the USA. The ASTM were instrumental in gaining acceptance of the approach with publication in 1994 of the “Emergency Standard Guide for Risk Based Corrective Action Applied at Petroleum Release Sites” which has since become a fully ratified standard. This guidance set out a tiered framework to provide a consistent decision-making process for the assessment and response to a petroleum release, based on the protection of human health and the environment. Whilst it was recognised that the RBCA process is not limited to a particular class of compounds, the guide focused on its application to petroleum product releases through the use of examples.

The RBCA approach is perceived as successful by both industry and regulators in the USA and has led to initiatives such as The Partnership In RBCA Implementation, or PIRI. This is a voluntary public-private partnership whose goals are to increase awareness of the benefits of RBCA, encourage the expedited adoption of RBCA by states, and help provide states with the technical RBCA training they need to effectively implement RBCA programs.

CONCAWE has recognised the usefulness of the RBCA approach, and this guidance aims to set out a framework for its use in a European context which could be adapted to the situations prevailing in the various European countries. It is also hoped that it may lead to the implementation of similar public-private partnerships as PIRI between European Member States and industry.

The underlying concepts of RBCA are described in this report. The technical aspects of key policy decision issues that need to be considered in implementing RBCA are covered in a number of discussion papers. These are appended to this report. CONCAWE recommends a three-tiered framework for deciding the most appropriate corrective action. This is summarised in **Figure 1**.

Figure 1 General Approach



Each tier involves increasingly sophisticated levels of data collection and analysis. The first tier consists in a simple screening step where the site conditions are compared with existing conservative screening criteria which have used generic assumptions. In subsequent tiers more site-specific information is used in developing remediation goals. In moving from a lower to a higher tier of analysis there is a reduction in the level of conservatism in the assumptions made but the degree of protection of human health and the environment remains the same.

The decision to move to a higher tier is determined by whether it is cost effective or practical to carry out corrective action based on the remediation goals determined at the lower tier. At the higher tier there is less uncertainty involved in establishing the appropriate remediation but the data and analysis required for the higher tier has to be obtained at an added cost.

The three-tiered approach is based on the principle of source-pathway-target. It starts with an initial assessment of the site which involves gathering general data including potential sources of contaminants, obvious evidence of contamination, land-use, presence of potable groundwater etc. The pathways by which contaminants could reach identified potential receptors or populations at risk are then identified. This enables a Tier 1 assessment to be performed, in which chemical data on the degree of contamination of the site is collected and compared with Risk Based Screening Levels (RBSL) and other relevant criteria. RBSLs comprise of a set of trigger concentrations for contaminated soil and groundwater. These figures are not intended to be soil standards or clean-up targets. If exceeded, they are simply an indication that further study is required. RBSLs are derived using conservative assumptions and, as such, are based on a generalised risk assessment. If the observed values are below these levels, then the risk is considered insignificant.

1. INTRODUCTION

This document presents a guideline for a uniform approach to corrective action decisions at contaminated European oil industry sites based on risk management. Whilst the guideline focuses on sites at which the production, use or storage of petroleum products may have resulted in accidental releases to soil and groundwater, it is expected that the process and its underlying principles can be applied to a broad range of industrial and commercial sites. The guideline provides details on how to identify whether or not corrective action is required at such sites and, if so, the form that this should take. The guideline links the principles of risk assessment with those of site investigation and corrective action decision-making.

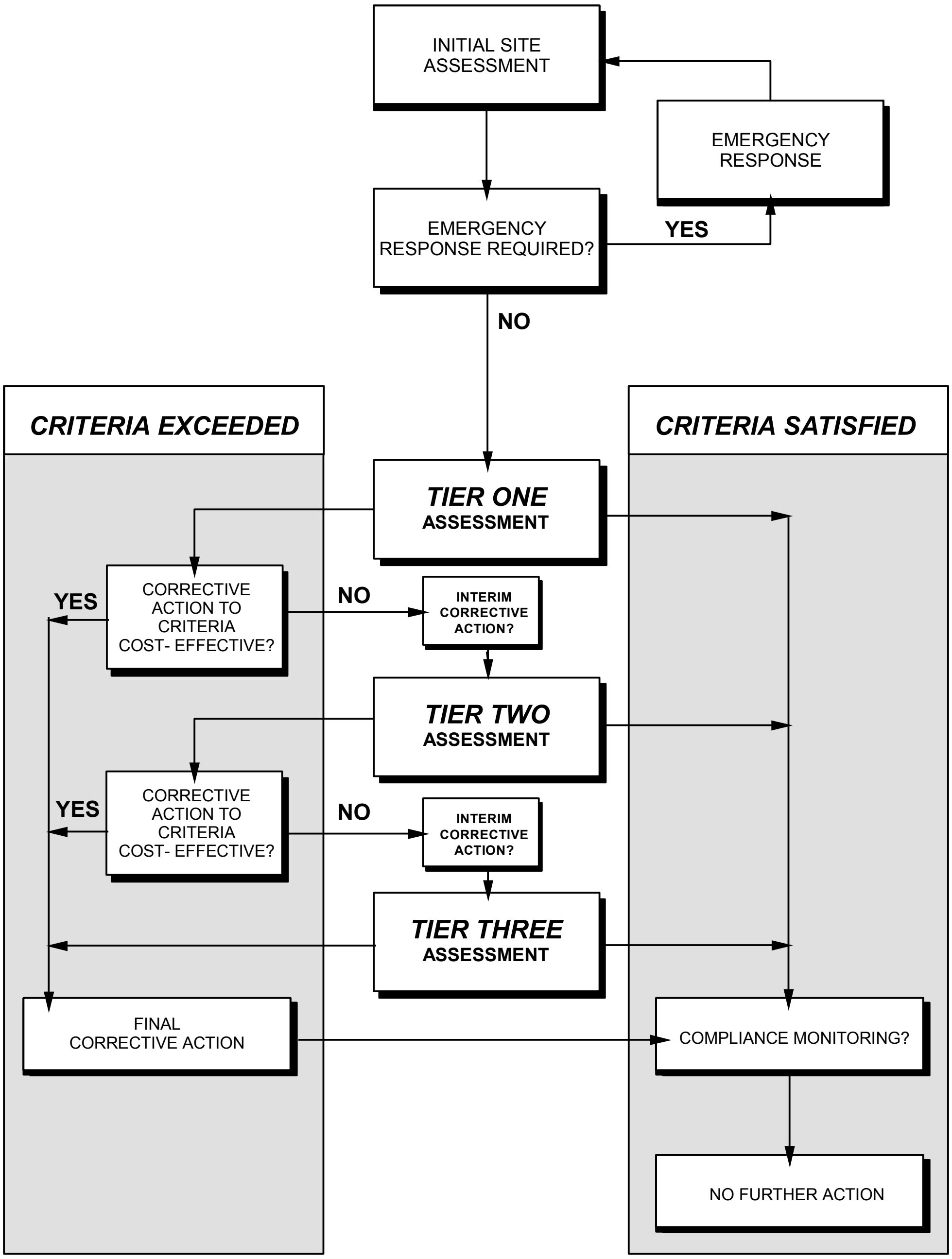
The guideline draws heavily on the principles of Risk-Based Corrective Action (RBCA) as they have been applied in other parts of the world, primarily in North America. It is an attempt to place these principles within a European context, in recognition of the specific circumstances pertaining both to the continent as a whole and to the individual countries within it. It reflects the European oil industry's promotion of a consistent risk-based approach to dealing with its contaminated sites.

Corrective action should only be applied to sites which are found to pose unacceptable actual or potential risks to human health and/or the environment. A risk-based approach allows the regulatory and regulated communities to focus their efforts on sites that pose actual risks, rather than uniformly applying non-site-specific criteria to all sites.

Contaminated oil industry sites vary widely in terms of their complexity, the physical and chemical characteristics of the contamination and the potential risk they may pose to human health and to the environment. The guideline recognises this diversity, and describes a three-tiered approach to decision-making in which site assessment, risk assessment and corrective action activities are appropriately tailored to site-specific conditions and hazards. This flexibility allows more focused and cost-effective solutions to be developed than have been used in the past, particularly those designed to achieve uniform standards and procedures. While the guideline is aimed specifically at oil industry sites, its general principles should be applicable across a broad range of industrial sectors and activities.

Under the guideline, site assessment becomes more detailed at each successive tier, and requires the progressive use of additional information and expertise. The approach is summarised schematically in **Figure 1**. It should be noted, however, that not all tiers have to be completed for a conclusion to be reached on the need for and scope of any corrective action. The tiered approach merely allows the level of analysis to be restricted to that needed to make an appropriate risk-based decision. Such an approach is consistent with the evolving contaminated land policies of several European governments and has the flexibility to be widely used.

Figure 1 General Approach



This report contains information on the process to be used. More detailed information on the methods to be used can be found in the appendices.

2. OVERVIEW

2.1. OBJECTIVES OF THE GUIDELINE

The objective of this guideline is to provide a simple-to-use, rational methodology for addressing potential contamination at oil industry sites in a manner which is protective of human health and the environment. It will allow risk-based decisions to be made in an efficient and cost-effective manner and can be used to prioritise remedial actions at numerous sites.

The guideline is designed to replace more traditional approaches to contaminated land assessment and remediation, in which investigation and corrective action activities have often taken place in isolation, with no clear linkage between the two. Such approaches have tended to lack any detailed scientific evaluation of the necessity of corrective action and of what form this should take to achieve adequate protection of human health and the environment in the most cost-effective manner. The blanket and uniform application of generic standards has compounded the problems of this approach since, when an exceedence has been identified, remedial measures have often been implemented with little regard for the actual objective, or how they should be targeted most effectively.

The guideline has been developed to provide a risk-based framework for consideration by European regulators and other interested parties across Europe as a scientifically defensible approach for dealing with contaminated land, specifically at oil industry sites. This is especially important at present since a number of countries are developing contaminated land policies which involve the use of risk assessment. The guideline provides a common framework that could be applied on a Europe-wide basis via an "evergreen" framework which integrates "state of the art" risk assessment techniques into a flexible decision-making methodology.

It should be noted that, until recently, risk assessment of contaminated sites often focused on the "worst case" or "reasonable worst case". This was especially so in the USA, where protecting the hypothetical "Maximally Exposed Individual" (MEI) has proved costly to industry, and ultimately society, with minimal positive impacts for the public. This situation can be visualised by considering sites where both soil and groundwater are contaminated, for example with volatile organic compounds. The MEI is assumed to be someone who lives on the site and is exposed to the contamination via all plausible exposure pathways. In reality, it is extremely unlikely that an individual would be exposed to all these pathways. These include drinking groundwater from a garden well, eating vegetables grown in the garden, coming into dermal contact with contaminated media and inhaling the vapours (both indoors and outdoors), as well as showering in the same contaminated water. It is only recently that the extensive resources committed to protecting this individual have been viewed in terms of the overall benefits to society and the environment. Such benefits are often low or even indefinable compared with those that are achieved in other areas of environmental improvement. This resulted in the risk-based corrective action (RBCA) process being adopted in the US.

It is the European oil industry's belief that corrective action at contaminated sites should be based on the practical application of risk-based methods. Clearly, it is impracticable, unrealistic and unnecessary to attempt to protect this hypothetical individual at all costs.

2.2. BACKGROUND TO RISK ASSESSMENT

Risk assessment with regard to contaminated land is based on a principle published by the US National Academy of Sciences (NAS) in 1983. This principle identifies four elements of the risk assessment process, as follows:

- hazard identification, in which the main potential adverse health effects are identified. In practice, hazard identification has been replaced by the term "site characterisation" and involves examination of the site and collation of relevant data and information. The process is illustrated in **Figure 2**.
- exposure assessment, in which the potential intake levels/exposures for target populations are calculated;
- dose-response assessment, in which the relationship between dose level and adverse health effects of chemicals are defined; and
- risk characterisation, which combines the exposure and dose-response information to predict the likelihood of adverse health effects arising in the target population.

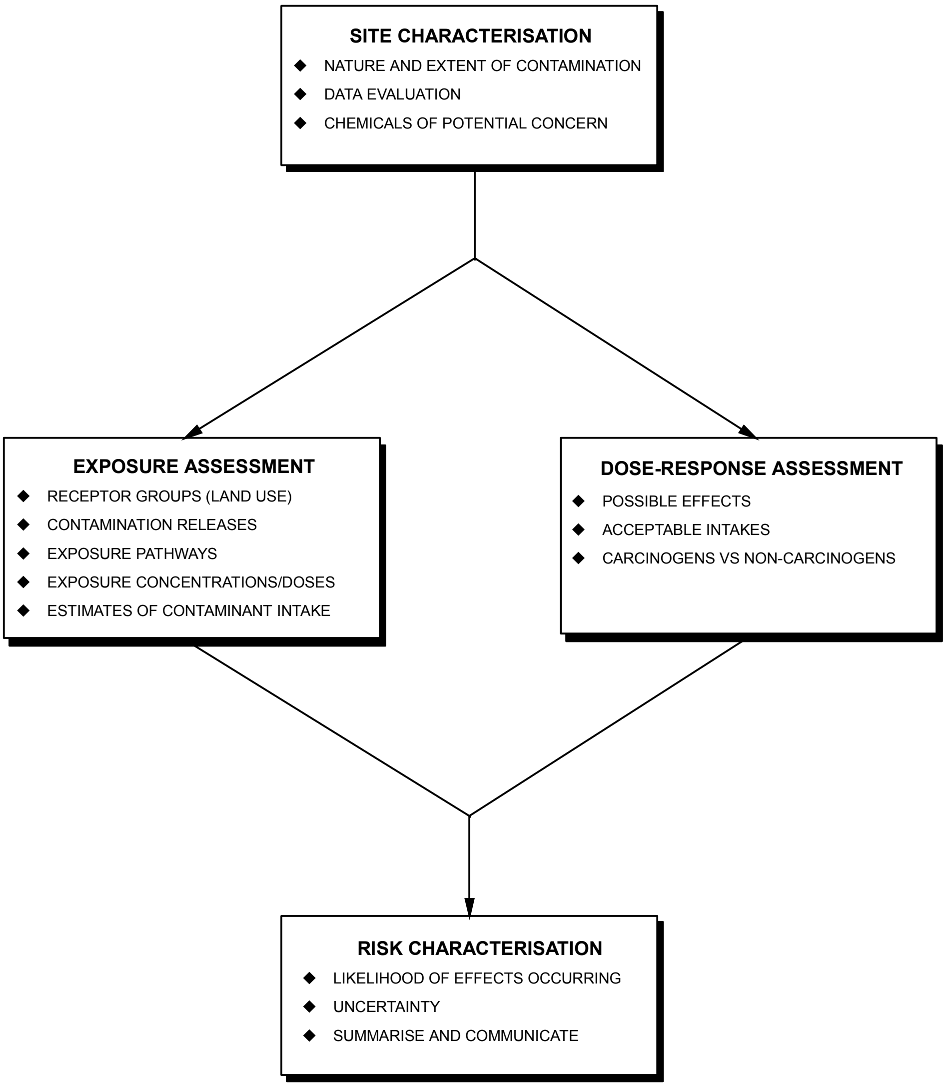
Fundamental to an understanding of risk assessment is the basic principle of toxicology, that "the dose makes the poison". This refers to the fact that every substance is toxic, no matter how benign it seems in everyday experience. The critical factors are the amounts which can be taken into the body before adverse effects occur and the probability of those effects occurring.

The purpose of a risk assessment is to carry out an evaluation of the possibility that toxic effects will occur, by quantitatively predicting exposure levels and then combining them with toxicity information. Well-established methods are available to predict the potential human exposure to substances present at contaminated sites, and suitable toxicity information (in the form of dose-response criteria) is available from authoritative sources, such as the World Health Organisation. The combination of predicted exposure levels with toxicity information provides an assessment of risk. In situations where it appears that there is a significant risk (i.e. the predicted exposure is in excess of the "tolerable" exposure), acceptable contaminant concentrations for soil, air, water, etc. can be derived or the exposure setting changed to bring the potential exposure levels down to within the tolerability limits. It should be noted that such limits are themselves subject to considerable uncertainty and so usually err considerably on the side of safety.

Risk assessment is now seen by regulators and industry in many countries as the best way forward in managing potential contaminated land issues. It has been incorporated into government environmental regulations in the USA, Canada, Australia, New Zealand, the Netherlands and the United Kingdom and is being considered in many others. In its broadest sense, risk assessment in relation to contaminated land can be defined as:

> *"an evaluation of whether there is a potential for adverse effects to occur, based on factual knowledge about a site and scientific evidence concerning the environmental behaviour and toxicity of the chemicals present."*

Figure 2 Traditional Risk Assessment Model



Risk assessment has developed rapidly since its initial use in addressing environmental issues in the USA in the mid-1980s. Historically, it was regarded as distinct from risk management, the latter being concerned with the implementation of measures designed to mitigate any issues identified by the former. This separation developed so that objective, scientific appraisals of risk could take place in isolation from issues such as economics or politics.

More recently it has been recognised that, while the separation of risk assessment and risk management makes sense philosophically, it can lead to problems in risk-based decision-making. This is because some sites present insignificant risk, whereas others may have the potential for significant risk, and so merit a more detailed examination. Clearly, with perhaps hundreds of thousands of potentially contaminated sites worldwide, risk assessment has to be streamlined to allow low risk sites to be screened out at an early stage and allow a more detailed investigation into sites which have the potential to pose higher risk.

The European oil industry believes that risk assessment is most cost-effectively applied within a tiered framework that is acceptable to both the regulators and regulated community. The amount of time and effort that is invested in assessing risk is therefore defined on a site by site basis, taking into account site conditions and the potential exposure pathways to the human and environmental receptors of concern. A tiered approach also allows the use of increasing amounts of site-specific data to replace the conservative generic assumptions that are initially made with less detailed site specific knowledge.

The risk-based approach to dealing with contaminated land has considerable advantages over the use of generic standards. It allows the assessment of site-specific conditions to determine whether or not there is a potentially unacceptable risk at a contaminated site and the need for, and scope of, any corrective action can subsequently be determined. Site-specific risk-based corrective action levels are typically less conservative than generic standards as they are calculated using site-specific data (the latter are designed to be applicable to the most sensitive of situations). As a result, corrective action is only carried out in situations where a need has been identified through a comprehensive evaluation of the associated risks, taking into account all local circumstances.

This guideline outlines a tiered risk assessment framework that provides a logical and technically defensible means of evaluating potential risks at petroleum sites. It also offers additional advantages since pre-defined risk assessment technical issues can be reviewed by regulators and/or independent technical consultants, and form the basis for established acceptance procedures. The guideline provides a framework into which new scientific information can be integrated as it becomes available, and allows where country-specific requirements and assumptions to be incorporated.

The final, and perhaps most important benefit of the risk-based process, is that it identifies the most important issues surrounding a site. This allows the exposure pathways of concern to be identified and any potential for exposure to be eliminated through institutional controls, natural attenuation and/or remedial techniques. The key is that the approach is flexible enough to facilitate the reduction or mitigation of potential site risks, as needed.

2.3. REGULATORY ACCEPTABILITY

Many countries in Europe have either adopted risk-based approaches to contaminated land corrective action decision-making or are in the process of doing so. It is important that, within developing legislation, the opportunity for using innovative techniques is left open. This will ensure that advances in knowledge and scientific developments can be incorporated into existing frameworks. Individual regulators may wish to make their own policy decisions and establish their own "best practice" but it is in everyone's interests that reasoned scientific principles should be allowed to prevail when deciding on the correct approach at a particular site.

The appendices to this report comprise a range of papers which discuss technical and policy issues which should be of interest and value to both regulators and their technical staff developing or reviewing risk-based approaches to the remediation of contaminated land.

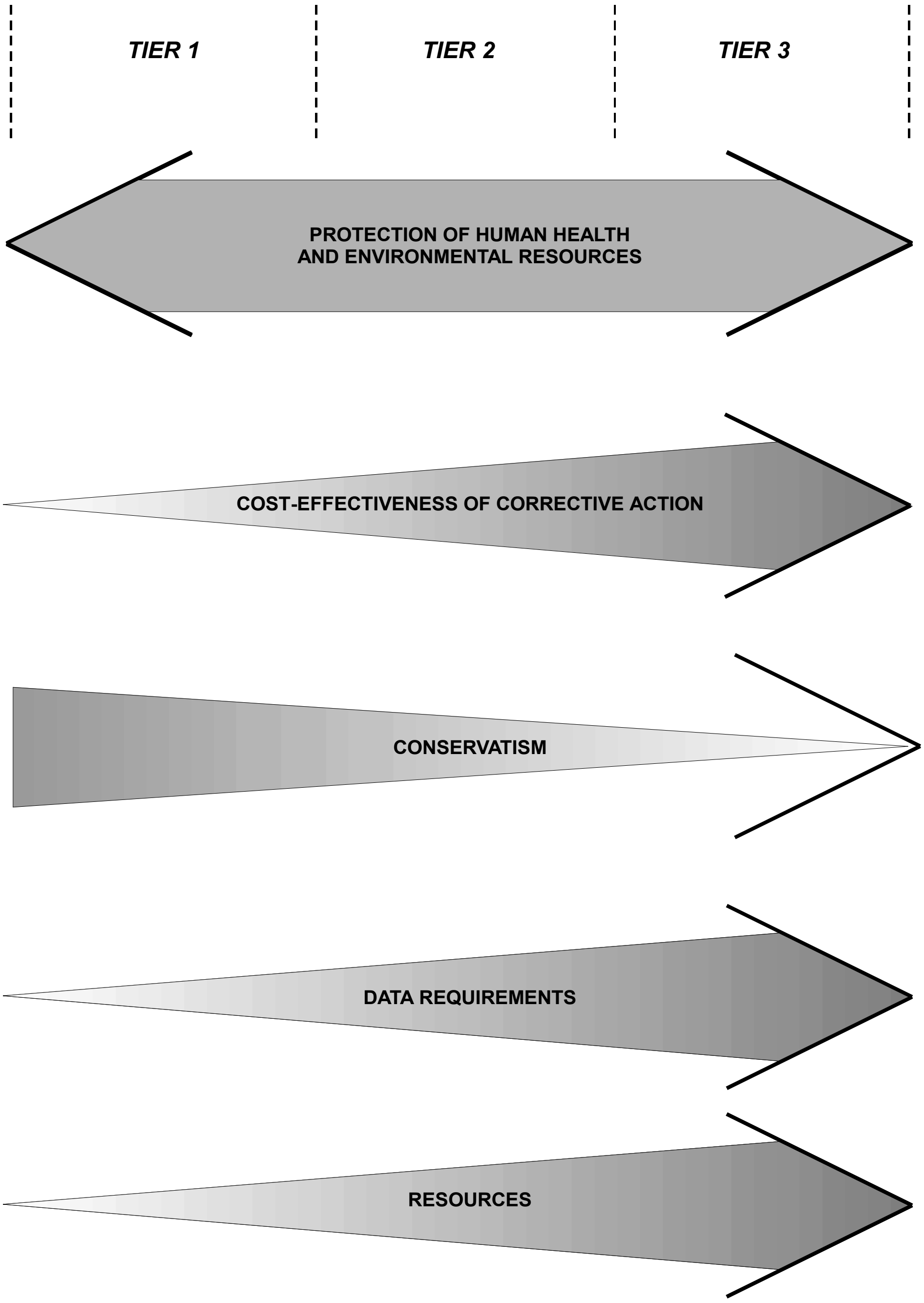
2.4. SUMMARY OF THE APPROACH

The approach developed for the European oil industry is of a tiered nature, based on ASTM Risk Based Corrective Action. It is summarised in **Figure 1** and a brief description of each of its elements is provided below, in advance of the remainder of this guideline, which describes it in detail.

The tiered approach to risk-based corrective action described in this guideline facilitates the best use of both private and public sector time and resources at oil industry sites in Europe. It is justified on the grounds that many sites do not need a detailed risk assessment to be performed in order that they can be declared safe, provided that conservative assumptions are made and any increase in the level of accuracy would not result in an increase in the estimated level of risk.

Figure 3 provides a visual representation of the key features of the tiered approach. As shown in the figure, progression through the tiers results in greater investments of resources (time and money) in order to attain the increasing data and analytical requirements. At the same time, conservative "generic" assumptions are replaced by site-specific values, producing less stringent targets for increasingly cost-effective corrective action. Throughout the process, the level of protection of human health and the environment remains constant.

Figure 3 Summary of Tiered Site Analysis



In broad terms the approach can progressively incorporate the following key steps, as required:

- Initial Assessment;
- Emergency Response Decision/Action;
- Tier 1 Assessment and Corrective Action Decision;
- Tier 2 Assessment and Corrective Action Decision;
- Tier 3 Assessment and Corrective Action Decision.

The outcome of each step can include tier upgrade, corrective action, compliance monitoring or a conclusion that no further action is required.

The first step, the "initial site assessment", involves the gathering of general data about the site. The assessor is required to identify the following:

- potential contaminant sources (e.g. equipment leaks);
- potential exposure pathways;
- obvious environmental impacts, if any;
- the presence of potentially impacted humans and environmental resources (e.g. workers, residents, surface water bodies, etc.);
- the current and proposed site land-use;
- the presence/absence of potable groundwater beneath the site; and
- conceptual site model(s).

This is followed by the collection of chemical data via intrusive investigations, and a comparison of the data with Risk-Based Screening Levels (RBSLs) and other relevant criteria (ORCs). It is also appropriate at this early stage to assess whether an emergency response action is required.

RBSLs represent chemical concentrations in soil and groundwater that, in the vast majority of cases, do not pose a significant risk to human health. ORCs relate to existing exposure media that have also been sampled (e.g. indoor air) and they are legal standards, guidelines or aesthetic criteria. RBSLs are typically derived using conservative assumptions and contaminant migration models. They are of an "evergreen nature" and subject to change as new modelling approaches and input parameters are developed. RBSLs are therefore conservative values against which measured contaminant concentrations can be compared. Where measured concentrations are below these screening criteria it may be assumed that the identified contamination does not pose a significant risk.

If the Tier 1 criteria (RBSLs and ORCs) are satisfied, then normally no further action is required. If the criteria are not satisfied, then the possibility of corrective action should be assessed for its cost-effectiveness. If it is clear that corrective action to achieve these levels would not be cost-effective, then the need for interim measures should be considered, before a Tier 2 assessment is carried out, involving the collection of additional data, if required. The decision to carry out a Tier 2 assessment should include a comparison of the cost of achieving Tier 1 corrective action goals with the cost associated with completing a Tier 2 assessment, bearing in mind that the achievement of the Tier 2 site-specific goals is likely to be significantly less costly to achieve than Tier 1 goals. It should also be considered whether the Tier 2 site-specific goals are likely to differ significantly from the generic Tier 1 goals, i.e. if the actual site conditions happen to be close to the generic assumptions made at Tier 1 then a Tier 2 analysis will not result in appreciably different remediation goals.

