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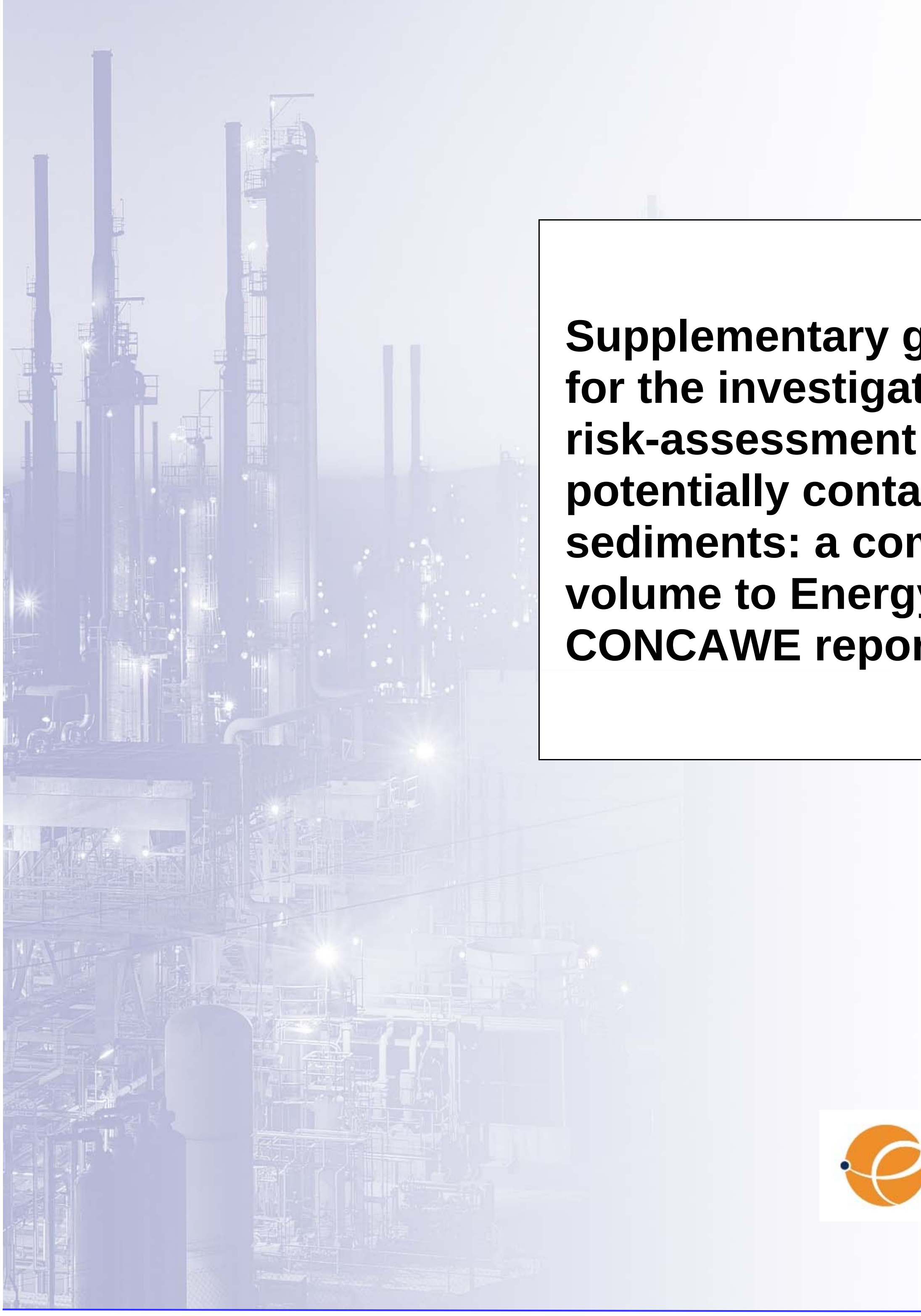

Supplementary guidance for the investigation and risk-assessment of potentially contaminated sediments: a companion volume to Energy Institute / CONCAWE report E1001

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conservation of **c**lean **a**ir and **w**ater in **e**urope

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Supplementary guidance for the investigation and risk-assessment of potentially contaminated sediments: a companion volume to Energy Institute / CONCAWE report E1001

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ABSTRACT

This report provides guidance on the investigation and assessment of potentially contaminated sediments, focusing on the inland, estuarine and coastal environments. It is designed as a complementary, technical companion document to Energy Institute & CONCAWE (2013) report '*Guidance on characterising, assessing and managing risks associated with potentially contaminated sediments*' (Report E1001). It highlights a number of significant challenges associated with assessing the aquatic and water bottom environment, which means that a sediment assessment should not be undertaken lightly.

Where a decision is taken to undertake a site assessment, this report promotes the use of an iterative process of Conceptual Site Model (CSM) development, data collection, data evaluation and a continuous CSM refinement, taking into account the results obtained.

Risk-based assessment is described throughout the report, entailing four tiers of assessment, which progress from a qualitative assessment (Tier 0) through to a detailed cause-attribution assessment (Tier 3), in which the decrease in uncertainty in the assessment process is balanced against the increased costs and timescales with progress to a higher tier assessment. The application of this evidence-driven risk-based approach to sediment site management, including remedial control measures, should help to overcome at least some of the challenges associated with contaminants in sediment sites in Europe, and promote a sustainable approach to sediment management on a case-by-case basis.

KEYWORDS

Sediment, Sediment investigations, sediment Conceptual Site Models, Risk-based site assessment, Remedial control measures

INTERNET

This report is available as an Adobe pdf file on the CONCAWE website (www.concawe.org).

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SUMMARY

This report provides guidance on the investigation and assessment of potentially contaminated sediments, focused on the inland, estuarine and coastal environments. While focused on practitioners from the energy sector, the concepts and guidance are broadly cross-applicable. It is designed as a complementary, technical companion document to Energy Institute & CONCAWE (2013) report '*Guidance on characterising, assessing and managing risks associated with potentially contaminated sediments*' (Report E1001). However, this publication can also be used as a standalone document, in particular to assist practitioners looking for techniques and solutions which reduce uncertainty in the assessment process.

Sediments are defined herein as being potentially contaminated when they contain substances derived from anthropogenic activities, and contaminated when they contain substances derived from anthropogenic activities at concentrations that are causing environmental damage or a significant threat of environmental damage.

The report highlights a number of significant challenges associated with assessing the aquatic environment, which means that a sediment assessment should not be undertaken lightly and unless careful consideration has been given to all potential outcomes and whether the objectives of the assessment can feasibly be met. Critically, it must be clear that there is real potential for contaminated sediments to be present, before an intrusive sediment assessment commences.

Where a decision is taken to undertake a site assessment, this report promotes the use of an iterative process of Conceptual Site Model (CSM) development, data collection, data evaluation and CSM refinement. To aid development of the CSM, a detailed overview of the theory relating to contaminant sources, fate and transport and receptor exposure in the sediment environment is provided, alongside practical examples of data collection and analysis techniques to help draw meaningful conclusions.

Risk-based assessment is described throughout the report, entailing four tiers of assessment, which progress from a qualitative assessment (Tier 0) through to a detailed cause-attribution assessment (Tier 3). The decrease in uncertainty in the assessment process is balanced against the increased costs and timescales with progress to a higher tier assessment. However, the publication also discusses the real challenge in quantifying risk – whether to humans or other living organisms – from contaminants in the sediment environment. Concluding that contaminated sediments are present at a site invariably requires multiple lines of evidence and a balance of probabilities that there is a relationship between observed or predicted environmental damage and a potentially contaminated sediment source.

Use of an evidence-driven risk-based approach to sediment site management should help to overcome at least some of the challenges associated with contaminants in sediment sites in Europe, and promote a sustainable approach to sediment site management.

1. INTRODUCTION

1.1. AIM OF THE PUBLICATION

There has been significant progress in the introduction of pan-European legislation aimed at protecting and improving the quality of inland, coastal and marine waters (e.g. the Water Framework Directive and the Marine Strategy Framework Directive). Evolving European legislation recognises that groundwater and surface water have environmental, economic and social value. The continued focus on the water environment has begun to highlight the importance of sediments within the aquatic system, which in turn is raising the profile of the potential impact of contaminants within sediments.

However, learning from other parts of the world where the investigation and assessment of contaminants in sediments is a more common occurrence, notably North America, it is clear that careful consideration of the legislative and regulatory context, and potential for a successful outcome prior to carrying out a sediment assessment and deciding that the assessment is required. Further, if an assessment is deemed necessary, there is a need for clear and well considered guidance to avoid risk management decisions being taken on the basis of poor or inadequate site conceptualisation, data and understanding.

This guidance document is designed as a complementary, technical companion document to Energy Institute & CONCAWE (2013) report '*Guidance on characterising, assessing and managing risks associated with potentially contaminated sediments*', hereafter referred to as '*Report E1001*'. This technical publication builds upon the key concepts and themes within Report E1001. However, this publication can also be used as a standalone document, in particular to assist practitioners looking for techniques and solutions which can be applied to understand and reduce uncertainty in the assessment process. Together these reports provide stakeholders with guidance to help answer the questions which include:

- Is the assessment of a potentially contaminated sediment site an appropriate course of action?
- Is it possible to define a clear endpoint to the assessment process and what will be the endpoint?
- What should be considered when developing the conceptual site model?
- What are the methods which can be used to assess a potentially contaminated sediment site?
- How can the data collected be evaluated to assess whether there is a potential risk to human health, ecology or the wider environment?
- What constitutes unacceptable risk in the context of the aquatic environment?
- What approaches can be used to manage unacceptable risks?

1.2. IMPORTANT DEFINITIONS

There is a wide range of definitions for contaminated sediments in the literature, however this document uses the following definition for "sediment" and "contaminated sediments":

Sediment

A ***sediment*** *is a material which has been eroded, transported and deposited on the bottom of a water body (lake, river / estuary, marine), resulting from natural processes that can also be affected by human activities.*

Because sediments are deposited as a result of natural processes, sediments will typically be biologically active. The US National Research Council (2003) estimated that the population of benthic organisms is greatest in the top few centimetres of freshwater sediment, although has the potential to be deeper in particular in marine deposits, which is important when understanding the potential effects of contaminants within a sequence of sediments.

Contaminated sediment

Any sediment is defined as contaminated when it contains substances, derived from anthropogenic activities, at concentrations that are causing environmental damage or a significant threat of environmental damage.

The definition of contaminated sediment can be applied where a substance or substances are identified as having a direct impact as a result of their toxicity or the hazard they present. However, the definition can also be applied to situations where the presence of substances in the sediments results in non-chemical stressors at levels which are causing or presenting a significant threat of environmental damage. It is noted that the use of the word "contaminated" is commonly replaced with the word "polluted" in some European Union Member States (Box 1.1)

The term "Environmental damage" is defined within the Environmental Liability Directive (2004/35/EC) which legislates against damage or imminent threat of damage to human health, water quality or protected communities/species. Sediments could also be considered contaminated, using the above definition, if it results in a breach of alternative European or national environmental legislation. For example, this could include:

- Degradation in water quality directly associated with the contaminants in sediments resulting in poor chemical or ecological status in an associated surface water body under the Water Framework Directive
- Presence of contaminants in fish-stocks or shellfish, directly attributable to contaminants in sediments, resulting in the need for restrictions on commercial fishing activities, or on consumption of caught fish
- Degradation in water quality directly associated with the contaminants in sediment, resulting in the need for restrictions related to recreational use of the waterway (e.g. bathing)
- Degradation in water quality directly associated with the contaminants in sediment, resulting in requirement for additional treatment of water abstracted for potable use.

The use of “significant” within the definition, deviating from the legal definition of Environmental Damage, implies the requirement to use a risk-based assessment to understand whether contaminated sediments are present. As such, the mere presence of an anthropogenically derived substance, or substances, within sediment does not equate directly to use of the term “contaminated sediment”. For example, it is not expected that the definition would be applied to:

- Deposits with a minimal thickness (e.g. insufficient thickness to be able to support biota);
- Deposits or contaminants present on the bottom of a water body for insufficient time to result in environmental damage to occur (e.g. defined on the basis of site specific knowledge regarding the ecological community); or
- Contaminants present at sufficient depth within the sediments such that a pathway to potential receptors is not plausible now or under predicted future conditions (for example, contaminants present at depth below the biologically active zone, where aquatic organisms have been identified as a receptor of concern in an environment not likely to be disturbed).

The term “contaminated sediments” has not been used to refer to sediments containing substances at levels which could result in the need for treatment prior to disposal following dredging activities, as the definition relates to potential risks relating to receptors associated with *in situ* sediments.

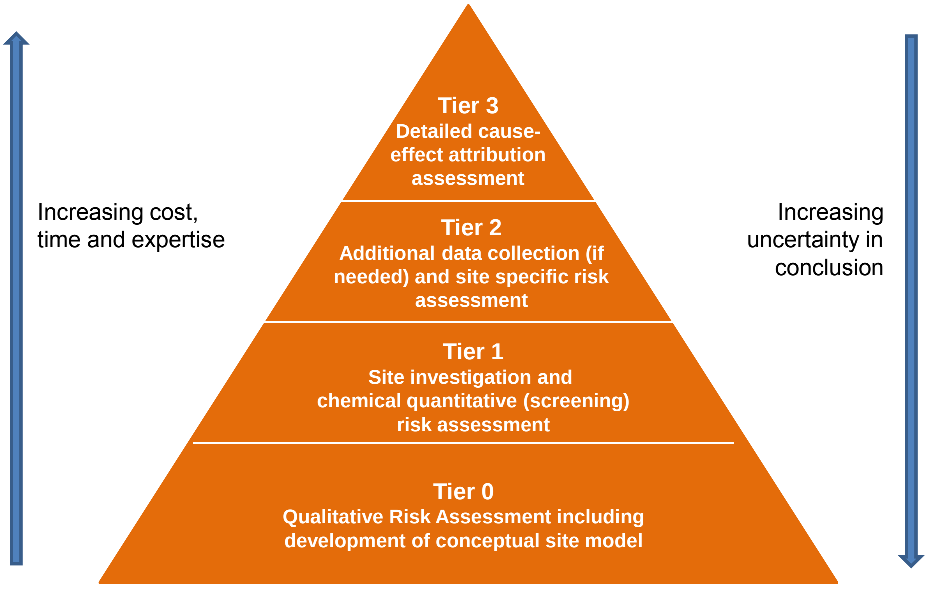
Box 1.1 The terms “contaminated” and “polluted”

Discussions are on-going in the European Union about the use of the terms “contaminated” versus “polluted”. In some countries, the term “contaminated” is defined legally (for example, “Contaminated Land” is defined within Part IIA of the Environmental Protection Act 1990 in England, Wales and Scotland) and is used to identify a site where significant risks to receptors have been identified. In other parts of the European Union, the terms contaminated or contamination are used to refer to sites where contaminants (derived from anthropogenic activities) have been identified but not considered to present significant risk. It is the term “polluted” which is used to combine together the presence of contaminants at a site with the potential for harm to occur. For example, European Directive 2010/75/EU on Industrial Emissions (Integrated Pollution Prevention and Control) defines pollution as *“…the direct or indirect introduction, as a result of human activity, of substances, vibrations, heat or noise into air, water or land which may be harmful to human health or the quality of the environment, result in damage to material property, or impair or interfere with amenities and other legitimate uses of the environment*”. It is not the intent of this guidance document to provide comment on which term should be used. As such, the term “polluted sediment” can be used interchangeably with the term “contaminated sediment” as defined within this document if more appropriate in a specific European Union Member State.

1.3. INTRODUCTION TO REPORT E1001

A tiered, risk-based framework to risk evaluation is proposed in Report E1001 (**Figure 1.1**), alongside recommended critical elements to consider when developing a conceptual model for a site affected by contaminants in sediments.

Figure 1.1 Report E1001 Tiered approach to assessment of sediment sites affected by contamination



A large toolkit of both investigation and remediation techniques are discussed and evaluated in Report E1001, including the advantages and disadvantages of each technique and where they are best applied.

The final chapter within Report E1001 identifies key points of learning from a number of global sediment investigation and remediation projects. This includes the importance of understanding the origin and nature of the sediment contamination (the ‘source’) and the mechanisms by which receptors can be affected by contaminants in sediments.

1.4. PUBLICATION STRUCTURE

The second chapter in this publication is designed to help practitioners answer the question as to whether a sediment assessment should be carried out. It is advisable to read the chapter prior to the remainder of the publication, which provides guidance where the decision regarding need for a sediment assessment has already been made.

Chapter 3 focuses on development of a robust conceptual site model, the first tier in the assessment process.