The Tier 2 assessment involves a refinement of the study to take into account more site-specific considerations with the collection of additional site investigation data if required. With regard to data interpretation, the replacement of "worst-case" assumptions with more site-specific information may be of particular importance. Different modelling techniques (which take into account chemical attenuation in the environment between source and receptor) may be employed or, alternatively, the models that were used to generate the RBSLs may be used, with appropriate refinement of the input values where site-specific data is available. It is recommended that the assessment takes place in a "forward manner" where quantitative risk estimates are generated for the site. The "forward calculation" of risk gives an overall perspective on the significance of potential risks to public health and the environment from measured chemical concentrations and is consistent with the "risk assessment" requirements of many European regulators[1].

Risk estimates are compared with appropriate acceptability criteria in order to determine the outcome of the Tier 2 assessment. This is in contrast to the Tier 1 analysis where measured contaminant concentrations were compared with RBSLs derived by taking an insignificant risk level and back-calculating a "safe" concentration. If corrective action target levels are needed, they may be developed using either the estimated risk levels or the same techniques as used in the original development of RBSLs, except that site-specific parameters are used in the equations. The new target levels, which incorporate site-specific assumptions and parameters, are termed Site Specific Target Levels (SSTLs).

If the acceptability criteria at Tier 2 are met, then no further action is required, except, perhaps, periodic monitoring for a finite period of time, if justified. If the criteria are exceeded by the site-specific risk estimates, the cost-effectiveness of achieving Tier 2 corrective action goals, which may include changes in land-use, exposure pathway control measures or Site Specific Target Levels (SSTLs), should be reviewed in relation to undertaking a Tier 3 assessment, bearing in mind that the achievement of Tier 3 site-specific goals will likely be less costly to achieve than Tier 2 goals. If corrective action is still not considered to be practical or cost-effective, a Tier 3 assessment should be carried out, although interim corrective action may still be needed. Such action could include obvious hot-spot remediation or temporary containment measures and focuses on reducing risks which, while as yet not quantified accurately, are judged by the assessor as likely to need addressing following Tier 3. By carrying out such interim measures, any potential risk posed by the site while the Tier 3 assessment takes place, is avoided, or at least reduced. Alternatively, interim measures may not be driven by real risk but by aesthetic considerations and the adverse publicity that could accrue if action is not taken where contamination has been identified.

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[1] Forward" means using the measured soil and groundwater contaminant concentrations to calculate actual risk levels to the identified receptors, at the points of exposure.
"Backward" means taking defined acceptable risk levels at points of exposure, and back-calculating soil contaminant levels which would achieve that level of risk.

The Tier 3 assessment evaluates further the risks posed by the site and provides the information required to more effectively focus any corrective action required. It will often require more site-specific data, more sophisticated modelling (such as numerical fate/transport models and pharmaco-kinetic modelling) or a combination of the two. The Tier 3 assessment provides forward calculations of risk which are then compared with acceptability criteria to assess the need for corrective action, as at Tier 2. If the risks are found to be unacceptable, the options for corrective action should be reviewed and appropriate control measures put in place and/or a remedial scheme designed and implemented. If the risks are not significant, then the situation may need to be monitored for a finite period of time, to make sure that it does not deteriorate.

It should be noted that throughout the assessment approach, a number of options are available under the heading of "corrective action" and can be summarised as follows:

- institutional controls (procedures or facilities that eliminate the possibility of exposure e.g. protective work practices or a restriction on use of the land – **see Appendix 10** for detailed discussion);
- natural attenuation **(see Appendix 1);**
- bioremediation; and
- technology-based remedial methods (e.g. pump and treat, air sparging).

Overall, this guideline represents a framework in which reasoned, risk-based decision-making can take place, rather than a prescriptive "how to" guide. As a result, it is hoped that it will provoke a search for yet more innovative and cost-effective approaches and techniques, all focused on achieving risk reduction.

2.5. COMPARISON WITH ASTM RBCA STANDARD

The approach outlined in this document is very similar to ASTM's RBCA framework[2]. Key similarities are as follows:

- Each provides a consistent and rational approach to corrective action;
- Both incorporate risk assessment into all aspects of investigation and corrective action;
- Both use a tiered approach which balances conservatism with site specificity;
- Both focus corrective action decisions on the reduction of risk on a site specific basis;
- Initial screening against Risk Based Screening Levels (RBSLs);
- Calculation of Site Specific Target Levels (SSTLs) based on site specific compliance points;
- Share many common pathways and algorithms for estimating exposures;
- In many cases use common data sets for physical/chemical, toxicological characteristics.

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[2] ASTM (1995) Standard guide for risk-based corrective action applied at petroleum release sites. ASTM E-1739. Philadelphia PA: American Society for Testing and Materials

There are certain differences between the two approaches, which reflect the regulatory situation, history and present understanding of contaminated land issues in Europe, versus that in the USA. However, these differences should not result in significantly different outcomes between the two approaches if they were applied to the same site.

One such difference between the current approach and ASTM's RBCA is that CONCAWE Tier 1 RBSLs can be derived using Monte Carlo simulation techniques. This reflects the increasing use of such techniques worldwide and it allows for the explicit consideration of uncertainty. The alternative to Monte Carlo based RBSLs is values based on point estimate assumptions, ostensibly made on a "reasonable worst case" basis but providing unknown levels of conservatism. Such conservatism may be extremely high, due to compounding effects, or low, depending on the scenarios considered in the risk model.

A further difference between the two approaches is the opportunity to carry out "forward" calculations of risk[3] at Tiers 2 and 3. (Under the ASTM approach, these tiers involve changes to clean-up target levels). A "forward" risk is consistent with European regulators' requirements for performing a risk calculation in support of contaminated land decision-making.

Minor differences between the two approaches include the use of European exposure/toxicity assumptions and the inclusion of a child receptor.

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[3] "Forward" means using the measured soil and groundwater contaminant concentrations to calculate actual risk levels to the identified receptors, at the points of exposure.
"Backward" means taking defined acceptable risk levels at points of exposure, and back-calculating soil contaminant levels which would achieve that level of risk.

3. INITIAL SITE ASSESSMENT

The initial assessment of a contaminated oil industry site involves the collection of data concerning site conditions. It is also an early opportunity to assess the need for carrying out any emergency measures. The individual components are described below.

3.1. DATA COLLECTION

The initial site assessment provides the building blocks upon which all other works at the site are based. A robust desk study, incorporating a good understanding of the site's history/operations and its environmental setting, will allow a focused data collection exercise to be planned and implemented. The desk study (which can include a questionnaire sent to site personnel) should be combined with a site reconnaissance visit to confirm or support its findings.

Key operational history information to collate and assess includes the following:

- site size and age;
- products stored;
- tank numbers, volumes, age, throughput and testing records;
- secondary containment detail;
- modes of product transfer (pipelines, loading gantries);
- drainage system information;
- interceptor configuration and maintenance history;
- wastewater treatment plant details;
- hardstanding distribution and condition;
- location of below-ground utility service lines and other preferential contaminant migration pathways (e.g. culverts);
- product spillage and leakage history;
- chemical storage / additive facilities;
- production area detail; and
- solid/hazardous waste management practices.

For larger/older sites in particular it will be appropriate to collect local historic topographic maps and aerial photographs of the facility to cross-check historical detail provided by site records.

An environmental setting assessment places the site within its local context. Key information to obtain here includes:

- land-use (on-site and adjacent areas, past, present and proposed future);
- regional and, if available, local geology and hydrogeology;
- proximity to and use of surface water bodies which may receive site-derived contamination and their use;
- local resource potential of groundwater and surface water bodies (e.g. potable supply, other supply purposes) including location of down-gradient wells;

- the location of sensitive ecological habitats (defined according to EC Directive 79/409/EEC or EC Directive 92/43); and
- data on local foundations and cellars.

Sources of information include local and regional geological, hydrogeological, aquifer vulnerability and topographic maps of an appropriate scale, along with site records (e.g. geotechnical and general site investigation). These can be supplemented by site-specific information prompted by a questionnaire and detailed inspection during the site reconnaissance visit.

The purpose of the environmental setting assessment is to identify: 1) the location of humans and environmental resources ("receptors") that could be impacted by the site; and 2) potentially significant exposure pathways. The latter should include a consideration of the possibility of preferential contaminant migration pathways, such as utility conduits.

3.2. ASSESSMENT OF NEED FOR IMMEDIATE ACTION

At a very small proportion of sites, it may become obvious during initial site reconnaissance and/or Tier 1 intrusive investigations, that there is an immediate potential threat of harm to human health or the environment. Examples include issues such as the ingress of large quantities of free product in adjacent waterways or off-site drainage systems, or significant vapour concentrations within buildings. If such threats exist, an action plan will need to be developed immediately to address such issues without waiting for the completion of the tiered sequence of tasks. Professional judgement will be needed on the urgency of response. **Table 1** shows examples of issues requiring emergency action and possible responses, although it should be noted that the table is for illustrative purposes only.

Table 1 Examples of Issues Requiring Emergency Response Actions

Criterion / scenario	Possible Emergency Response Action
Overpowering odour indicating the possible presence of explosive levels or concentrations of vapours that could cause acute health effects.	Evacuate occupants and immediate vicinity of site. Check vapour concentrations using a PID and/or LEL detector. If suspicions are confirmed, then begin abatement measures such as subsurface ventilation, or building pressurisation.
Visual signs of off-site contaminant migration (e.g. oil seepage, surface water plumes)	Minimise further impact using containment measures. Recover free product. Assess the need to restrict area access.
Substantial product loss (e.g. fractured pipe, substantial dip losses in storage tanks)	Minimise further impact using containment measures. Recover free product. Assess the need to restrict area access.
Visual signs of ecological harm (e.g. damaged vegetation, dead fish)	Minimise further impact using containment measures.
Third parties affected (e.g. nearby wells impacted, preferential contaminant migration along electrical conduits, through sewers)	Assess impacts using drinking water criteria. Minimise further impact using containment measures. Notify affected third parties. Assess the need to restrict area access.

3.3. DEVELOPMENT OF CONCEPTUAL SITE MODEL

The data collected during the initial site assessment should be used to develop a "conceptual site model" (CSM) that will be refined as the analysis proceeds. The CSM is a description of how potential chemical sources at the site could contribute to increased levels of risk in potentially exposed receptors. It is a qualitative evaluation of the sources, exposure pathways and receptors identified during the desk study and site reconnaissance visit and can be used to test assumptions and field data to produce a complete view of the site-specific situation. The most important potential human exposure pathways that can exist at contaminated sites are as follows (depending on land-use):

- accidental soil/dust ingestion (indoors and outdoors);
- skin contact with soil/dust (indoors and outdoors);
- inhalation of vapours from soil sources (indoors and outdoors);
- inhalation of vapours from groundwater sources (indoors and outdoors);
- inhalation of vapours from free product;
- leaching of chemicals from soil or free product to groundwater or surface waters;
- domestic or recreational use of groundwater or surface waters (potentially leading to ingestion and inhalation of contaminants);
- consumption of home-grown fruits and vegetables.

This list of potential pathways is not exhaustive and should be reviewed for appropriateness and possible omissions based on the conceptual site model.

Where appropriate, the site should be divided into discrete areas, each with its own CSM, in addition to an overall CSM for the site as a whole. Flow charts and schematics can be used to illustrate the processes considered in the CSM.

Early development of the CSM and constant reassessment in the light of investigative results can have a profound influence on the investigation and sampling activities. This can enhance the latter's cost-effectiveness by making sure that samples are taken from the areas that are most likely to be contaminated and from the media that are most relevant to those contaminant migration/exposure pathways likely to pose a significant risk (this is especially important for Tiers 2 and 3). It can also guide the sampling of off-site receptor locations that may have already been impacted by the migration of contaminants.

The CSM's focus is on which pathways for a given site are complete. A complete pathway exists only if there is a source of sufficient strength, a pathway for migration of Contaminants of Concern (COC) from source to receptor, **and** an exposure point for the receptor. The process of progressing from Tier 1 to Tier 2 or Tier 2 to Tier 3 involves a more complete analysis of whether these pathways are complete and should be retained in the CSM.

The appendices to this report discuss this issue in more detail.

4. TIER ONE ASSESSMENT

4.1. INTRODUCTION

The Tier 1 assessment involves the collection of data concerning site conditions, the interpretation of chemical data by reference to suitable Risk Based Screening Levels (RBSLs) and other relevant criteria (ORCs) and an evaluation of the overall results. The individual components of the assessment are described below.

The Tier 1 data collection exercise relies on the conceptual site model to ascertain the distribution and character of existing chemical contamination. A balance must be struck between the provision of sufficient information to allow an appropriate Tier 1 evaluation and the minimising of detail which can, if required, be collected during subsequent tiers. In general, the amount of information necessary for the Tier 1 assessment is less than that collected for Tier 2 and certainly Tier 3 assessments. At some sites, however, the benefits of collecting sufficient information during the initial site assessment to allow subsequent Tier 2 assessment without a need for further site works may be considerable (e.g. due to site access issues).

4.2. SAMPLING AND ANALYSIS

Most Tier 1 assessments should include the sampling of on-site soils and shallow groundwater, if present. Soil vapour surveying may be used to screen a site to help pinpoint potential "hot-spot" areas which hopefully will have already been highlighted by the desk study and site reconnaissance. The preferred option at most sites is to bias the sampling programme towards identifying the maximum levels of on-site contamination by focusing on most likely source areas (e.g. locations of old spills). In rare cases where site information is absent (e.g. an old derelict site or site area long since demolished) systematic sampling may have to be applied. In such cases a statistically appropriate number of samples must be collected.

In many cases the Tier 1 intrusive site investigation will be limited to within the site boundary. However, it may be necessary to sample nearby off-site wells/water courses and local buildings/basements. This is especially important with regard to the identification of immediate hazards requiring an emergency response (see below) and it should be guided by the initial site reconnaissance. To some degree the extent of migration can also be assessed by including down hydraulic gradient boundary locations in the sampling plan.

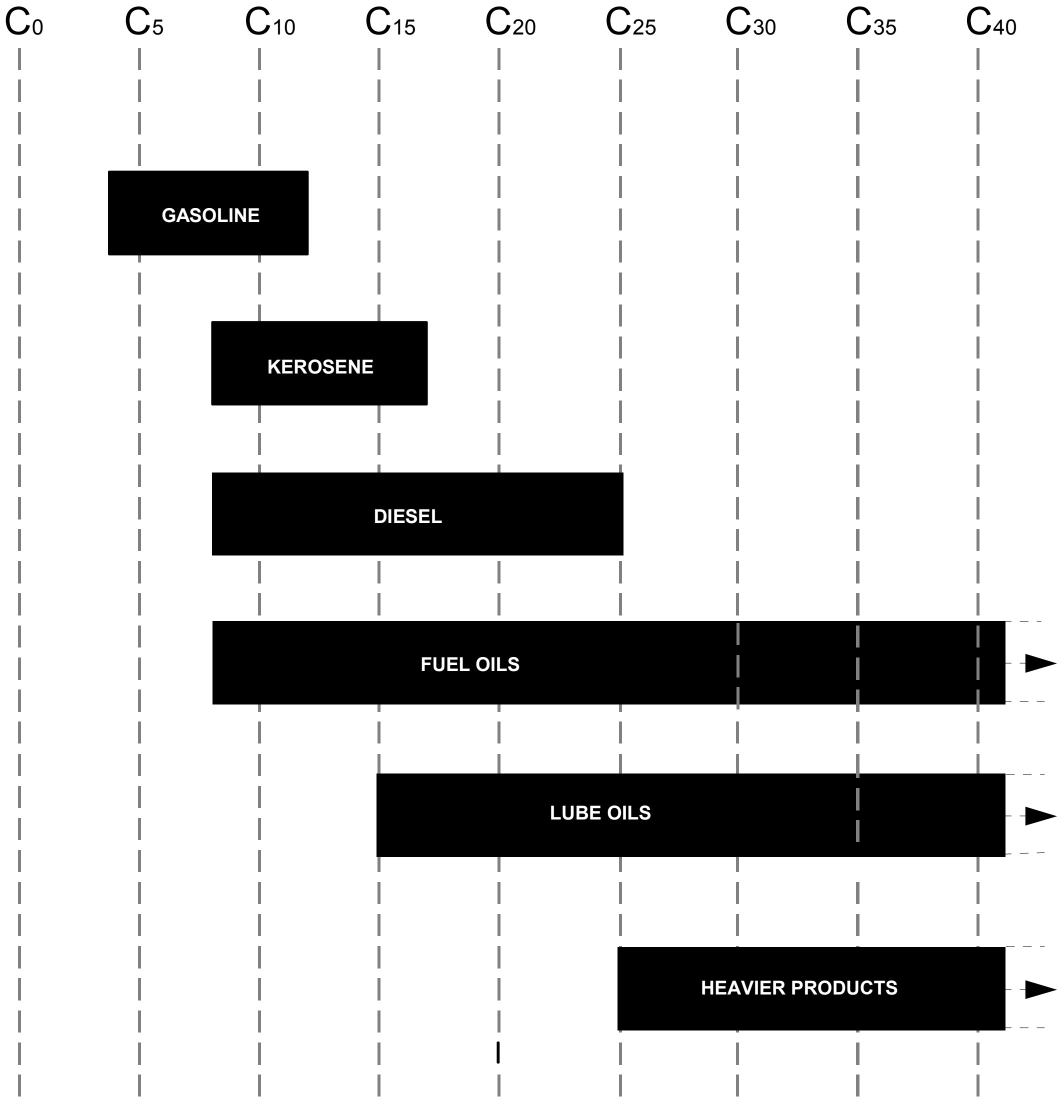
The laboratory analysis of samples should initially focus on chemicals known to have been used or stored on-site which are relevant to the particular medium being evaluated. Soil samples may be sent to a laboratory for detailed gas chromatography (GC) analysis, while vapour samples from a utility conduit may be analysed by a portable explosimeter, where the objective is to evaluate the potential for immediate hazard (it should be noted that this can take place before the collection of Tier 1 samples). An example list of chemicals is provided in **Table 2**, along with the reasons for their likely evaluation at petroleum industry sites. It is good practice to include a wide range of suspected contaminants at the Tier 1 stage, with progressively fewer being needed at subsequent levels of analysis. To this end, data pertaining to site history, especially any information regarding product usage, leaks and completed or ongoing corrective action, should be used. It is important that all key hazardous chemicals which have been stored or used on-site are included for analysis at this stage because a site which passes the Tier 1 assessment should not require any additional evaluation.

Table 2 Example list of compounds that are likely to be encountered at petroleum industry sites

Compound	Reason for inclusion
Benzene	Carcinogenic constituent of light-end fuels (e.g. gasoline)
Benzo(a)anthracene	Carcinogenic constituent of mid-range fuels (e.g. diesel)
Benzo(a)pyrene	Carcinogenic constituent of mid-range fuels (e.g. diesel)
Benzo(b)fluoranthene	Carcinogenic constituent of mid-range fuels (e.g. diesel)
Benzo(k)fluoranthene	Carcinogenic constituent of mid-range fuels (e.g. diesel)
Total petroleum hydrocarbons	Measure of total oil content of soils
Chrysene	Carcinogenic constituent of mid-range fuels (e.g. diesel)
Dibenzo(a,h)anthracene	Carcinogenic constituent of mid-range fuels (e.g. diesel)
Ethylbenzene	Non-carcinogenic constituent of light-end fuels (e.g. gasoline)
Indeno(1,2,3-cd)pyrene	Carcinogenic constituent of mid-range fuels (e.g. diesel)
Methyl-tertiary-butyl-ether	Non-carcinogenic gasoline additive
Tetraethyl lead	Non-carcinogenic gasoline additive
Toluene	Non-carcinogenic constituent of light-end fuels (e.g. gasoline)
Xylene	Non-carcinogenic constituent of light-end fuels (e.g. gasoline)

It should be noted that any analysis of Total Petroleum Hydrocarbons (TPH) should focus on either: 1) establishing concentrations of specific groupings of compounds, or 2) the identity of the TPH mixture (e.g. weathered diesel – **see Appendix 3**). This is because petroleum products are composed of a multitude of chemicals, which vary depending on factors such as product type and age. **Figure 4** illustrates the diversity of chemicals found in petroleum products, in terms of the carbon numbers of specific products. TPH measurements which meet neither of the above objectives are less useful for risk assessment purposes but can still be utilised in a qualitative manner to assist in the identification of the boundaries of contamination and the location of hot-spots. Samples from such areas could subsequently be taken and subjected to more complex analysis.

Figure 4 Carbon Number Ranges of Petroleum Products



4.3. INTERPRETATION OF DATA

4.3.1. Introduction

The data collected during Tier 1 are interpreted by reference to Risk-Based Screening Levels (RBSLs) and other relevant criteria (ORCs). RBSLs are used to screen chemical concentrations in on-site environmental media (soil, air, surface water and groundwater) while ORCs are used to interpret data for additional media that have been sampled, for example, off-site well water. RBSLs are most commonly developed based on human health considerations but they can also be based on other environmental considerations.

4.3.2. Comparison of Data with Health-Based RBSLs

The comparison of data with RBSLs is a relatively straightforward exercise in which measured on-site soil and groundwater concentrations are assessed against RBSLs taking into consideration the potential human exposure pathways identified. RBSLs are typically calculated using conservative assumptions applicable to the country in which the site is situated. They can either be based on conservative exposure assumptions for individual pathways or on the sum of the exposure pathways that could co-occur under a specific land-use scenario. A discussion of the relative merits of the two approaches is given in the appendices to this report.

For simplicity, soil RBSLs are land-use specific (i.e. different RBSLs are set for different land-uses) and can be applied with a minimum of background knowledge on the risk assessment of contaminated sites. Most commonly RBSLs only take into account human health risk and do not address aesthetic, ecological and other criteria. Thus these factors need to be considered separately **(see Appendix 1).**

The main focus of RBSLs is the prevention of long-term (chronic) dose levels from repeated exposure to chemicals in environmental media (air, soil, surface water and groundwater). As acute toxicological effects occur at higher concentrations than chronic effects, RBSLs based on chronic exposure are necessarily protective against acute effects. Thus any site at which chemical concentrations are less than the appropriate RBSLs can be assumed to pose no significant risk of either acute or chronic effects.

Tier 1 RBSLs will be highly conservative and err considerably on the side of caution. This is a result of the methodology and assumptions used in their derivation. They need to be developed using simple, effective and clearly understood procedures in order to demonstrate that they are protective of both human health and the environment.

In order to use the RBSLs the assessor must establish:

1. the current and proposed site land-use;
2. inventory of complete pathways for the site;
3. whether the assumptions made in deriving the RBSLs are potentially under-conservative in relation to site-specific conditions (this is most unlikely, but not impossible).

The RBSLs normally relate to various land-uses and incorporate exposure assumptions specific to these land-uses. As a result, it is essential that the correct values are used in the comparison exercise. Assertions regarding future land-use must be supported by legally binding instruments such as deed restrictions, which prevent or manage certain types of development.

If a targeted intrusive investigation has been carried out (as would normally be the case), the maximum detected chemical concentrations should be compared with the RBSLs, on the grounds that if there is an insignificant risk from these, then there is an insignificant risk from the entire site. If random data have been collected, statistical techniques can be used. It should be noted that the use of maximum values from targeted investigations places considerable importance on the quality of the data collection activities. At sites where there is more than one chemical present, the possibility of additive toxic effects can be considered, although this is generally part of a more refined Tier 2 or 3 analysis. It may also be important to consider background concentrations of chemicals in soil and air, along with potential up-gradient sources for groundwater, to enable the assessment to focus on site-related contamination only.

4.4. LIMITATIONS

Although the comparison of measured concentrations with human health based RBSLs represents a suitable Tier 1 screening tool, there are several limitations which must be considered in order to decide whether they are to be relied on to decide on risk-based corrective action specific to the particular site. These are as follows:

- Risks to ecological receptors. Sensitive ecological habitats must be confirmed as being absent or an ecological risk assessment developed as part of the assessment (**see Appendix 7**).
- The assumptions used in generating RBSLs are conservative in almost all cases. However, as mentioned above, there may be rare occasions where this is not the case and a check is therefore necessary as to their applicability to the site in question.
- Risk of damage to materials through corrosion, geotechnical issues such as ground stability, environmental impacts from ongoing industrial processes, flooding risk, construction worker safety, aesthetic issues (e.g. soil staining), business risk, liability or reputation. These must be dealt with separately, where appropriate.

RBSLs should not be viewed as a definitive list of standards. They are based on current knowledge and assumptions concerning exposure parameters and toxicology and, consequently, should be viewed as "evergreen" sets of values that can be continually updated whenever new methodologies and parameters are developed. Where required, fate and transport estimations are based on conservative models.

It should be noted that certain regulators have their own standards that may need to be used in place of RBSLs as part of a Tier 1 assessment. For example, the Netherlands has published "Intervention Values", which, if exceeded, trigger further risk assessment to determine the urgency of response at contaminated sites. In the UK, Guideline Values are being developed which will fulfil roughly the same role as the RBSLs described above. Such values are derived using certain assumptions and models which may not be appropriate at all sites - this is an important aspect that must be considered in trying to reconcile two apparently conflicting values for the same compound.

4.4.1. Comparison of Data with Other Relevant Criteria (ORCs)

At certain sites, data may have been collected from off-site wells, local basements/buildings and local water courses. These data can be compared with suitable criteria for the particular contaminant of concern. For example, the comparison of off-site well concentrations with legal standards or drinking water guidelines may indicate whether a potential risk already exists via the off-site groundwater migration pathway, while the use of odour thresholds can enable the existence of a potential nuisance to be assessed. Examples of ORCs are provided in **Table 3**.