Chapters 4, 5 and 6 cover the topics of source characterisation, system hydraulics and contaminant fate & transport, and exposure scenario assessment respectively.

Data collection and risk assessment methods are explored in Chapter 7.

Finally, the publication ends with Chapter 8 which explores the link between the findings of a risk-based assessment and the decision to implement a risk management/remediation strategy.

2. SHOULD AN ASSESSMENT FOR POTENTIALLY CONTAMINATED SEDIMENTS BE CARRIED OUT?

Report E1001 provides an overview of legislative and regulatory drivers which may result in an evaluation as to the need for a potentially contaminated sediment assessment. In theory, examples of scenarios where a potentially contaminated sediment investigation and assessment may at first seem a logical route to follow include:

- Failed chemical status or poor/bad ecological status for a watercourse under the Water Framework Directive
- Recorded or suspected impacts to a receptor which cannot be explained by know point or diffuse sources
- Following an unpermitted release to the aquatic environment.

However, in each case, the question as to whether potentially contaminated contaminants could be present, or are likely to be present, should be asked, as the key driver behind the need to undertake an assessment.

In some countries, there may be a legal or regulatory requirement to undertake a sediment assessment for each of the example scenarios, or comparable, scenarios. In such cases, compliance with the local legislative or regulatory requirements is standard. However, it should be recognised that there are significant challenges associated with assessing the aquatic environment. As such, where there is no legal or regulatory requirement to undertake a sediment assessment, such an assessment should not be undertaken unless careful consideration has been given to all potential outcomes and whether the objectives of the assessment can feasibly be met. Critically, it must be clear that there is real potential for contaminated sediments to be present, as opposed to contaminants present in sediment as a result of anthropogenic activity but which do not meet the definition of contaminated sediments.

Even where there is in theory a legal or regulatory requirement to undertake the work, efforts should be made to engage the relevant stakeholders, and discuss the challenges before deciding whether a sediment assessment is an appropriate course of action. This approach fits with the increased emphasis on sustainable decision-making for sites affected by contamination, whether in the terrestrial or aquatic environments.

2.1. WHAT FACTORS INFLUENCE THE DECISION-MAKING PROCESS?

When deciding whether an assessment for potentially contaminated sediments is warranted, there are a number of questions which can be asked, which include:

(1) Is there a legal or regulatory requirement for the assessment?

(2) Can the works be undertaken safely?

(3) Have the relative costs and benefits to carrying out the work been evaluated and discussed between the relevant stakeholders?

(4) Can the assessment be carried out within the desired timescale?

(5) Will it be possible to draw meaningful conclusions from the data?

(6) Is there a clear endpoint to the assessment, i.e. a defined point at which the decision as to whether contaminated sediments are present (based on the definition provided in Chapter 1) can be made?

(7) Are there any feasible risk management solutions which could be employed if contaminated sediments are found to be present?

In most cases, unless the answer to each of the questions is 'yes', then carrying out an assessment for potentially contaminated sediments is unlikely to have a successful outcome. In answering each of the questions, it is important to understand the challenges involved with undertaking an assessment of potentially contaminated sediments.

2.2. WHAT ARE THE CHALLENGES ASSOCIATED WITH ASSESSING A SEDIMENT SITE?

Report E1001 highlights key issues affecting the investigation and assessment of potentially contaminated sediment sites, ranging from access difficulties to multiple legislative regimes (**Figure 2.1**).

Figure 2.1 Key issues affecting the investigation, assessment and remediation of potentially contaminated sediments

However, three of the key issues are of particular importance when evaluating whether a sediment assessment is warranted, and can be carried out successfully:

1. Multiple sources in a dynamic environment
2. Uncertainty in science
3. Potential for remediation exacerbating the problem.

2.2.1. Multiple sources in a dynamic environment

Inland, coastal and marine sediments across the whole of the European Union contain a wide range of substances derived from anthropogenic activities: these can be historical or current activities, and substances may be present as a result of permitted or unpermitted releases. For example, there is a legacy of centuries of industrial activity in some parts of the European Union (e.g. Example 2.1), and a long history of permitted discharge to surface water across the European Union. This means that almost any sediment investigation will encounter concentrations of substances in sediment or sediment pore water, presenting real challenges in terms of distinguishing between different source inputs. It is critical that this is considered carefully when evaluating whether a contaminated sediment assessment should be carried out, and what form the assessment should take. This should help to prevent contaminated sediment assessments which result in the collection of large volumes of data which cannot be interpreted and evaluated, thus not meeting the assessment objectives.

Example 2.1: Heavy metals associated with medieval silver mining, Germany
Lead and silver ore was mined in the Harz Mountains in Germany between the 12th and 15th centuries for a range of uses, including glass production (Wedepohl and Baumann, 1997). This early medieval industrial activity not only resulted in the deposition of heavy metals in soils (e.g. Clemens, 2001) but also a long history of heavy metal discharge to the Aller and Weser rivers (e.g. Förstner et al, 1982). The heavy metals released are still present in the sediments and floodplain (meadow) deposits alongside sediments in the ports of Bremen and Bremerhaven (e.g. Matschullat et al, 1997, Monna et al, 2000). Today, the presence of these metals in the harbour sediments affects the requirements for handling and disposal of dredged material.

2.2.2. Uncertainty in science

While scientific knowledge continues to advance, and targeted data collection helps to reduce poor decision-making regarding potential risks, uncertainty is still inherent throughout the assessment process. This starts with the ability to be able to accurately characterise the sources (see Section 2.2.1) and predict the migration of contaminants in the aquatic environment, and ends with debate as to what constitutes “environmental damage”. This challenge is often compounded by policy decisions based on conservative assumptions – which run the risk of remediation efforts being carried out for sites where only hypothetical, rather than real, risks are present – or an absence of a clear policy on acceptable versus acceptable risk.

2.2.3. Potential for remediation to exacerbate the problem

One potential outcome from the assessment process is a recommendation to undertake remediation or risk mitigation works. However, if it is shown that the feasible risk mitigation techniques are likely to exacerbate the problem (or create a new problem), and then the value of carrying out the assessment has to be questioned. For example, dredging of sediments or installation of a capping system could have a significant impact on the existing ecosystem. In some cases, it may be appropriate to consider the costs and benefits of potential risk mitigation solutions prior to works commencing, so that a decision can be reached between all relevant stakeholders that the cost, environmental footprint and social impact of remediation – if warranted – is acceptable.

2.3. USE OF THE TIERED, RISK-BASED FRAMEWORK

Where it is determined that a sediment assessment is appropriate, the next step is to decide what form the assessment should take. The tiered, risk-based framework (**Figure 1.1**) illustrates that while moving from a lower to a higher tier usually incurs additional cost, time and expertise, there is a reduction in uncertainty associated with the conclusions reached.

In theory, while a lower tier assessment can be used to demonstrate that contaminated sediments are not present, a higher tier assessment is needed to be able to conclude with certainty that contaminated sediments are present (based in part on the uncertainties in both science and policy). However, the decision as to whether remediation or risk mitigation measures should be implemented does not have to rely on a robust conclusion that contaminated sediments are present. The relevant stakeholders may agree that the balance between increased costs for continued investigation and assessment outweigh the costs for implementing a risk mitigation solution, thereby exiting the risk framework at a low tier of assessment. It should also be recognised that the framework is not linear (i.e. requiring progression from Tier 0 to Tier 3). In some cases, it may be appropriate to carry out a Tier 3 assessment to gather empirical evidence on cause-attribution (e.g. sampling of specific receptors), in preference to relying on the collection of data on sediment quality or fate and transport modelling to indicate whether a higher tier assessment is warranted.

2.4. SUMMARY

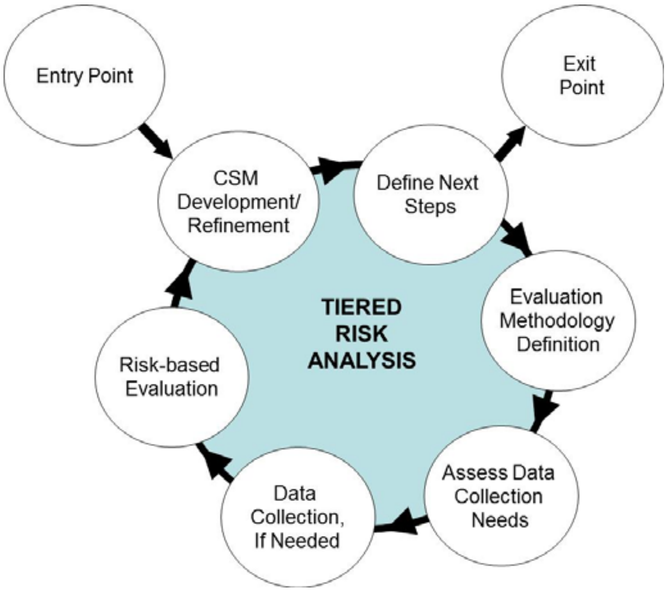
Considering the requirement for, and value of completing, a sediment assessment will help all relevant stakeholders understand the likely outcomes which could be achieved. In many cases, the evaluation may lead to the decision that it is not appropriate to carry out an assessment. However, where all relevant stakeholders agree that the works are warranted, the first step is to develop a Conceptual Site Model, which is explored further in Chapter 3.

3. CONCEPTUAL SITE MODELS – UNDERPINNING THE ASSESSMENT PROCESS

3.1. ROLE OF THE CONCEPTUAL SITE MODEL

The identification and evaluation of potential risks associated with contaminants in sediments is a tiered and iterative process (**Figure 3.1**). Section 2 highlighted that the first step in the assessment process, where contaminated sediments are suspected as being present and it has been decided that an assessment is required, is the development of the Conceptual Site Model (CSM).

Figure 3.1 Risk analysis – an iterative approach (taken from Report E1001)



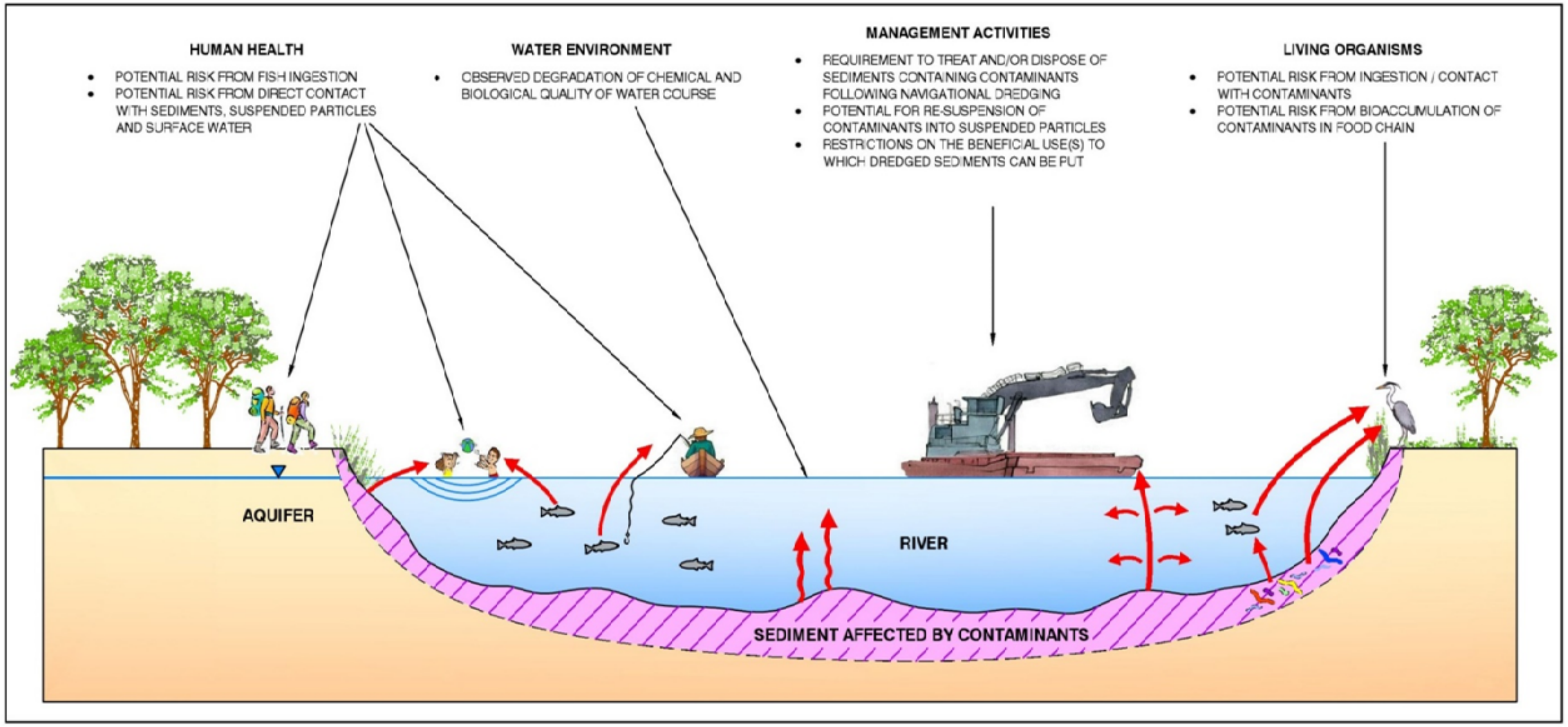
A CSM can take many forms, but fundamentally is designed to identify and lead to a greater understanding of the potential receptors and the routes by which the receptors could be affected by contaminants in sediments. The CSM may be descriptive, take the form of a flow chart or be represented as an image or graphic. The concepts of site characterisation and risk analysis are inherent within the CSM development, which should underpin the risk management strategy for a site.

Report E1001 identifies three receptor-types which may need considering when developing the CSM:

- Living organisms associated with the aquatic environment (see also Section 6.4, Practical Application 6.1)
- Human beings
- The water environment (e.g. water quality)

The CSM may also need to take into consideration whether site conditions could, or are, impacting upon watercourse management activities. A hypothetical scenario which highlights how each receptor-type may need considering within the CSM development is shown as **Figure 3.2**. It is noted that the CSM in **Figure 3.2** is illustrative only, and not all potential pathways have been identified.

Figure 3.2 Hypothetical conceptual site model – receptor identification



The question underpinning an evaluation for each of type of receptor is whether potentially contaminated sediments are present, and whether there is a plausible linkage (whether a fate and transport mechanism and/or exposure route) between the contaminants and the receptors. Such a link needs to be present before it can be concluded that there is potential for contaminated sediments to be present.

Where contaminants in sediments have the potential to impact upon living organisms or human health, the development and refinement of the CSM will typically rely on collection of data to support a quantitative risk-based evaluation. Where there is concern that contaminants in sediments are impacting the water environment, the focus of the CSM development may instead be on whether a linkage between the contaminants in sediment and chemical quality of the surface water can be proven. The assessment should still follow a risk-based, tiered approach, but may focus instead on comparison of the soluble or leachable constituents in the sediment with water quality standards rather than evaluation of potential of harm to specific receptors. Further, the relationship between the sediment and overlying water column cannot be considered a one-way potential migration route; the potential for the sediment to act as a sink for contaminants as well as the potential for it to act as a source of contaminants may need to be considered.

If contaminants in sediments are impacting upon river management activities, such as securing safe navigation, the assessment is again likely to differ, requiring an understanding of the economic or social impact incurred as a result of the contaminants in sediments. For each case, while data evaluation methods may differ, the management of contaminants in sediments should still be underpinned by the CSM to make it clear to all stakeholders the reasons for which investigation, assessment and – if necessary – remediation works are being undertaken.

3.2. COMPONENTS TO A SEDIMENT SYSTEM CSM

The three components which inform the development of the CSM, as for a terrestrial site affected by contamination, are an understanding of the source characteristics, identification of potential receptors (and, where applicable, exposure mechanisms) and the link between these (the pathways). The latter requires the identification and evaluation of the routes by which the source can impact upon each receptor. Sections 3.2.1 to 3.2.3 explore this concept, and highlight where more detailed discussions relating to each element can be found within this document.

3.2.1. Source characterisation

CSM development often begins by characterising the source, asking questions such as what contaminants could be present, where could they be present and are there single or multiple contaminant inputs? The greater the understanding of the source and distribution of contaminants in sediment, the better able an assessor is to quickly screen out those sites and/or contaminants where there is no hazard, and those sites where more detailed assessment of the whole system (or specific contaminants) is appropriate. Section 4 identifies a number of key areas to consider when developing, and refining, the understanding of the source, namely:

- **Sediment contaminant inputs** (Section 4.2): in order to assess and manage potential risks from contaminants in sediments, all pertinent sediment contaminant inputs – both historical and still active – should be kept in mind. This may include a need to use tools and techniques to distinguish between different system inputs (e.g. laboratory forensic analysis).

- **Contaminant “partitioning”** (Section 4.3): understanding how different contaminants partition in the sediment environment (e.g. capacity to sorb to organic matter, the influence of different forms of carbon including black carbon, solubility) helps to predict where contaminants may be present, where and what to investigate, and how different receptors may be exposed to the contaminants.
- **Bioavailability** (Section 4.4): For a human or ecological receptor to be affected by contaminants in sediment, the contaminant must be in a form which is bioavailable. Assuming that all contaminants are bioavailable is a conservative assumption frequently made at the outset of an investigation, but potentially leads to an over-prediction of the actual risks present.
- **Lateral distribution** (Section 4.5): Input of contaminants to a surface water system may occur at more than one location, but since the water and sediment move (e.g. sediment redistribution during flood events) the zone of sediment contamination may extend beyond the immediate point of entry. Furthermore, fluvial processes may repeatedly mobilise and deposit sediment as it is mobilised by floods or other processes. In tidal estuaries contaminant transport up-stream may occur and this should be included with investigation design.
- **Vertical profile of contaminants in sediments** (Section 4.6): in building the CSM, and developing a risk management approach, the vertical profile of sediments may be equally as important as an understanding of the lateral profile. Understanding the vertical contaminant distribution may provide, for example, information relating to current versus historical sediment and contaminant inputs and changes in biological activity as a result of different redox conditions. Considered early in the assessment process, it will help investigation design (for example, analysis for specific radiochemical markers in sediment layers). The vertical profile may provide evidence of depositional sequences, and of the dynamism of the sedimentary environment, which may help to establish whether buried sediments are currently, or are likely, to be exposed in the future. Within historical context the river flow may have altered and current zones of deposition may differ from historical zones. Temporal issues of deposition must be acknowledged in assessment design.

3.2.2. System hydraulics and contaminant fate & transport

The second element to the CSM is an understanding of the system hydraulics and the fate and transport of contaminants which are present in the sediments. For example, if contaminants are believed to be present in sediments as a result of discharge of contaminated groundwater, what are the routes for contaminants to migrate in the system, and what are the controls on this migration? Section 5 focuses on these two elements:

- **System hydrodynamics** (Section 5.2): areas explored are sediment depositional environments, groundwater-surface water interactions and onshore to offshore system interaction. There is often a much greater potential for contaminant migration (including as a result of sediment disturbance) in the sediment environment than for terrestrial (soil) sites, as a result of changing depositional/erosional environments, water management activities and cyclical changes (e.g. tidal activity). These can all impact upon the fate and transport of contaminants in the sediment environment, which if not considered, result in poor site characterisation and conceptualisation.

- **Contaminant fate & transport** (Section 5.3): while understanding the system hydrodynamics is critical to developing a robust CSM, it is also important to understand the other factors which will impact upon contaminant fate and transport. Factors to consider include contaminant transport methods, contaminant transformation mechanisms (e.g. methods of degradation), flux modelling (e.g. moving from groundwater to surface water) and where empirical data provides significantly greater confidence in the CSM compared to theoretical calculations.

3.2.3. Exposure scenario conceptualisation

The final element to developing and refining a CSM is to identify the potential receptors and the exposure mechanisms by which they could plausibly be impacted. This includes a need to focus on the potential routes of exposure for different receptor types (human health, Section 6.5 and ecological receptors, Section 6.4); using site specific receptor behaviour combined with an understanding of the system or habitat they inhabit to compile a defensible CSM.

3.3. THE IMPACT OF THE CSM ON INVESTIGATION DESIGN

The CSM underpins the design of the site investigation strategy, identifying what the critical data collection requirements are in order to confirm assumptions included in the CSM, or to refine it if the data do not support previous assumptions. Each time an investigation is completed, the CSM should be revisited, challenged and refined as necessary.

To manage and where possible reduce uncertainty in the assessment process, the limitations with investigation design must be kept in mind. In some cases, innovative techniques may be used to improve efficiency of the investigation process, or to collect data which would not be possible to obtain using more conventional investigation tools. This is discussed in greater detail in Sections 7.2 and 7.3.

3.4. REFINING THE CSM AND EVALUATING POTENTIAL RISKS

Use of a tiered, phased approach to evaluating potential risks from contaminants in sediments is underpinned by the need to revisit and refine the CSM throughout the process. The consequence of not doing this might be that the data collected are misinterpreted based on a pre-existing CSM, leading to a poor risk-assessment and the potential for incorrect decisions on the need for remediation, whether to undertake unnecessary remedial action, or to fail to take remedial action when it is really needed. This also highlights the importance of evaluating the data within the risk-based framework and providing clear end point criteria for the assessment (Sections 7.4 to 7.8).

4. SOURCE CHARACTERISATION

4.1. INTRODUCTION

The first element in characterising a site is to develop and refine an understanding of the source. The "source" can refer to two aspects within the CSM, namely:

- Indirect "source"; The actual source of the contaminants in the sediments (e.g. discharges into surface water, contaminated site run-off, or leakage of a chemical from a storage container to ground); and
- Direct "source"; The contaminants in sediments themselves, acting as a secondary source to which receptors may become exposed.

Report E1001 provides an overview of the potential routes by which contaminants can migrate into (in dissolved phase or transport of liquid phase substance), or be deposited into (e.g. deposition of contaminants bound to suspended particles), the sediment environment, and subsequently partition between the different phases (liquid, solid, air) within the sediment matrix. An understanding of both the primary source of contamination alongside the behaviour of the contaminants once in the sediments is important in characterising the site.

In this section, areas of uncertainty which may arise during the characterisation process, from the development of the CSM through to quantitative risk-based analysis, are highlighted. Methods which can be used to understand and in many cases reduce the uncertainties are described, discussed within the following groupings:

- Sediment contaminant inputs (Section 4.2);
- Contaminants in the sediment matrix (Section 4.3);
- Bioavailability (Section 4.4);
- Lateral distribution of contaminants in sediments (Section 4.5); and
- Vertical profiling of contaminants in sediments (Section 4.6).

4.2. SEDIMENT CONTAMINANT INPUTS

An understanding of the likely sediment contaminant inputs assists with initial CSM development, but also aids design of investigations, risk evaluation and, if required, design and implementation of a remediation solution. The sediment environment is typically dynamic, which needs to be taken into account throughout the assessment process, in particularly when characterising the source of the contaminants in the system (Example 4.1).

Example 4.1: Man-made cooling water ponds, northwest England

A large former chemical manufacturing site in northwest England has a series of man-made ponds (**Figure 4.1**), which were excavated into the natural geology but only partly lined, to allow storage of cooling water for use in the manufacturing process. Sediments (described as such due to the partial lining of the cooling ponds) were present in the base of the cooling ponds which contained a range of contaminants at mg/kg concentrations. The same contaminants were also found in the overlying surface water and within a nearby stream to which the cooling ponds discharge. The concentrations in surface water were considerably higher than Environmental Quality Standards, and remediation was considered necessary by all stakeholders involved, on the basis of degradation of water quality within the stream system and potential harm to aquatic organisms.

The initial proposed remediation solutions comprised sediment removal from the ponds or a capping solution. However, the uncertainties associated with the CSM – in particular the sediment contaminant inputs – were highlighted early in the evaluation process, resulting in the completion of a Tier 0 assessment (including development of a robust CSM).

Figure 4.1 Man-made cooling pond, England

The water within the ponds was known to be fed from a natural watercourse, but site investigation data also demonstrated a component of groundwater discharge into the ponds. Surface water samples collected up-gradient of the ponds did not contain the same contaminants as present in the pond sediment. Therefore, this was discounted as a potential contaminant source although it was identified as a contributing source of the sediment materials present in the ponds. Groundwater discharging into the ponds was demonstrated to contain elevated concentrations of the contaminants, thereby acting as an indirect source to the ponds. There were no known historical product leaks in the vicinity of the ponds and former stack emissions would not have contained the contaminants encountered in the system. Interviews with previous site workers identified the possibility that contaminated soils had been deposited in the ponds historically (forming a sludge), and could also be acting as an indirect source to the system. Finally, small drainage pipes were identified discharging water from across the site into the ponds. The quality of the water, including the presence or absence of suspended particles, was unknown.

On the basis of the Tier 0 assessment, further evaluation of the contaminant source inputs was recommended, focused on understanding the importance of the groundwater source input, historical contaminated soil input and drainage pipe input. This required collection of additional site data, including more detailed profiling of the vertical contaminant profile in the pond sediments and sampling of the pipe discharge water. Without further data collection, the CSM was used to illustrate that source removal or a capping solution was unlikely to be successful due to the continued input of contaminants into the sediment environment from uncontrolled sources (potential for recontamination).

The uncertainties (Practical Application 4.1), which may arise as a result of not considering the sediment contaminant inputs include challenges in interpreting site investigation data (e.g. accounting for varying contaminant concentrations with depth in the system), evaluating potential risks (e.g. could the risks change in the future as a result of differing contaminant inputs?) and assessing remediation feasibility (e.g. if source removal is implemented, are there additional uncontrolled source inputs that will result in re-contamination occurring?).

Practical Application 4.1: Sediment contaminant inputs
Each site should consider whether there could be a historical or on-going contaminant input (at the site, in the vicinity of the site or in the upstream part of the catchment area), possibly as a result of: • Atmospheric deposition; • Groundwater discharge; • Surface run-off; • Point discharges (which may or may not be permitted); • Deposition of suspended particles (e.g. originating from urban waste water treatment plants, or naturally occurring contaminants present as a result of riverbank erosion); • Waste disposal activities, including combined sewer overflows; or • Temporal changes to watercourse morphology (e.g. scouring of riverbed resulting in contaminants buried in sediments below the biologically active zone becoming re-exposed). In many cases, it may be possible to rank the sediment contaminant inputs to identify which are the greatest contributors, potentially underpinned by use of simple mass balance calculations (Box 4.1) related to groundwater discharge, atmospheric deposition rates etc.

4.2.1. Contaminant source history

Characterising historical contaminant inputs into the sediment system can be a challenge, in particular where multiple pressures have been present (for example, industrial sites, road run-off, ports and harbours), and where the input period stretches back over decades or even centuries. At a Tier 0 level of assessment, reliance may be placed on literature source in developing the CSM, such as:

- Site records (e.g. historical processes, location of production plants, location of site drainage, site staff interviews);
- Aerial photographs;
- Historical topographic maps; or
- Public records (e.g. existing environmental investigation reports, building control records, records of release events, discharge permits).

Progressing to a higher Tier of assessment, conceptualisation of the contaminant source history may be possible through vertical profiling of the sediments (Section 4.6) or source attribution (Section 4.2.3) alongside mass balance calculations to estimate changing contaminant input with time. Such calculations may be relatively basic (Box 4.1) at lower tiers of assessment, but more complex at higher tiers of assessment where system hydrodynamic modelling or multivariate statistical testing (Section 7.4) may be required to provide the greatest degree of certainty in the evaluation.

Box 4.1: Simple mass balance calculations

There are multiple forms of mass balance calculations which could be undertaken to evaluate the likely importance of different contaminant input routes.

Where contaminants are input as a result of groundwater discharge to surface water, Darcy's Law could be used to predict the flux of contaminant, assuming the concentration of contaminant in groundwater over time is known (or can be reasonably estimated). The conservative assumption would be that all the contaminant input via this route is retained in the sediments. However, the large number of variables that can affect this fate and transport route means that any such assessment will typically have a high degree level of uncertainty.

Under the more unusual circumstance of atmospheric deposition being an input route of concern, it may be possible to estimate the historical rate of deposition (e.g. site records relating to stack emissions, regional public data regarding particulate concentrations) which can be combined with the estimated (e.g. literature sources) or measured rate of sedimentation (e.g. through isotopic testing, such as ^{210}Pb or ^{137}Cs in a stable system, Section 5.2.1) within the watercourse to predict the contaminant input flux from this route. This may change over time, especially where the historical source is a stack emission relating to former activities on a site, or surrounding sites.

However, it is recognised that such simple mass balance calculations have associated uncertainties and limitations. For example, when considering a groundwater contaminant input, attenuation is likely to occur as the groundwater discharges through the anaerobic/aerobic interface, and it is possible that this will reduce the contaminant flux into surface water by a considerable amount.

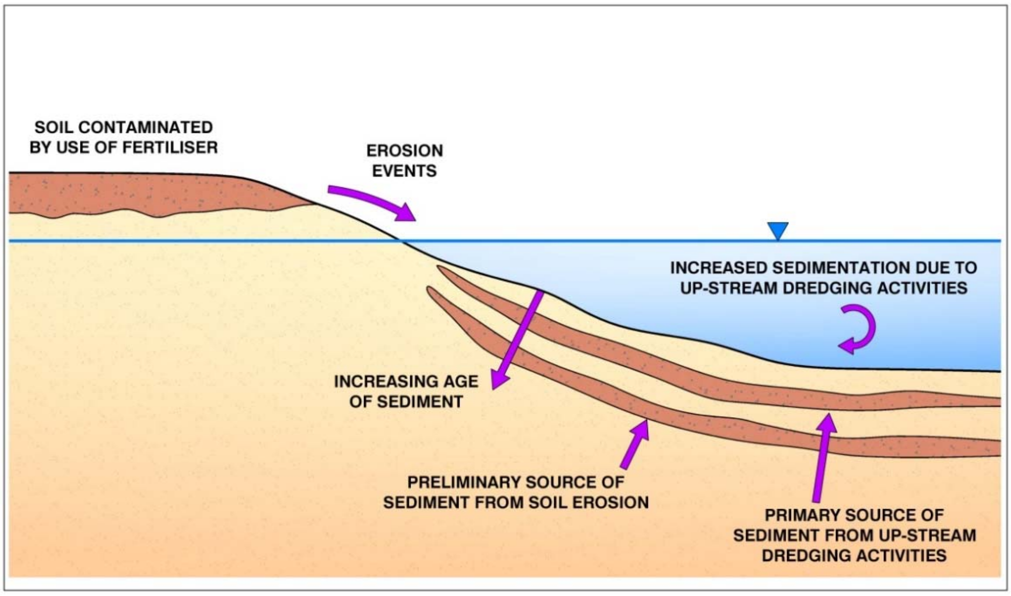
When collating information on the contaminant source history, it is helpful to distinguish between dynamic versus stable contaminant inputs (Section 4.2.2), but also current inputs versus historical inputs. Given the long legacy of industrial activity in the European Union, including the consented discharge of many contaminants to watercourses, all these factors should be considered during development of the CSM and the potential influence they may have on the viability of completing a successful assessment evaluated.

An understanding of the contaminant source history also helps to highlight at an early stage in the assessment whether contaminants may be present that could affect the data assessment process and/or that may restrict remediation options if remediation is found to be warranted.

4.2.2. Dynamic versus stable contaminant inputs

Understanding whether a contaminant input is a dynamic process or a stable input is important in characterising the contaminant input to the system over time, and whether this needs to be factored into investigation design and risk evaluation. Linked in with understanding historical contaminant inputs (Section 4.2.1), techniques such as vertical profiling of the sediments may help to identify both changes in contaminant input and changes in sedimentation rates, for example as a result of more predictable cyclical factors (e.g. increased surface run-off during periods of heavy rainfall) or less predictable factors (e.g. waterway dredging leading to suspension and re-deposition of sediments in the watercourse). If the possible temporal effects on contaminant input to the system are not considered, there is potential for the true system condition to be masked (**Figure 4.2**).

Figure 4.2 Schematic showing a theoretical site with dynamic sediment and contaminant inputs



When an investigation was designed to collect surficial sediment samples from the example system in **Figure 4.2**, taken after a period of upstream dredging activities, the uppermost sediments would show low concentrations of contaminants (assuming the suspended particles re-deposited did not contain the same contaminants). If the samples were collected after sufficient time had elapsed such that soil erosion was the dominant contributor to the sediment formation (and therefore contaminant input), a different view might be concluded of the sediment quality. Use of sub-surface sediment sampling techniques (i.e. to collect a sediment core to profile the vertical contaminant distribution, Section 4.6) or repetition of the surficial sampling over time can help to build up an understanding of the relative importance of each deposition layer in the risk evaluation.