Table 3 Other Relevant Criteria (ORCs) – Examples

Compound	WHO Drinking water standard	Occupational Exposure Limit - Air (ACGIH) [b]		WHO Air Quality Guideline	Odour Threshold [c]		Lower Explosion
	(µg/l)	ppm v/v	mg/m^3	(mg/m^3)	ppm v/v	mg/m^3	Limit (%)
Benzene	10	10 [d]	32 [d]		1	3.26	1.4
Ethylbenzene	300	100	434		0.092	0.4	1.2
Toluene	700	50	188	8 [a]	0.156	0.6	1.27
Xylene	500	100	434		0.069	0.3	1.0
Benzo(a)pyrene	0.7						

a Time-weighted average (averaging time = 24 hours)

b ACGIH - American Conference of Governmental and Industrial Hygienists

c 50% detection threshold (lowest value taken from Verschueren, 1983)

d EU OEL currently 3 ppm v/v to become 1 ppm v/v (3.2 mg/m^3) in 2003

4.5. EVALUATION OF TIER 1 RESULTS

If the measured on-site chemical concentrations exceed the RBSLs the possibility of corrective action should be reviewed in relation to its cost-effectiveness. The review should focus on the following alternatives:

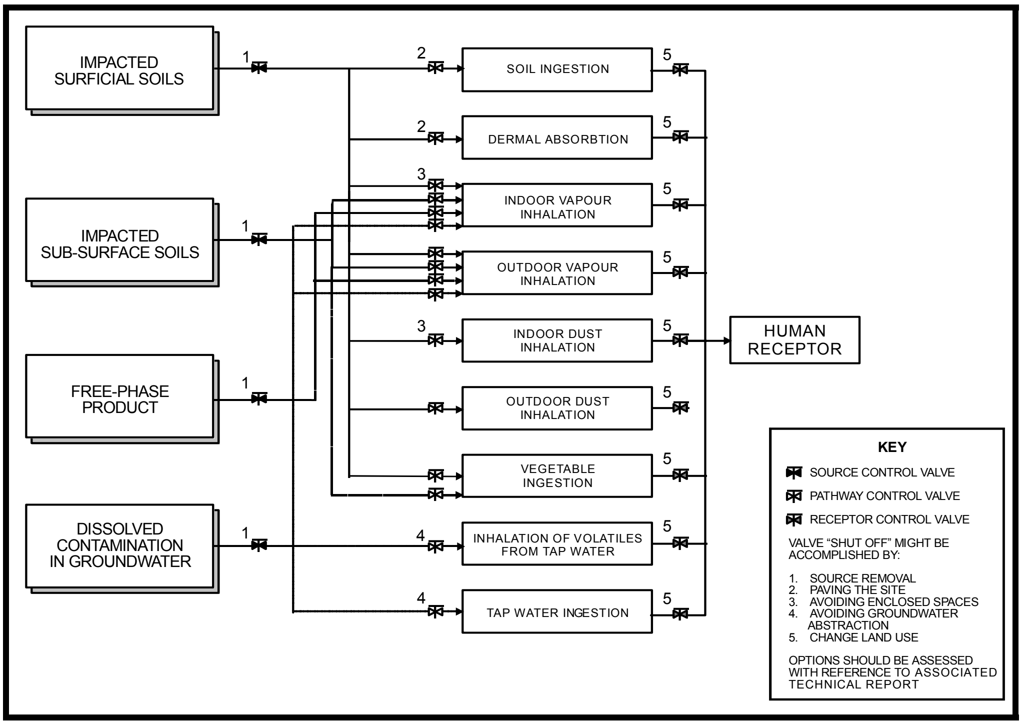
1. reducing the concentrations to below RBSLs;
2. controlling certain exposure pathways; or
3. changes in land-use, backed up by deed restrictions or other institutional controls (a more detailed review of the options available for corrective action is provided in **Section 7**).

If any of these measures would be more cost-effective than a Tier 2 assessment, bearing in mind that the latter may point to substantially less costly corrective action, then they may be carried out. If, however, they are judged to be inappropriate and subsequent corrective action goals are likely to be significantly different to those of Tier 1, then the process should proceed to Tier 2. If any measured receptor point concentrations exceed ORCs, it is possible that this would trigger corrective action.

A useful tool in the development of corrective action goals is a diagram such as that in **Figure 5**. This illustrates the relationship between contaminant sources, exposure pathways and receptors and how, by applying corrective action measures to the source, pathway or receptor, risks can be reduced to acceptable levels. In terms of controlling pathways, a valve symbol denotes where such action can take place - all the assessor needs to do is establish the best way of shutting off the valve, which will break the source-pathway-target link.

If the on-site chemical concentrations do not exceed the RBSLs, the assessment finishes, and the site can be considered to represent no significant risk and normally no further action is required. Compliance monitoring may be implemented, subject to the views of the regulatory authority, to confirm that current conditions persist or improve with time.

Figure 5 Example Pathway Control Measures



5. TIER TWO ASSESSMENT

5.1. INTRODUCTION

The Tier 2 assessment involves a more detailed evaluation of the site focusing on exposure pathways that have caused exceedence of RBSLs and addressing other issues identified at Tier 1, such as land use. It also offers the opportunity to evaluate the risk at more remote locations from the site, the so called points of compliance (or points of determination) or at potential receptor locations. This may require the collection of more data and/or the completion of a more sophisticated risk assessment.

Tier 2 provides the opportunity for the assessor to consider contaminant fate and transport in more detail than is the case at Tier 1. This is achieved by the replacement of the generic site data used in Tier 1 with site-specific information and the use of more sophisticated chemical fate and transport models. In this way, the Tier 2 assessment provides a more realistic examination of the specific issues surrounding a site.

It is important to note that both Tier 1 and Tier 2 corrective action goals are based on achieving similar levels of human health and environmental resource protection. The development of Tier 2 goals should lead to more cost-effective corrective actions.

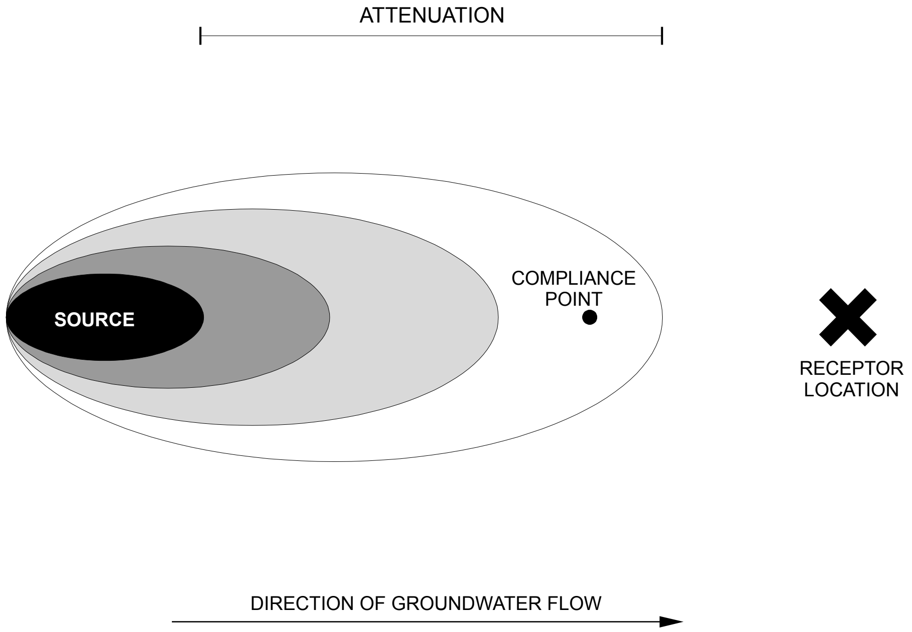
5.2. ISSUES OF CONCERN

The first step in a Tier 2 assessment is to identify the issues of concern requiring further analysis. This is accomplished by revisiting the CSM and reviewing which pathways are complete and contribute to receptor exposure. Incomplete pathways or Contaminants of Concern which do not contribute to risk can be eliminated from further analysis. Tier 2 assessment will include the sources, chemicals and exposure pathways which caused the exceedence of the RBSLs in Tier 1.

The chemical sources could include known or assumed areas of high concentration (hot-spots) or contaminated groundwater which contains the chemicals that exceeded the RBSLs. The human exposure pathways include all those which made a significant contribution to the RBSLs that were exceeded in Tier 1. They are identified by means of pathway contribution tables.

An important aspect of Tier 2 is the consideration of potential exposure at "compliance points", as opposed to anywhere in an environmental medium. Such points include property boundaries or locations between source areas and reasonable potential receptors, or they could be receptor locations themselves. Corrective action goals for source areas are then based on the demonstrated and predicted attenuation (reduction in concentration with distance) of compounds that migrate away from the source area. **Figure 6** illustrates this concept.

Figure 6 Natural Attenuation of Contaminants Dissolved in Groundwater



5.3. DATA COLLECTION

Tier 2 data collection activities are designed to build upon the information collected as part of Tier 1 in order that the site assessment can focus on the most important issues. The Tier 1 data set should be re-appraised and summary tables produced which highlight the chemical and physical characteristics of the various environmental media, within all relevant site areas and depth zones. In cases where it is believed the data set is suitably robust to facilitate an adequate Tier 2 assessment then this should proceed. If this is not the case then an appropriate Tier 2 site investigation programme should be planned to fulfil the additional data needs.

Tier 2 investigations could be directed towards better characterising the magnitude and distribution of contamination along the migration pathway(s) identified to be of concern. This may involve the collection of geological, hydrogeological and chemical data to replace conservative assumptions made in the previous tier. The amount of Tier 2 data required could also depend on factors such as the degree of site contamination (the extent to which Tier 1 investigation data failed the RBSLs), the suitability of the generic assumptions used at Tier 1, site environmental sensitivity, and the proposed land-use.

During the Tier 2 data collection activities, every effort should be made to collect samples from exposure or compliance points as such locations represent points at which potential receptors could actually become exposed. Amongst other things, such data may assist in the calibration of chemical fate and transport models, if required. In many cases it can be used to eliminate the need for, or to check the validity of, sophisticated pathway-specific modelling by providing actual exposure data. However, it must be remembered that such measurements are only "snapshots" in time and that, although the detection of high concentrations may indicate a potential problem, the interpretation of low contaminant concentrations is much more difficult. An assessment needs to take into account at least the physical-chemical properties of the particular contaminants and appropriate toxicity data so that the significance of such low concentrations can be determined.

5.4. INTERPRETATION OF DATA

5.4.1. Introduction

The interpretation of data at Tier 2 takes the form of

1. site-specific risk assessment;
2. the development of Site-Specific Target Levels (SSTLs); and/or
3. comparison of measured or predicted concentrations with ORCs or RBSLs;
4. comparison of measured or predicted compliance point concentrations with ORCs or RBSLs.

Where estimated risks exceed acceptable levels, or where the measured concentrations exceed ORCs or RBSLs, Site-Specific Target Levels can be developed to aid in the setting of Tier 2 corrective action goals. Tier 2 focuses on all chemicals detected at the site at concentrations which exceed the Tier 1 RBSLs, as discussed above.

5.4.2. Site-Specific Risk Assessment

The Tier 2 site-specific risk assessment should take place in a "forward manner", in which quantitative risk estimates are generated for the site and compared with appropriate acceptability criteria. This allows the statistical treatment of data, if required, and it should enable a clear view of the presence or absence of a significant risk at the site (often required by regulators). Examples of acceptability criteria for a Tier 2 risk assessment are currently under development - these should normally be the same as those used in the derivation of RBSLs.

The Tier 2 risk assessment techniques involve the use of either:

1. the algorithms used to generate RBSLs; or
2. other models and approaches.

In either case, site-specific data should be used in the place of conservative assumptions, wherever possible. Within the Tier 2 assessment it is also possible to evaluate whether a potential risk exists by predicting contaminant concentrations at the off-site receptor or compliance point, and comparing these to the RBSLs.

The models are used to predict attenuation of contaminants away from the source area. They are based on interpolating and extrapolating site-specific data through the use of conservative "screening" mathematical models. In general the better the site investigation data the more accurate the modelling results. These models are characterised by the following:

- the models are relatively simplistic, and are often algebraic or semi-analytical expressions;
- model input is limited to practically attainable site-specific data, or easily estimated quantities (e.g. soil porosity, soil bulk density);
- site-specific validation/calibration studies are not necessary provided worst-case assumptions are used in setting the input parameters;
- source depletion due to physical removal mechanisms (e.g. leaching) can be considered;
- biodegradation can be considered provided either: 1) site-specific data is available to demonstrate its occurrence; or 2) documented evidence is available from other, similar sites;
- the models are based on descriptions of relevant physical/chemical phenomena. Any mechanisms that are neglected result in predictions that are conservative relative to those likely to occur.

For above-ground exposure pathways, the chemical data which form the input to a Tier 2 risk assessment should be health-conservative estimates of the concentrations present across the relevant exposure area (e.g. garden). These are typically either maximum detected values or 95% upper confidence limits of arithmetic mean values, calculated using algebraic or geostatistical techniques. Alternatively, certain risk assessment software can accept whole data sets or probability distributions of contaminant concentrations. For groundwater modelling, the maximum detected on-site concentration (soil or groundwater) should normally be used as the source concentration in the model, in order to be conservative.

5.4.3. Comparison of Data with Other Relevant Criteria (ORCs)

If additional data have been collected from off-site wells, local basements/buildings and local water courses as part of a Tier 2 assessment, they can be compared with ORCs, as at Tier 1. For example, the comparison of off-site measured groundwater concentrations with RBSLs will indicate whether a potential health hazard exists via this migration pathway at the time of measurement.

5.4.4. Assessing the Risk from Free Product (See Appendix 4)

The risk from free product should be addressed. These allow the modelling of indoor air and groundwater impacts (if present), based on known product characteristics. Groundwater quality data obtained from the site could also be used to assess the effects, if any, on groundwater. Again, "real" data are preferred over modelled contaminant concentrations, where they are available.

5.4.5. Assessing the Risk to Surface Water

The risk to surface water can be assessed by measuring contaminant concentrations in lakes, rivers, etc. or modelling them using computer software available for this purpose.

5.4.6. Ecological Risk Assessment

An ecological risk assessment is the process of evaluating the likelihood that adverse ecological effects will occur. If an ecological risk assessment is deemed necessary, a tiered approach is recommended to ensure the cost-effective protection of ecological resources, mirroring the approach taken to protecting human health **(see Appendix 7)**.

5.5. EVALUATION OF TIER 2 RESULTS

If the site-specific risk assessment acceptability criteria are met and there are no exceedences of ORCs then no further action is required, except, perhaps, periodic monitoring for a finite period of time. If the criteria are exceeded, SSTLs can be derived from the results of the risk assessment. Following this, the cost-effectiveness of achieving Tier 2 corrective action goals, which may include SSTLs, should be reviewed, bearing in mind that Tier 3 site-specific goals will likely be less costly to achieve than Tier 2 goals. If corrective action is still not considered to be cost-effective and Tier 3 corrective action goals likely to be significantly different to Tier 2 goals, a Tier 3 assessment should be carried out, although interim corrective action may be needed (this could include hot-spot removal, localised containment or institutional controls). A review of the options available for corrective action is provided in **Section 7**.

Corrective action goals could include source removal or the blocking of individual exposure pathways based on the results of the risk assessment. In the case of the former, SSTLs should be developed from the predicted attenuation of contaminants away from the source area. For example, if the risk assessment model predicts exposure/compliance point groundwater concentrations which are 100 times lower than the measured on-site concentrations (and the relationship between on-site and off-site concentrations is linear), then the SSTL for on-site groundwater should be 100 times greater than the relevant RBSL or ORC (e.g. drinking water standard). Measured exposure/compliance point concentrations can be used to corroborate the model's predictions.

It should be noted that, while a Tier 3 assessment may represent the best way forward at a site, there may be interim corrective measures that could be carried out while this is going on. Such action could include obvious hot-spot removal or temporary containment measures that focus on reducing risks which, while as yet not quantified accurately, are judged by the assessor to be likely to need addressing following Tier 3. By carrying out such interim measures, the potential level of risk posed by the site is reduced while the Tier 3 assessment takes place. Alternatively, interim measures may not be driven by real risk but by aesthetic considerations or the adverse publicity that may accrue if action is not taken. In some cases, the implementation of corrective action can exacerbate the risks associated with the contaminants identified. Therefore, the potential benefits of carrying out interim corrective action should be considered in the light of the potential risks (and associated costs) before deciding to proceed.

6. TIER THREE ASSESSMENT

6.1. INTRODUCTION

The Tier 3 assessment involves the collection of more site-specific data, if necessary, and a further evaluation of the potential risks from site-related contamination using advanced techniques including, for example, numerical fate/transport models and pharmaco-kinetic considerations. In some cases this can result in a conclusion being reached that no corrective action is required with the likely exception of a finite period of monitoring. In others, the on-site concentrations may still be found to pose a significant risk and corrective action goals need to be developed. These could include the calculation of, and remediation to, Tier 3 SSTLs, which are normally higher (less conservative) than their Tier 2 counterparts.

It is important to note that both Tier 2 and Tier 3 corrective action goals are based on achieving similar levels of human health and environmental resource protection. However, in moving to Tier 3 the assessor is able to develop more cost-effective action plans because certain conservative assumptions and modelling techniques used in Tier 2 are replaced with site specific data and more realistic approaches.

6.2. ISSUES OF CONCERN

The first step in a Tier 3 assessment is to identify the issues of concern requiring further analysis. These could include sources, chemicals, exposure pathways and receptors, as indicated by the results of the Tier 2 assessment.

In most cases it would be expected that source area hot-spots including soil, groundwater and free phase contamination will have been adequately characterised during Tier 2. However for the principal contaminant migration pathways additional media specific chemical and physical property data may need to be collected. The exposure pathways assessed should include all those which make a significant contribution to the Tier 2 estimated risk levels - pathway contribution tables can be used for this purpose.

6.3. DATA COLLECTION

Field investigation data requirements for Tier 3 assessment should be defined on a site-specific basis. It is not appropriate to give even indicative requirements since this tier of assessment will be very focused on one or more key aspects.

In advance of any Tier 3 site investigation which involves the collection of additional media samples for chemical analysis and/or physical property testing, geostatistical analysis of the existing data set could be considered. This allows data gaps to be identified and an appropriate sampling plan to be developed to fill such data gaps. Geostatistics incorporates procedures to describe and evaluate clustered (hot-spot) and non-random sampling regimes. The mathematical procedures of geostatistics allow estimates of a given parameter at unsampled locations to be made within known limits. This allows quantitative assessment and statistical validation of proposed (Tier 3) sampling plans.

6.4. INTERPRETATION OF DATA

6.4.1. Introduction

The interpretation of data in Tier 3 takes the form of site-specific risk assessment, the further development of SSTLs and/or the comparison of measured receptor point or compliance point concentrations with ORCs and RBSLs. It generally focuses on all chemicals detected at the site which contribute to the exceedence of Tier 2 risk acceptability criteria although it may also be necessary to consider others where additive effects are possible.

6.4.2. Site-Specific Risk Assessment

The Tier 3 risk assessment approaches may involve the use of Tier 2 techniques, with added refinements made, or the utilisation of additional techniques, as follows:

- revised treatment of non-detect values;
- calibration of models with measured data;
- numerical modelling of groundwater pathways;
- revisions to toxicity criteria; and
- site-specific bioavailability/leachability data.

Clearly, there is considerably more flexibility in exposure assessment than in toxicity assessment, since the latter is often set by regulators. In certain circumstances, however, industry-derived dose-response criteria may be felt to be more appropriate than other published values. Where this is the case, the use of such values must be justified to the relevant authorities and their agreement obtained.

6.4.3. Comparison of Data with Other Relevant Criteria (ORCs)

If additional data have been collected from off-site wells, local basements/buildings and local water courses as part of a Tier 3 assessment, they can be compared with RBSLs or ORCs, as at Tier 1. For example, the comparison of off-site measured groundwater concentrations with RBSLs will indicate whether a potential health hazard exists via this migration pathway.

6.5. EVALUATION OF TIER 3 RESULTS

If the site-specific risk assessment acceptability criteria are met and there are no exceedences of ORCs or RBSLs then no further action is required, except a possible need for periodic monitoring for a finite period of time. If the criteria are exceeded, the cost-effectiveness of achieving Tier 3 corrective action goals, which could include SSTLs should be reviewed. A review of the options available for corrective action is provided in **Section 7**; the concept of Best Practical Environmental Option (BPEO) is a useful guiding principle.

7. CORRECTIVE ACTION MEASURES

7.1. INTRODUCTION

This section provides a summary of the range of corrective action measures that are available for contaminated sites representing the Risk Management options. These include the following:

- traditional remediation processes that reduce contaminant concentrations;
- exposure pathway elimination methods, such as capping and hydraulic containment;
- land-use restrictions (administrative and institutional controls - these are especially important at larger facilities – **see Appendix 10**);
- monitoring of natural attenuation between sources and receptors (for the purpose of validating the conclusion to take no further action) **(see Appendix 1)**.

All of these options are equally valid within the risk-based corrective action framework, provided they are implemented correctly, as they are all capable of reducing risks to acceptable levels.

It should be noted that

- the measures described in this section should only be utilised in connection with the tiered assessment approach described above;
- other measures may become available and be developed as "best practice" in the remediation of contaminated sites as risk-based corrective action evolves.

7.2. SELECTION OF MOST APPROPRIATE CORRECTIVE ACTION TECHNIQUES

Following the identification of an unacceptable risk associated with site-related contamination, a number of risk management strategies may be considered. The works may vary from simple risk mitigation measures to large-scale site remediation. The management tool used in the selection of the most appropriate corrective action approach for a site is a technical (engineering) feasibility study, incorporating design and costing. Other factors such as business reputation, liability and aesthetics may also need to be considered.

It is also necessary when comparing corrective action options to consider short-term risks to health and the environment during their implementation, such as exposure due to vapours and dust, and accident hazards to site personnel. Clearly, a corrective action programme must not, in addressing one set of risks, create others that negate the gains to health and the environment that remediation was intended to bring about.

It is inherent within the tiered approach that potential corrective action options and approaches are evaluated, and their merit revisited as analysis proceeds (i.e. as part of assessing the need for tier-specific corrective action, whether interim or final). A technical (engineering) feasibility study should be carried out to assess the site specific practicalities associated with undertaking one or more potential corrective action measure(s), which also forms part of the cost-benefit analysis.

Once the selection of one or more appropriate options has been made a detailed design can be drawn up and budget cost estimates made. In cases where highly technical solutions may be required, simple benchscale or field pilot studies (i.e. pilot plant testing) may be required to better assess the feasibility of a particular scheme prior to full scale design and costing (e.g. for dual phase extraction or bioremediation).

7.3. EXAMPLES OF CORRECTIVE ACTION TECHNIQUES

The following techniques represent the principal methods by which corrective action at oil industry sites can be achieved, whether as an interim measure or a long term solution. They may be applied in isolation or in combination.

- ongoing monitoring of the natural attenuation of contaminated media (in particular in cases where source removal has been achieved and/or where natural processes (e.g. biodegradation) are expected to reduce the contaminant levels over time) **(see Appendix 1);**
- contractual instruments or physical barriers limiting the use of property or land to avoid a potentially unacceptable exposure to current or future site users

  includes fencing-off contaminated areas, restricting access to subsoils and restricting site land-use;
- physical isolation measures for existing buildings or their incorporation into the design of new buildings during site redevelopment

  includes vapour exclusion membranes, removal of ducting, passive venting techniques;
- installation of specialist physical isolation barriers to restrict exposure /migration pathways at existing or redeveloped sites

  includes the capping of contaminated areas where direct exposure pathways drive the risk assessment or where the leaching of soil contaminants to groundwater via rainfall infiltration is a concern;
- construction of physical barriers or collection systems to restrict contaminant migration to surface and or groundwater

  includes cut-off walls or collection drains, vitrification, stabilisation;
- in-situ treatment of contaminated materials to reduce the source volume or concentration

  may include vacuum extraction for volatiles and semi-volatiles, air sparging or bioremediation;
- receptor point corrective action

  includes the treatment of contaminated water as it is abstracted from a groundwater supply well;

- removal and disposal/treatment of contaminated soils

  includes ex situ bioremediation, landfilling, incineration, soil washing, thermal desorption.

7.4. MONITORING AND POST-CORRECTIVE ACTION REQUIREMENTS

Following the implementation of corrective action measures, a site monitoring system should be considered as a part of the corrective action assurance process. For example, at those sites where estimated risks are acceptable, but where significant residual contamination is known to exist, a requirement to monitor may be set by the regulatory authority. The purpose and duration of any such activity would be negotiated on a site specific basis and should depend upon the sensitivity of a particular site setting. If conditions change in the future then further corrective action measures may be necessary.

Monitoring can take one of two principal forms. Firstly, validation monitoring is designed to ensure that contaminated material has been removed or treated to an acceptable degree leaving residual concentrations at acceptable levels. This is usually performed at the time of (or immediately after) the remedial programme of works. Secondly, longer term monitoring is often implemented to prove that the site condition, post-corrective action, does not represent an ongoing risk for the wider environment. It is important to pre-define the period of time for which monitoring is required.

8. GLOSSARY

Acceptability criteria	RBSLs, SSTLs or IRLs.
Air sparging	*In-situ* volatilisation of dissolved or sorbed-phase organic compounds by the injection of air.
Algorithm	Procedural model or rule for calculation.
Analytical data	Data pertaining to the chemicals for which a sample is analysed.
Aquifer	A water-bearing bed or strata, either by virtue of its porosity or because it is pervious.
Attenuation	See "Natural Attenuation".
Backward	Taking defined acceptable risk levels at points of exposure, and back-calculating soil contaminant levels which would achieve that level of risk.
Bioavailability	The degree to which chemicals present in a soil matrix may be absorbed or metabolised by a human or ecological receptor.
Biodegradation	The breakdown of a substance or chemical by living organisms, usually bacteria.
Bioremediation	Breakdown and removal of contaminants by microbial action.
Capping	Placing a layer of material over an area of contamination to remove exposure pathways and/or prevent infiltration.
Compliance point	Negotiated location where target concentrations are to be achieved.
Conservative	Erring on the side of safety.
Contaminant migration pathway	The mechanism by which a contaminant moves in the environment from source to target.
Corrective action	Any activity conducted in order to address an actual or perceived contamination problem.
Deed restriction	Legal method for preventing particular types of developments on a specific site.
Dose	The amount of a chemical which enters the body of an individual, expressed in the form of mass per unit body weight per unit time (e.g. mg/kg-day).
Dose-response relationship	A numerical expression of a chemical's dose-response relationship that is used in risk assessments. The two toxicity criteria used in this assessment are reference doses (for non-carcinogenic effects) and slope factors (for carcinogenic effects).
Ecological receptor	Habitat or species (non-human) that is potentially exposed to site-related contamination.