4.2.3. Source attribution

Where there are multiple inputs of the same groups or suites of contaminants into a sediment system, the need to be able to attribute these contaminants to specific primary or secondary inputs can be critical in understanding the original “polluter” and, therefore, which stakeholder or stakeholders are liable. Because many sediment systems are dynamic (i.e. sediment re-suspension and re-deposition is an active and on-going process), identification of a contaminant adjacent to a known source alone (e.g. site affected by groundwater contamination) is not always sufficient evidence to link the contaminant in sediment to that particular source. It is also possible that suspended particles originating from elsewhere in the watercourse, also containing the same contaminant have been deposited adjacent to the site as a result of the system hydrodynamics. However, there is an increasing toolkit which can be used to try to attribute sources of contaminants in sediments, which includes accounting for the variability in observed conditions affected by natural processes (see Section 4.3.1 and 4.3.2). This helps to ensure that appropriate comparisons between sample locations are made, including through the process of normalisation. Additional tools include statistical testing (such as principal component analysis) to evaluate correlations between datasets (see Section 7.3).

Chemical fingerprinting, or forensic testing, methods are summarised by the US Naval Facilities Engineering Control (2003), and include:

- Use of geochemical relationships including stable isotope analysis to attribute contaminants to specific sources and to understand source distribution (Section 4.3, see also Bertine and Golderberg, 1977; Ackerman et al, 1983; Trefry et al, 1985, Klamer et al, 1990, Schropp et al, 1990 and Daskalakis and O'Conner, 1995, which are all summarised and reviewed by the Naval Facilities Engineering Control, 2003);
- Use of contaminant ratios, for both organic and inorganic contaminants, to distinguish between naturally occurring and anthropogenic sources (Practical Application 4.2);
- Laboratory analysis to assess state or weathering or ageing of organic contaminants (Practical Application 4.3);
- Laboratory analysis for indicator contaminants, contaminant isomers/congeners or product additives (Practical Application 4.4); or
- Forensic laboratory analysis of a reference sample (primary source, Practical Application 4.3) and comparison to analysis of samples obtained from site.

Practical Application 4.2: Chemical Fingerprinting – contaminant ratios

Different ratios of contaminants can be used for organic and inorganic contaminants as an indicator as to the primary source. Typically, the output will provide an indication as to whether the primary source is naturally occurring or anthropogenic, although analysis methods are becoming more sophisticated. Three examples of chemical fingerprinting through evaluation of contaminant ratios highlighted by the Naval Facilities Engineering Control (2003) and summarised here.

Metals

Evaluation of metal-aluminium ratios can indicate where metals are present as a result of naturally occurring, "background" conditions. This is based on the presumption that naturally occurring metals are typically part of an alumina-silicate mineral structure. A regression analysis of naturally occurring metal concentration against aluminium concentration should provide a linear correlation. Where such a relationship is not observed, then it is probable that there is also an anthropogenic input into the system.

Polycyclic Aromatic Hydrocarbons (PAH)

There are well recognised methods by which the source of PAH can be investigated, primarily related to the fact that two forms are typically found in the environment. The two forms are typically referred to as "petrogenic PAH" and "pyrogenic PAH". Firstly, "petrogenic PAH" is a definition used for PAH that are formed slowly and under low to moderate temperatures (often related to a natural source, such as coal deposits). Secondly, "pyrogenic PAH" is a definition used for PAH that are related to higher temperature events, such as combustion of fuels (e.g. from automotive or power plants, or incomplete combustion of wood or charcoal burning) or from processing of coal to form coal tars and coal tar products (Boehm and Saba, 2008). It is also recognised in literature that as the formation temperature increases, so the type and complexities of PAH forms changes (Lima *et al*., 2005). Taking this into account, simple forms of PAH ratio screening have been used to distinguish between petrogenic and pyrogenic sources. For example, a ratio of phenanthrene/anthracene greater than 10 typically indicates a petrogenic source, but a ratio less than 10 indicates a pyrogenic source. Boehm (2006) built on this to develop a more sophisticated toolkit. This includes increasing the range of PAH analysed (e.g. increased number of alkyl carbons), testing for alkylated homologues (e.g. C1-C4 naphthalene), testing for biomarkers (e.g. steranes) and the use of “double ratio” plots to evaluate trends in PAH datasets across an investigation area.

Practical Application 4.3: Chemical Fingerprinting – Laboratory Product Analysis

Forensic testing of product samples, obtained from the field (e.g. from a monitoring well) or even forensic testing of a reference sample, can be used to understand the possible origin of the product. The testing needs careful interpretation by an expert.

The following are examples of analysis which can be undertaken in order to distinguish the type of petroleum hydrocarbon product present, its likely age and degree of weathering:

- Carbon number range/boiling point range
- Pristane/phytane ratio
- nC17/pristane ratio
- Density
- Rb (cumulative ratio)
- Presence/absence of specific compounds e.g. additives such as:
    - methyl tert-butyl ether [unleaded gasoline, 1990s to current];
    - ethyl tert-butyl ether [unleaded gasoline, mid 2000s to present]
    - 1,2-DCE, 1,2-DBA, tetra-ethyl lead [leaded gasoline, pre-mid-1990s]

Practical Application 4.4: Chemical Fingerprinting – Congener Analysis for PCBs

PCBs were manufactured from 1930 to 1977 and sold under the trade name Aroclor®. Each Aroclor was numbered, and comprised a consistent mixture of specific PCB congeners. An initial form of chemical fingerprinting is to test for an aroclor mixture, based on knowledge about the Aroclor mixture suspected as the source. However, there may also have been additional contaminant inputs to the system, for example another industry using the same Aroclor mixture. Where this is the case, more detailed analysis of the specific congeners present can be undertaken, but it is recognised that forensic testing for PCBs is complicated by the often complex environmental degradation and transformation processes (abiotic and biotic) which PCB congeners slowly undergo in the natural environment. Advanced forms of forensic testing include double ratio plots for specific congener ratios, regression analysis of Total Petroleum Hydrocarbons (carrier oil) versus specific congeners and isomer analysis (related to differing de-chlorination rates for ortho-, meta- and para- PCB isomers), alongside use of statistical analysis tools such as principal component analysis.

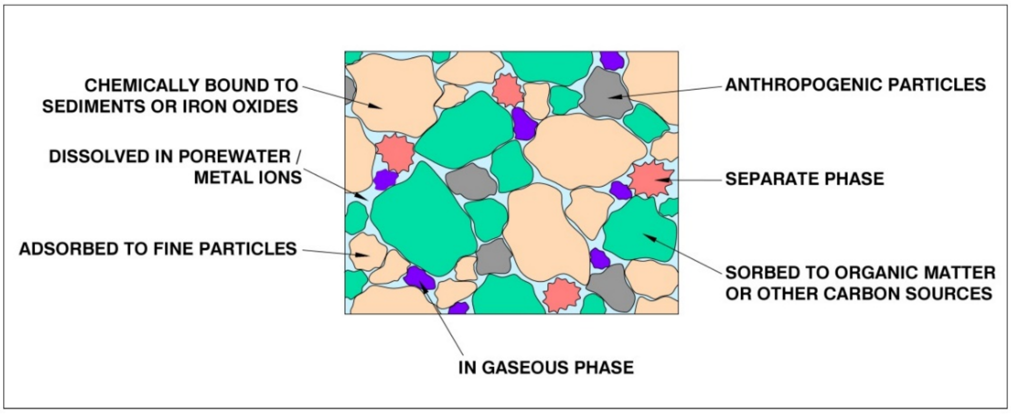
4.3. CONTAMINANTS IN THE SEDIMENT MATRIX

Sediments are made up of multi-phases, comprising a combination of particles and organic matter (both naturally occurring and anthropogenic in origin – the sediment matrix), pore water (interstitial water) and gases. Contaminants may be present sorbed to the sediment matrix (e.g. sorbed to the surface of particles), dissolved in pore water, within gas “bubbles” or, in some cases, as a separate phase which displaces the pore water (**Figure 4.3**).

The phase(s) in which a contaminant resides in a sediment is dependent on physical-chemical properties of the contaminant, the physical properties of the sediment (e.g. particle type, percentage of organic matter content) and the biochemical and geochemical properties of the sediment (see also Section 4.3.1, contaminant "form"). Predicting the distribution of a contaminant between each of the phases helps guide investigation design to target data appropriate date collection. For example, where a contaminant is predicted to largely reside in pore water, an investigation focused on collection of interstitial water may be required. For a contaminant which will sorb preferentially to organic matter, the investigation may include detailed assessment of the percentage and form of organic matter in the sediment.

Understanding where the contaminant resides within the sediment is important to predict the potential fate and transport pathways for contaminants, alongside the likely bioavailability of a contaminant based on its distribution in pore water (Section 4.4).

Figure 4.3 Illustration of the sediment matrix "compartments"



Contaminants present as a result of precipitation processes and absorption into the solid matrix of a sediment (e.g. structural collapse of the mineral around the sorbed contaminant) are generally stable. In contrast, partitioning of contaminants through surface adsorption and organic partitioning are more likely to be reversible. As a result, contaminant partitioning throughout the sediment compartment may change with time, influenced by contaminant concentrations, physical/mechanical stress on the sediment matrix, changing geochemical properties (e.g., pH) or chemical speciation.

There is still debate as to the best method to predict contaminant partitioning through multi-phase modelling, with a general acceptance that the complexities of the natural environment means that model predictions only provide an estimation of conditions in the field. A number of authors believe that prediction of contaminant partitioning within the sediment matrix from a bulk sediment concentration using predictive mechanistic approaches is actually unreliable (e.g. ECHA, 2011; USEPA, 2008), for a number of reasons, which may include:

- Limited focus on the contaminant form present
- Variable water content throughout the system
- Non-linear desorption, typically involving both a fast and a slow rate over time
- The importance of dissolved phase organic matter

- No differentiation based on the type and quality of organic matter present and impact this can have on sorbtive capacities (e.g. black carbon, Section 4.3.3)
- Variable particle size and the impact this can have on contaminant distribution
- Reliance on literature-based partition coefficients derived under different conditions to those present at a site
- Difficulties with accounting for separate phase contaminants or contaminant particles in the sediment matrix.

Relatively simple equations can be used to predict the partitioning of organic and inorganic contaminants within the sediment matrix, but the limitations associated with modelling as opposed to collection of empirical data should always be kept in mind.

Two approaches are used to predict partitioning behaviour (Mackay, 2001):

- Use of contaminant-specific empirical or experimental partition coefficients (e.g. promoted by the Environment Agency, 2009a, for assessment of soils)
- Relating the concentration in each phase using an intermediate quantity as a measure of equilibrium, for example level III fugacity model described by Mackay et al (1985) (e.g. promoted by RIVM, Lijzen et al, 2001).

The simplest form of equation is used to predict the concentration of a contaminant in sediment pore water, which is of particular importance when evaluating the potential bioavailability of the contaminants (Section 4.4) relying purely on use of the sediment-water partition coefficient.

$$C_{porewater} = C_{sediment} / Kp$$

Where:

$C_{porewater}$	is the predicted concentration of a contaminant in porewater ($\mu g_{contaminant}/L$)
$C_{sediment}$	is the measured concentration of a contaminant in sediment (µg/kg)
Kp	is the sediment-water partition coefficient ($L_{water}/kg_{sediment}$), which in turn is typically calculated using the simple relationship: Fraction of organic carbon in sediment multiplied by the Koc (soil organic matter to water partitioning coefficient).

4.3.1. Contaminant “form”

Understanding the contaminant “form” present allows more robust CSM development and more accurate prediction of potential risks. This is particularly the case for inorganic contaminants, where both contaminant speciation (e.g. chromium III versus chromium VI) and contaminant form (e.g. mercuric chloride versus mercuric sulphate versus mercuric cyanide) influence the fate and behaviour of the respective elements. The contaminant form present is likely to be an important control on contaminant partitioning to sediment, thus affecting its bioavailability (Section 4.4) or its migration through the environment (Section 5). Different contaminant forms may also present a greater or lesser risk to the identified receptors as a result of their inherent toxicity.

When developing the CSM, the potential for different forms of contaminants to be present should be taken into account (Practical Application 4.5).

Practical Application 4.5: Contaminant forms (CSM Development)

When developing the CSM, identifying known or potential contaminants which may be present in the sediment matrix, the following should be considered:

- Are there multiple isomers which could be present?
- Are there different metal species which could be present?
- Which metal salts may be present?
- What is the sediment redox condition and the likely oxidation state of specific metals?
- What species of dissolved phase ions could be present?
- Which of the isomers, species or salts is likely to present the greatest risk (e.g. consider use of the HydroCarbon Block method, King et al, 1996)?

Each question may be answered by reviewing available information relating to the site history and likely sources of contaminants (e.g. knowledge about industrial processes in the area), alongside a prediction as to the salts or species which may be there given the predicted (or known) sediment geochemical conditions. This directly impacts upon investigation design and implementation (Practical Application 4.6).

For inorganic contaminants, the salts or species present may be dependent on the geochemical conditions within the sediment. These conditions may change laterally and with profile depth, and include pH, oxidation reduction potential, acid volatile sulphides (AVS), salinity and alkalinity (Practical Application 4.6). The importance of three of these parameters (pH, oxidation reduction potential and acid volatile sulphides) is explored in further detail, with a good overview also provided by the Naval Facilities Engineering Control (2003).

Practical Application 4.6: Contaminant forms (Investigation Design)

When designing the sediment investigation, if specific substances isomers, speciated metals or salts could be present, the following should be incorporated where appropriate:

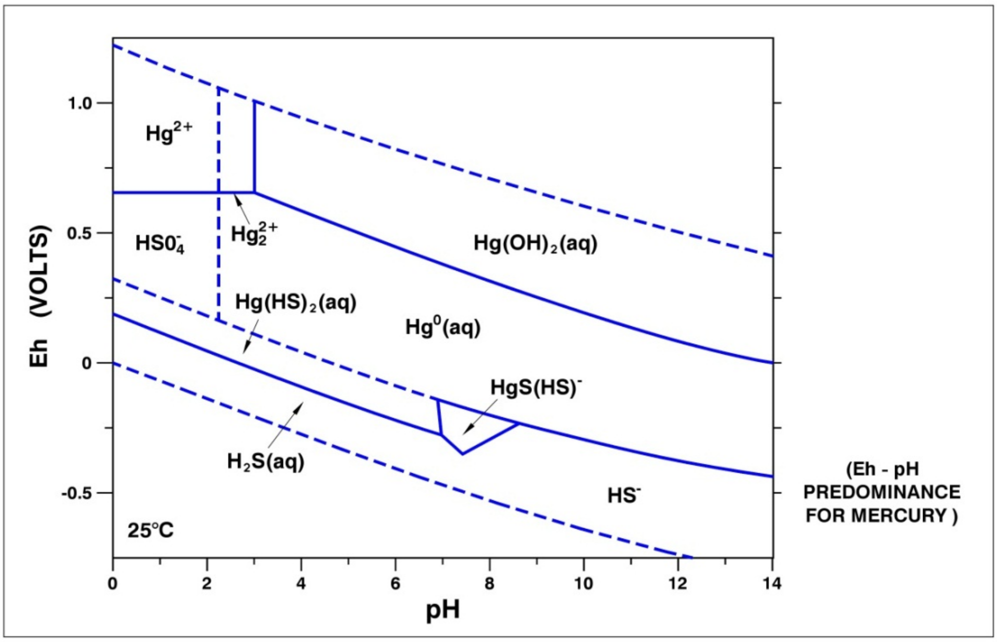
- Sample collection and preservation to maintain in-situ geochemical conditions
- Appropriate storage and transportation to maintain sample integrity
- Appropriate sample preparation at the laboratory to ensure it is not adversely affected prior to analysis
- Laboratory analysis to test for the different isomers, species or salts which are anticipated to be present (see also Section 4.2.3)
- Measurement of pH (in the field)
- Measurement of salinity
- Measurement of alkalinity (in the field and/or laboratory)
- Measurement of redox conditions (in the field)
- Measurement of AVS

The data collected can be used to inform the contaminant bioavailability assessment (Section 4.4), alongside interpretation of potential differences in bulk sediment concentrations with depth and laterally across the investigated are which may be due to variable geochemical conditions rather than varying concentrations of contaminants in sediment.

pH and oxidation-reduction potential (Redox or Eh)
These geochemical parameters can be important in understanding the form of certain contaminants and whether conditions are appropriate for microbial degradation of particular contaminants to take place.

An Eh (activity of electrons, oxidation-reduction potential)-pH (activity of hydrogen ions) diagram, also known as a Pourbaix diagram, (e.g. **Figure 4.4**) is a method of illustrating the fields of stability of contaminant species (Pourbaix, 1974 and Brookins, 1988).

Figure 4.4 Eh-pH stability chart for mercury



Inorganic contaminants may undergo transformation as a result of changing geochemical conditions; the conditions may change temporally or spatially. Eh-pH charts are readily available within literature (e.g. Pourbaix, 1974 and Brookins, 1988) or can be calculated using freely available software tools, and can be used to predict which species may be present under a combination of pH and redox conditions. This knowledge can then be used to predict the likely bioavailability of the inorganic contaminant, its potential for migration in the environment and its toxicity to different receptors – both for current conditions and should conditions change.

For organic contaminants, microbial degradation is a relevant mechanism for changing the distribution, concentration and form of contaminants in sediments (e.g. ITRC, 2011a; Hambrick et al, 1980; DeLaune et al, 1980; DeLaune et al, 1981). There is a correlation between the geochemical conditions, notably the pH and redox, and what microbial degradation processes are active in sediments. Microbial activity itself impacts upon the geochemical conditions; different microbes are suited to differing geochemical environments, therefore, the microbial population will change over time as degradation of an organic contaminant takes place and geochemical conditions are modified. An understanding of the geochemical conditions can help predict whether degradation of a specific contaminant is likely to take place (Example 4.2).

Example 4.2: Degradation of petroleum hydrocarbons, Barataria Bay, Louisiana
Studies were undertaken in a number of sediment environments – inland, estuarine and marine – by a group of researchers in the 1970s to 1980s, focused on understanding the relationship between microbial degradation of petroleum hydrocarbons and geochemical conditions. DeLaune et al (1980) reported on a study in Barataria Bay, Louisiana, where the microbial mineralization rates of two petroleum hydrocarbons were assessed, under changing pH and oxidation-reduction potential conditions. The study relied upon use of ^{14}C-labelled hydrocarbons, inferring the rate of degradation through the activity of respired $^{14}CO_2$. The first conclusion of the study was the importance of pH; the rates of mineralisation were highest at pH 8.0 and lowest at pH 5.0. The second conclusion of the study was that rates of mineralisation decreased as the conditions became more anoxic. The authors explained the findings of the study as providing evidence for the more ready degradation of petroleum hydrocarbons under thermodynamically-favourable aerobic conditions than anaerobic conditions.

Acid volatile sulphides (AVS)

As a precipitant of certain metals, sulphide is important in controlling the partitioning of metals in anoxic sediments. AVS can provide an indicative measurement of the amorphous iron sulphide (FeS) present within sediments (e.g. Schulz and Zabel, 2006). Iron is generally present in sediments as pyrite (FeS_2) or mackawinite (amorphous FeS). If amorphous FeS is present in sediments, many dissolved metal species present will adsorb to the FeS content, which is generally stable in reducing environments. As such, in anoxic conditions, the potential for heavy metal dissociation from sediment into pore water generally decreases with increasing AVS concentrations. However, if the redox conditions changes to oxidising conditions, the metals sorbed to FeS can be released back to the dissolved phase.

As a simple form of analysis, the molar concentrations of the metal and AVS measured in each sediment sample can be compared to determine if there is an excess in metal concentrations. If an excess is predicted, the likely form of the residual content should be made, evaluating its physical-chemical and toxicological properties. Alternatively, the extractable metal concentrations can be normalised to AVS (ITRC, 2011a) using the same method provided for particle size and organic carbon normalisation (Sections 4.3.2 and 4.3.3). The difference in metal concentration and AVS itself can also be normalised to organic carbon content. This data can be used to inform an assessment of contaminant bioavailability.

4.3.2. Particle size distribution

Organic and inorganic contaminants are typically concentrated onto the finer particles (silt / clay) within sediments, where the increased surface area and organic carbon content results in greater contaminant adsorption than will occur within coarser granular sediments. Therefore, consideration of sediment stratigraphy and particle size should be factored into the investigation design. A common method for compensating for particle-size differences in suites of sediment samples, in order to enable a more sophisticated assessment of potential trends in the lateral and/or vertical distribution of contaminants, is to normalise contaminant data, either through physically separating the fines and analysing for the contaminants, or by regression using particle size analysis (Practical Application 4.7). There is debate as to whether the normalisation band should be the <20 micron fraction (e.g. Krom et al, 2002, Szava-Kovats, 2008) or <63 micron fraction (e.g. Grant and Middleton, 1998). Szava-Kovats (2008) argues that <63 micron fraction is not small enough, as does not accurately represent the clay content where the bulk of the contaminants will reside. However, a larger normalization target is preferable if normalisation is to be carried out physically rather than relying on particle size analysis, as preparing and testing <20 micron fraction of the sediment takes longer and has greater potential for laboratory errors (Herut and Sandler, 2006).

Practical Application 4.7: Normalisation to particle size

Particle size distribution analysis should be undertaken (dry weight) for each sediment sample for which the normalisation process is planned. Typically, such testing is completed with reference to include BS EN ISO 17892 Part 4 (Geotechnical Investigation and testing – laboratory testing of soil. Determination of particle size distribution). The percentage silt/clay content of each sediment sample can be calculated from particle size distribution analysis, and the corresponding contaminant concentrations divided by the fraction of silt/clay content measured within each sample, resulting in a 'normalised' data set:

$$C_{N\text{-}GS} = C_M / GS_{SC}$$

Where:
$C_{N\text{-}GS}$ is the concentration of contaminant ($mg/kg_{dry\ weight}$) normalised to % silt/clay
C_M is the measured concentration of contaminant in sediment ($mg/kg_{dry\ weight}$)
GS_{SC} is the fraction of particles <63 micron in size (i.e. % silt/clay content, expressed as a fraction)

The sediment analysis data can then be evaluated for potential trends in lateral or vertical distribution, but without bias introduced as a result of variable particle sizes.

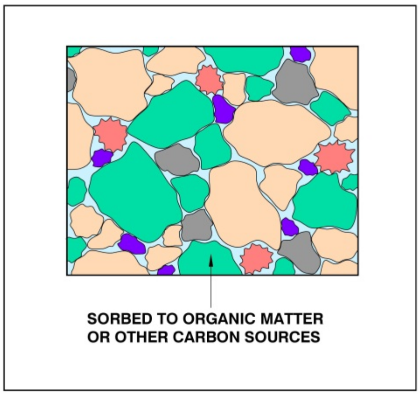
This method of analysis is well documented and applied (e.g. Example 4.3), and is typically considered alongside normalisation to organic matter content (Section 4.3.3).

Example 4.3: Particle size normalisation, Ria de Vigo, Spain

Rubio et al (2000) reported the findings of a sediment investigation (66 samples) collected from the funnel-shaped embayment in Galicia, Spain. The samples were analysed for major and trace elements to investigate whether the conditions encountered could be attributed to polluting activities on the foreshore or whether they could be attributed to (naturally occurring) background conditions. The authors concluded that there were two clear groupings present in the data; a sand-rich sediment with less than 10% fines and "mud-rich" samples from the central part of the Ria basin. The normalisation of element concentration to particle size highlighted that Al, Fe, Ti, Cu and Zn were between 5 and 7 times greater in the muddy sediments than the average concentration in the sandy sediments. Pb and Cr were found to be close to 4 times higher in the muddy sediments, with Ni, Co and As approximately twice as high. Principal component analysis was also completed, with the aim of identifying trends in the observed conditions relative to expected background concentrations. The findings of the assessment were that the Ria harbour was moderately contaminated by Pb, Zn, Cu, Cr and Fe, relating to anthropogenic contaminant input, and highlighted importance of adjusting for particle size when studying metal contamination.

For more information, see Rubio et al (2000).

4.3.3. Organic carbon



Organic carbon plays an important role in controlling the partitioning of dissolved organic contaminants (including nonpolar organics, such as polychlorinated biphenyls) onto solid organic matter in sediments (**Figure 4.1**). Generally, the higher the percentage of organic carbon present, the higher the potential for contaminants to be bound to the sediment matrix. However, the type of organic carbon present also dictates the degree of sorption which can occur. Natural organic matter, such as vegetative debris, humic and fulvic acids and decayed remains of plants and animals, contains non-pyrogenic organic carbon. A general rule of thumb is organic matter comprises approximately 58% organic carbon (e.g. Environment Agency, 2009a). Organic carbon may also be present in sediments as a result of anthropogenic sources ("black carbon" particles such as coke, charcoal, and soot). Black carbon particles are known to have high sorption capacities (e.g. Grathwohl 1990; Gustafsson et al, 1997; Ghosh et al, 2000; Accardi-Dey and Gschwend, 2002; Moermond et al, 2005; Koelmans et al, 2006). Therefore, where black carbon is suspected or known to be present, and the evaluation will rely on prediction of the partitioning of organics in the sediment compartments, it is prudent to undertake analysis which distinguishes between the different organic carbon types.

While the focus of organic carbon analysis is on the bulk organic carbon content of a sediment sample, it can be useful to understand the dissolved organic carbon content within the sediment pore water, as this can still act as a sink for contaminants, impact upon contaminant mobility and impact upon contaminant bioavailability (Section 4.4). As such, the distribution of contaminants within the sediment matrix can be influenced by dissolved organic carbon. Dissolved organic carbon distribution coefficients (K_{doc}) can be used to theoretically evaluate the impact of dissolved organic carbon on the contaminant partitioning (e.g. Böhm and Düring, 2010).

Due to the role that organic carbon content plays in controlling organic partitioning and bioavailability (and in some cases metal binding and bioavailability) in sediments, measured concentrations of contaminants can be normalised to organic carbon content (Practical Application 4.8) in order to aid assessment of potential trends in the lateral and/or vertical distribution of contaminants (see also Section 4.3.2).

Practical Application 4.8: Normalisation to organic carbon

Organic carbon analysis should be undertaken for each sediment sample for which the normalisation process is planned, and to support the wider site conceptualisation (giving consideration to the value of analysis for dissolved organic carbon and black carbon in sediment). Assuming a comparable form of organic carbon is present throughout the sediment matrix, the organic carbon content can be estimated through laboratory analysis of each sediment sample, and the corresponding contaminant concentrations divided by the organic carbon content measured within each sample, resulting in a 'normalised' data set:

$$C_{N\text{-}OC} = C_M / f_{OC}$$

Where:

$C_{N\text{-}OC}$ is the concentration of contaminant (mg/kg$_{\text{dry weight}}$) normalised to organic carbon content

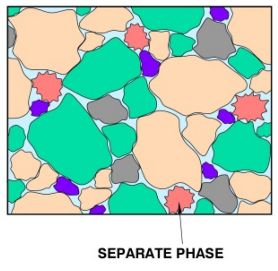
C_M is the measured concentration of contaminant in sediment (mg/kg$_{\text{dry weight}}$)

f_{OC} is the organic carbon content (fraction)

The sediment analysis data can then be evaluated for potential trends in lateral or vertical distribution, but without bias introduced as a result of variable organic carbon content.

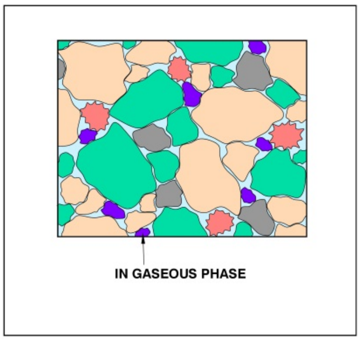
4.3.4. Separate phase contaminants

Contaminants may be present in the sediment as a separate phase (liquid or solid). Where present as a solid, it may be possible to identify the solids through visual inspection of sediment samples (e.g. coal particles, plastics etc.). Understanding whether solids are present may be important for evaluating the potential for disassociation of contaminants from the sediment matrix, and whether the solids are too large for ingestion by a human or ecological organism to be a plausible pathway (e.g. Hoeger, 2011). Screening sediment samples by particle size can help to identify larger solid particles.



Where separate phase liquids are present, or suspected, the source characterisation should consider the lateral and vertical extent of the liquids in the sediment, the degree of saturation of the sediment by the liquid, thereby helping to answer question such as whether the liquid is functionally mobile or immobile, and whether migration of the liquid is (or could) occur. For example, the concepts of mobility, plume stability and recoverability of light non-aqueous phase liquids have been well studied for aquifers (e.g. ITRC, 2009, API, 2006), concepts which can be applied to the sediment environment. There are a range of testing kits (e.g. separate phase detection dyes) and *in situ* probing tools which can be used to delineate the presence and degree of saturation of a sediment by separate phase liquids (e.g. Membrane Interface Probe or Laser Induced Fluorescence probes, which can be barge-mounted or operated from the land/foreshore), highlighted in Report E1001. These can be used to build up a 3 dimensional understanding of the distribution of the liquid within the sediments (see Sections 4.5 and 4.6).

4.3.5. Contaminants in gaseous phase



Gases can be present in sediments as “bubbles” which have the capacity to act as a transport mechanism carrying contaminants through the sediment profile (ebullition) or promote the migration of separate phase liquids (Examples 4.4 and 4.5). This can include gases acting to transport separate phase contaminants on the gas bubbles themselves.

This is likely to be of greatest concern in sediment systems where bulk gases such as carbon dioxide or methane are being generated, and should be considered in development of the CSM, design of investigations and the potential impact this could have on a proposed remediation solution.

Example 4.4: Ebullition and Separate Phase Liquid Migration, US

Gas bubbles were observed during the investigation of a sediment site in the US, with separate phase hydrocarbon liquid also present. Preferential migration pathways were identified in the sediment (utility corridors) which allowed the gas bubbles to migrate towards the sediment surface (ebullition) acting as a transport mechanism for the separate phase liquid (entrained within or on the gas bubbles). A reactive cap was proposed for the site, to break the pathway between source and potential receptors, but the cap had to be carefully designed to take account of greater levels of loading (and therefore, potential to saturate the reactive cap more rapidly) which would occur in the vicinity of the preferential pathways. Had observations relating to ebullition not been made during the early stages of site assessment, a remediation solution could have been employed which was not fit for purpose.

Example 4.5: Ebullition, Upper Main Harbour, Frankfurt

Field tests were undertaken at the Upper Main Harbour of Frankfurt (Main River), Germany, to investigate the source of gases observed in the harbour water.

Figure 4.5 Test site, Upper Main Harbour, Frankfurt

A 0.8-1.6 m thick sediment layer is present in the northwest of the harbour. Particle size distribution analysis determined that on average, 46.5% of the sediment comprises particles less than 20 µm (clay and fine silt) and 40.2% comprises silt (20-63 µm). Dry matter content of all sediment samples ranged between 28 - 54% (average 42%). The average organic carbon content was

3.9%, ranging from 3.1 to 8.4%. The sediment was predominately contaminated by petroleum hydrocarbons (total petroleum hydrocarbons at a maximum concentration of 19 g/kg). Polycyclic aromatic hydrocarbons (PAH), organo-halogens, and heavy metals were detected but at lower concentrations.

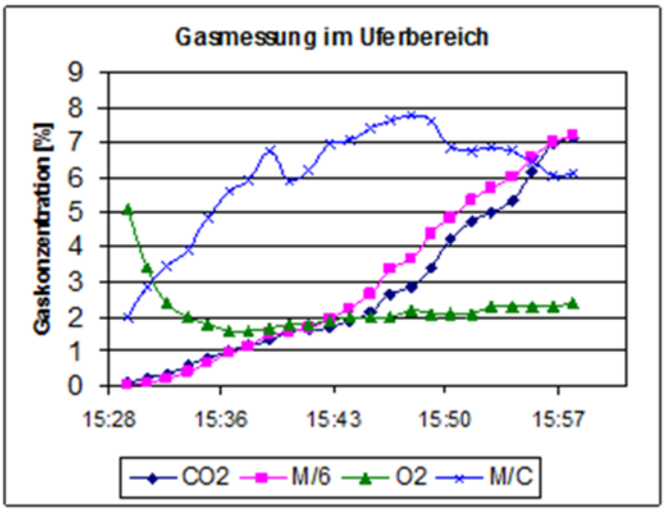
Sediment cores showed a distinct layering, with a thin unconsolidated upper layer (a recent deposit), a consolidated mid layer and a basal layer. In the basal layer, a high organic content (parts of plants, shell fragments etc.) and high petroleum hydrocarbon concentrations were detected. Field observations indicated elevated gas production in the sediment. During periods of decreased water levels, water turbulence caused by ship traffic on the river Main was observed to result in gas emissions from the sediments.

During sediment surface emission tests, sediment gases were sampled by a floating gas trap (**Figure 4.6**) and analysed for oxygen (O_2), carbon dioxide (CO_2), methane and volatile organic compounds (VOCs).