Ecological risk assessment	The process of evaluating the likelihood that adverse ecological effects may occur due to exposure to one or more stressors.
Exposure	The opportunity to receive a dose of a chemical.
Exposure assessment	The process of establishing whether, and how much, exposure will occur between a receptor and contamination.
Exposure assumption	An assumption made to aid in the process of exposure assessment.
Exposure pathway	The course a chemical takes from a source to a receptor. Each exposure pathway includes a source, a transport medium (or media) an exposure point and an exposure route.
Fate and transport model	A mathematical model used to describe and simulate the movement of a chemical in the environment.
Forward	Using the measured soil and groundwater contaminant concentrations to calculate actual risk levels to the identified receptors, at the points of exposure.
Free product	Petroleum product (e.g. gasoline, diesel) which is present in either its original or weathered state at a concentration above the residual saturation level.
Geostatistics	Statistical methods specifically related to characterising geological conditions.
Groundwater	Water occupying openings, cavities, pores and spaces in rocks, beneath the topographic ground level.
Hot-spot	Area containing a higher concentration of contaminant(s) than the surrounding area.
Insignificant risk level (IRL)	A measure of risk which has broad public or regulatory acceptance (e.g. via legislation).
Intake	Same as dose.
Intrusive investigation	Procedures incorporating techniques such as boring and trenching to facilitate the investigation of subsurface conditions.
Maximally exposed individual (MEI)	Hypothetical individual who has a combination of characteristics (body weight, soil ingestion rate, etc.) such that the total exposure is unlikely to be exceeded by any other individual.
Monte Carlo analysis	Method for calculating the range of solutions to an equation, when the input variables can be characterised by probability density functions (PDFs).
Natural attenuation	Reduction in contaminant concentrations as a result of naturally occurring processes, such as dilution, evaporation and biodegradation.
Other relevant criteria (ORCs)	Officially recognised chemical concentrations in environmental media for the protection of specific adverse effects (e.g. odour thresholds, drinking water standards).

Pathway	The mechanism by which a contaminant travels from source to target in the environment.
Pharmaco-kinetic	Pertaining to the internal physiological/biochemical responses to a chemical dose.
Risk-based screening level (RBSL)	Chemical concentration in a specific environmental medium that can be used to make a judgement on the absence of a significant risk.
Reasonable worst case	An estimate of the plausible maximum (or minimum) value that an exposure assumption can achieve.
Receptor	Potentially-exposed organism.
Reference dose	Dose-response parameter for non-carcinogenic effects, equal to "safe" level of exposure.
Remediation	The completion of practical measures with agreed end-points for the purposes of rendering a contaminated site suitable for the use to which it is desired to be put.
Residual contamination	Contamination remaining on a site following corrective action.
Risk assessment	The process of establishing, to the extent possible, the existence, nature and significance of a risk.
Risk estimate	A quantitative or qualitative statement as to the level of risk, with no attempt made to interpret its meaning.
Risk management	The process of interpreting and controlling assessed levels of risk.
Significant risk	A risk which is considered worthy of concern and/or remedial action.
Significant risk level	A quantitative expression of what constitutes a significant risk.
Site-specific target level (SSTL)	A chemical concentration derived on a site-specific basis which does not pose a significant risk.
Soil vapour	Airborne chemicals present in the soil that may or may not be due to contamination.
Source	The activity or entity from which a chemical is released for potential human exposure.
Subsoil	A layer of shattered and partly weathered rock between the soil proper and the bedrock.
Surface water	Rivers and streams, lakes and reservoirs and tidal estuaries.
Target organ	The site where the toxic injury manifests itself in terms of dysfunction or overt disease.
Total petroleum hydrocarbons (TPH)	The sum of all petroleum-related compounds present in a sample, according to a specific analytical technique.
Vacuum extraction	Removal of contaminants by creating a vapour flow through the soils by applying a vacuum.

APPENDIX 1 NATURAL ATTENUATION OF CONTAMINANTS IN GROUNDWATER

1.1 INTRODUCTION

Contaminants in groundwater are subjected to several natural processes (both physico-chemical and biological) which reduce their concentrations. Given sufficient travel distance and time, these processes can result in complete attenuation of contaminants before any sensitive receptor is reached, and can thereby alleviate the need for costly engineering solutions. Natural attenuation is thus one of several remediation options possible at a site. As with any remediation option, natural attenuation should be evaluated for its appropriateness based on the risks, the site characteristics, and the potential to achieve remedial objectives at each individual site. Natural attenuation is not a “do nothing solution”. It should not be assumed to be occurring at a site simply because the contaminants present have been demonstrated to attenuate naturally at other sites. Sufficient monitoring needs to be done to conclusively demonstrate that it is taking place at a rate that will mitigate any risk to a potential receptor. For this reason the corrective action is often referred to as monitored natural attenuation (MNA).

1.2 NATURAL ATTENUATION PROCESSES

1.2.1 Physico-chemical processes

The physico-chemical processes which can bring about natural attenuation of groundwater contaminants are adsorption, dispersion, diffusion and volatilisation. Contaminants can be adsorbed onto the surfaces of soil particles, thereby reducing concentrations that would be observed if only a pure aqueous phase were present. Those contaminants, which adsorb most strongly to the soil, migrate more slowly in groundwater than those which are only weakly sorbed. This process is referred to as retardation.

The extent of sorption depends on the chemical nature of the contaminant and the composition of the soil. Hydrophobic organic chemicals such petroleum hydrocarbons adsorb to organic matter coating the soil particles. Polar organics and metals may sorb to clay particles under the right pH conditions. The parameters that are required to assess the retardation of organic chemicals in soils and aquifers are: the soil bulk density, the mass fraction of organic carbon in the soil and the octanol/water partition coefficient of the contaminant.

The dilution of contaminants in groundwater resulting from spreading and mixing caused by microscopic variations in groundwater velocities within and between pores is termed dispersion. Diffusion (migration resulting from concentration gradients) plays only a minor role (compared to dispersion) in contaminant dilution in permeable strata, but can be a dominant transport mechanism in low permeability conditions. Although the processes of adsorption, dispersion and diffusion do not result in decreased contaminant mass, they contribute to risk reduction by reducing the concentration reaching a particular receptor.

The concentration of volatile contaminants in groundwater declines over time as they volatilise out of the groundwater up through the unsaturated zone. Hydrocarbons are likely to biodegrade if the residence time is long enough. The contribution of volatilisation to contaminant mass reduction is small compared to biodegradation for most petroleum hydrocarbons.

1.2.2 Biological processes

Biodegradation is the major natural attenuation mechanism for readily biodegradable organic contaminants such as petroleum hydrocarbons. In this process, naturally occurring micro-organisms use the contaminants as a food source, breaking them down into the carbon dioxide and water. When this process occurs naturally without the interference of man, it is termed natural biodegradation or intrinsic bioremediation. When it is enhanced by the use of engineering techniques to alleviate as many of the rate limiting factors as is practically feasible, it is termed bioremediation or engineered bioremediation.

When microbes degrade organic contaminants, they require a terminal electron acceptor such as oxygen. Most organic contaminants, such as petroleum hydrocarbons, biodegrade faster in the presence of oxygen (aerobic conditions) than its absence (anaerobic conditions). However, many contaminants will degrade under the latter conditions so long as alternative electron acceptors such as nitrate, iron, sulphate and bicarbonate are present. Some contaminants are preferentially biodegraded under anaerobic conditions (e.g. the more highly substituted chlorinated solvents).

Oxygen is frequently the major factor limiting aerobic biodegradation in the subsurface. Oxygen is replenished naturally in the vadose zone by air exchange between the above ground atmosphere and the soil atmosphere caused by barometric pressure and water table fluctuations. Following this the oxygen is redistributed within the vadose zone principally by diffusion. Dissolved oxygen in the groundwater is replenished by hydrodynamic dispersion, diffusion and re-aeration at the interface between the capillary fringe and the vadose zone.

A groundwater contamination plume will most likely contain both aerobic and anaerobic zones. Aerobic conditions will generally be found at the periphery where contaminant concentrations are at their lowest. Moving back through the plume towards the source one will encounter anaerobic regions where several different types of alternative electron acceptor activity may be found.

1.3 IMPLEMENTING NATURAL ATTENUATION AS A REMEDIAL OPTION

Every remediation action plan must have clearly defined objectives. These objectives include identifying cleanup levels or performance requirements, determining points of compliance, and establishing acceptable time-frames for cleanup. Once the remediation objectives are established, natural attenuation can be evaluated for suitability as a remediation alternative. Natural attenuation may be the sole remediation option, a component of the remediation action plan, or unsuitable - depending on the site.

Many groundwater contaminants (e.g. petroleum hydrocarbons, chlorinated solvents and phenols) have the potential to undergo natural attenuation. A life cycle of a dissolved phase groundwater plume typically goes through four phases:

- Expansion, where dissolution from the source exceeds the rate of biodegradation;
- Steady state, where dissolution from the source equals the rate of biodegradation;
- Collapse, where the plume contracts because the rate of biodegradation exceeds the rate of dissolution from the source;
- Exhaustion, where the plume has disappeared.

The Lawrence Livermore National Laboratory (LLNL) in California have analysed soluble hydrocarbon plumes containing benzene, toluene, ethylbenzene and xylenes (BTEX) at 271 sites with leaking underground gasoline tanks. They found that the length of BTEX plumes stabilised at relatively short distances from the source and rarely exceeded 75 metres. They concluded that natural attenuation can provide corrective action that is at least as efficient as actively engineered remediation processes such as pump and treat for a fraction of the price. The findings of the Lawrence Livermore study have been confirmed by similar studies in Texas and Florida. An excellent summary of these three studies can be found in a report of the API Soil & Groundwater Technical Task Force [1].

Evaluating natural attenuation is an active process that includes site characterisation, risk assessment, and monitoring of remediation progress.

1.3.1 When is natural attenuation an appropriate corrective action?

The criteria which make monitored natural attenuation an appropriate corrective action include:

- No currently impacted or immediately threatened receptors;
- All on-going leaks have been eliminated;
- The rate of contaminant migration is relatively slow due to low groundwater gradients, low permeability soils or a soil type which retards migration of the soluble plume;
- Evaluation of natural attenuation is not likely to increase the costs of corrective action when compared to other alternatives;
- The impacted groundwater is not used as a source of drinking water.

There is much debate as to whether free product removal should be a pre-requisite to implementing natural attenuation for groundwater contamination. Site-specific conditions can often render significant free product removal impractical **(see Appendix 4**). Even where it is possible it may bring little risk reduction benefit, although less time may be needed before the soluble plume starts to shrink. A consistent approach would be to consider the free product in the same risk-based manner. It may be possible to demonstrate that migration of the free product is either not occurring or does not pose a risk. It should be remembered that the free product might also be subject to natural attenuation and thus degrade over time and distance.

1.3.2 Monitoring natural attenuation

To determine whether natural attenuation is a feasible corrective action strategy a well-developed and proven conceptual site model is required (source-pathway-target relationships), supported by field data about the hydrogeology of the site and the contaminant plume. The hydrogeology data may include some of the following:

- Direction and gradient of groundwater flow;
- Hydraulic conductivity;
- Porosity;
- Definition of lithology;
- Locations of nearest groundwater recharge areas;
- Seasonal fluctuations in water table;
- Aquifer thickness;
- Depth to groundwater;
- Organic carbon content of the soil.

Examples of data on the plume which may be required include:

- Delineation of the source and the soluble plume;
- Date of contaminant release (not essential but useful for predicting expected extent of plume migration);
- Concentrations over time along the primary flow path from the source to the leading edge;
- Geochemical data (electron acceptors for aerobic or anaerobic biodegradation).

Several parameters can be monitored to determine the extent to which natural attenuation is controlling the migration of a contaminant plume. The primary line of evidence that natural attenuation is taking place is provided by monitoring the concentration of contaminants in a series of monitoring wells on a quarterly basis, or less frequently where the rate of groundwater flow is low, the distance to the receptor is large or the time history of the data suggests that changes to the plume are slow to occur. These wells should be located both within the plume and at its periphery. At sites where a predominant direction of groundwater flow and plume migration has been established monitoring wells should be located along the centre line of the plume comprising the primary axis of migration from the source to the leading edge.

When evaluating plume behaviour four different scenarios are possible: it recedes, it remains stable (steady state plume), it migrates slower than expected or it migrates faster or at the same rate as expected. The first three are indicative of natural attenuation. Trends should be established from multiple monitoring events to discount the effects of seasonal fluctuations in contaminant concentrations and data variability.

If there is a sensitive receptor in the vicinity it is advisable to place a sentinel well between the leading edge of the contaminant plume and nearest down gradient receptor to act as an early warning that the plume threatens the receptor. The location and frequency of sampling of the sentinel well should be such that it allows adequate time to implement an alternative corrective action should natural attenuation prove to be insufficient to protect the receptor. A contingency plan should be drawn up to facilitate this action if it becomes necessary.

So-called secondary lines of evidence for natural attenuation are provided by indirect measurements of biodegradation such as electron acceptors and their conversion products and intermediary degradation products. Electron acceptors and reduction products which are commonly measured include: dissolved oxygen, nitrate, ferrous iron, sulphate and methane. The ones measured at any particular site will depend on the nature of the contamination. They should be measured inside and outside (including up-gradient) the plume and correlated with contaminant concentrations.

An inverse relationship between, say, dissolved oxygen for aerobic degradation in an aerobic aquifer and contaminant concentration is indicative that natural attenuation is taking place. The reason for this is that dissolved oxygen will be low where contaminant concentrations are high (in the centre of the plume) due to the high biological oxygen demand and dissolved oxygen will be high where contaminant concentrations are very low at the leading edge.

Since the stoichiometry of biodegradation for many contaminants is well understood, it has been proposed that quantification of alternative electron acceptors can be used to estimate biodegradation capacities of aquifers. There are many pitfalls in this and it should be used with extreme caution. The measurement of intermediary breakdown products can also provide supporting evidence for natural attenuation. Chlorinated solvent degradation is a good example of this.

Long-term monitoring of natural attenuation is usually unnecessary, with two to three years being a typical time-frame. However, since natural attenuation is a new concept to many regulators it is possible that more monitoring of the plume will be required in the short-term until confidence develops in this approach.

1.4 MTBE AND NATURAL ATTENUATION

Until very recently, MTBE was thought to be recalcitrant in the environment. This has led to some states in the US precluding the use of natural attenuation as a remediation option when MTBE is present as a contaminant of concern. However, evidence is now coming to light which indicates that some aquifers have the potential to attenuate MTBE both aerobically and anaerobically, albeit much more slowly than BTEX. Therefore, natural attenuation may be an appropriate risk reduction option for MTBE under certain circumstances. In any event the presence of MTBE at a site should not preclude natural attenuation as a remedy for other contaminants (e.g. BTEX) at that site. There is also evidence that the presence of MTBE at sites is unlikely to present a threat to drinking water [2].

1.5 ADVANTAGES AND DISADVANTAGES OF NATURAL ATTENUATION

The potential advantages of natural attenuation as a remediation option include:

- the generation of less remediation wastes;
- elimination of exposure of remediation contractors to potentially harmful contaminants;
- less disruption of the environment;

- ease of use in conjunction with other remediation technologies;
- no equipment down time;
- likelihood of lower overall costs than from active remediation.

There are, however, a number of disadvantages including:

- Longer time-frames may be required to achieve remediation goals;
- the public may not perceive the process correctly (seen as “doing nothing”);
- site characterisations can be more costly and complex;
- responsibility must be assumed for performance monitoring and the potential exists for continued migration.

In the current climate (lack of demonstration sites and regulatory experience of natural attenuation in Europe) it is most likely that a contingency plan that uses a more active remediation alternative will need to be provided. This would need to be implemented if monitoring shows the situation is not as predicted and natural attenuation will fail to meet the remedial goals. The contingency may be something as simple as a perimeter monitoring well(s) or sentinel well that could be pumped to “buy more time” for the natural processes to work.

The disadvantages can have economic implications: Property transfers may be delayed or stopped; longer time-frames may not be compatible with future land uses; active remediation may be more economic than performance monitoring at certain sites and liability could be an issue for present and future land users. In addition, the owner and / or operator may find it more difficult to obtain insurance.

It may be possible to overcome some of these issues on a Europe-wide or country basis through dialogue with the relevant interested parties (regulators, industry, academia, banking, insurance, general public), but many of them will need to be resolved on a case-by-case, site-specific basis.

Quite often engineered remediation simply will not work and there is no option but to let nature take its course. There is some very sobering evidence from the LLNL and Texas ‘plumathon’ studies on this point. Both these studies looked at plumes at sites which had undergone some form of engineered remediation of the groundwater and compared these to plumes receiving no treatment. The conclusions are very revealing. For LLNL: "An analysis of plume length categories shows that none of the remediation treatment variables have a significant impact on the relative frequencies of the different categories of plume (expanding, stable or shrinking). For the Texas study. "We found no difference in plume length between different remediation techniques and sites with no remedial action."

Published guidelines on monitoring natural attenuation can be found in the literature [3,4,5].

1.6 REFERENCES

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APPENDIX 2 TARGET RISK LEVELS AND COMPOUND / PATHWAY ADDITIVITY

2.1 INTRODUCTION

One of the key issues facing a policy maker concerned with regulating soil and groundwater quality is the question of what level of risk is acceptable. In practice, the driving risk factor is usually carcinogenicity. The decision on the quantitative number identifying this target risk (i.e. the acceptable risk level) should be weighed against other policy issues. In particular, those concerned with what to do if multiple carcinogenic compounds are present, or if more than one route of exposure is possible (e.g. direct ingestion of contaminated groundwater and inhalation of vapours entering a house from a groundwater plume. This paper will provide some insight on these questions to help focus the policy debate.

2.2 DEFINITION OF RISK

In the remediation community, environmental risk generally is separately defined depending on whether the chemicals of concerns are cancer-causing (carcinogenic) or not. Policy decisions regarding non-carcinogens are usually less controversial because such compounds have an assumed safe dosage level, i.e. an amount that can be ingested, absorbed or inhaled each day for every day of a person's life without causing a problem. The target risk level is normally set so that the exposure dose does not exceed this safe *reference dose*. Common terminology refers to the ratio (exposure dose divided by reference dose) as the Hazard Quotient (HQ). Typically, an exposure is considered safe if the HQ is equal to, or less than, one.

Carcinogens are assumed to have no safe dosage, so any exposure contributes to some cancer risk. The question then becomes what level of incremental exposure is acceptable. Here, incremental refers to the increased probability (but not certainty) that an individual will contract cancer over his/her lifetime due to chronic (long-term) chemical exposure. A range commonly used is an increased cancer risk of 1 in 10,000 to 1 in 1,000,000, i.e. a target level of 10^{-4} to 10^{-6}. This means that if 10,000 or 1,000,000 people, respectively, were chronically exposed to a designated concentration (chemical-specific), then one person may expect to contract cancer. Of note, the concentrations corresponding to a 10^{-4} to 10^{-6} risk are typically obtained by evaluating data from animal bioassays using low-dose extrapolation algorithms, that generally result in quite conservative toxicity thresholds.

It is important to recognise that this latter risk is incremental to the background rate of cancer development, i.e. cancers from smoking, diet or from hereditary reasons. Since approximately 30% of the population dies from cancer, the policy decision actually reduces to whether the cancer risk to an exposed individual should be 0.3001 or 0.300001.

2.3 ADDITIVITY CONSIDERATIONS

If a person were exposed to multiple carcinogenic/non-carcinogenic compounds, one approach could be to add the individual compound risks to arrive at a cumulative carcinogenic and non-carcinogenic risk. However, there are subtle issues to consider regarding compound additivity:

This idea is potentially applicable only if the compounds affect the same organ in the body, e.g. the liver or the blood.

- The no safe threshold assumption for carcinogens directionally lends itself to additivity, i.e. the more exposure (from both the size of the dose and the number of compounds) an individual experiences, the higher the risk;
- The safe threshold assumption of non-carcinogens implies minimal risk at or below a certain level, directionally making use of additivity more questionable (adding zero risk from one compound to zero risk from another compound still gives zero risk);
- There remains a question of whether the additivity should be a straight linear mathematical process, or whether non-linear influences should be considered. Non-linear behaviour would be applicable if the compounds act synergistically (heightening the bodily response due to their combined presence) or antagonistically (where the individual compound effects offset each other).

Some insight on these important issues is available from the literature review of Seed et al [2]. The toxicological studies evaluated in this paper suggest that compound additivity is an appropriate model for mixtures of carcinogens that impact the same target organ, even at relatively low doses. However, additive non-carcinogens effects are not apparent when the hazard quotients of the individual compounds in the mixture are well below one. But as the hazard quotient of a mixture component or number of components approaches one, additive effects are more likely, including synergistic or antagonistic interactions.

Risk additivity is also a consideration when exposure may occur via more than one pathway. Pathway additivity can be described by the following example. Contaminated surface soil in gardens could lead to exposure of residents by dermal (skin) contact. Furthermore the contaminants in the soil could leach to the groundwater table via rainfall and enter a well used by the household for drinking and bathing purposes. Conceivably then, this same soil source could expose an individual to any or all of the following pathways: 1) accidental ingestion of the soil; 2) dermal contact with the soil; 3) ingestion of vegetables grown in the soil; 4) ingestion of contaminated groundwater; and 5) vapour inhalation of groundwater when it is used for indoor showering.

2.4 POLICY QUESTIONS

Since multiple compounds and/or pathways may be present at a contaminated site, a policy maker faces a philosophical choice:

- Should the target risk level be set for individual compounds and individual pathways, with the inherent assumption being that any increased risk due to multiple compound or pathway exposure will be compensated by choosing a conservative individual target?
- Should a less conservative overall target risk level be specified if the policy specifies that risks due to individual compounds and/or pathways are to be added?

2.5 INDIVIDUAL COMPOUND / PATHWAY TARGET RISK LEVELS

Formulating policy based on specification of individual compound and pathway target risk has at least three advantages:

At most contaminated sites, overall risk is dominated by one compound and pathway - this approach focuses attention on these major influences. This is particularly relevant given the exposure model that establishes that a source-pathway-receptor relationship must exist to have a risk. Risk targets set for individual pathways allow for focused remedial solutions.

A second advantage of this approach is that it simplifies the calculation of cleanup levels. This is commonly referred to as the *backward* calculation, i.e. identifying the acceptable risk level and then computing a *safe* source (soil or groundwater) concentration, allowing for fate and transport effects between source and receptor. If multiple compounds are to be considered in a backward calculation, the contribution each compound makes to total risk must be somehow apportioned. This requires qualitative judgement and more involved computational steps.

The third argument for individual compound/pathway risk targets is that it is consistent with existing drinking water guidelines, as promulgated by the US EPA (under the Safe Drinking Water Act) and the World Health Organisation [6]. Drinking water standards for individual compounds are listed by these bodies independent of whether other compounds may be present.

2.6 RISK ADDITIVITY

Three arguments can be made favouring the use of risk additivity, including:

- In many situations, exposures to multiple carcinogenic/non-carcinogenic compounds do occur simultaneously via more than one pathway;
- Taking account of additivity removes the need to rely on the assumptions that a single compound or pathway dominates the process, or that a conservative individual risk target will compensate for the risk contributions of other compounds or pathways;
- Use of additivity eliminates the possibility that a site could fall just below a risk target when only the most dominant compound or pathway is considered, but that the threshold could be exceeded (perhaps triggering a need for corrective action) when the risk from more than one compound or pathway is added.

Use of additive compound risk does however require some caution. As pointed out earlier, there is a logical basis and data to support the concept of adding the risk of different carcinogens, but there is the question as to whether this should be done linearly or non-linearly. Addition of non-carcinogenic compound risk is supportable only when the dose from one or more individual compounds approaches its acceptable threshold level. Finally, compound additivity is applicable only where the target organ and the effect on the organ are broadly similar.

It is of interest to note that not all countries in Europe distinguish between carcinogenic and non-carcinogenic effects. In the Netherlands, for example, the toxicity of all compounds is expressed in terms of a *tolerable daily intake*. This has the same units as *reference dose*, and at first glance it implies that all compounds are treated as non-carcinogens. But this is not necessarily the case. Non-zero drinking water standards exist even for carcinogens which theoretically have no safe dosage. This means that a tolerable daily intake can easily be derived for carcinogens by simply multiplying the drinking water standard by the average number of litres of water consumed per person per day and dividing by the average individual's body weight (assuming ingestion as the only pathway). Policy decisions on additivity of compound risk that distinguish between carcinogenic and non-carcinogenic effects should take this peculiarity into account.

2.7 BACKGROUND RISK

Another policy issue concerns the way to treat background risk, i.e. the risk due to levels of contamination naturally occurring or otherwise normally present in an area. The approach in the US and in some European countries (e.g. The Netherlands) has been to regulate on the basis of incremental risk above background. This is normally accomplished by subtracting background concentrations of chemicals of concern from the input concentrations in a forward risk calculation. The CLEA (Contaminated Land Exposure Assessment) model, which was funded by the UK Environment Agency, specifies however that background concentrations are to be included in the risk calculations, thus lowering the acceptable dose from anthropogenic contamination. This latter approach may be more holistic is dealing with overall risk, but it raises the possibility that a site owner could be unfairly penalised by having to initiate corrective action for low levels of contamination where background concentrations are close to risk-based action levels.

2.8 NUMERICAL RISK LEVELS

The common application of 10^{-6} risk in local contaminated land legislation stemmed from two factors. One is the perception that hazardous waste is a more serious public issue than other sources of exposure (e.g. automobile emissions or radon which are regulated less stringently). The second reason is that, unlike decisions about air emissions or pesticides which are made at the federal level, hazardous waste cleanup rulings are made locally where cost/benefit analysis does not feature as strongly as it would where decisions have more of a nation-wide impact.

In fact, with regard to federal environmental legislation on hazardous waste sites, the concept of 10^{-6} as a criterion of acceptable risk has never been mandated in any US EPA regulations. In fact the range of 10^{-4} to 10^{-6} has been adopted as *generally acceptable risk*, forming the basis to determine remedial need of US. Superfund sites in the 1990 National Contingency Plan [3].

Under this guidance, risks below 10^{-6} are considered to be negligible while risks above 10^{-4} are considered unacceptable. This still leaves a hundred-fold difference in risk which, in application, could mean more than a hundred-fold difference in site-specific remedial costs. Unless regulatory flexibility is granted to set the risk target on a case-by-case basis, there is the dilemma of how to choose a specific number.

Because this is a judgement decision and not a scientifically derived value, the only available guidance stems from examples where specific numbers have been adopted. Malander [1] lists a series of US examples pointing to a trend of acceptable risk levels above 10^{-6} as *'the conservative nature of risk assessment calculations has been recognised'*. In one of his quoted examples of hazardous waste standards, the US EPA selected 10^{-5} as the basis for its rule on characterising when a substance is considered hazardous [4]. In legislation involving air emissions of the carcinogen benzene [5], a standard of 10^{-4} was adopted.

Another benchmark is to compare environmental risk against generally accepted principles used for industrial safety risk, i.e. risk due to explosions, fire, etc. One common guideline is a target (not to exceed) value for safety risk to the public of 10^{-4} per exposed individual. But it should be noted that safety risk is calculated on a yearly basis whereas environmental risk is calculated over an individual's lifetime. For an average 70 year lifetime, this means that environmental risk is 70 times more conservative (more stringent) for the same numerical benchmark, e.g. for a standard of 10^{-4}, the equivalent safety risk is actually $70x10^{-4}$ or $7x10^{-3}$.