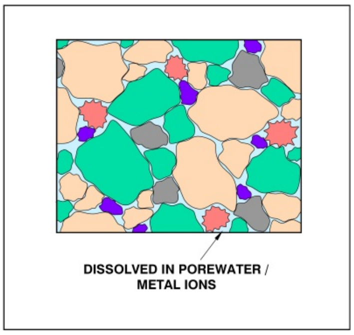
Figure 4.6 Surface emission gas trap

The data indicated that the gas composition was dominated by methane and CO_2 (**Figure 4.7**), believed to be associated with both the elevated organic matter in the basal layer alongside the biodegradation of petroleum hydrocarbons. Note, in **Figure 4.7**, O_2 is plotted as O2, CO_2 is plotted as CO2, methane levels have been divided by six for ease of comparison (M/6), and methane divided by CO_2 is plotted as M/C.

Figure 4.7 Gas emissions with time, Upper Main Harbour



4.3.6. Contaminants in sediment pore water



There is a general preference to characterize sediments by measuring, rather than predicting, contaminant concentrations in sediment pore water since contaminants in pore water represent the bioavailable fraction (Section 4.3). Pore water may be impacted as a result of contaminants already present in the sediments (tending towards equilibrium conditions for undisturbed sediments) or as a result of system input (ground water discharge). Report E1001 provides an overview of the range of tools and techniques which can be used to measure sediment pore water quality. The sample collection approaches recommended by ITRC (2011a) fall into two categories, standard and advanced (Box 4.2).

Box 4.2: Methods for analysis of pore water quality (adapted from ITRC, 2011a)	
Standard approaches	• Shoreline ground water wells • Seep/direct samplers e.g. piezometers • Sediment sampling followed by filtration and centrifugation of samples to separate pore water for analysis
Advanced approaches	• Passive *in* situ samplers for nonpolar organics, e.g. Solid Phase Micro-extraction (SPME) fibres, Polyethylene (PE) devices, Polyoxymethylene (POM) devices • Sediment centrifuge to extract pore water followed by analysis using SPME • Passive sampling for metals, e.g. peepers, Diffusive Gradient Thin Films (DGTs) • Passive sampling for polar organics, e.g. semi-permeable membrane devices (SPMDs).

The sampling devices may be deployed from a boat, from land in an intertidal zone or deployed by a diver. ITRC (2011a) provides a detailed evaluation of direct and indirect pore water sampling devices. The requirement for collecting pore water samples depends on the acceptable level of uncertainty (and likely conservatism) which will be introduced into the assessment through reliance on model predictions rather than an empirical dataset (Practical Application 4.9).

Practical Application 4.9: Measurement of sediment pore water quality

The decision as to whether to investigate sediment pore water quality should take into consideration:

- The receptors which are potentially at risk, and whether understanding the pore water quality – and inferred contaminant bioavailability - is a critical lement to the assessment
- The value of collecting such data, given the investigation data quality objectives (Report E1001)
- The ease by which the data can be collected, and whether it can be collected safely
- The toolkit which is available to deploy, and the familiarity of the stakeholders in understanding how to collect and interpret the data.

ITRC (2011a) provides detailed advice on design of investigation, depending upon the environment and receptor-type under consideration.

Once the data have been collected, it can be used within a risk-based evaluation process in place of predicted concentrations of contaminants in sediment pore water (Section 7).

4.3.7. Surface water and suspended particle quality

The final element of the sediment system, which will need considering throughout the assessment process, is the interaction between the sediments and the overlying surface water (including suspended particles). While contaminants within the sediment may be a secondary source resulting in deterioration in surface water quality, the converse is also possible, with pre-existing poor surface water quality or suspended contaminant particles resulting in the deposition of sediments which contain contaminants. In a dynamic system, evaluation of both the surface water conditions and suspended particles is prudent, with a range of investigation techniques and methods for data collection described in Report E1001. It is noted that the terms “suspended sediments”, “suspended matter” and “particular matter” are often used in literature to refer to suspended particles (mineral constituents), while the term “suspended solids” is typically used to refer to the suspended mineral and organic components (UNEP and WHO, 1996). In this publication, suspended particles are assumed to comprise both mineral and organic components.

4.4. BIOAVAILABILITY

4.4.1. Introducing the concept

If there is a plausible route for receptors to come into contact with contaminants in the sediment, the bioavailability of the contaminant should be factored into the assessment of potential risks. There is potential for over prediction of the risk to human health or ecological receptors if inadequate consideration is given to the bioavailability of the contaminants. The traditional approach to evaluation of the risks posed through exposure of organisms to contaminants in sediments relied on consideration of bulk (total) constituent concentrations in sediment, under the assumption that there is a linear relationship between constituent concentration in sediment and risk presented (ITRC, 2011a), and that all of the contaminant present has the potential to enter and be absorbed by the organism. This is known to be unrealistic and can lead to over-prediction of the actual risk to biological organisms.

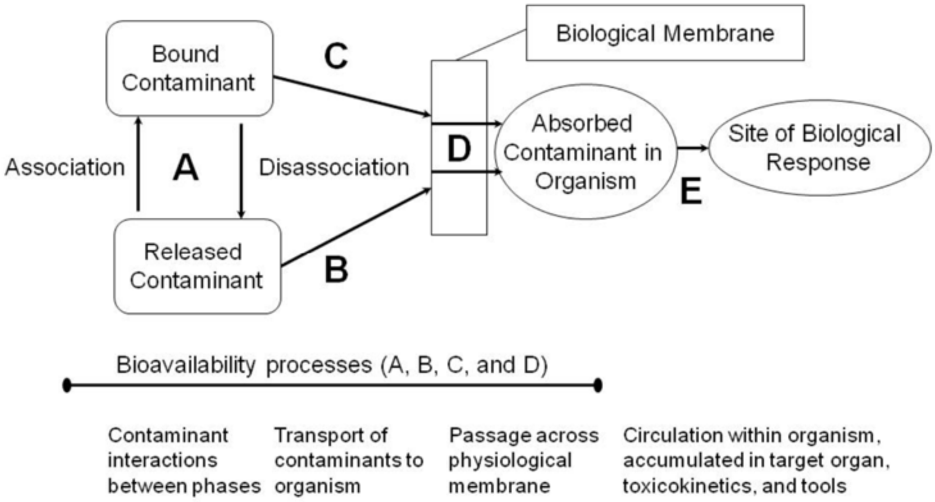
The Interstate Technology and Regulatory Council released a comprehensive guidance document (ITRC, 2011a) on the topic of how to incorporate bioavailability considerations into the evaluation of sediment sites affected by contamination. It is not the intention of this publication to reproduce the ITRC guidance, rather to highlight some of the key concepts. The first step is to understand what is meant by "bioavailability processes" and "bioavailable contaminants" (Box 4.3), before identifying how and where in the assessment process the concept of bioavailability can be accounted for.

Box 4.3: The concept of bioavailability

The USEPA (1992a) defines "bioavailability" as the "*state of being capable of being absorbed and available to interact with the metabolic processes of an organism*". The implication of this concept is that the presence of a contaminant in the sediment does not automatically equate to potential for harm, because it depends on the contaminant form present and whether/how the contaminant can be taken up and metabolised by a receptor (i.e., biological organism). It may be that only a fraction of the total contaminant mass is bioavailable.

The US National Research Council (NRC 2003) defines the term "bioavailability processes" as "…*individual physical, chemical, and biological interactions that determine the exposure of plants and animals to chemicals associated with soils and sediments*". This highlights that there are a number of processes which impact upon the bioavailability of a specific contaminant. **Figure 4.8** (taken from NRC, 2003) identifies the fate and transport elements to consider when assessing the bioavailability of a contaminant.

Figure 4.8: Bioavailability processes in sediment



The first element is to consider if and how a contaminant can be released from the sediment. For example, if sediment containing contaminants sorbed to organic material is ingested, to what extent will the contaminant desorb from the organic material? In other cases, the contaminant may already be present in a form which can be ingested without the need for desorption or disassociation, such as when present in dissolved phase in sediment pore water.

The second element to consider is whether the contaminant, once exposure has occurred, can come into contact with, and permeate through, a membrane (such as skin, lungs, intestines) into the organism.

Finally, the third element is to consider if there is a possibility for the contaminant to reach a sensitive organ within the receptor, with the potential to result in an adverse effect.

It is noted that a distinction is typically made in the European Union between oral bio-accessibility and bioavailability, with definitions which differ slightly from the definition of bioavailability provided by the USEPA. Oral bio-accessibility is defined by the Bio-accessibility Research Group of Europe (BARGE) as the fraction of the contaminant released from the environmental medium (in this case, sediments) into solution during processes such as digestion, making it available for absorption. Bioavailability is described by BARGE as the fraction of a contaminant that can be absorbed by the organism – a ratio of absorbed to administered dose – through the gastrointestinal system, pulmonary system and the skin.

The concept of bioavailability and bio-accessibility differ from the concept of bioaccumulation (see Section 6.2.2) but each play a role in understanding the potential for intake and uptake by different receptors in the food chain.

4.4.2. Where to account for bioavailability in the assessment process

ITRC (2011a) recommends consideration of bioavailability throughout the assessment process, from development of the CSM (Section 3) through to quantitative risk evaluation. It recommends that "*if contaminants are present but not bioavailable, they should not be included in the calculation of risk*". Taking into account the bioavailability processes in **Figure 4.4**, it is clear that different methods of approach will be needed to fully evaluate the bioavailable fraction of a contaminant in sediment, recognising that in many cases, it may not be plausible to assess each of the processes.

Data can readily be collected during a sediment investigation, focused on improving the understanding of how a contaminant could be released in a form which allows exposure to occur. This requires an understanding of the likely contaminant partitioning (building on information provided in Section 4.3) to identify site specific data which can be collected (Practical Application 4.10).

Practical Application 3.10: Bioavailability – investigation data

The distribution of contaminants within the sediment system can be predicted using a bulk sediment measurement, but there are recognised limitations with performing such a calculation (Section 4.3). As such, the following data can be collected alongside bulk measurements of contaminants in sediment, to improve the site-specific understanding of the contaminant distribution between different environmental media. Such data could be collected at a Tier 1 or higher level of assessment:

- Geochemical data to predict changing contaminant forms in the sediment (e.g. pH, redox, AVS; Section 4.3.1)
- Particle size distribution (Section 4.3.2)
- Organic carbon content (Section 4.3.3)
- Concentration of contaminants in pore water, either measured directly or using techniques such as sequential extraction on sediment samples (Section 4.3.4)

Further detailed advice on design of investigation to provide appropriate information to evaluate contaminant bioavailability is provided by ITRC (2011a).

A Tier 1 risk evaluation will typically rely on literature estimates for the second and third elements of a bioavailability assessment (e.g. literature-sourced dermal absorption factors or literature-sourced *in vitro*/*in vivo* studies). However, a more detailed analysis of contaminant bioavailability may be appropriate for high tiers of assessment (Tiers 2 and 3), which may include laboratory analysis or commissioned studies, to understand the potential for contaminant uptake versus intake and contaminant bioaccumulation (including potential for contaminant metabolism). These concepts are explored in greater detail Section 6.2.1.

4.5. LATERAL DISTRIBUTION OF CONTAMINANTS IN SEDIMENTS

It is clear why an understanding of the lateral distribution of contaminants in sediments is an important part to the site evaluation, as this can impact upon the receptors which may be affected by the site. It is also evident that, in a dynamic environment with the potential for multiple contaminant inputs, identifying the actual extent of contamination can prove challenging. Poor source characterisation, including a failure to consider contaminant source inputs (Section 4.2) and contaminant forms in the sediment (Section 4.3), may lead to over-extensive investigations and the collection of data which cannot be readily evaluated or attributed to a specific source. A reference area can be considered analogous to a “control” site, allowing collection of reference data which describes the underlying (background) conditions in the sediment system under evaluation. The USEPA (2002) defines reference or background conditions as “*constituents or locations that are not influenced by the release from a site, and is usually described as naturally occurring or anthropogenic (not specifically related to the site under assessment)*”. Selection of an appropriate reference area(s) should try to match the site conditions (sediment type, hydrodynamics and ecosystem) as closely as possible. For example, for a site located within a port or harbour setting, with a known release event of a contaminant to sediments, a reference area within the port/harbour is likely to be appropriate to understand the reference/background conditions. For larger sites, it is possible that the reference area(s) could be located within the site boundaries.

To investigate the lateral distribution of contaminants in sediments, there is a large toolkit available (see Report E1001). Employed by a competent person, with well-defined data quality objectives, there may be multiple tools fit for purpose. However, to provide the greatest resolution datasets more careful planning may be required. For example, it may be possible to use on-site screening tools (hand held devices, biological testing kits, separate phase detection sprays, immunoassay kits which rely on reactions between introduced antibodies to specific chemical compounds) to quickly evaluate multiple samples without the need for laboratory analysis for each location. Real-time investigation tools (see Section 3.3.6) not only provide data for immediate interpretation but also high resolution datasets. Use of such tools may avoid a conservatism characterisation of the contaminants in sediment (i.e. present “throughout” based on limited number of sampling locations, rather than understanding how system heterogeneities have resulted in variations in contaminant concentrations).

A real challenge to investigating the lateral extent of contamination occurs where the land requiring investigation belongs to a different land owner. This may require legal agreements to obtain access, regulatory involvement and a clear communication strategy (including the likely timescales for an investigation to be completed, lead-in time before works can commence, different evaluation end-points, and how these will be communicated).

4.6. VERTICAL PROFILE OF CONTAMINANTS IN SEDIMENTS

4.6.1. Importance of the vertical contaminant distribution in the CSM

Sections 4.2 (contaminant inputs) and 4.3 (contaminant forms) have showed that an understanding of the vertical profile of contaminants in sediment is valuable in identifying and attributing contaminant sources, variable degradation or attenuation processes, and the form of contaminants which are likely to be present.

The profile is also important to understand for the purposes of detailed risk evaluation. If contaminants are present at depth within the sediment profile, beneath the uppermost sediments in which benthic organisms live [the 'Biologically Active Zone'], it may be possible to conclude at an early tier of assessment (e.g. Tier 0 or 1) that no plausible link exists with the identified receptors. For example, when sufficient thickness of "clean" sediments are present, it may be possible to conclude that there is no potential direct exposure of benthic organisms to the buried potentially contaminated sediment, and that further assessment of remediation to mitigate risks to those receptors in unnecessary. As the sediment system under evaluation may be dynamic, care must always be given to assess the potential for buried sediments to become uncovered and exposed in the future, for example as a result of routine waterway dredging activities.

4.7. SUMMARY

This Section has provided an overview of the challenges involved in the characterisation of contaminant sources in sediment, alongside methods by which these challenges can be overcome and uncertainties reduced in the assessment process. Example 4.6 shows a number of these elements in practice.

Example 4.6: Source characterisation for a fishing pond, southern England

A privately owned fishing pond was identified hydraulically down-gradient of a former chemical manufacturing site in southern England. Investigations undertaken beneath the manufacturing site had identified a range of contaminants (organics and inorganics) present in soils and groundwater, with concern that these could have migrated beyond the site boundary and entered the pond. A sediment and surface water sampling investigation was planned, with the aim of identifying whether site-derived contaminants were present in the pond, and the potential risk these could pose to water quality (the pond), ecological receptors (wildlife associated with the pond, including birds) and human receptors (for example, through indirect exposure to sediments or fish ingestion).

Contaminant inputs

Multiple potential historic and current contaminant inputs were identified, including:

- Groundwater to surface water discharge (organics and inorganics);
- Atmospheric deposition (inorganics);
- Land erosion (land surrounding pond, historic landfilled area); and
- Naturally occurring inputs (inorganics).

Monitoring data indicated the current contaminant distribution was relatively stable, but it was acknowledged that inputs may have been dynamic historically, for example while stack emissions were on-going when the site was active. As a result, it was important to understand the lateral and vertical distribution of contaminants in the pond, in particular to identify potential trends which may indicate one source being prevalent. It was noted that distinguishing between a groundwater input and atmospheric/sedimentation input may prove challenging, as the hypolentic zone could be acting to attenuate the contaminants entering the system.

Contaminant forms

The organic contaminants present in groundwater were known to be relatively recalcitrant in the environment, meaning that limited degradation or transformation was expected. However, the potential for variable redox and pH conditions meant variable metal salts could be present throughout the depth profile.

Environmental media

As there were plausible S-P-R linkages identified, and insufficient data to demonstrate that no unacceptable risks existed, the decision was taken to undertake a Tier 0 and Tier 1 assessment, collecting sediment and surface water data for comparison against conservative generic screening criteria. Suspended particles were not tested, although provision was made for additional testing if found to be needed.

Geochemical analysis

The redox and pH conditions through the sediment profile were recorded using a hand-held probe, and AVS analysed by an external laboratory. Particle size distribution and organic carbon content were also tested; there was no concern that black carbon could be present, given the surrounding land use history.