Outside the US the most notable numerical example of environmental risk acceptability is the standard of 10^{-5} for drinking water adopted by the World Health Organisation [6]. In Europe, the trend of acceptable risk levels above 10^{-6} is also evident in emerging legislation/technical guidance in relation to contaminated land in France, Germany, the Netherlands, the United Kingdom and parts of Spain.

2.9 CONCLUSIONS

There is no absolute basis upon which to answer the question of how much risk is acceptable. The safe dosage assumption for non-carcinogens alleviates some of the controversy for these compounds as it is defensible to argue that chronic exposure should not exceed the safe reference dose. Historically, acceptable risk targets for carcinogens have ranged between 10^{-4} and 10^{-6}, but selection of a specific number is a value judgement decision.

Recent trends both in the US and in Europe at large show movement away from the commonly applied but very conservative figure of 10^{-6} carcinogenic risk. But selection of an admitted arbitrary acceptance level should not be taken in isolation. An equally important decision is whether the risk target should be applied to individual compounds and pathways or whether risk via different chemicals and pathways should be additive. Justifiable arguments can support either approach, although additivity of compound risk should perhaps be limited to mixture compounds that impact and have a similar effect on the same target organ in the body.

One plausible starting point in the debate could be the following. Consistent with the World Health Organisation's drinking water guidelines, a legislative framework that defines acceptable risk on the basis of individual compounds and pathways could utilise 10^{-5} as the standard. A policy recognising the contribution other compounds or pathways make to total additive risk could adopt a less stringent overall standard of 10^{-4}. Both approaches remain consistent with the historical trend of specifying acceptable risk within the 10^{-4} to 10^{-6} range but reflect the understanding that 10^{-6} represents almost zero risk (which therefore may not be technically achievable or economically defensible). In fact, both philosophies converge to the same level of human health protection when the number of compounds and pathways considered under the additive case approaches ten in total.

2.10 REFERENCES

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APPENDIX 3 THE USE OF TOTAL PETROLEUM HYDROCARBONS IN RISK-BASED CORRECTIVE ACTION

3.1 INTRODUCTION

Total Petroleum Hydrocarbon analysis (TPH) is widely used as a general measure of the presence of crude oil or petroleum product in soils. TPH is defined as the measurable amount of petroleum-based hydrocarbon in an environmental media (e.g. soil, water, and sediments) and thus, is dependent on analysis of the medium in which it is found. While providing an overall concentration of petroleum hydrocarbons, TPH itself is not a direct indicator of the risk (i.e. mobility, toxicity, and exposure to human and environmental receptors) posed by petroleum hydrocarbon contamination. Both mobility and toxicity are strongly dependent upon the relative amounts of the individual (or groups or families of) constituents within a hydrocarbon mixture. For example, a crude oil may contain different types and amounts of aromatic compounds than does a gasoline. Other analysis or information in addition to a single TPH number must be used to relate TPH concentrations to risk.

This paper presents an overview of the measurement of TPH and the methods that have been used in the past to estimate the risk from TPH contamination. More recent developments, including those of the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG), which is an ad hoc committee that was formed in the USA to develop a technically defensible risk-based approach to TPH, are also discussed. The paper concludes with examples of how these more recent developments have been used by environmental regulatory agencies or authorities to incorporate TPH into a risk-based corrective action program. Risk-based approaches for TPH range from detailed site-specific assessment to generic criteria based on typical compositional data for petroleum hydrocarbon products. In some cases, regulatory agencies have concluded that TPH does not pose a significant human health risk in the absence of a small set of specific indicator compounds (e.g. benzene, etc.) and thus, have established screening criteria for TPH based on aesthetic or other non-human health risk-based criteria.

3.2 MEASUREMENT OF TPH

There are in excess of 50 methods or variations for which the result is a measure of “TPH”. Historically, TPH has been measured by extraction of the environmental medium (e.g. soil or water) with a chlorinated solvent such as carbon tetrachloride or Freon 113, followed by quantification based on absorption of infra-red (IR) light by the hydrocarbons in the solvent extract. Examples of methods which are based on this approach include: USEPA 418.1 (new designation 5520), ISO TR 11046 (infra-red screening), DIN 38409 (Germany), NEN 6675 (Netherlands). These methods provides a “one number” value of TPH in an environmental medium; they do not provide information on the composition (i.e. individual constituents such as benzene) of the hydrocarbon mixture. Some of these methods are not specific to hydrocarbons and can give false positive results when organic matter (e.g. humic acid) is extracted from the environmental medium for analysis. In other words, TPH measurements by IR methods do not always indicate petroleum contamination.

In recent times, gas chromatography based methods have replaced IR based methods for quantification of TPH. Examples include USEPA Method 8015 Modified and ISO method TR 11046. EPA 8015 reports the concentration of purgeable and extractable hydrocarbons which are also sometimes referred to as gasoline and diesel range organic compounds (i.e. GRO and DRO) because the boiling point ranges of the hydrocarbon in each roughly corresponds to that of gasoline (i.e. C_6 to C_{10-12}) and diesel fuel (i.e. C_{8-12} to C_{24-26}), respectively. Purgeable hydrocarbons are measured by purge-and-trap gas chromatography (GC) analysis using a flame ionisation detector (FID), while the extractable hydrocarbons are analysed by GC following extraction with a solvent and subsequent concentration of the extract by evaporation. While more detailed information is generated by these methods (e.g. GC chromatograms which are sufficient for generation of a boiling point distribution or a finger print of the TPH), the results are most frequently simply reported as single numbers for purgeable and extractable hydrocarbons.

The Massachusetts Department of Environmental Protection (MADEP) has developed a method based on 8015 Modified which gives a measure of the aromatic content of the hydrocarbon in each of several carbon number ranges. In the MADEP method, the lighter hydrocarbon fractions (i.e. carbon numbers from C_6 to C_{12}) are analysed by purge-and-trap GC analysis using a flame ionisation detector (FID) to measure the total hydrocarbons and a photo ionisation detector (PID) to measure the aromatics (e.g. benzene) with the aliphatic (e.g. hexane) component of the TPH being found by difference. The aromatic and aliphatic fractions are divided into carbon number fractions based on the normal alkanes (e.g. n-octane) as markers. The heavier hydrocarbons (i.e. C_{12} to C_{26}) are analysed using an extraction procedure followed by a column separation of the aromatic and aliphatic groupings or fractions using silica gel (Modified EPA Method 3630). The two fractions are then analysed using GC-FID. PAH and n-alkane markers are used to divide the heavier aromatic and aliphatic fractions, respectively, by carbon number.

The MADEP method is based on standard EPA methods (i.e. 8020/8015 Modified) which allow it to be easily implemented by contract laboratories. However, there are some concerns or issues about the method. One issue is that the PID is not completely selective for aromatics (i.e. it does respond to aliphatic compounds). Thus, this approach can lead to an overestimate of the more mobile and toxic aromatic content of the petroleum hydrocarbons. Another issue with this analytical approach is that the results from the two analyses (i.e. purgeable and extractable hydrocarbons) can overlap in carbon number and thus may not be simply added back together to get a total TPH concentration. The performance of this method has only been tested on single compounds (e.g. benzene, naphthalene, etc.) and may be limited for real hydrocarbon products that are mixtures. In addition, the definition of the fractions based on different markers for the aliphatic and aromatic fractions may also cause confusion.

The TPH Criteria Working Group in the USA has developed an analytical method for identifying and quantifying the presence of groups or fractions of hydrocarbons with similar mobility in soils. The technique is based on EPA Method 3611 (Alumina Column Cleanup and Separation of Petroleum Wastes) and EPA Method 3630 (Silica Gel Cleanup), which are used to fractionate the hydrocarbon into aliphatic and aromatic fractions. A gas chromatograph equipped with a boiling point column (non-polar capillary column) is used to analyse a whole soil extract (i.e. prior to column separation) as well as the aliphatic and aromatic fractions. The normal alkanes are used as markers to resolve and quantify various groups or fractions. The use of a single GC run to analyse both the purgeable and extractable range hydrocarbons overcomes some of the limitations of the MADEP analytical method and leads to easier identification of the hydrocarbon contamination as well as consistent definition of the various fractions or groups of hydrocarbons. The method is versatile and performance-based and, therefore, can be modified to accommodate data quality objectives. However, this direct approach does result in higher detection limits since no concentration step is used (i.e. to limit the loss of volatile hydrocarbons). Thus, separate analyses for some of the indicator compounds may be required in some cases. Although, the detection limits are adequate compared to typical screening levels for TPH.

3.3 ESTIMATES OF RISK FOR TPH

There are three basic approaches that have been used in the past to estimate potential human health risks posed by TPH contamination. The one most generally applied and most appropriate for evaluation of the carcinogenic risk from TPH is an “Indicator” approach. This approach assumes that the estimated risk from TPH is characterised by a small number of indicator compounds (e.g. BTEX, PAHs, etc.). This approach was necessitated by the inability to analyse for the large number of constituents in TPH and the lack of toxicological and other relevant data for many of those constituents that could be individually identified. The indicator approach is generally accepted and used by many regulatory agencies for carcinogenic risk posed by petroleum hydrocarbon contamination. The use of the indicator approach for determining non-carcinogenic risk has, however, not been fully developed.

Another approach, the “Surrogate” approach, assumes that a single surrogate compound can characterise TPH. This approach can overestimate toxicity and mobility because of the toxicity and mobility of the compounds typically available for use as surrogates. For example with respect to toxicity, benzene is often used as a surrogate compound for all aromatics; it is also one of only a few hydrocarbons that is assessed as carcinogenic. Thus, its use as a surrogate can significantly over estimate the potential risk. With respect to mobility, benzene is, again, often used as the surrogate compound because it travels at a faster rate than other petroleum constituents. Benzene, however, represents only a small fraction of the constituents found in petroleum mixtures (i.e. it is one out of a large number of aromatic hydrocarbons that only represent a small fraction of the total mixture) and its use as a surrogate can result in inaccurate estimates of the fate and transport of petroleum hydrocarbons.

A variant of the “Surrogate” approach is the “Whole Product” approach in which the toxicity and mobility of the TPH product are based on that of a whole product of similar characteristics. Neither the “Surrogate” nor the “Whole Product” approach is capable of taking into account the effects of weathering (i.e. changes in composition, toxicity, and mobility over time) and the wide range of mobility of the constituents of the typical hydrocarbon product. Because the lighter and more mobile constituents tend to weather faster, weathered crude oils and hydrocarbon products are typically less mobile and, thus, typically pose a lower risk (although mobility is only one of several factors used to determine risk). The “Surrogate and the “Whole Product” approaches are similar to the “Indicator” approach in that they use specific knowledge of a single or a few constituents to characterise the many constituents in a hydrocarbon mixture.

More recently, approaches have been developed which are a compromise between the “Indicator” and the “Surrogate” or “Whole Product” approaches. In these approaches, carcinogenic risk is estimated based on indicators (e.g. benzene and the carcinogenic PAHs) while the non-carcinogenic risk from the TPH is estimated based on a relatively small number of groupings or fractions. Each of these groups or fractions is composed of constituents of TPH that have similar toxicity and mobility characteristics. The risk as a result of TPH contamination can be estimated for each of the groupings or fractions as individual contaminants or for the measured TPH (i.e. the sum of all the groups or fractions) by assuming additivity of the risk from each of the fractions. The approaches developed by the Massachusetts Department of Environmental Protection and the Total Petroleum Hydrocarbon Criteria Working Group are examples of this compromise approach [1,2].

3.4 THE MADEP AND TPHCWG APPROACHES

Both the MADEP and the TPHCWG approaches are combined indicator and grouping or fraction approaches, where the carcinogenic risk is evaluated based on a small number of indicators and the non-carcinogenic risk is evaluated based on a small number of groups or fractions. Note that indicators other than the carcinogenic hydrocarbons may also be appropriate for some petroleum hydrocarbon contaminated sites (e.g. lead, etc.). For example, the non-carcinogenic indicators (i.e. TEX and non-carcinogenic PAHs) can be included in the grouping or fraction analysis or treated as indicators if they represent a significant faction of the risk. If they are treated as indicator compounds, they should be backed out of the TPH analysis so that the risk is not double counted. In general, indicator compounds should be used when individual constituents represent a significant fraction of the potential risk from contamination by petroleum products.

In both the MADEP and the TPHCWG Approach, the TPH is split into a small number of groups or fractions that have similar properties. The main difference between the approaches is that in the TPHCWG approach, the groups or fractions of TPH are defined based on the potential mobility of the hydrocarbons within each group, while in the MADEP approach, they are based on the available toxicity data. Since its original development, the MADEP approach has been modified to incorporate the fate and transport data developed by the TPHCWG. However, it has retained the original broader definition of the fractions and thus does not account for the variability in environmental behaviour as well as the TPHCWG approach. The approach developed by MADEP does an adequate job of assessing the risk from TPH for direct exposure scenarios. In comparison, the approach developed by the TPHCWG as well as adequately assessing direct exposure risk, is better suited for addressing cross media exposure pathways such as leaching of contaminants from soil to groundwater, since it specifically takes into account the variability in the potential mobility of the petroleum hydrocarbon groups or fractions.

The other main difference between the MADEP and the TPHCWG approaches is that the MADEP approach assigns the toxicological properties for the various groups or fractions based on single surrogate compounds. In comparison, the TPHCWG approach is not a surrogate approach. In the TPHCWG approach, the physical/chemical and toxicological properties of each of the groups or fractions are based on all available data for individual constituents, well defined mixtures, and/or whole products that are representative of each group or fraction. The MADEP is currently reviewing the toxicological properties developed by the TPHCWG, which are based on a more complete database of toxicological properties. While developed first, the MADEP approach to risk assessment of TPH can be viewed as a specific application of the more general approach developed by the TPHCWG.

3.5 INCORPORATING TPH INTO A RISK-BASED CORRECTIVE ACTION PROGRAM

The fraction or group approach (i.e. the petroleum fate-and-transport fractions and toxicity criteria as developed by the TPHCWG) can be used in the ASTM/RBCA framework or any other risk-based decision making framework to develop mixture-specific risk-based screening levels (RBSL) for TPH. The soil risk-based screening levels (RBSLs) that are calculated for the indicator compounds and for the fate-and-transport fractions can be used individually as a basis for the management of a contaminated site. In this instance, site remediation will be governed by the most restrictive or lowest soil RBSL. Alternatively, the composition of the total petroleum mixture present at a site can be used to yield a soil RBSL for TPH (i.e., based on a composite target hazard index that it the sum of the hazard quotients from all the fractions). Since this composite RBSL for TPH is based on the non-carcinogenic risk, the RBSLs for the carcinogenic indicator compounds must still be considered separately. The RBSL for TPH is calculated by assuming that the risk for the individual compounds and fate-and- transport fractions can be added, each weighted by their composition in the total petroleum mixture. A thorough discussion of how the group or fraction approach may be used within the RBCA framework, including risk calculations and results from demonstration sites where this new approach has been used, are presented in Volume 5 of the TPHCWG documentation [2].

The approach developed by TPHCWG is intended to provide the technical basis for application of the group or fraction approach within a broad range of regulatory programs. Thus, while it can be used to develop risk-based analysis for the individual TPH groupings, the approach can also be used to develop a risk assessment or risk-based screening levels for TPH (i.e. the sum of the fractions). In addition, the application of the full analytical method and risk analysis may not be needed for all soil samples collected at a petroleum-contaminated site. Once the petroleum composition has been fully characterised at a site, additional sampling can rely on traditional, less expensive TPH analysis rather than the more complex group or fraction analysis (if the TPH fingerprint is similar across the site). This simplification can be carried further if process knowledge for a site can be used to characterise the hydrocarbon contamination such that the composition of the petroleum hydrocarbons at the site can be based on non-site specific analysis (e.g. typical jet fuel at an Air Force base).

These simplifications are important for application of the group or fraction approaches at sites where the cost of the more detailed analysis is not justified. For example, the full group or fraction analysis may not be cost effective at heavy hydrocarbon sites where significant concentrations of the indicator compounds are not anticipated, historical data for TPH does not allow identification of the individual groupings, and/or additional analysis is not cost effective. The full group or fraction analysis may also not be cost effective for sites such as retail/marketing sites with underground storage tanks where information about the type of hydrocarbon is available (i.e. the contamination is known to be gasoline from an underground storage tank). For these cases, generic risk-based TPH screening levels based on typical composition data (i.e. a typical weathered gasoline) can be developed, and less expensive TPH analysis and/or indicator analysis can be used to characterise the site. The group or fraction approach (e.g. the TPHCWG technical findings) can be adapted to fit within and support a broad range of regulatory programs.

One possible use of the group or fraction approach is to provide the technical basis for the assumption that the risk from TPH other than the indicator compounds (e.g. BTEX and the PAHs) is not significant under certain exposure scenario assumptions. In this case, the risk from TPH contamination would be evaluated based on the analysis of indicator compounds or on some non-risk-based criteria such as the potential mobility of the TPH as a non-aqueous phase liquid or NAPL. Regulations in the state of Ohio are a good example where a look-up table for TPH was developed based on soil types and the boiling range of the hydrocarbon contamination. The criteria were developed using models to estimate the percent of saturation required for the non-aqueous phase liquid (NAPL) hydrocarbon to be mobile. The States of Hawaii and Louisiana have developed similar policies where the upper limit for TPH screening levels (i.e. 5000 mg/kg and 10,000 mg/kg, respectively) are based on aesthetics or some other non-risk-based criteria.

Another possible use of the group or fraction approach is to develop generic criteria for TPH based on typical compositions of fresh and/or weathered hydrocarbon mixtures. A good example is a recent analysis of crude oils in the State of Michigan. Analyses of five representative crude oils from across the State were used to support cleanup levels of 10,000 mg/kg. At this concentration of TPH (i.e. 10,000 mg/kg), the concentrations of the carcinogenic indicator PAHs and the TPHCWG fate-and-transport fractions are below levels of concern (i.e. concentrations are less than RBSLs). The state regulatory agency has adopted 10,000 mg/kg as a generic screening level for TPH at all crude oil contaminated sites, and has retained indicator screening for benzene at non-weathered sites.

The technology is now available to develop risk-based approaches to address contamination of soils and groundwater by TPH. The technical findings of the TPHCWG provide the basis for application of a combined indicator and group or fraction approach within a broad range of regulatory programs. However, many technical and policy issues must be resolved prior to adoption of a risk-based approach for TPH within a particular regulatory program. The technical and policy issues include (but are not limited to): the acceptable risk level (e.g. 10^{-6}, 10^{-4}, etc.), the definition of potential receptors and exposure pathways to be considered as well as the associated parameter values, the selection of appropriate indicator compounds and the definition of the groups or fractions and associated physical/chemical and toxicological properties to be included in the analysis, etc. Once the technical and policy issues have been resolved, the findings of the TPHCWG can be used to develop a risk-based approach to TPH that is cost effective, protective of human health and safety and the environment and consistent with the overall regulatory program. These approaches can range from detailed site-specific assessment to generic criteria based on typical compositional data for petroleum hydrocarbon products or even conclusions that in some cases, TPH does not pose a significant human health risk in the absence of a small set of specific indicator compounds (e.g. benzene, etc.).

3.6 TPHCWG REFERENCE LIST

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APPENDIX 4 LIGHT NON-AQUEOUS PHASE LIQUIDS (LNAPL)

4.1 INTRODUCTION

Petroleum hydrocarbon products such as gasoline, kerosene, diesel and fuel oil are water-immiscible. They are referred to as light non-aqueous phase liquids (LNAPL), because they float on water. When they enter the ground, they partition into four phases. Small portions evaporate into the air, or absorb onto soil, or dissolve into groundwater, while the majority exists as neat product.

The LNAPL migrates downwards through the unsaturated zone of the ground as long as the residual saturation of the soil (i.e. the soil's holding capacity of the product) is exceeded. Below the residual saturation level, the LNAPL is immobile. If sufficient product enters the ground for it to reach the capillary fringe of the first encountered water table, downward migration of the LNAPL will cease and it will form a layer of so-called "free product". The presence of "free product" in the ground is inferred when a layer of LNAPL is detected above the groundwater in a monitoring well screened across the water-table.

When free product LNAPL is detected in groundwater monitoring wells it is not straightforward to determine the amount of material actually residing in the subsurface, or its potential to move, and the level of risk it poses. It is also not straightforward to predict the amount of material that can be removed by conventional means and the risk reduction benefits provided by this removal.

Often the answers to these questions are surprising. Free product LNAPL is not as easy to remove as might be thought. Recoveries in the region of 20%-30% are generally the best achievable. Those reporting higher recoveries may have either underestimated the amount of free product LNAPL in the ground, or based their recovery estimations on the volume of oil and water emulsion removed rather than on the volume of LNAPL itself.

Early on, attempts at free product removal were initiated without a firm technical understanding of the subsurface migration and the recoverability of these materials, and without a context of risk reduction or risk management. Consequently, many remedial efforts were initiated in situations, which presented little or no risk, and many remedial approaches resulted in little or no appreciable reduction in risk levels. In short, mass reduction did not necessarily equate to risk reduction.

The intent of this paper is to provide an indicator to the major factors associated with the risk and recoverability of "free product" LNAPLs in the subsurface. This paper will discuss the topic without dependence upon mathematics or diagrams of saturation curves. It presents a simplified picture of what is a complex subject in order to communicate the basic principles and messages.

4.2 MODELLING LNAPL BEHAVIOUR

The movement of LNAPL in the subsurface is a multi-phase problem (LNAPL, water and air). Complex multi-phase flow models are required to predict the consequences of LNAPL spills in detail. Unlike dual phase modelling of groundwater flow, the effect of the unsaturated zone and the capillary zone cannot be ignored in LNAPL modelling. These models require a high degree of mathematical expertise to understand and use them. Given the variability and uncertainty that surrounds subsurface parameters, it is more appropriate to use simplified models to assess LNAPL migration at sites.

4.3 LNAPL MOVEMENT IN THE SUBSURFACE

If an LNAPL is released to the ground it will infiltrate due to the action of gravity and capillary forces. The greater the viscosity of the oil, or the smaller the spaces between the soil grains (soil pores), the slower the rate of entry into the ground. Just as with water, LNAPL will move and be retained in the soil pores along with some air and water. For most purposes, relative to air, LNAPL acts as the wetting fluid and displaces air from the tighter spaces. However, relative to water, LNAPL is the non-wetting fluid, meaning water will preferentially be drawn into the tighter spaces leaving the LNAPL to occupy the larger pores. As these spaces fill they reach a large enough saturation that the LNAPL can then enter adjacent pore spaces. This saturation level is known as residual saturation.

LNAPL cannot move further if the quantity of fluid at its front in a porous medium is below the residual saturation level. Thus only a limited quantity of LNAPL can spread vertically through a certain volume of material demonstrated in sand box models, where the release of LNAPL into dry sand produced a spherical zone of contamination. (The movement-limiting effect of the residual saturation level is the reason why sand is used to mop up surface spills on non-porous surfaces). Likewise, the amount of LNAPL left behind as it travels through soil is equivalent to the residual saturation level. For small releases a trail of residual oil is absorbed in the soil and never reaches the groundwater table.

The quantity of material released and the residual saturation level are key parameters for estimating the depth of penetration and volume of material that may be affected by a surface or sub-surface LNAPL spill. Residual saturation levels are a function of the properties of both the LNAPL and the soil.

If the quantity of product released is large or a slow leak continues for a considerable time, the LNAPL will continue to move downwards, leaving a percentage of its mass behind at residual saturation levels, until it meets a lower permeability material or the capillary zone above the first water table. Once prevented from moving downwards it will start to produce a lens of so-called free product with saturation above the residual level. This lens of free phase product will then expand laterally to produce a circular shape in a homogenous deposit or an irregular shape (more likely) in a heterogeneous deposit. Since LNAPL is lighter than water the lens will depress and ultimately eliminate the capillary zone, depressing the water table underneath in a similar way as a saline / fresh water system. For a large volume one-off spill, lateral movement will continue until the force required to enter pore spaces is equal to the force provided by the thickness of product at the centre of the lens. In such cases the oil saturation within the lens is above the residual level but further lateral movement ceases, because there is insufficient energy left in the system. In the initial spill, gravity provides an extra force to encourage vertical movement reducing saturation to residual levels.

As with the vertical flow case, horizontal movement of a spill is contained within a limited distance from its origin. This is an important point for those new to the subject who may believe that the LNAPL will move over a very large distances as a thin sheen in a similar way to that observed on surface water bodies.

In examining LNAPL movement it is important to remember that the system exhibits multi-phase behaviour. Air and LNAPL reduce the rate of any movement, and moisture in the system, inhibit movement further. This interference is referred to as a relative permeability and is lower than the hydraulic conductivity. It is important to understand the difference between intrinsic permeability (units of length, measured in darcies), hydraulic conductivity (units of length/time) and relative permeability (unitless). Charbeneau and Weaver have produced a useful USEPA funded, simplified model (HSSM) for understanding NAPL movement in a homogenous deposit with saturated and unsaturated zones [1].

In any review of a field situation and model simulation, the effects of heterogeneity must also be considered since these modify behaviour. Effects are often counter intuitive, since they are dependent upon the interaction of viscosity, capillary effects, wetting and non wetting phases, hysteresis and relative permeability. All are explained in more detail in the references.

4.4 ESTIMATING QUANTITY OF FREE PRODUCT IN THE SUB-SURFACE

It is important to recognise that the thickness of LNAPL floating on the surface of the water in a groundwater monitoring well is not an accurate reflection of the thickness of free product in the formation. Indeed, the thickness in the well is always greater than the thickness in the formation and often considerably so. For this reason, the thickness in the well is referred to as the apparent thickness. In the early days it was believed that the thickness in the well was about 4 times the thickness in the formation; this is now known to be an over-simplification. It severely overestimates the thickness of free product in the ground in silty or clay soils. It is well known that the relationship between well thickness and formation thickness for free product depends on the permeability of the soil. The more permeable the soil, the closer the well thickness reflects the thickness in the ground. For example a well thickness of 1 m in a sandy soil may reflect a true thickness of 0.2 - 0.3 m, whereas the same well thickness in a silty or clay soil would represent a negligible thickness in the formation.

Another problem to consider is that LNAPL in a well can appear as an artefact of ground disturbance during well construction, even when the amount of free product is below residual levels in the undisturbed ground. Once in a well LNAPL cannot migrate outward unless the water table raises the oil lens above a previous level or falls into areas where oil has not been present. Often removal of oil from a monitoring well will demonstrate that quantities of removable oil are limited, since when removed by pumping, or a skimming recovery system, no new oil appears.

4.5 EFFECTS OF A FLUCTUATING WATER TABLE

Once an LNAPL reaches the water table it forms a lens. The water table will fluctuate naturally, moving the LNAPL in the lens into areas where it has not been present before. Thus it will smear product throughout the entire zone of water table fluctuation increasing the area containing residual phase LNAPL, and reducing even further the quantity that may be recoverable by pumping. Also, the residual saturation of oil below the groundwater table is greater than in the vadose or unsaturated zone, allowing more oil to become trapped and immobile as the water table rises.