Findings

Concentrations of a limited number of organic compounds, consistent with those previously manufactured at the site, were found in sediment samples from across the pond, with comparable distribution with depth. These were not encountered in the overlying surface water, providing evidence for hypolentic zone attenuation and/or dilution of pore water in the surface water. Normalisation to particle size and organic carbon did not identify a different distribution from the bulk dataset. It was considered unlikely that these could be present as a result of any source other than groundwater discharging to sediments, suggesting a wide and diffuse dissolved phase plume was the contributing source. This matched with data obtained from on-site and off-site groundwater monitoring wells. However, the concentrations were below conservative screening criteria, and the concentrations in the groundwater plume were not expected to increase in the future. No further works were recommended to address the organic contaminants, on the basis that they did not pose an unacceptable risk to human health, ecology or the wider environment.

Concentrations of a range of metals were also found in sediment samples from across the pond, again with comparable distributions with depth. Redox and pH readings indicated increasingly anaerobic conditions with depth. Normalisation to particle size and AVS did not identify a different distribution from the bulk dataset. The same metals were encountered in the overlying surface water, but at concentrations below environmental quality standards. Review of historic and current groundwater data from the site indicated that groundwater was unlikely to be a significant contributor to the metals observed in sediments or water. The absence of active stacks emitting particles for a number of years meant that these were unlikely to be the primary source, as elevated metal concentrations were present in the shallowest sediments at comparable concentrations to those at a greater depth. It was concluded that alternative sources (erosion of adjacent landfilled material and natural occurrence) were the more plausible sources. As the concentrations were not above conservative screening criteria, no further detailed forensic analysis was considered warranted, on the basis that the site did not pose an unacceptable risk to human health, ecology or the wider environment.

Section 5 follows the same format, focusing on the routes by which contaminants, once present in the sediment environment, can migrate to a point of exposure.

5. SYSTEM HYDRAULICS AND CONTAMINANT FATE & TRANSPORT

5.1. INTRODUCTION

There are two elements to consider in conceptualising, investigating and assessing the migration of contaminants in the sediment environment. The first element is the system hydraulics and the second is the fate and transport of contaminants.

Failure to understand the flow regime can lead to spurious and incorrect interpretation of chemical data. It is important to understand the flow regime (system hydraulics) as a precursor to subsequent (bio and geo) chemical data interpretation. This Chapter explores the factors to be considered when assessing both the system hydraulics and contaminant transport elements which are required to accurately estimate risk to receptors.

5.2. SYSTEM HYDRAULICS

Hydraulics describes the science of hydrodynamics in general, including its practical application (Chambers, 1999). There are a number of ways that the term hydrodynamics can be defined, but for the sediment environment it is used to describe (qualitatively or quantitatively) the interactions and motion of fluids (including water) and sediments throughout the system. Such underlying transport mechanisms need to be understood before the fate and transport of contaminants within that system can be factored into the assessment. The following elements are considered in more detail:

- Sediment depositional environments and water balances;
- Geomorphology;
- Hydraulics in the hyporheic and hypolentic zones, including heterogeneity in distribution of flow; and
- Onshore to offshore hydraulics.

5.2.1. Sediment depositional environments and water balances

The location and rate of formation of a sediment deposit is dependent on a range of factors, which include:

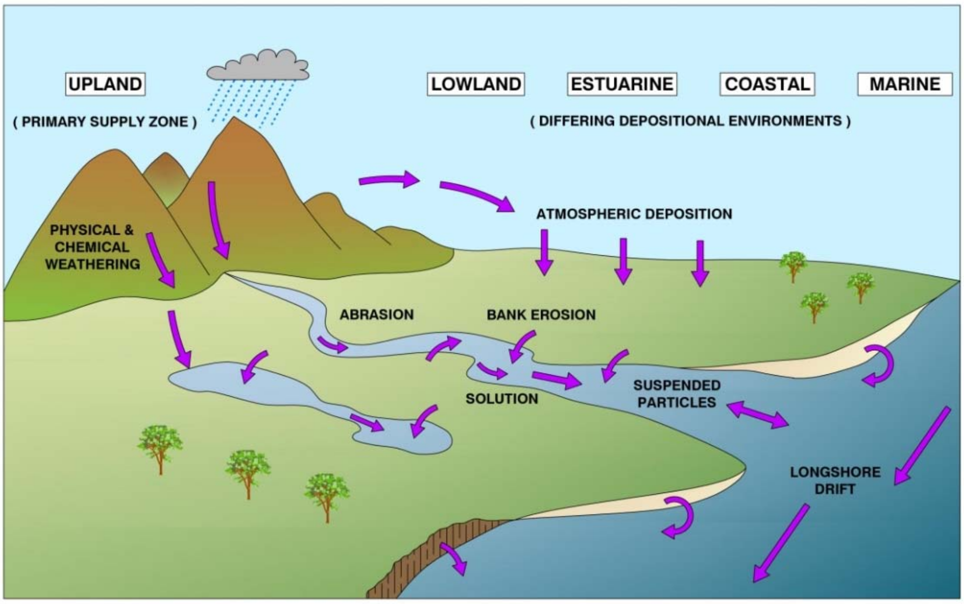
- The source (and size / density) of the particles being deposited (e.g. erosion of riverbed, atmospheric particle deposition, deposition of suspended particles);
- The water environment (e.g. upland stream, lake, estuarine/intertidal, coastal), and specifically whether it is a low-energy depositional, or a high-energy erosional environment;
- The rate of deposition versus the rate of sediment erosion (i.e. is it a net depositional environment, whereby sediment thicknesses will increase over time?); and
- Anthropogenic effects (e.g. re-suspension of particles following dredging activities).

Fundamental principles governing the deposition of sediments are described in Box 5.1.

Box 5.1: Background Information: sediment deposition as a result of natural processes

The source and input of particles is different in different environments, illustrated by a schematic, "typical" watershed in **Figure 5.1**.

Figure 5.1 Schematic showing origin and transport of sediment particles



Using this generalised schematic, the **upland** area in a watershed system is the primary source of particle input, generated through physical/mechanical (e.g. frost shattering) and chemical/biological (e.g. dissolution of carbonates) weathering of rocks. The parent rock composition, determined by its initial method of formation (i.e. igneous, sedimentary or metamorphic), dictates the nature, volume, shape and size of particles which are formed.

The particles are eroded and transported away from the site of origin as a result of gravity-driven or precipitation-driven migration, potentially entering an **upland** stream/river-system or lake. Close to the point of origin, the particles are typically more angular. In a stream/river-system, large particles will typically be deposited in the upper reaches of the waterway, close to the upland region, with smaller particles transported further downstream towards the **lowland** region. Particle transport is a combination of **bed-load contribution** (**traction** and **saltation**, or "sliding" and "bouncing") alongside **suspended particle transport** where the waterway turbulence is sufficient to prevent deposition of smaller particles from occurring. In the upper and transitional regions, the deposition rate, location and potential for re-suspension of even the largest particles is particularly affected by natural events (e.g. flood events caused by heavy precipitation or glacial melts). This is most dynamic in a river system, but even an upland lake can see variable depositional rates, particles types and composition with time.

In the **lowland** region of a stream/river system, particles of decreasing size are deposited as sediments as the energy within the system dissipates, with lessening topographic gradients and widening channels leading to a decreased river velocity. Larger particles may break up through the process of **attrition** (reduction in particle size caused by collisions during transport). This also results in particles becoming rounder and more homogeneous in shape and size. Additional particle inputs to the system originate through the **erosion** of river or lake banks, **solution** of underlying bedrock (in particular for carbonate systems), **abrasion** (erosion of the stream/river bed) and tributary loadings. Each of these processes factor into a stream/river system being a dynamic environment, resulting in lateral movement of the system and change to the stream/riverbed geomorphology over time (e.g. formation of ox-bow lakes, migrating river meanders, braided river systems). This is in contrast to a lake system, which may maintain a relatively stable geomorphology and depth with time. In a lake setting, the near-bank deposits are likely to include a wider variety of particle sizes, influenced by bank erosion and overland inputs. The central area of the lake, with a more static water column and reduced turbulence, will typically exhibit a more homogeneous sediment formed of fines (e.g. silt, clay). In both environments, flood events can result in the removal of sediment from the system and deposition on the surrounding land to form a soil layer.

In the **estuarine** environment, the river system is typically at its widest, with the reduced water velocity and turbulence (except where affected by tidal activity) allowing even fine particles to be deposited (e.g. mudflats). Added complications include the impact of tidal movement on the deposition regime and system geomorphology, alongside the impact of anthropogenic activities such as navigation channel dredging or river-side development. This can result in deep channels which extend to the coastal region, to allow shipping, less intuitive areas of particle deposition (e.g. related to tidal influence and freshwater/brackish water/saline water interactions), shifting sand banks etc.

Moving from the brackish estuarine region into the saline **coastal** environment, factors such as long-shore drift which transports particles along the coastline as a result of oceanic currents, prevailing wind directions and coastal morphology.

Further recommended reading, relating to sedimentation environments alongside water balance estimates, includes Clowes and Comfort (1987), Waugh (2000) and Environment Agency (2009b).

These concepts can be used to estimate the system “sediment balance” (i.e. the sediment inputs, outputs and sinks) in a similar way that the system water balance can be estimated (i.e. identifying water inputs, outputs and storage in the system). Understanding the primary, and most critical, inputs and outputs to the system will help in defining the reference area (Sections 4.5 and 7.3).

When developing and refining the CSM, a choice has to be made as to the scale of the evaluation. Box 5.1 provides an overview of the inputs and outputs for an entire watershed, which may need consideration when, for example, an entire river system or length of river system is under evaluation. However, this is unlikely to be either practicable or necessary for a discrete site. The scale of the evaluation, i.e. defining the extent of the reference area in terms of sediment and water inputs and outputs, is partly driven by the system hydraulics but also driven by the likely contaminant inputs to the system (Section 4.2) and contaminant fate & transport (Section 5.3).

At the start of the assessment process, it may only be possible to provide a qualitative assessment of the sediment and/or water balances. However, the qualitative assessment can then be used to identify the most sensitive or pertinent data needed to help quantify the balance, including how to estimate or measure sedimentation rates (Practical Example 5.1).

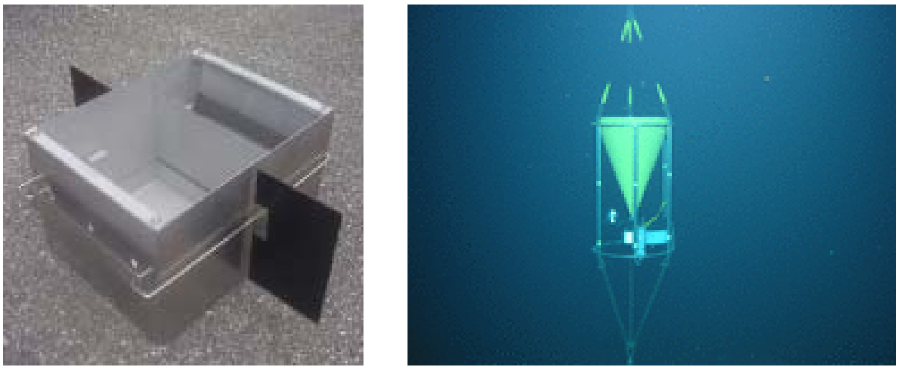
Practical Application 5.1: Sedimentation rates

There are multiple literature sources which provide data on sedimentation rates in different depositional environments. The impact of anthropogenic activities (notably in stream/river systems) such as construction of weirs or dams, farming and gravel extraction, can also be significant in terms of sedimentation location and rates, and is becoming more widely studied (e.g. Kusimi, 2008). However, where site specific data are required, there are three typical methods which can be used – calculated rates using radionuclides (e.g. ^{137}Cs, ^{210}Pb, ^{14}C and ^{7}Be), calculated rates using other marker compounds where appropriate (e.g. DDT) and physical measurements of particle deposition.

There are a range of radionuclides present in the sediment environment and a number are described by the United States Geological Survey (USGS, 1998) as "*short-lived isotopic chronometers*". The USGS highlight that a for a radionuclide to be a useful indicator of sedimentation rates, (a) the isotope chemistry must be well understood, (b) the half-life of the isotope is known, (c) the initial amount of isotope in the sediment at the point of deposition must be known or accurately predicted, (d) the only change in isotopic concentrations are as a result of radioactive decay and (e) it must be relatively easy to investigate. Some radionuclides are present in sediments as a result of natural, on-going processes, whereas others are associated with known events in history (acting more as an event marker). The concept is that the radionuclide will decay at a given rate over time, therefore, the depth of burial can be equated to the time since that layer was deposited. This is a well-recognised technique (e.g. Naval Facilities Engineering Control, 2003) but typically provides deposition estimates over a medium to long term period (typically tens of years). The same concepts have been used by authors investigating the deposition of particles on floodplains (e.g. He and Walling, 1996; Du and Walling, 2012).

Physical measurements of sedimentation rates (e.g. using a plate trap) are typically more challenging, due to the need to install and monitor equipment in the aquatic environment. The data collection may take a period of weeks to months, but should provide an estimate of short-term deposition rates (e.g. Kozerski, 2002). Examples of tools used to "trap" sediment or suspended particles are shown as **Figure 5.2** (a: Tidal sediment trap", developed by the FU Berlin for the Hamburg harbour, b: sediment net (source: University of Vienna 2006) for lakes and/or deep sea)

Figure 5.2: Examples of Sediment Traps


(a) (b)

The data might be used to estimate the depth at which contaminants may be present in the sediment profile as a result of historical inputs, or to quantify the impact of sedimentation on a monitored natural remediation strategy.

An understanding of the sediment depositional regime aids design of an investigation strategy (e.g. locations to investigate, depth to investigate, geochemical conditions which might be expected). The depositional regime will affect the type of material deposited (e.g. percentage of organic material), the particle size deposited and the likely geochemical conditions present. Sections 4.3.1-4.3.3 illustrated the importance of understanding these elements within the source area, but the same considerations apply when investigating the lateral and vertical migration of contaminants over time from the source through the sediment system (Practical Application 54.2, predicting particle size distribution throughout the sediment system).

Practical Application 5.2: Predicting Particle Size Distribution

Example 4.3 illustrated the importance that particle size can play in evaluation of sediment quality data, with a greater proportion of “muddy” sediments in the centre of the Ria de Vigo river basin and thus a higher average concentration of metals in the sediments. This distribution of particle size in the river basin will be dependent on site specific factors, but if the distribution can be predicted, it may be possible to target the specific zones in the vicinity of a site or at least ensure that appropriate samples are collected. Questions which may be asked during the investigation design include:

- Has a sediment and water balance estimate been made for the system?
- What are the critical sediment inputs?
- Is the system highly dynamic or more stable?
- Can the particle size distribution (laterally and vertically) be predicted?
- How can the change in particle size distribution be represented, for example on a cross section?
- Can this information be used to design the investigation, in terms of investigation locations and data requirements?

An understanding of the depositional environment can also enable estimates as to the extent of other sediment components, such as organic carbon, likely to be present (see Section 4.3.3).

5.2.2. Geomorphology

The geomorphology of the sediment system, which describes its structure and topography, impacts upon a range of factors, including:

- The **system hydraulics:** e.g. areas of turbulence as a result of the riverbed topography, or “riffles” along a riverbed can identify zones of upwelling and downwelling of groundwater (Environment Agency, 2009b);
- The **sediment depositional environment:** see Section 5.2.1, for example a scour or dredged channel in a river may result in a different lateral and vertical sediment deposition profile; and
- The **distribution of contaminants** in the sediments: e.g. sediments with lateral or vertical permeability differences may promote the migration of contaminants along preferential flow routes.
- The geomorphology may also indicate the movement of sediments from the aquatic environment onto a floodplain. The system geomorphology can be investigated using a range of tools (**Table 5.1**) which are described in more detail in Report E1001.

Table 5.1: Examples of methods for investigating the system geomorphology

Approach	**Data collection techniques**
Desk-top study	Data which can be collected to evaluate both the topography and structure of the sediments include Admiralty/naval charts (bottom morphology, water line), port authority records, regulatory records, aerial photographs and existing site boring logs.
Bathymetric survey (sediment topography)	A number of techniques can be used to perform a bathymetric survey, such as underwater photography, sediment probing, multi-beam (“swath”) bathymetry, side scan sonar and sub-bottom profiling. All techniques are non-intrusive.
Intrusive investigation	Surficial samplers provide information about the sediment structure in the upper centimetres of the deposit, providing a disturbed sample which can be logged or tested by a laboratory (for example, particle size distribution). Examples of surficial samplers include Orange Peel, Birge-Ekman and PONAR. Sub-surface samplers can enable collection of a relatively undisturbed sediment sample (sediment core) providing information on the sediment structure with depth. Examples of sub-surface samplers include hand corers, box corers, vibratory corers and gravity corers.