It is well known that the thickness of an LNAPL layer in a groundwater monitoring well fluctuates up and down as the water table rises and falls. This corresponds to free product movement within and outside the smear zone in the vicinity of the well.

In general, the thickness increases as the water table falls and decreases as it rises. The reduction in product thickness can be explained by the trapping of oil in a monitoring well below the water table. Water rising, for example in response to a recharge event, finds that it is easier to flow round a LNAPL lens rather than moving the LNAPL upwards and through an area with reduced permeability caused by varying LNAPL saturations. Once it has flowed round the lens it can move into the previously unsaturated area on top of the oil. This prevents any further movement of the oil upwards, since the vertical force produced by the lower density of the oil is insufficient to move the product through the water. However if the water level falls below the lens, for example during groundwater recession, the oil can re-mobilise to a thickness sufficient to overcome pore entry pressures and move downwards.

4.6 LNAPL REMOVAL / CONTAINMENT

Removal of LNAPL by pumping is difficult because of the residual saturation level. If a lens of LNAPL exists, a portion of the free product may be removed from it by very careful low rate pumping. However once the degree of saturation reaches the residual saturation level, all flow will stop. The efficacy of free product removal system is dependent upon the number and spacing of locations used to extract the oil, rather than their size. Furthermore, since most lenses are thin, if the pumping rate is too high, ‘up-welling’ will occur, producing a number of smaller lenses. It may even trap oil in pockets below the water table. It is partly for this reason that dual fluid pumps are used to depress the water table and aid removal of free product. If water table depression is too large, the oil will smear and increase the zone of residual saturation.

The consequence of these effects is that not all the oil present below ground can be removed by pumping, which has been known to petroleum engineers for many years. Hence a source cannot be fully depleted and the effect of oil removal will be small since a large quantity of the mass spilt will remain at residual levels. Removal efficiencies rarely exceed 20%-30%. The efficacy and necessity of LNAPL removal by pumping must therefore be questioned before being used at any site.

Other available methods for LNAPL removal include soil removal and treatment / landfill or in-situ techniques such as soil vapour extraction. Before considering removal, it should be considered whether or not the risk truly merits this, taking into account exposure of the remediation workers during excavation, generation of dusts and vapours and the energy and resources required.

4.7 RISK ASSESSMENT AND REDUCTION

In risk-based management, the problems are managed when unacceptable risks are shown to exist and where there is a practical means of reducing the risk significantly. Given that LNAPLs leave a proportion of their mass in the material through which they move as a residual phase, potential risks are presented either by vapours, the soluble constituents or the LNAPL itself reaching a receptor via, for instance, a basement, surface water course, or service trench. Hence these issues are of more importance than the presence of the liquid, per se. The presence of LNAPL does not preclude the use of many of the risk assessment methodologies since vapour equilibrium and leachate saturation concentrations can be calculated for the contaminant.

If residual or free phase liquid is present, vapour problems may occur, usually from light hydrocarbon products such as gasoline. Simply reducing the mass of free product by pumping may not cure the problem entirely, since much of the cotamination will still be present as residual phase. However if significant risks exist from light products soil vapour extraction can remove the volatile components from both free product and the residual phase such that the risk from vapour movement can be minimised.

In the case of water-soluble components, the solubility of an individual component is limited by its presence in a mixture (the actual solubility is lower than that of the pure compound solubility in proportion to the mole fraction of the compound in the mixture – this is known as Raoult's Law).

Providing conditions are suitable, natural attenuation may limit the actual migration of dissolved phase components, such as BTEX, to a fairly small area. The questions to be addressed are: is a receptor present, are conditions for natural attenuation favourable, is there sufficient travel distance (and hence time) to the receptor at risk, and will the legislative framework permit use of natural attenuation. It is often assumed that monitored natural attenuation of contaminants in groundwater cannot be applied until free product has been removed. However, it has recently been demonstrated that in many soils, aggressive removal of free product via pump and treat has little or no effect on:

- reducing dissolved plume concentrations or lengths; and
- may not significantly reduce remediation time-frames, because of residual saturation.

Movement of free phase over any significant distance generally only occurs when:

- the volume lost from a single event is large, or slow continuous losses have occurred over a long time; and
- the permeability of the soil is high, or preferential flow paths such as service piping or fissures exist.

In these circumstances free product removal or interception may be required to prevent any further spread. If the material is very heterogeneous, locating the free product and ensuring its interception is unlikely to be simple. In such circumstances consideration must be given to the practicality of proposals and the optimum location for remedial action.

To summarise, free phase and residual phase management may be required if a risk-based review of the situation has shown that:

- There is a significant risk to a receptor from vapour or from the water soluble components;
- It is known that natural attenuation will not prevent an unacceptable risk to a receptor;
- There is risk of free product migrating along service trenches or the water table and reaching a receptor;
- There is risk of an explosion;
- The threat to an aquifer is long term and significant.

Risk management may consider a variety of options, one of which may be removal of free phase. However this may be technically difficult in-situ and alternatives such as plume containment, recharge reduction and treatment at the receptor should also be considered.

4.8 CONCLUSIONS

LNAPL movement in the sub-surface is an extremely complicated process. Accurate modelling requires detailed understanding of physics, mathematics, field parameters and the implications of assumptions and simplifications that are often not stated explicitly in the model documentation. However, complex accurate modelling is rarely required and simplified models when used appropriately can be perfectly adequate for understanding the movement and recoverability of LNAPLs.

LNAPL can only move if the concentration is above the residual saturation level for a particular soil type. If the unsaturated zone is thick enough downward migration may halt before the LNAPL reaches the groundwater table. For situations where sufficient LNAPL has been released to reach the water table, vertical movement is translated into lateral movement, but this movement is more difficult than vertical movement. This limits the lateral spread of the LNAPL producing a lens with concentrations above the residual saturation level, creating a "free product pool".

LNAPL cannot be fully removed by pumping from the subsurface since it is immobile at concentrations below the residual saturation level. Often, 80% or more of the NAPL will remain trapped in the soil pores and resist removal. Alternative source reduction methods such as soil vapour extraction can reduce these levels if products are volatile and sub-surface deposits are somewhat permeable. Any pumped removal of free product requires careful management to prevent water up-welling and the entrapment of oil below the water table. Likewise, excessive groundwater drawdown and resulting smearing by free product should be avoided.

Proposals for removal of "free product" at a site should explicitly state the expected result and the benefit, including the risk reduction that will be achieved, since mass reduction does not necessarily equate to risk reduction. LNAPL at residual saturation levels may still produce both vapour and groundwater contamination from soluble components, which may or may not pose unacceptable risks.

In cases where the LNAPL is not migrating substantially either vertically or laterally, and no significant risk exists, a monitored natural attenuation approach is likely to be appropriate. Alternatively, if a risk does exist, and if pumping and treating will not substantially address the risk, alternative management approaches such as containment, hydraulic control, vapour extraction, or enhanced bioremediation may be appropriate.

Vapour from an LNAPL may reach explosive levels or cause asphyxiation if it enters confined spaces and thus can be an immediate threat to human health. The potential for this risk must be evaluated and corrective action taken if it exists. In such cases soil vapour extraction can be an effective means of reducing risk to acceptable levels.

4.9 REFERENCES

1. Charbeneau, R.J. et al (1999). Free-product recovery of petroleum hydrocarbon liquids. API Publication 4682, p. 178. Washington DC: American Petroleum Institute

APPENDIX 5 TOXICITY ASSESSMENT FOR HUMAN HEALTH

5.1 INTRODUCTION

The purpose of the toxicity assessment is to collect and weigh the available evidence regarding the potential for particular contaminants to cause adverse effects in exposed individuals and to provide an estimate of the relationship between the extent of exposure to a contaminant and the increased likelihood and/or severity of adverse effects. Adverse effects are broadly characterised as carcinogenic (resulting in tumour development or other forms of cancer) or non-carcinogenic (all other forms of toxicity unrelated to cancer effects).

Several authoritative organisations (e.g. the World Health Organisation, WHO) including specific countries (e.g. the US Environmental Protection Agency (USEPA) and the UK Committees on Toxicology (COT) and Carcinogenicity (COC) have developed toxicity criteria for several chemicals. Unfortunately, toxicity criteria are not available for all potential contaminants, in which case, a mechanism must be available to develop these. This paper will describe, in general, the methods used for developing human toxicity criteria and suggests that these criteria be developed using the most recent and available peer review data and methodology. In addition, some general discussion on specific issues is provided, including the use of bounding estimates when toxicity criteria are not available, benchmark dose methodology, and bioavailability.

5.2 CURRENT METHODS OF TOXICITY ASSESSMENT

During the past 20 years, risks from exposure to carcinogens and non-carcinogens have been assessed using fundamentally different approaches. Carcinogenic risks have typically been quantified using mathematical modelling approaches such as the linear low-dose response model. On the other hand, acceptable exposures to non-carcinogens have been estimated by applying uncertainty or adjustment factors to no-observed-adverse-effect levels (NOAELs). The use of this dual approach is currently being questioned and evaluated.

As stated above, toxicity criteria for non-carcinogenic effects have been developed based on the concept that there is a "safe" (threshold) level of material to which humans can be exposed without adverse effects. These criteria are often derived for chronic exposures (usually over a lifetime) by applying uncertainty and/or adjustment factors to intake levels observed to have little or no effects in human or animal studies. These are typically expressed as a tolerable daily intake (TDI) or reference dose (RfD) or reference concentration (RfC).

The first step in evaluating the potential carcinogenicity of a material is to determine if the material has been shown to produce tumours in exposed humans or in controlled animal studies. The EC Dangerous Substances Directive (67/693/EEC) provides three categories (1, 2, and 3) corresponding to designations of materials as a proven human, suspected human and suspected animal carcinogen, respectively. The USEPA and International Agency for Research on Cancer (IARC) organisations also have classification schemes.

Depending on mode of action, carcinogenic materials may be divided into genotoxic (having the ability to mutate genetic material and eventually initiate tumours, also referred to as mutagenic) or non-genotoxic (non-mutagenic). It is generally accepted that whereas non-genotoxic materials may exhibit a threshold, any exposure to genotoxic materials may potentially lead to tumour formation. For materials classified as carcinogenic, a determination of an "acceptable" (genotoxic) or "safe" (non-genotoxic) exposure level is driven by the mode of action of producing the carcinogenic effect.

Thus, for non-genotoxic materials, a TDI ("safe" level) may be derived from no (or lowest) observed adverse effect levels, i.e. NOAEL or LOAEL (typically from animal studies) combined with uncertainty/adjustment factors. The process is comparable to that used for non-cancer effects. This general approach is favoured by the WHO and several European countries. It has not traditionally been used by the USEPA until recently (1996) when the USEPA proposed its new cancer guidelines which take a more mechanistic approach (taking into account how the specific cancer is formed).

For genotoxic materials (where it is assumed that no thresholds exist), extrapolation methods are often used to calculate a sufficiently low level that is "acceptable". WHO and USEPA typically use mathematical modelling methods (e.g. one-hit, linear multi-stage) to calculate this value, often expressed numerically as a slope factor (SF) or a unit risk factor (URF). Not all countries favour this method. For example, in the United Kingdom, a mechanistic approach is typically used rather than a mathematical modelling approach. In fact, efforts are currently underway both in the US as well as in other parts of the world to harmonise toxicity methods. It is expected that mechanistic evaluations will continue to gain acceptance.

5.3 SOURCES OF TOXICITY DATA

Typically, toxicity assessments are not performed for individual chemicals at individual sites. Rather, as far as possible, toxicity values are obtained from the peer reviewed literature, preferably from an authoritative source that used a scientific consensus process to develop appropriate values. In Europe, the World Health Organisation is a useful source for such data, if values are not generated on a country-specific basis, e.g. Germany, the United Kingdom. In the US, the Environmental Protection Agency's Integrated Risk Information Service (IRIS) is the primary toxicity database and can be used as a supplemental data source in Europe. However, because the approaches for developing these criteria are not yet harmonised globally, care must be taken when transferring criteria between the regions.

The major sources of compiled data (excluding country-specific one) include:

- World Health Organisation/International Program on Chemical Safety (WHO/IPCS) Environmental Health Criteria documents;
- WHO Guidelines for Drinking Water Quality and Air Quality in Europe;
- USEPA Integrated Risk Information Service (IRIS);
- Monographs of the International Agency for Research on Cancer (IARC);
- Reports of the Agency for Toxic Substances and Disease Registry (ATSDR).

5.4 GENERAL GUIDANCE ON DERIVING TOXICITY CRITERIA

The following discussion provides an overview of a process that might be used when toxicity data are available for a specific chemical but toxicity criteria have not been developed by an authoritative organisation.

Available data should first be evaluated to determine the likelihood that the agent is a human carcinogen. If the chemical is determined to be a likely or possible human carcinogen then a toxicity value (e.g. slope factor or TDI) should be calculated based on most recent and available information from peer reviewed journals. The most relevant and current scientific methods should be used in making these determinations. A toxicity value (e.g. TDI, RfD, RfC) should also be developed for the potential non-carcinogenic effects using standard methods from the WHO or from country specific guidelines, e.g. UK COT and COC, USEPA.

For many chemicals, toxicity data exist for only one route of exposure, usually ingestion. Extrapolation to other routes must be done with appropriate care and only if the toxicological endpoints or mechanism of action is the same irrespective of route.

The toxicity value must be based on peer reviewed literature that includes all relevant sources of data and must be a balanced description of both positive and negative findings on the toxicity of the chemical, the weight of evidence supporting the toxicity value, and the main sources of uncertainty of the toxicity value documented in the risk assessment report's uncertainty section.

5.5 BOUNDING ESTIMATES (USEPA / AIHC DEMONSTRATION PROJECT, 1998)

Humans are exposed to many compounds of toxicological interest for which risk estimates have not been derived. Bounding estimates are a simple mechanism that provides a means to estimate a range of risk from exposure to these substances.

Bounding estimates based on acute dose-response data may be useful for estimating a range of risk for exposure to chemicals lacking adequate subchronic (less than a lifetime) or chronic (long-term, lifetime) toxicity studies. Bounding estimates are derived using default uncertainty factors as opposed to data-derived uncertainty factors. Estimated toxicity values using this approach are expected to be more conservative than values based on a more substantial database.

The use of this technique generally leads to an imprecise risk estimate that is conservative, necessitated, in part, by the uncertainties inherent in extrapolating from acute to chronic exposures.

5.6 BENCHMARK DOSE (USEPA / AIHC DEMONSTRATION PROJECT, 1998)

A key concept in toxicity assessment is the use of some critical effect level adjusted by uncertainty and modifying factors to derive a "safe" dose estimate. Traditionally, the critical effect level is the no-observed-adverse-effect-level (NOAEL) or lowest-observed-adverse-effect-level (LOAEL) developed from chronic or subchronic animal studies or human exposure information. In either case, this approach has an inherent limitation: the critical effect level may simply be an artefact of the doses utilised in the study. This limitation may be addressed by the application of the benchmark dose (BMD) concept.

A BMD is defined as a statistical lower confidence limit on the dose producing a predetermined level of change in adverse response compared with the response in untreated animals (the benchmark response, or BMR). The benchmark dose method utilises data for the critical effect to fit a dose-response curve. The 95% lower confidence limit of this curve is used to estimate the in 10% of the test population (LED10). This is the benchmark dose. Application of appropriate uncertainty and modifying factors to the benchmark dose results in a reference dose estimate. In other words, the BMD is used in place of the NOAEL to derive the reference dose.

The benchmark dose methodology is a valuable tool because it applies data from the dose-response curve in which effects are observed to determine a point of departure for estimating the reference dose. With an understanding of mechanism of toxicity and an adequate model, estimating potential risks associated with exposure lower than the benchmark dose might also be possible. This approach is preferable over the use of a NOAEL when data are sufficient to generate credible benchmark doses, or where determinations of the NOAEL are problematic. It is particularly useful when the data and model are consistent. The benchmark dose methodology is a powerful and welcomed addition to the tools available to risk assessors.

The benchmark dose methodology should be used on a chemical-specific basis depending on the adequacy of the toxicity database for given endpoints. Work remains to be done in two areas: 1) determine the effect of sample size, dose placement, and model selection on the final estimates of the reference dose estimate, and 2) the relationship of the benchmark dose estimate to the NOAEL.

5.7 BIOAVAILABILITY (USEPA / AIHC DEMONSTRATION PROJECT, 1998)

Bioavailability can be defined in two ways: 1) absolute bioavailability - the fraction of a substance that is absorbed into the body, or 2) relative bioavailability - the ratio of absolute bioavailability in an environmental medium (e.g. soil) relative to the absolute bioavailability in the medium of a reference toxicity study. Acceptable contaminant limits for the ingestion of soil are often established using an assumption of 100% absolute bioavailability. However, specific forms of a contaminant (e.g. metal species) present in soil may have different bioavailabilities, thus presenting the opportunity to develop more realistic risk-based soil cleanup standards. A specific form of a contaminant with low bioavailability results in decreased exposure to humans, and, therefore, decreased risk. Bioaccessibility, or the solubility of a chemical in the liquid phase of the gastrointestinal tract, can be estimated using in vitro methods and is likely a conservative surrogate for bioavailability.

Bioavailability has traditionally been a consideration for metals, but can also be applied to semi-volatile or non-volatile organics and inorganics. Bioavailability can be a factor in the assessment of risk by the inhalation and dermal routes and in various types of environmental media.

Bioavailability can be a major data gap in risk assessments of contaminated sites. Using an assumption of 100% absolute bioavailability can result in high estimates of risk, an increased quantity of soil to remediate, and increased costs. If bioavailability data are available, certainty in the risk estimates may be improved. This added certainty confers greater confidence in risk management decisions.

Use of bioavailability data generally requires greater knowledge of the chemical form of the constituents of concern (e.g. speciation of metals), as well as increased knowledge of the physical characteristics of the environmental media. This knowledge is important to risk managers because it provides greater understanding of the potential health risks posed by chemicals remaining after remediation.

Bioavailability has been considered in many remediation decisions; however, it has not been universally applied. The major limitation is the need to obtain site-specific data that typically increases assessment costs and time. On the other hand, when site-specific data are collected, decisions are generally easier to make are more defensible.

APPENDIX 6 PROBABILISTIC RISK ANALYSIS IN ENVIRONMENTAL SITE MANAGEMENT

6.1 INTRODUCTION

Exposure factors used in environmental health risk assessments include human exposure factors (physiological, contact/intake rate, time/activity patterns); physical parameters (e.g. room sizes and volumes) and fate and transport parameters (e.g. organic carbon, hydraulic conductivity). These factors are typically represented by a range of possible values either because of measurement error (uncertainty) or true variability in the "populations" from which they are determined. Depending on the availability of data and the goals of the analysis, exposure factors may be described using a single point value, a range of values representing different possibilities, or a distribution of values. Probabilistic evaluations of risk use distributions of exposure factors in the risk algorithms to produce a probability distribution of risk. This paper will describe the role of probabilistic risk analysis in environmental site management.

6.2 PROBABILISTIC RISK ANALYSIS (PRA)

Often risk assessments are performed using a deterministic (single point) approach to estimating risk. The single point estimates of the various input parameters are often each conservative, thus leading to a compounding of the conservatism and a very conservative overall risk estimate.

Exposure-related variables such as duration or frequency of exposure, are generally recognised as having a range of possible values that exhibit both variability and uncertainty. Variability represents true heterogeneity in a well-characterised phenomenon that usually cannot be reduced through further measurement, while uncertainty represents ignorance about a poorly characterised phenomenon that may be reduced through additional measurements. Probabilistic analysis can account for both variability and uncertainty and, thus, is a useful tool for estimating risk or conversely estimating an acceptable environmental target concentration based on an acceptable risk level.

Using ingestion of drinking water as an example, groundwater target concentration (safe/acceptable level) could be defined by the following equation:

$$\text{Groundwater Target Concentration} = \frac{\text{Allowable Intake of Toxin x Body Weight}}{\text{Water Ingestion Rate x Days at Exposure Location}}$$

Each of these exposure factors, e.g. body weight, water ingestion rate, duration, can be described by a single point, a range or a distribution. **Table A1** below provides some values for an adult residential receptor (i.e. point value, distribution, mean, range). Substituting a random point from the distribution for each of the four variables into the equation and solving for the target groundwater concentration results in a deterministic evaluation. Repeating this process many times results in an overall distribution of groundwater concentrations depicted in **Figure A1**. This distribution describes the relative frequency (probability) with which these concentrations would occur in the population described by the four variables.

Table A1 Typical Values for an Adult Residential Receptor

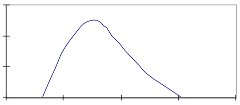
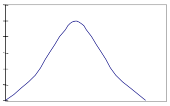
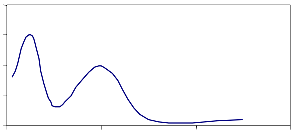
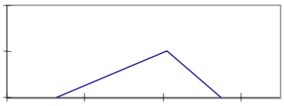
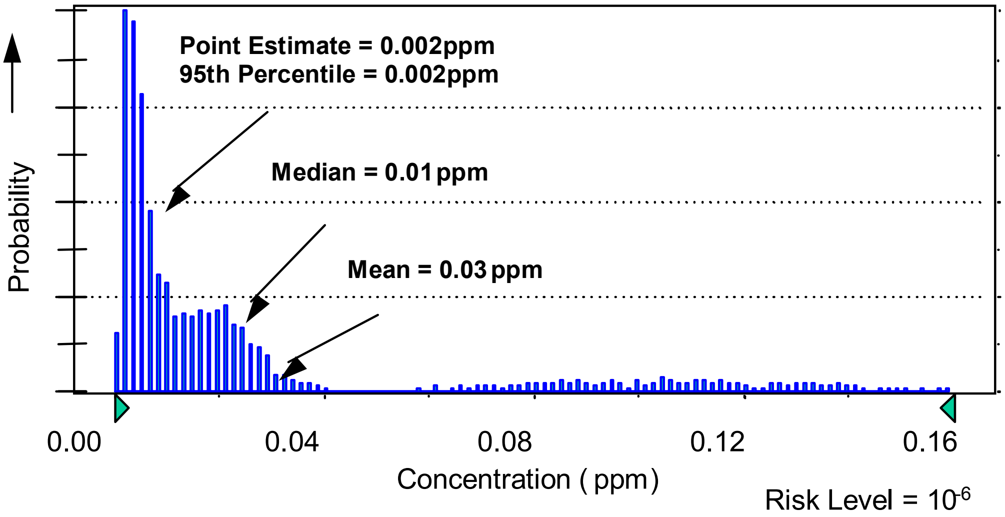
Factor	**Reasonable Maximum Exposure Value**	**Distribution**	**Mean**	**Range**
Body Weight (kg)	70		71	32 - 115
Ingestion Rate (l/day)	2		1.4	0.1- 4
Years at Home (yrs)	30		8	1 - 50
Days at Home per Year (days/yr)	350		351	323 - 365

Figure A1 Forecast Groundwater Target Concentration



A major benefit of using PRA comes from the ability to use the full range of data in the assessment and present the full range of results for complex risk management decisions. The 95th percentile of the overall calculated risk distribution above corresponds to the reasonable maximum exposure (RME), a typical regulatory risk management decision point. However, other estimates of risk (e.g. central tendency, and maximum) are readily available from the distribution. It should be emphasised that the use of RME, the 95th percentile or some other percentile point value from the probability distribution is strictly a policy decision.

6.3 THE ROLE OF PRA IN ENVIRONMENTAL SITE MANAGEMENT

When adequate supporting data are available, PRA is an important tool that can assist risk assessors in evaluating and characterising the variability and uncertainty in risk estimates.

In addition, PRA may be useful when site conditions exceed screening criteria calculated using conservative point estimates; when it is necessary to rank exposures, exposure pathways, sites or contaminants; or when the cost of regulatory or remedial action is high and management decisions may depend on the details of the risk assessment. Thus, PRA can be quite useful for defining generic (Tier 1) screening levels as part of a regulatory program.

The use of PRA to develop site-specific cleanup goals is resource intensive and is thus inappropriate for simple evaluations. Although, the use of probabilistic analysis for risk assessments associated with site remediation has advanced significantly in the last five years, there are still data gaps, which also limits its utility on a routine basis. It is suggested that probabilistic analysis be considered as part of a Tier 3 approach to risk assessment in the environmental site management process.

An often forgotten component of the risk assessment process is the characterisation of uncertainty. Uncertainty represents ignorance (or lack of perfect knowledge) about poorly characterised phenomena or models (Burmaster and Anderson, 1994). The concept is important and indeed implicit in the risk-based approach but is often ignored in practice. For example, the generic environmental targets (e.g. acceptable groundwater concentration) in risk-based decision-making approaches are acknowledged to be conservative and one of the rationales for being conservative is to account for the uncertainty inherent in developing the standards.

At an initial level (Tier 1), point estimates of exposure and risk (or site-specific standards) may be developed that describe both the sensitive individual receiving the "reasonable maximum exposure" (RME) or the "most likely exposed" individual (MLE). The RME portrays the highest level of human exposure that could reasonably be expected to occur and is calculated using a mixture of conservative default assumptions (e.g. 70 kg body weight, 70 year lifetime) and upper bound (e.g. 95th percentile) exposure estimates. In contrast, the MLE is calculated using "median" exposure estimates. It has been argued that in estimating the RME, the use of many conservative assumptions results in exposure estimates that are unrealistically high. This is clearly illustrated in **Table A2** where the use of RME exposure estimates rather than the more reasonable MLE estimates results in an overall daily exposure estimate that exceeds the MLE by a factor of 1203. In spite of this, many risk managers use the RME rather than the MLE as the decision point (i.e. for many regulators only exposures below the RME are considered acceptable).

Table A2 Illustrative Comparison of Two Single Point Exposure Estimates

Exposure Factor	**MLE (best estimate)**	**RME (upper bound estimate)**	**Overestimate**
Chemical concentration in soil (from a random site)	40 mg / kg	361 mg / kg	9 times
Rate of soil ingestion	25 mg / day	100 mg / day	4 times
Frequency of exposure	35 days / year	350 days / year	10 times
Duration of exposure	9 years	30 years	3 times
Life time exposure	0.315 mg	379 mg	
Exposure per day and per kg bodyweight (70 kg and 70 years)	1.8 x 10^{-7} mg / kg day	2.1 x 10^{-4} mg / kg day	1203 times

It is strongly recommended that a qualitative evaluation of the uncertainty in the risk assessment input parameters is undertaken. Such an evaluation should indicate the most uncertain and most sensitive parameters and how they may impact the final results. It is important that the uncertainties inherent in the both the toxicity assessment as well as in the exposure assessment be put into perspective.

At some middle level of effort (Tier 2), statistical estimates (experimental estimates, population variability, and estimation error) could be listed and the impact of these on the results discussed. A more formal sensitivity analysis may be performed to rank the input parameters on the basis of their contribution to the uncertainty.

At the highest levels (Tier 3), methods to quantitatively address variability and uncertainty (including but not limited to probabilistic analysis) could be used to carefully determine the overall precision of the risk estimates as they relate to scenarios, models and inputs.

The EPA Risk Assessment Forum has developed a policy on the use of probabilistic analysis (May 1997). This policy in part states:

> *a "tiered approach" may be helpful in deciding whether or not a Monte Carlo [probabilistic] analysis can add value to the assessment and decision. In a tiered approach, one begins with a fairly simple screening level model and progresses too more sophisticated and realistic (and usually more complex) models only as warranted by the findings and value added to the decision. Throughout each of the steps in a tiered approach, soliciting input from each of the interested parties is recommended. Ultimately, whether or not a Monte Carlo analysis should be conducted is a matter of judgement, based on consideration of the intended use, the importance of the exposure assessment and the value and insights it provides to the risk assessor, risk manager, and other affected individuals or groups.*

Several user-friendly computer programs (add-ins to spreadsheets) are currently available to facilitate the use of PRA in both fate and transport and human exposure modelling.

Although tools (e.g. software models such as “Crystal Ball” and guidelines on how to use the technique) are becoming increasingly available to implement probabilistic approaches, three major areas that require attention have been identified:

- A need exists for "consensus" reference distributions for key parameters and mechanisms to determine when site-specific distributions are appropriate;
- Additional efforts are needed to address minimum data requirements to support distributions;
- Because the results of the assessment are more complex, effort is needed to ensure that the results are appropriately interpreted and communicated.

APPENDIX 7 ECOLOGICAL RISK ASSESSMENT IN SUPPORT OF RISK MANAGEMENT OF CONTAMINATED SITES

7.1 INTRODUCTION

Ecological risk assessment (ERA) is a process for evaluating the likelihood of undesired ecological effects as the result of exposure to chemical contaminants. Properly planned ERAs provide a means of balancing and comparing risks associated with environmental problems and can facilitate informed risk management at contaminated sites. In contrast to human health risk assessment which considers individuals of a single species, ERAs assess the likelihood that impacts may occur or are occurring to an array of potential ecological receptors that may include diverse taxa with varying sensitivities to contaminants.

This paper provides an overview of ERA components and identifies considerations which are important to effective implementation of the process and use of information in risk management decision making. It should be noted that ERA issues are very site specific, and may be subject to regulatory requirements. Included in the paper is a discussion of desired ERA attributes or elements including: a tiered approach, reliance on a weight-of-evidence, use of screening criteria and modelling, and incorporating flexibility and reasonableness with professional judgement.

7.2 ERA COMPONENTS

Although there exist a variety of approaches and guidance for conducting ERA, in general, the majority consist of three basic components: problem formulation, risk analysis, and risk characterisation. During the implementation of an ERA, chemical, toxicological, and ecological information are systematically evaluated and, as far as possible, science-based conclusions are reached on the potential risks. This is frequently an iterative process, meaning that ERA components may be repeated, so that uncertainties can be reduced and more accurate conclusions reached to support decision making. The ERA results are used in conjunction with the many other inputs needed for informed risk management of contaminated sites.

7.2.1 Problem formulation

This is the planning phase of the ERA where the objectives and scope are established. Important considerations such as the technical, regulatory, and policy contexts of the assessment are integrated during this phase. Discussions between the risk manager and risk assessor should take place to ensure that the ERA is conducted in a manner that will provide useful information for risk management decision-making for the site. The contaminants of potential concern (COPCs), relevant ecological receptors or habitats, and potential complete exposure pathways are identified and incorporated into a conceptual model. Other constituents and parameters that are not of concern can be removed from further consideration.

7.2.2 Risk Analysis

This phase consists of the science-based assessment of exposures and potential effects. In order for ecological receptors to be at risk, contaminants must have the ability to cause an adverse effect and must come into contact with an ecological receptor for a sufficient duration and intensity to cause the adverse effect (i.e. a complete exposure pathway exists) (USEPA 1997). The ERA should focus on the contaminants and relevant ecological receptors only where complete or potentially complete exposure pathways exist.

7.2.3 Risk Characterisation

The results of the risk analysis are evaluated and explained in the context of the ERA's scope and objectives. The risk characterisation includes a description of the assumptions and uncertainties associated with the analysis. The potential risks are identified and the ecological significance (i.e. potential seriousness and permanence) of the risks or impacts are described.

7.2.4 Risk management

This is the final component of this process. It is here that risks to valued ecological receptors are considered during the decision-making process. Risk management must balance the benefits and costs (including adverse impacts) of the various alternatives. However, risk management decisions are not based solely on technical merit of the ERA, but also include consideration of other factors such as societal values, economics, politics, and regulatory policy. The goal of risk management process is to select the most reasonable and acceptable alternative to meet risk management objectives.

7.3 CONSIDERATIONS

The effective design and implementation of an ERA requires flexibility to meet site-specific risk management goals. The ERA activities should integrate sound scientific approaches with reasonableness and professional judgement. There are a number of key issues that should be considered during the risk assessment process. These are discussed below in the context of the value that they may add to the risk management process.

7.3.1 A Tiered Process

A tiered or phased process is a rationale and efficient approach for implementing ERAs. Each tier involves increasingly sophisticated levels of data collection and assessment. Most sites require no more than a simple, subjective assessment to demonstrate that they do not pose unacceptable risks. In some cases it may be necessary to proceed to higher tiers to reach scientifically defensible conclusions.

The first tier consists of a preliminary assessment to determine whether site conditions, applicable regulations, or other considerations indicate that an ERA is appropriate for a site. If the site merits further evaluation, a screening or baseline ERA would be conducted as part of the next assessment tier. Screening criteria (described below) are used during these early tiers to focus or prioritise the assessment on contaminants and ecological receptors of concern. If later assessment tiers are needed, progressively more site-specific data and sophisticated tools are used to assess risk.

7.3.2 Screening Criteria

Screening criteria are effective tools to aid decision-making during an ERA. Screening criteria can provide the basis for decisions on whether further ERA is appropriate for a site, and if so, help focus the assessment by identifying issues of potential concern and eliminating from further consideration those that are not of concern. Criteria used to screen sites include: the existences of complete exposure pathways, the current or future use of the site, or the proximity of the area to important ecological resources. For instance, screening criteria could be used to identify industrial or other properties that would not serve as habitat for wildlife, and remove them further consideration during the ERA.

Ecotoxicological benchmark values and regulatory criteria can also be used as screening criteria. These values are the concentrations of chemicals which do not pose unacceptable risks to certain ecological receptors which are normally invertebrates or plants in a terrestrial setting. Benchmarks may be useful for ERAs because their application can narrow the evaluation to chemical constituents of significant ecological concern, thus saving time and resources. However, since benchmarks are generic, normally highly conservative, and not derived for site-specific conditions or higher trophic level species, it is inappropriate to apply them as cleanup levels for a site.

Contaminants may occur naturally at some locations. These 'background' sources of contaminants may include both naturally occurring components of soil (e.g. iron, arsenic), as well as non-site related anthropogenic releases (e.g. PAHs from fossil fuel emissions). Measures of background levels of the chemicals of interest also serve as effective screening criteria. Chemicals of interest that occur at levels at or below background concentrations can be removed from further assessment because potential ecological effects from these chemicals cannot be attributed to site-related activities. The use of background levels as a screening criterion focuses the ERA on those site-related contaminants that pose potential risks to ecological receptors.

7.3.3 Relevant Ecological Receptors and Habitats

Since it is not feasible to assess risks to each and every organism that may occur at a site, representative or relevant species and habitats must be identified. Relevant ecological receptors and habitats for ERA are those that are valued or must be protected to meet management goals. These receptors and habitats may include those that are protected by regulatory mandate (e.g. endangered species), valued by society (e.g. game species), or key components of the ecosystem. Valued habitats may include aquatic habitats such as streams, lakes, and estuaries, wetlands, and ecologically important areas that serve as feeding areas, breeding grounds, or refuge for species of concern. Typically, commercial or industrial properties would not be considered valued habitats, nor would invasive, non-native, or non-desirable species be considered relevant ecological receptors for ERA purposes.

7.3.4 Basing Decisions on a Weight-of-Evidence

ERA conclusions should be based on the weight-of-evidence (also known as lines of evidence); meaning that information which is more applicable to a site and / or less uncertain, is considered with greater emphasis than information which is less applicable to a site, or less certain. As with a tiered assessment approach, a weight-of-evidence uses adequate quantities and types of information to support conclusions with an acceptable degree of uncertainty. In general, four primary lines of information can be used to assess ecological risks: 1) measures of contaminant levels at a site, 2) results obtained from laboratory ecotoxicity studies, 3) field observations and ecological measures, and 4) modelling. If any line of information is inconclusive, additional information can be used to supplement the assessment. Understanding of the relative strengths and limitations of different sources of information is used to focus the investigation on areas providing the greatest benefit to the assessment.

Contaminant concentration measurements often provide the first information on whether potential risks exist. Comparison of contaminant levels in media to appropriate ecotox benchmarks and background values can be done early in the assessment. Contaminants that exceed these screening values are considered for further assessment. Due to the variability in chemical concentrations that often occur at a site, the mean concentration or the upper confidence level of the mean (UCLM) may be used as a conservative estimate of contaminant levels.

Laboratory ecotoxicity studies, or bioassays, are often used to assess potential contaminant risks. Laboratory bioassays provide a more realistic assessment of effects than benchmarks. While these studies can effectively demonstrate that a contaminant or contaminated media may pose adverse impacts, care must be taken before extrapolating the results to conclude that risks exist under the site-specific conditions. Laboratory bioassays are conducted under controlled environmental conditions that tend to maximise exposures, and usually rely on surrogate species to make indirect assessments of site risks. As such, they are less robust than direct measures because they fail to establish whether the ecosystem itself is adversely impacted and do not account for site-specific factors. Due to their artificial nature and the uncertainties associated with laboratory bioassays, the results are typically conservative and often produce overly protective cleanup criteria.

Field observations and ecological measures are useful for indicating if there is impact associated with site contamination. They represent direct, qualitative or quantitative measures of overall ecosystem conditions. Natural mechanisms that allow ecosystems to adapt to environmental stresses can only be assessed by field observation. While direct field measures provide an important line of information concerning risks, these methods also have limitations and uncertainties than need to be considered. For example, it might be concluded that the observed ecological effects are due to natural variability in the local ecosystem, and not due to the contaminants present.

Modelling is a useful and powerful tool for estimating potential exposure and effects of contaminants on ecological receptors and in some cases may be the only mechanism to evaluate risks to some receptors, such as wildlife. Models are mathematical equations that represent relationships within an ecosystem. Due to the complexities in natural systems, all models are simple representations of ecosystem relationships. One advantage of using models is that they allow assessment of the relative importance of different factors and can used to evaluate risks under a variety of conditions. The appropriate application of models requires that assumptions be made concerning the nature of the ecosystem. Generally, the absence of appropriate input data for models limits their usefulness.

Models may be applied both deterministically or probabilistically. Deterministic modelling uses a single-point estimate for each exposure input variable and generates a single-point estimate of exposure or effects. In contrast, probabilistic modelling uses distributions that can be expected for each input variable to estimate a distribution of exposure or effects. Deterministic modelling is generally more suited for screening assessments, because uncertainty and variability are not addressed, so the resulting estimates are likely to overestimate actual risks. This technique is appropriate as a screening tool in order to focus attention on contaminants which can require further assessment, however it is not suitable for definitive risk assessments that will be used to support the development of remediation plans for complex sites. For definitive assessments, the probabilistic approach is generally preferred.

7.3.5 Consideration of Bioavailability

The bioavailability of a chemical is a major factor dictating the risk posed to receptors. A contaminant's bioavailability is affected by its interaction with the environment and biological receptors. To accurately characterise risks posed by contaminants, bioavailability should be considered as early as possible in a risk assessment, and can be readily incorporated into the tiered assessment process, moving from more conservative assumptions at lower tiers to more site-specific factors at higher tiers. Consideration of bioavailability will result in a more quantitative exposure assessment, reduce uncertainty in the assessment, and aid the selection of appropriate remedial measures.

7.3.6 Risk Associated with Remedial Actions

The ERA can include an assessment of potential impacts of remedial action measures. It is quite possible that remediation will cause greater damage to the ecosystem than leaving contaminants in place, and risk managers should balance the relative costs and benefits of remedial alternatives. In many instances, natural remediation will be the alternative that best meets risk management goal for protection of ecological values at a site.

7.3.7 Uncertainty

Risk estimation entails degree of uncertainty. Assumptions, extrapolations, and interpretation of results all contribute to the uncertainties involved in characterising ecological risk. As part of the risk characterisation, the degree of uncertainty should be identified and communicated along with the risk estimate. This will allow the risk manager to weigh these results with other considerations, thus producing decisions that produce environmental benefit, and direct resources to highest priorities.

APPENDIX 8 THE CONCEPTUAL SITE MODEL AND EXPOSURE PATHWAY ANALYSIS IN RISK-BASED CORRECTIVE ACTION

8.1 INTRODUCTION

The conceptual site model (CSM) is an often misunderstood and misused element of a Risk Based Corrective Action (RBCA) programme [1]. Many contaminated land professionals have concentrated on the use and comparison of various risk algorithms without comprehending how to relate the results to practical guidance on managing contaminated sites. A CSM is formulated as a final product, whereas it should really be an initial product that is refined as further information comes to light. The process underpins all subsequent work and analysis. It is the CSM that integrates the site characterisation data with the exposure pathway analysis data and provides a means of identifying acceptable options for corrective action [2].

The CSM may be presented as a series of diagrams (plan and/or cross sectional views), source-pathway-receptor valve diagrams, pathway-related chemical worksheets, maps or written explanations. The requirement is to produce a holistic view of the site, based on sufficient data for the size of the problem under study, that is quickly and easily understood. Uncertainties will be identified and then, if necessary, actions taken to reduce the magnitude of the uncertainty. It should be demonstrated at the end of the project that nothing of significance has been missed or under reported.

8.1.1. Development of the CSM

Development of the CSM starts with the initial collection of base data, which enables data gaps and uncertainties to be identified. Base data include information on the site history, surroundings (industrial, agricultural, residential), underlying geology, previous owners, materials and chemicals produced, stored, transported or used, and current and possible future land use. This base data is used to formulate the initial CSM. It is this model that focuses future field investigations. It is during this initial formulation stage that potential chemicals of concern (COCs) that may be present are identified, potential pathways and receptors identified, and exposure assumptions defined explicitly. Alternative corrective actions for particular contamination types are also introduced for consideration. In addition to evaluating potential human and environmental health risks, the CSM should also attempt to identify any safety risks that could result from contamination. For example, under certain conditions, explosive mixtures may be formed in confined spaces. Such risks that pose an immediate threat to human and/or environmental receptors and should be addressed and remediated immediately. In conclusion, all the data and assumptions are iteratively tested for reasonableness and if necessary, the CSM is refined. Thus, the major components of the CSM are:

- Site History;
- Geology and Hydrogeology;
- Land and groundwater use (current and reasonably potential future);
- Fate and transport properties of the COCs;
- Identification of receptors;

- Exposure pathway analysis; and
- Potential corrective actions.

The initial development and then iterative testing of the CSM is the key to correct application of risk based corrective action.

8.1.2. Exposure Pathway Analysis

The exposure pathway analysis quantifies or evaluates the magnitude, frequency, duration and routes of exposure. It is the key element of the CSM in risk based corrective action since only sites representing a risk need to be remediated and risks do not exist if exposure pathways are not complete.

The exposure analysis is typically performed in three steps:

- Characterisation of the exposure setting including:
    - the physical setting; and
    - potential exposed populations.
- Identification of exposure pathways which includes the integration of:
    - sources and receiving media;
    - fate and transport in the release media;
    - exposure points and exposure routes.
- Quantification of exposure at the receptor including:
    - environmental concentration; and
    - intake.

The exposure analysis process is well defined in various guidance documents from the US EPA and so is not reiterated here. However, background is provided on key concepts in exposure analysis needed to understand the role of generic versus site-specific pathway evaluation.

The exposure pathway describes the mechanism by which receptors (individuals or populations) may be exposed to the source. Pathways consist of a route of exposure and a transport mechanism, if the exposure point is not the same as the source. Typically, only complete or potentially complete pathways are included in the CSM.

A fundamental consideration in defining potential pathways is land use (e.g. residential, industrial, agricultural, etc.) and water use (e.g. potable, non-potable, recreational) scenarios. Activities that occur as a result of a given land use (or water use) scenario provide the basis for determining appropriate receptors and exposure assumptions about these receptors. For example, residential settings are likely to have children playing in soil and so direct ingestion of soil is a likely pathway for children in the residential setting. For industrial sites, direct ingestion of soil is also possible but the use of protective equipment and activity restrictions may reduce these exposures significantly to only incidental occurrences. The soil cleanup criteria for a residential vs. industrial CSM vary significantly.

8.2 CURRENT UNDERSTANDING OF SOME COMMON PATHWAYS

There are a number of potential exposure pathways at contaminated lands. Some of these are considered direct, i.e. contact with the source requiring little (e.g. direct inhalation of vapours) or no (e.g. direct ingestion of soil) transfer across media. Others are considered indirect because exposure occurs via a different medium than the source and there may be significant fate and transport mechanisms that may need to be taken into account. In general, it is simpler to determine the applicability of direct pathways as well as to evaluate them. Thus, the direct pathways are often used by regulatory agencies in the development of Tier 1 (generic) cleanup criteria. To use these generic targets, site conditions must reasonably conform to the default site conceptual model. If other relevant pathways exist, further site-specific evaluation may be warranted. For example, the site conceptual model for the generic evaluation may not be able to appropriately account for ecological receptors. However, ecological receptors may be identified on a site-specific basis and would have to be addressed (see Appendix on Ecological Risk Assessment).

Some direct pathways, such as direct ingestion of soil or groundwater and direct inhalation of volatiles and/or particulates from soil, are fairly well established and can be modelled routinely where they have been identified as complete pathways. At issue would be defining appropriate exposure factors (such as intake rate for the given population) since these factors exhibit a range of possible values. Typically, the level of conservatism desired defines the choice of exposure factors (maximum exposure versus average exposure). ECETOC has recently published a technical report on this subject [3].

Dermal contact (with soil or groundwater), on the other hand, is less well-defined particularly in terms of estimating intake (the mass of substance in contact with the body per unit body weight per unit time) and more importantly absorbed dose (intake multiplied by an absorption factor to account for mass actually present in the body). This pathway is best addressed at a site-specific level when identified as relevant. Although there is some guidance professional judgement may play a significant role in estimating dermal exposure.

Simple analytical models can address certain indirect pathways (e.g. soil leaching to groundwater and subsequent ingestion of groundwater). Although site-specific data inputs to these models are typically favoured as producing a more realistic estimate of exposure, site-specific data may not always be accessible. This is problematic for some specific indirect pathways, especially inhalation of vapours via intrusion into enclosed spaces. Modelling of this pathway is quite sensitive to site-specific factors such as soil moisture content and natural degradation of the vapours. Without this site-specific data, a monitoring approach may be preferable to the use of models that have been shown to be imprecise using generic assumptions. However, some modelling may have to be performed to meet future scenarios. The use of a combination of default and site-specific parameters may be the best approach provided the rationale for the choice of values is included.

8.3 USE OF THE CSM IN DEVELOPMENT OF TIERED CLEANUP CRITERIA

In general, the approach which is favoured by both industry and regulators, is one in which the Tier 1 clean-up numbers are derived using a generic CSM that includes pathways that are common (for given land uses). Sites that do not fit the "generic" CSM should have a refined CSM for developing clean-up goals based on site-specific data.

Finally, it is recommended that generic criteria (Tier 1) be based on a set of well established and validated pathways/routes of exposure selected to provide adequate protection of human health, safety and the environment. These targets should be consistent with specific land and water use scenarios. The generic CSM may include, but not be limited to groundwater ingestion, direct inhalation of volatiles, and direct ingestion of surface “soils”. The criteria for selecting alternate site-specific pathways (Tiers II and III) should include the availability of the scientific knowledge needed to mathematically model the pathways. In addition, adequate data should be available to provide for realistic model inputs. The models and their accompanying assumptions and data should be subject to validation with field data.

8.4 REFERENCES

1. ASTM (1995) Standard guide for risk-based corrective action applied at petroleum release sites - E1739-95e1. Philadelphia PA: American Society for Testing and Materials

2. ASTM (1995) Standard guide for developing conceptual site models for contaminated sites - E-1689-95. Philadelphia PA: American Society for Testing and Materials

3. ECETOC (2001) Exposure factors sourcebook for European populations (with focus on UK data). Technical Report No. 79. Brussels: European Centre for Ecotoxicology and Toxicology of Chemicals

APPENDIX 9 POINTS OF COMPLIANCE

Points of compliance are locations selected to be either at a contaminated source area or between it and the potential point of exposure of a receptor. Concentrations of the chemicals of concern must be at or below the determined target levels in the relevant environmental media (e.g. air, soil, groundwater, surface water) at this compliance point. Points of demonstration are locations where samples of the relevant environmental media are collected to demonstrate that compliance is achieved.

In a risk-based corrective action approach the initial phase of site assessment involves a conservative evaluation of the risks to human health and environment that a site may pose. Conservative screening levels are used and any potential receptors are assumed to be exposed at the point where the environmental media is worst affected. In other words the point of compliance is set at the source of contamination and the point of demonstration is each sampling location.

In reality the site-specific conditions are often such that the above assumption is not realistic. For example it is unlikely that a drinking water well would have its catchment zone in the shallow aquifer present beneath a refinery or that a child would have access to surface soils on a chemicals plant. In these instances a more realistic and yet still protective approach could be to set the point of compliance at the nearest point to the source at which a receptor could potentially come into contract with the contaminated media. Physical transport mechanisms can be modelled or measurements taken in order to estimate a more realistic exposure to any potential receptors.

Even in the case of stringent generic clean-up standards being in force there may be the opportunity to apply the fate and transport effects by extending the points of compliance and demonstration beyond the point of release. Many regulatory environments allow for natural attenuation to be considered in setting surface water discharge consents. Similarly, groundwater clean-up standards based on drinking water guidelines may still accommodate processes that dilute contamination emanating from source areas. As an example, drinking water guidelines are usually intended to refer to water quality at the tap (or relevant point of use) and not in the aquifer. So effects due to groundwater migration can be incorporated in the derivation of clean-up targets that remain protective of human health and the environment at the likely receptor locations (i.e. the point of compliance).

In order to determine the appropriate location of points compliance the following actions are required:

- Identify locations of current receptors;
- Identify locations of reasonable potential receptors;
- Identify current and projected land and usage;
- Identify areas where resource usage can be controlled or restricted through institutional controls;
- Estimate rate of contaminant transport.

Points of compliance should normally be located in areas where there will be long-term rights of access to the problem holder. This is to ensure actions such as monitoring and (if shown to be necessary) remedial measures, can be carried out without hindrance. If downstream of a source, points of compliance should be located at a distance associated with a reasonable travel time (e.g. one year) during groundwater transport. This is to allow sufficient time for further corrective action to be taken if the compliance criteria are not met. In the case of groundwater, local or regional restrictions on water use and/or physical limitations of the aquifer (e.g. low yield or water quality) should also be taken into account when establishing a point of compliance and/or demonstration.

APPENDIX 10 INSTITUTIONAL CONTROLS IN RISK-BASED CORRECTIVE ACTION

Institutional controls refer to non-engineering remedial measures; usually intended to influence human activities in such a way that they prevent or reduce exposure to hazards which may exist at the site. These are often a key element of the site remediation strategy.

The role that institutional controls play in the risk management approach for a facility is based on site-specific conditions and should be considered during the selection process. Like any other remedial alternative, they should be rigorously evaluated to determine their appropriateness, feasibility, and long-term effectiveness in protecting human health and the environment.

Institutional controls are often used in conjunction with, or as a supplement to, other measures such as treatment or containment to prevent or reduce exposure. An institutional control or a group of institutional controls, under certain circumstances, may serve as the sole remedy at a facility, although this is rare. However, institutional controls are not intended to be used as secured abandonment (i.e. physically securing a site and preventing exposure while making little or no effort to ensure that COCs do not migrate to and beyond the property boundary). Institutional controls are not normally appropriate as the sole remedy for off-site releases.

US EPA has developed guidance on the use of institutional controls at Superfund and RCRA corrective action sites, and the guidance may provide additional information regarding their applicability and use.

The following are examples of situations where institutional controls may be an appropriate component of a remediation strategy, or may be necessary to ensure that a remediation is protective:

- Where cleanup is protective for industrial but not residential exposures, requiring future use of the site (e.g. building houses);
- Where groundwater abstraction is to be prevented because of contamination;
- Where surface water is contaminated such that fishing restrictions should be imposed;
- Where soils are remediated at the surface but contamination at higher concentrations remains in the subsurface, thus requiring excavation depths to be limited;
- Where contaminant concentrations in soils are reduced to a level appropriate for residential use but a specific activity, such as gardening, might result in an unacceptable exposure;
- Where contamination is capped to prevent exposure and/or reduce leaching to groundwater, and activities that may damage the cap must be prohibited.

The use of an institutional control to meet a performance standard should include a mechanism to ensure the maintenance of the control. Such mechanisms are vital to ensuring that exposure to unacceptable levels of hazardous constituents is prevented.

10.1 TYPES OF INSTITUTIONAL CONTROLS

The following information is provided to help identify the various types of institutional controls that may be available and the tools that may be available to create them. The authorities should also be consulted to provide assistance in identifying the controls available for use, and which are acceptable to them.

Generally, there are three ways to control land and resource use: property controls, which rely on property law; regulatory enforcement controls, which rely on the authorities (usually local); and information mechanisms:

- **Property controls**: Property law provides a variety of mechanisms that can restrict or affect the use of property. Common examples include covenants and restrictions that limit future land use or prohibit activities that may compromise specific engineering remedies. For example, a restriction can be used to prevent an owner from developing a site for residential use. Property controls are based on generally applicable property law. As a result, they can be implemented without the need for intervention by regulatory authorities.
- **Regulatory controls**: Regulatory controls rely on the authorities to impose restrictions on the citizens and resources under their jurisdiction. Because they are implemented by third parties (normally local government), monitoring, maintenance, and enforcement are the most important considerations. Their effectiveness is dependent on the ability and desire of the governing authority to undertake such efforts. Examples of the mechanisms available to governmental authorities are zoning restrictions; restrictions on groundwater use; building restrictions; issuing of notices warning of potential risk; and creation of registries of contaminated sites.
- **Information mechanisms**: Information mechanisms such as deed notices are mechanisms for ensuring that parties to a property transaction (purchasers, tenants, and lenders) have an opportunity to be made aware of the environmental condition of the property prior to finalising a transaction. For example, a deed notice can disclose the specific location of contaminants at a site, and list any restrictions on site use, access, and development. A properly drafted and archived deed notice can be effective by ensuring that future landowners and users are aware of all relevant environmental information on the site.

10.2 OTHER CONSIDERATIONS FOR USE OF INSTITUTIONAL CONTROLS

Institutional controls should be robust over the time period required. This may come at some cost, and may justify re-examination of the costs of alternative remediation options.

Consultation with authorities should also include the Planning Authorities, to ensure that the institutional controls proposed are not in conflict with local development plans.

Where assurance of the effectiveness of the institutional controls requires periodic site inspection, provisions should be made for lawful access to the site.

Where the level of contamination is expected to reduce over time, e.g. by natural attenuation, then it may be possible at some stage for the institutional controls to be lifted. It is therefore important to set the criteria for the lifting of such restrictions.

APPENDIX 11 EUROPEAN GEOLOGY

11.1 INTRODUCTION

This paper presents a review of European geology. An important consideration in the generation of Risk-Based Screening Levels (RBSLs) at Tier 1 and site-specific risk assessments (at Tiers 2 and 3) are the assumptions that are made for the physico-chemical parameters of specific rock types underlying a site. In generating new tables of RBSLs on a site-specific or country-specific basis (or when performing site-specific risk assessments) attention must be paid to the geology underlying the site or geographic area in question.

This paper contains a review of the broad patterns of geological deposits that occur within Europe at large and a detailed discussion of each of the main parameters of concern as follows:

- fraction of organic carbon;
- porosity;
- hydraulic conductivity;
- bulk density;
- thickness of capillary fringe; and
- thickness of the saturated zone (depth to groundwater).

The values assigned to these parameters directly influence RBSLs and the outcome of site-specific risk assessments, and the values of site-specific target levels (SSTLs) calculated when risk estimates exceed acceptable levels.

A wide range of geological conditions exist across Europe and it is therefore very difficult to characterise each and every rock type that may be encountered beneath a specific site. Such an objective is outside the scope of this paper. What is summarised are the rock types commonly encountered in Europe, including a discussion on how rock types influence the values of each of the parameters listed above and the ranges of values that are likely to be encountered. It is important to note that made ground is not covered in this review. Many industry sites are, however, underlain by made ground which will characteristically be of uncertain and often variable composition. It is therefore important that, where such materials underlie a site, close attention is paid to their make-up so that realistic (conservative) parameter values can be assigned. This places considerable importance on the site investigation phase of any study.

11.2 ROCK TYPES

The geology of Europe is complex, comprising a diverse collection of rock types arising from the Precambrian to Quaternary times. In simple terms, however, the rock types can be grouped into three broad classifications as follows:

- unconsolidated sediments;
- consolidated sediments; and
- crystalline and metamorphic rocks.

Unconsolidated and consolidated sediments are formed from the weathered remains of older rocks. Sediments containing coarse-grained rock fragments are called clastic sediments, while sediments containing fine rock fragments are known as argillaceous sediments. Crystalline rocks are formed from the melting and fractionation of rocks deep beneath the earth's surface, which slowly migrate upwards, where they are either extruded at the surface, or cool beneath it, eventually becoming exposed as a result of weathering.

Within each broad category there are a number of diverse sediment types formed in a broad range of geological environments. Unconsolidated sediments, which are commonly referred to as soils, can be deposited in fluvial (rivers), lacustrine (lakes), glacial, aeolian (wind blown) and marine environments. Upon subsequent burial these sediments may become consolidated (harden into a soft rock, such as limestone) due to compaction and cementation processes. Further burial may result in the sediments being subjected to high pressure and temperature and, as a consequence, may undergo physical and chemical alteration to produce metamorphic rocks. Crystalline rocks are formed from the hardening of magmatic material, i.e. molten rock. These rocks are normally intruded into the subsurface as, for example, plutons or batholiths, or extruded at the surface as a result of volcanic activity. In a similar manner to sedimentary rocks, these rocks can also be buried and metamorphosed. Consolidated, crystalline and metamorphic sediments are sometimes termed `bedrock'.

The nature or energy of the depositional environment controls the type of sediment deposited. For consolidated and unconsolidated sediments, coarse-grained material (such as sands and gravels) are deposited within high energy environments such as rivers, while fine grained materials (such as clays and shales) are deposited within low energy environments such as lakes. “Poorly sorted” sediments, containing a mixture of fine and coarse-grained material, are typically deposited in high-energy environments. Examples of poorly sorted sediments are Boulder Clays and conglomerates. Boulder Clays are associated with glacial activity where deposition occurs in a high-energy pulverisation environment beneath a slow moving glacier. Conglomerates are formed in short duration high-energy events such as flash floods. Crystalline and metamorphic rocks are generally denser than unconsolidated or consolidated sedimentary rocks. However, certain extruded crystalline rocks may be less dense as they contain large pores resulting from 'degassing' of the magma as it cools.

The three broad categories of rock types found within Europe are discussed below.

11.2.1 UNCONSOLIDATED SEDIMENTS

These sediments are typically alluvium and river terrace sands and gravels and they can form extensive deposits within river valley systems. Alluvium is composed of silts and clays with isolated sand and gravel horizons. River terrace sands and gravels mainly comprise sands and gravels with occasional silt and clay layers. Glacial sand and gravel deposits and Boulder Clay form extensive and occasionally thick deposits across northern Europe. Boulder Clays are predominantly composed of dense clays with isolated sand and gravel horizons, while the sand and gravel deposits have a similar composition to those described above.

Unconsolidated sediments are generally found across Europe in the form of valley sands and gravels and alluvium. These deposits provide thin cover over consolidated and crystalline bedrock, although regional occurrences are occasionally thick, for example, in parts of the Po valley in Italy. Extensive glacial sands and gravels occur over much of northern Europe, especially across Holland, northern Germany, Poland and Scandinavia. Associated with these deposits are glacial Boulder Clays which form extensive deposits, especially in Scandinavia, Wales, Scotland, Ireland, and Northern and Eastern England. Glacial deposits are also found in the vicinity of the major mountain belts across Europe.

11.2.2 CONSOLIDATED SEDIMENTS

These sediments are classified into the following major rock types:

- **Sandstones** - mainly composed of sand with occasional clay or marl layers. Deposited within aeolian or fluvial environments, prior to consolidation due to burial;
- **Limestones** - mainly consist of calcium carbonate, with occasional clay or marl layers. Deposited within marine environments, prior to burial and consolidation;
- **Shales** and **mudstones** - mainly comprise clay minerals with silts and occasional sandstone and limestone horizons. These deposits are normally formed within marine and lacustrine environments prior to consolidation by burial.

The various types of consolidated sediment described above are often found in close proximity to each other. Sandstones and limestones form prominent hills across much of Europe and are extensively exploited for water resources. Large areas of limestone are, for example, found along the Apennine Mountains and on the southern foothills of the Alps in Italy and across large areas of central and eastern Spain. Within England, France and Germany, they are associated with large sedimentary basins such as the London and Paris basins. Within Italy and Spain weathering has resulted in extensive Karst environments (limestone formations with large cavities and high permeability) forming within the limestone deposits, which is less significant further north in countries such as England and Germany. Associated with these sedimentary basins are extensive deposits of clays, shales and sandstones.

11.2.3 CRYSTALLINE AND METAMORPHIC ROCKS

Crystalline rocks are dense rocks that are normally composed of interlocking crystals with little or no pore spaces and include granites, dolerites, gabbro’s, pegmatites and basalts. Extruded rocks, such as basalt, may contain a high number of unconnected pores or vesicles.

Metamorphic rocks include schists, gneiss, quartzite (metamorphosed sandstones) and marble (metamorphosed limestone). Due to the compaction and alteration of these rocks, the original pore structure is drastically altered, resulting in very low porosities.

Crystalline and metamorphic rocks are generally found in regions of very ancient rocks such as Scandinavia and Scotland, as well as being exposed by tectonic activities associated with the Pyrenees, Alps, Carpathians and the Sierra Nevada.

11.3 CHARACTERISTICS OF DIFFERENT ROCK

The characteristics of rock vary considerably and are described by various parameters. The main parameters of interest for risk assessment are:

- fraction of organic carbon;
- porosity;
- hydraulic conductivity;
- bulk density;
- thickness of capillary fringe; and
- thickness of the unsaturated zone (depth to groundwater).

Climatic conditions will have a significant impact on the values that the parameters listed above can take in a particular geographic area. A wide variety of climatic conditions are encountered within Europe, ranging from sub-arctic within Scandinavia and the Alps, through temperate humid Atlantic climates of western Europe to the semi-arid climate typical of parts of Spain and the Mediterranean. These conditions influence the amount of water which is available to infiltrate these sediments. Also, the sediment types listed can be physically and chemically altered by weathering.

All of the parameters under consideration are complex and are not easy to describe or quantify in the broad European context. In addition, many are site-specific and depend upon the physical characteristics of the geological material as well as the prevailing climatic conditions. The following sections provide brief definitions of each parameter and present the ranges of values likely to be encountered. It should be emphasised that, for a given sediment type, some of these parameters can vary by several orders of magnitude. It is therefore important that, when deriving RBSLs or performing quantitative risk assessments, detailed attention is paid to the values that are assigned to each parameter. It may be appropriate in many cases, to collect field data to substantiate any assumptions that are being made.

11.3.1 TERMINOLOGY

Definitions of terms are as follows:

- **Unsaturated zone** - the zone above the water table where air and water co-exist in the pore spaces at pressures less than atmospheric. Within the unsaturated zone water is held by capillary forces. The unsaturated zone is also known as the vadose zone;
- **Saturated zone** - the zone below the water table where pore spaces are filled by water at pressures greater than atmospheric. Movement of water occurs through the connected pore spaces when a hydraulic gradient exists;
- **Capillary fringe** - the zone immediately above the water table where capillary forces are strong enough to saturate the soil or rock matrix with water. This water, however, possesses a pressure head less than atmospheric and is not free draining under the influence of gravity alone;

- **Water table** - the upper surface of the saturated zone, where the water pressure head is identical to atmospheric. Below this the water pressure head is greater than atmospheric. Water within the saturated zone is free draining and can flow under gravity;
- **Soil** - top and sub soils or agricultural soils. Soil is not used to describe the subsurface which is referred to in terms of sediments and rocks.

The key parameters which control the movement of vapour in the various rock types are discussed in the following sections.

11.3.2 FRACTION OF ORGANIC CARBON

The fraction of organic carbon (Foc) is defined as the mass of organic carbon per unit weight of soil (g-C / g-soil). However, the majority of data available in the literature relates to organic matter and not to organic carbon. The weight of the organic matter is greater than that of the organic carbon alone, due to the presence of additional elements including hydrogen, nitrogen, sulphur and oxygen. Organic matter can be converted to organic carbon using an approximate conversion factor of 0.58.

The range of Foc measurements likely to be encountered in soils is typically far greater than that for consolidated sediments or rock. These are summarised in **Table A3** as follows:

Table A3 Fraction of Organic Carbon (Foc) for Various Rock Types

Rock Type	**Foc Range**
Sands and Gravels [a]	0.0002 to 0.001
Silts [a]	0.001 to 0.03
Clays [a]	0.005 to 0.17 [c]
Sandstones [b]	0.0002 to 0.005
Limestones [b]	0.0002 to 0.02
Shales and Siltstones [b]	0.005 to 0.02
Crystalline and Volcanic rocks	0.00005 to 0.0002

[a] unconsolidated deposits

[b] sedimentary rocks

[c] organic rich clay assemblage within the Jurassic Age Oxford Clay of the UK

The distribution of organic carbon can be very uneven for some geologic materials. For example, the majority of the matrix of limestone rocks (e.g. the Cretaceous chalks and Jurassic Limestones) may possess very low levels of organic carbon, with higher concentrations being found within thin isolated clay or shale horizons. Also, by their nature, crystalline and volcanic rocks are created within an environment devoid of organic life. However, Foc is unlikely to be equal to zero as some of these lithologies may be derived from rocks originally containing organic carbon, or may, during their emplacement come into contact with organic carbon rich geologic materials. Organic carbon may also be deposited by infiltrating water on to fracture surfaces. Some rocks, such as coal and peat, are almost entirely composed of organic carbon.

11.3.3 POROSITY

The porosity of a rock consists of void spaces between solid fragments and is defined as the ratio of the void space to the total volume of the rock. Porosity is normally reported as a decimal fraction or a percentage.

Porosity can range from zero or near zero to more than 0.60 (see below). Higher values are characteristic of recently deposited sediments whereas the lower values are typical of dense crystalline rocks or highly compacted soft rocks such as shales. In general, for sedimentary materials, the smaller the particle size, the higher the porosity.

There is a strong relationship between texture and porosity, which can be altered by burial and tectonic effects. Well sorted (similarly sized) geological materials generally have a high porosity, while poorly sorted materials have low porosities. This results from the spaces between large grains being occupied by smaller particles. This is known as primary porosity. Burial of these sediments leads to a complex process known as diagenesis which, generally, acts to reduce the primary porosity. Diagenesis includes compaction and deposition of cementing materials (such as calcite, dolomite and silica), which act to close the volume of pore space, but also includes dissolution of material which acts to increase porosity. The porosity of geological materials can be enhanced through solution by water, structurally-controlled regional fracturing and weathering. This enhancement is termed secondary porosity.

The rock types described above all have, to a greater or lesser extent, spaces or pores between the grains, this is the porosity. Many of these pores may not be connected and so contribute little to the movement of water and gases through the rock. For example, crystalline rocks are formed from interlocking crystals which result in very low primary porosities. Tectonic activities can result in dense fractures which act to increase porosities to approximately 0.02 to 0.05. This can be further enhanced at the near surface by weathering to give porosities as high as 0.3 to 0.6 in extreme cases. Extrusive volcanic rocks are often deposited at the near surface and cool quickly. This results in radically different porosity characteristics. The rapid cooling can often trap degassing products which results in a vesicular texture, with little interconnectivity. For example basalt normally contains little gas resulting in porosities of between 0.01 to 0.12, while porosities as high as 0.87 can occur within high gas content rocks such as pumice. Many lava flows can leave tubes and tunnels and joints formed from shrinkage cracks when the lava cools. Fracturing caused by tectonic effects can result in secondary porosity which again can be enhanced by weathering to result in porosities as high as 0.60.

Table A4 Porosities of Various Rock Types

Rock Type	**Porosity Range**
Gravel [a]	0.25 - 0.40
Sand [a]	0.25 - 0.50
Silt [a]	0.35 - 0.50
Clay [a]	0.40 - 0.70
Sandstone [b]	0.05 - 0.30
Limestone, Dolomite [b]	0.00 - 0.20
Limestone, Karst [b]	0.05 - 0.50
Siltstone [b]	0.20 - 0.40
Shale [b]	0.00 - 0.10
Anhydrite and Salt [b]	0.005 – 0.05
Fractured Basalt [c]	0.05 - 0.50
Basalt [c]	0.03 - 0.35
Fractured Crystalline Rock [c]	0.00 - 0.10
Dense Crystalline Rock [c]	0.00 - 0.05
Weathered Granite [c]	0.34 - 0.57
Weathered Gabbro [c]	0.42 - 0.45

a unconsolidated deposits
b sedimentary rocks
c crystalline and volcanic rocks

Pore spaces can be filled with either water or air. The former constitutes the volumetric water content of the sediment and the latter the volumetric air content. For a saturated sediment, the volumetric water content equals the porosity of the sediment. As the water content within a sediment declines the volumetric air content increases. The volumetric air content is defined as the ratio of the volume of air to the total volume of the rock and is less than the porosity. Logically the highest volumetric air contents should equal the porosity of the sediment i.e. all the water has been removed. However, in reality, there is always a proportion of water which cannot be removed. This is usually associated with the smallest pores within a sediment in response to capillary forces, which, at the near surface, can be reduced by evapotranspiration but not removed.

An important distinction is the difference between total porosity, which does not require pore connections, and effective porosity, which is defined as the percentage of interconnected pore space. Many rocks, crystalline in particular, have a high total porosity, most of which may be unconnected. Effective porosity can be over an order of magnitude lower than total porosity with the greatest difference occurring for fractured rocks. This has significant implications for the movement of both vapours and fluids through those deposits and hence contaminant transport and subsequent human exposure.

11.3.4 POROSITY OF UNSATURATED ZONE SEDIMENTS

The **volumetric water content** is defined as the ratio of the volume occupied by water to the total volume of the rock. Above the capillary fringe increasing proportions of the sediment matrix become unsaturated as progressively smaller and smaller pores drain. As with the capillary fringe, the capillary forces increase as the pore size declines. This results in different soil drying behaviours for each type of sediment which are related to the pore size distribution of that sediment. There are no values available within the literature to quantify the minimum volumetric water content for a given geological material, although it is generally true that the coarser the material the lower the minimum water content. Data is available for agricultural soils which, although not included in this discussion, illustrate the minimum volumetric water content.

Typical volumetric water characteristics for agricultural soils are shown in **Table A5** below. The table indicates that as the proportion of small particles increases the amount of free draining water declines.

Table A5 Volumetric Water Characteristics of Various Rock Types

Soil Type	Clay Content (%)	Porosity	Field Capacity
Sand	3	0.40	0.06
Loam	22	0.50	0.29
Clay	47	0.60	0.41

The **Field Capacity** is the volume fraction of water after the saturated soil has drained under gravity to equilibrium. This is, in effect, the capillary water which is not free draining under gravity as discussed previously in the context of geological sediments. Within an agricultural soil this water can be reduced by evapotranspiration, which does not concern the discussion. The agricultural soil types described above are composed of a combination of sand, silt and clay size fractions (**Table A6)** which themselves are composed of particle sizes as follows - Clay < 2 µm, Silt 2 to 60 µm and Sand 60 to 2000 µm.

Table A6 Composition of Various Soil Types

Soil Type	Sand %	Silt %	Clay %
Sand	> 90	0 – 10	0 - 10
Loam	22 - 52	28 – 50	8 - 28
Clay	0 - 50	0 – 40	> 40

The Volumetric Air Content is defined as the ratio of the volume of air to the total volume of the rock and is always less than the porosity. It increases with the coarseness of the geologic material and, for a given sediment, will not decline within wet and humid climates as much as it would for more arid climates. Under arid conditions the volumetric water content can decline to levels approaching the capillary water content.

11.3.5 POROSITY OF CAPILLARY FRINGE SEDIMENTS

By definition, the capillary fringe is essentially saturated with water, such that the volumetric water content is effectively equal to the primary porosity of the geological sediment. Secondary porosity features such as fractures and karst features have much greater pore sizes (void space) than the surrounding matrix. These features, if large enough, can remain unsaturated within the capillary fringe and only become saturated as the water table rises. Examples of sediments which exhibit such behaviour are fractured fine grained geological materials. The chalk found in France and England is a classic example where the fractures within the unsaturated zone remain drained while the matrix, due to its very small pore size distribution (<1 µm), forms the capillary fringe and is effectively saturated. The fractures form the secondary porosity component within the chalk. Typical values for such porosity normally range between 0.00 to 0.05, although higher amounts may be present within karstic environments and volcanic rocks containing pipes. The resultant volumetric air content within the capillary fringe can be assumed to equal the secondary porosity.

11.3.6 HYDRAULIC CONDUCTIVITY

As described in the previous sections, geological sediments generally contain some void space and thus exhibit porosity. In most cases, these voids are interconnected to some degree. Water or other fluids contained within these voids is capable of moving from one void to another under the influence of a pressure gradient (usually described as head or hydraulic gradient), thus flowing through the sediment. This flow may be very difficult within sediments possessing low interconnected porosity or very small diameter void spaces.

Hydraulic conductivity is defined as the volume of water that will flow through a unit cross-sectional area of sediment in unit time, under a unit hydraulic gradient, at a given temperature. The hydraulic conductivity, with units of velocity, characterises the capacity of a sediment to transmit water.

Hydraulic conductivity depends on the properties of both the sediment, through which flow occurs, and also the density and viscosity of the fluid, which are both greatly affected by temperature. For example, an increase in water temperature from 5°C to 30°C will double the hydraulic conductivity. However, this is normally not a significant problem as the temperature of groundwater generally remains relatively constant, except in some shallow aquifers in regions of climatic extremes or in particular situations involving contaminated groundwater. The density of a fluid can also be affected by the amount of minerals dissolved within it (for example saline groundwater).

Representative values of hydraulic conductivity for various sedinal types at 15.6°C. (60°F) are provided in **Table A7** below:

Table A7 Hydraulic Conductivity of Various Sediment Types

Sediment Type	**Hydraulic Conductivity (m/s)**
Unconsolidated	
Gravel	3.0 x10-4 - 3.0 x10-2
Coarse Sand	9.0 x10-7 - 6.0 x10-3
Medium Sand	9.0 x10-7 - 5.0 x10-4
Fine Sand	2.0 x10-7 - 2.0 x10-4
Silt, Loess	1.0 x10-9 - 2.0 x10-5
Till	1.0 x10-12 - 2.0 x10-6
Clay	1.0 x10-11 - 4.7 x10-9
Unweathered Marine Clay	8.0 x10-13 - 2.0 x10-9
Consolidated	
Karst and Reef Limestones	1.0 x10-6 - 3.0 x10-2
Limestone and Dolomite	1.0 x10-9 - 6.0 x10-6
Sandstone	3.0 x10-10 - 6.0 x10-6
Siltstone	1.0 x10-11 - 1.4 x10-8
Salt	1.0 x10-12 - 1.0 x10-10
Anhydrite	4.0 x10-13 - 2.0 x10-8
Shale	1.0 x10-13 - 2.0 x10-9
Crystalline Rocks	
Permeable Basalt	4.0 x10-7 - 2.0 x10-2
Fractured Igneous and Metamorphic Rock	8.0 x10-9 - 3.0 x10-4
Weathered Granite	3.3 x10-6 - 5.2 x10-5
Weathered Gabbro	5.5 x10-7 - 3.8 x10-6
Basalt	2.0 x10-11 - 4.2 x10-7
Fractured Igneous and Metamorphic Rock	4.0 x10-14 - 2.0 x10-10

As noted in the above listing, hydraulic conductivity can range in value over about 12 orders of magnitude, with the lowest values for unfractured crystalline rocks and the highest values for gravels and some karstic or reef limestones and permeable basalts. The range in hydraulic conductivity within a given rock type is greatest for crystalline rocks and smallest for the unconsolidated materials. In general, a hydraulic conductivity approaching 10^{-9} m/s and smaller can be characterised as a low permeability material. Clay, Shale and unfractured limestones and crystalline rocks as well as poorly sorted unconsolidated materials such as Till (eg Boulder Clay) fall within this category. However, if these rocks are fractured, the conductivity can easily exceed this limiting value by two or three orders of magnitude. The Cretaceous chalk of Southern England is a classic example of this. Typical hydraulic conductivities for the unfractured matrix range between 10^{-7} and 10^{-9} m/s. However, the hydraulic conductivity of the fractured component typically ranges between 10^{-5} and 10^{-3} m/s, with extreme values as high as 10^{-2} m/s. It is the fractured component which results in the chalk being an aquifer. Many crystalline basement rocks and some sandstones and limestones are also aquifers as a result of this phenomenon. Near surface weathering can also increase the hydraulic conductivity of sediments. Within an aquifer, or any geological sediment for that matter, hydraulic conductivity can vary significantly both spatially and vertically as a result of the complex nature of the sediment composition as well as by of fracturing and weathering.

11.3.7 BULK DENSITY

The dry bulk density of a rock is defined as the mass of the rock per unit volume. Bulk density is influenced by the density of the rock particles and the number of grains per unit volume. Thus for a given rock, bulk density is inversely related to the porosity.

For the majority of geological materials dry bulk density varies from 1.2 to 2.5 g/cm^3, the highest values being associated with dense crystalline rocks and the lowest with unconsolidated sediments.

11.3.8 THICKNESS OF CAPILLARY FRINGE

The capillary fringe is the portion of the unsaturated zone where the pores are saturated with water which is not free to drain under gravity and the pressure heads are less than atmospheric. The pressure head becomes equal to atmospheric at the water table. Capillary movement in soils refers to the movement of moisture through minute pores between the soil particles which act as capillaries. These capillary forces take place as a consequence of surface tension and are termed matrix suction or matrix potential. This "surface tension pull" results in water being raised against the force of gravity, the degree of saturation decreasing from the water table upwards. Equilibrium is attained when the forces of gravity and surface tension are balanced. The zone immediately above the water table is referred to as the capillary fringe. Above this, air and water are held by capillary forces and exist together within the remainder of the unsaturated zone.

The thickness of the capillary fringe is largely dependent on the particle size distribution and density of the sediment, which in turn influence pore size. In other words, the smaller the particle size, the greater the thickness of the capillary fringe. For example, clay deposits and fine grained limestones such as the chalk possess very thick capillary fringes which can extend from the water table to within a couple of metres of the surface. In sediments which are poorly sorted the thickness of the capillary fringe generally varies spatially whereas in uniformly textured soils it attains a roughly uniform height.

The height of the capillary fringe is very hard to measure in the field but estimates are provided in **Table A8** below:

Table A8 Estimates of Height of Capillary Fringe

Sediment	**Pore Size Range (µm)**	**Capillary Rise (m)**
Coarse gravel	20,000 - 60,000	up to 0.1
Fine gravel	2000 - 6000	0.10 - 0.50
Medium sand	200 - 600	0.15 - 0.30
Fine sand	60 - 200	1.00 - 10.00
Clay	sub 2.0	over 10

11.3.9 THICKNESS OF THE UNSATURATED ZONE (DEPTH TO GROUNDWATER

The greatest controls on the depth to groundwater are topography and climate. In very general terms the groundwater table normally follows closely the direction of the topographic gradient. The groundwater table does not, however, mirror the topographic surface. In areas of high relief the groundwater table may be at some depth below the surface, even in wet climates. An example of this is the chalk in the UK, where in the relatively high areas of the Chiltons, The Downs and the Lincolnshire and Yorkshire Wolds, the water table can be found at depths in excess of 40m below the surface. Under arid conditions the depth to the water table may extend to hundreds of metres. As relief declines, for example as one moves toward the valley floor, the depth of the water table will decline, eventually reaching the ground surface. Areas of marshland and wetlands can form, at such locations, or springs and streams can develop. These areas are known as discharge points. The majority of urban and industrial developments are located in relatively flat areas close to rivers or the sea. In such circumstances the groundwater table may be only a few metres below the surface.