The topography and morphology of the surrounding land can affect the sediment environment, for example changes land use can alter runoff intensity. Anthropogenic activity, such as the construction of dams, will also alter sediment transport characteristics and the system geomorphology.

Practical application 5.3 illustrates the role system geomorphology can play throughout the sediment evaluation process.

Practical Application 5.3: System geomorphology
The system geomorphology can affect: **Investigation design** For example, the geomorphology will impact upon the variable depths of investigation which may be required, with changing system geomorphology, which in turn may influence the selection of investigation tool. Report E1001 provides an overview of different investigation tools, including those which can be used to investigate the system geomorphology alongside the advantages and disadvantages of each technique. **Risk evaluation** Site specific data regarding the system geomorphology can be used to inform development of models to predict the migration of sediments and flow of water within the aquatic environment (Section 5.4), thus helping to evaluate the migration of contaminants (see Sections 5.3 and Section 7).The system geomorphology can also impact upon the risk evaluation once site specific data have been collected, due to the importance it plays in the overall CSM (e.g. Smith and Lerner, 2008). **Remediation design** For example, the design of a capping system needs an accurate understanding of the depth to sediment and how this changes spatially. This was highlighted by Blake (2009) as a key area of learning from the Port of Tyne dredging and capping project (see also Report E1001).

5.2.3. Hydraulics in the hyporheic and hypolentic zones

A zone of particular importance for many sediment sites is the hyporheic or hypolentic zone. The Environment Agency (2009b) defines the hyporheic zone as "*that part of the groundwater-river interface which is water-saturated and in which there is exchange of water from the stream into the riverbed sediments and then returning to the stream, within timescales of days to months*". The hypolentic zone is the comparable part of the system in a lake setting. A comprehensive introduction to the hyporheic zone, and factors to consider when conceptualising this element of the aquatic environment, is provided in the Hyporheic Handbook (Environment Agency, 2009b) and CL:AIRE (2011).

The hyporheic and hypolentic zones can play an important role in the attenuation of contaminants entering the aquatic environment (see Section 5.3.4) both as a result of the organisms present but also the hydraulic properties and how these affect the interaction between groundwater and surface water. The Hyporheic Network (http://www.hyporheic.net/index.html) aims to transfer knowledge in this area of research, identifying existing and innovative methods by which the groundwater-surface water interaction can be better evaluated and understood. Understanding this element of the system hydraulics help to clarify factors such as:

- The temporal variability in water flux at the groundwater-surface water interface;
- Spatial variability in water flux at the groundwater-surface water interface; and

- The likely changes in geochemical conditions as groundwater interact, through the hyporheic/hypolentic zone, with surface water.

Characterisation of the hyporheic or hypolentic zone hydraulics needs an understanding of the “up-gradient” (i.e. terrestrial) geology and hydrogeology as well as an understanding of the hydrodynamics and geomorphology of the receiving watercourse. However, based on the Environment Agency definition, the importance of understanding the true interaction between groundwater and surface water is highlighted. The relationship is rarely simple and linear for a stream/river system (groundwater discharging to surface water), rather there is a continued interaction between groundwater and surface water which can vary temporally and spatially.

Temporal and spatial variability in water flux at the groundwater-surface water interface

In a dynamic aquatic system, temporal variability in water flux at the groundwater-surface water interface is documented as occurring, and is important in understanding contaminant fate and transport in this zone (e.g. Winter, 2002) which may change over a period as short as hours (e.g. Harvey et al, 1991; Wroblicky et al, 1998; Hollender et al, 2011). Keery et al (2007) suggest that temporal variability could be due to:

- Variable hydraulic gradients responding to changes in groundwater head variations;
- Hydrological events (including tidal variation);
- The effect of macrophyte (plant) growth;
- Plugging of the streambed by fines; and
- Geomorphological changes to the watercourse as a result of flooding events, animal or human intervention.

Spatial variability in water flux at the groundwater-surface water interface also occurs in a dynamic aquatic system, with Keery et al (2007) identifying the following as potential causes:

- Channel bed deposit hydraulic conductivity varying spatially (e.g. Cardenas and Zlotkik, 2003);
- Variability in streambed topography (e.g. Harvey and Bencala, 1993);
- Variability in the fluvial geomorphologic sequence (e.g. Gooseff et al, 2005);
- The effect of stream curvature (e.g. Cardenas et al, 2004); and
- Variable groundwater gradients (e.g. Storey et al, 2003).

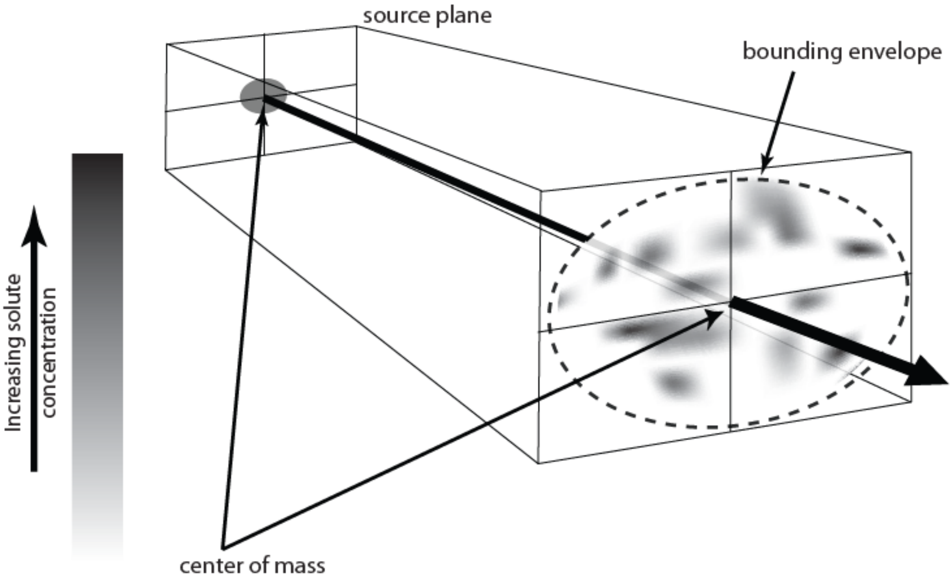
Investigation of the flux of water at the groundwater-surface water interface has traditionally been carried out by a number of methods (e.g. seepage meters, tracer tests; see **Table 5.2**). One of the more innovative approaches, which was first considered in the 1960s (Anderson, 2005) but not adopted widely across industry, is the use of temperature profile measurements. Anderson (2005) reviewed different methods for estimating vertical groundwater flow from temperature measurements. Using a similar approach, watercourse and watercourse bed temperature time series (e.g. Hatch et al, 2006; Keery et al, 2007) can be used to calculate the change in water fluxes. The method proposed by Keery et al (2007) relies on measuring temperature oscillations in watercourses, allowing the vertical rates of water flow in sediments to be estimated (Example 5.1).

Table 5.2: Examples of Groundwater-Surface Water (Water Flux) Investigation Tools

Tool/technique	**Description**	**Advantages**	**Disadvantages**
Seepage meter	A chamber is installed into the upper surface of the sediment, and the volume of water flowing up from the sediment over time is recorded using a collection container (bag).	• Simple and relatively inexpensive to install in shallow waters • Additional probes can be introduced (e.g. salinity probe)	• Provides measurement at one discrete location, so multiple locations may need investigation • Can be difficulties in certain locations (e.g. gravelly sediments, heavy vegetation)
Darcian flux estimates	Monitoring wells are installed along the waterway bank, groundwater head and hydraulic gradients used to estimate water flux based on Darcy's Law	• Monitoring wells may be needed as part of terrestrial characterisation programme • Relatively simple to install in most locations	• Multiple monitoring wells needed to cover a waterway reach, to evaluate spatial differences • Requires multiple monitoring visits or use of down-well continuous monitoring equipment to understand temporal variability • Reliance upon a predicted rather than measured flux
Tracer solutions	A tracer solution or dye is introduced into the aquifer or watercourse, and breakthrough of the tracer identifies interaction zones and variability in interaction (e.g. Triska et al, 1993; Castro and Hornberger, 1991)	• Existing monitoring infrastructure may be usable	• Difficulties in investigation design to ensure that tracer is identified • Heterogeneous systems result in unpredictable discharge of tracer • May require permit to introduce tracer to the system
Temperature profiling	At its simplest, use of Thermal Infrared Imagery (TII) can identify zones of groundwater discharge. Alternatively, temperature sensors (e.g. waterproof temperature loggers or thermal sensors) are used to record both the water temperature and sediment temperature (temperature probes installed into narrow diameter tubes driven into the streambed). See Example 5.1.	• Heat is a natural tracer • Temperature variations can be accurately measured with inexpensive and simple equipment • Some equipment can allow remote recording of temperature over time	• Requires installation of temperature arrays along watercourse, or terrestrial/aerial survey using TII • Mathematical solutions may be required, needing a level of expertise to calculate water fluxes
Stable isotopic analysis	Stable isotopes of hydrogen and oxygen can be analysed and used to distinguish between different water chemistries, including groundwater versus surface water (e.g. Deshpande et al, 2003).	• Isotopic analysis is reasonably well established as a form of forensic testing • Water samples can be collected for a wide range of analysis, alongside isotopic analysis	• Relatively new technique so expertise still being developed for its application • Requires collection and analysis of water samples

Understanding the potential, and scale, of temporal variability is important in developing a water balance evaluation alongside identification and measurement of locations where contaminants may be discharging to the sediment system (e.g. areas of upwelling or down-welling). Use of an over-simplistic conceptualisation of continuous and homogeneous discharge of groundwater along a river reach not only has the potential to introduce uncertainties and errors into the water balance evaluation, but can also leads to an assumed homogeneous discharge "front" for dissolved phase contaminants within a plume. This traditional view of contaminant plumes in groundwater discharging to surface water is changing to one of a heterogeneous and time-variable flux through the aquifer towards area of discharge (**Figure 5.3**).

Figure 5.3: Schematic - concept of a heterogeneous dissolved phase contaminant plume front (courtesy: Payne et al, 2008)



Spatial variability in contaminant transport will be influenced by a range of factors, including the heterogeneities within the aquifer geology (from a millimetre to metre scale) and the presence of natural or anthropogenic preferential transport routes (e.g. along the routes of utilities or drainage channels). Temporal variability will also occur, for example caused by heavy precipitation events resulting in the periodic "flushing" or filtration of the river bank, by surface water ingress and groundwater egress (Example 5.1).

Example 5.1: Groundwater-surface water interaction, River Tern, UK
Keery et al (2007) describe the use of heat profiling to assess the temporal and spatial variability of groundwater-surface water fluxes for the River Tern. The channel width is between 4 m and 8 m, is significantly incised along the reach, has significant bank vegetation during summer months and the streambed comprises sand and gravel with occasional poorly consolidated sandstone boulders. Time series measurements of temperature in the watercourse sediments and stream flow were taken, from five locations along the river reach. Temperature of the stream water was recorded using Tidbit® thermistor logging devices, which were attached to posts driven into the riverbed. The authors

recorded the temperature of the streambed sediments using "*Hobo® TMC50-HD thermocouples, with stainless steel sensor casings, connected to four channel Hobo U12 data loggers…thermocouples were installed in probes constructed from 14 mm diameter iron tube, which were driven into the streambed to depths of up to 1 m* [and] *sealed with non-setting plumber's mastic to minimise convection*". Wooden tubing was also found to be successful to contain the probes. The watercourse flow rate was measured using a Sontek® acoustic Doppler flow meter. Finally, seepage meters "*constructed from plastic bowls of diameter 300 mm, linked to polythene collection bags with 9 mm diameter plastic tubing*" were installed in five locations in groups of three, and used to monitor the temperature series and record water flux volumes.

The temperature series showed variation with depth (**Figure 5.4**), and temporal variation, along two locations of the stream reach (note, measurement locations distributed evenly along the 1 km investigated stretch of river, which included both river bends and straight stretches). The data were evaluated using mathematical devices, including Dynamic Harmonic Regression, which were used to calculate the seepage flux (**Figure 4.5**).

Figure 5.4: Temperatures from the stream and below the streambed recorded at two locations (taken from Keery et al, 2007)

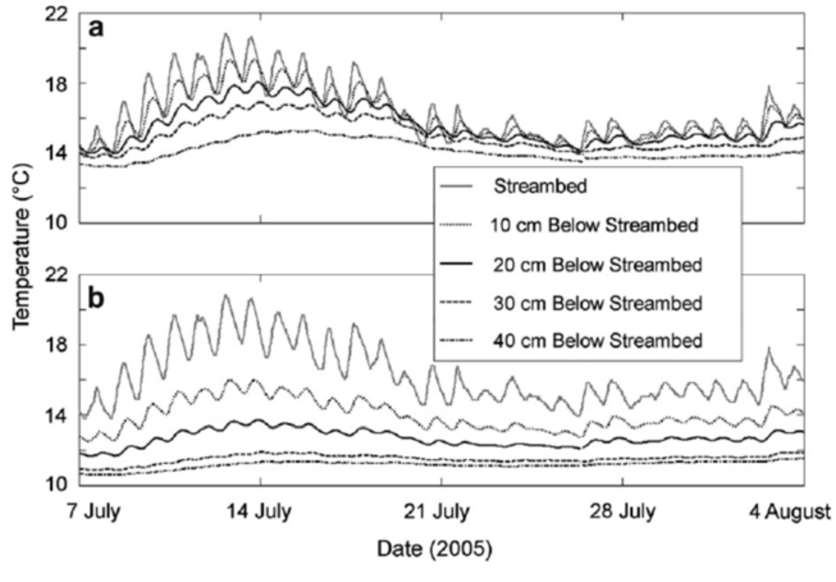
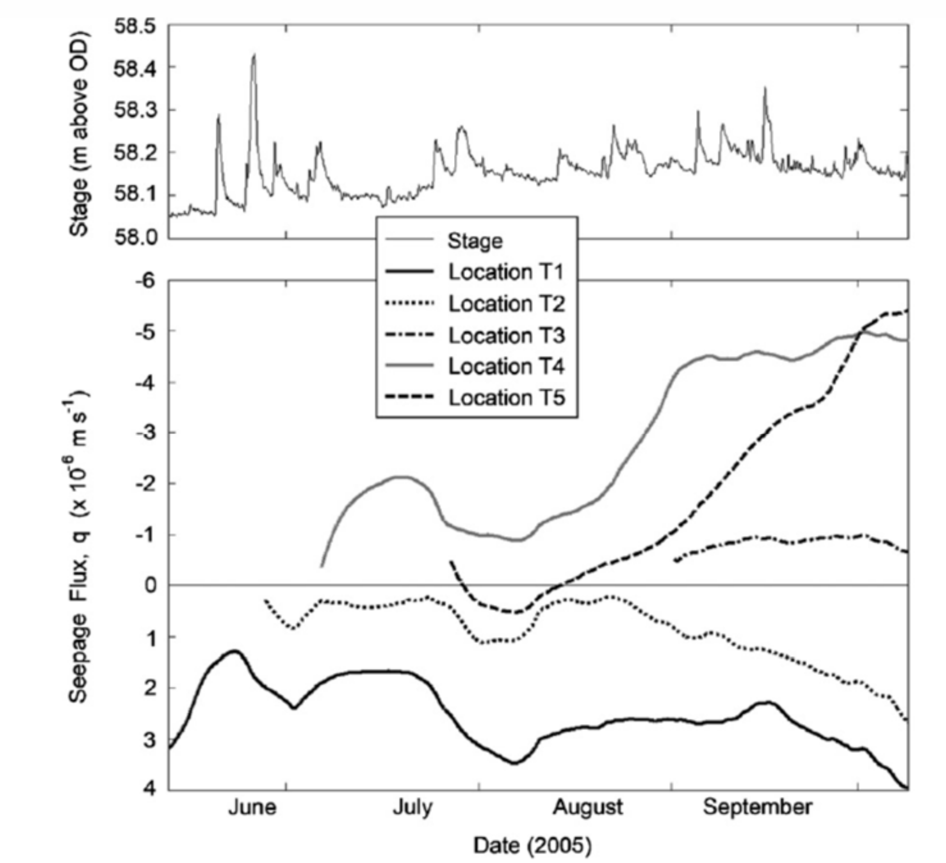


Figure 5.5: Stream stage (one location) and seepage flux (taken from Keery et al (2007)



A negative flux in **Figure 5.5** illustrates flow upwards to the stream. Fluxes recorded using temperature evaluations were comparable to those derived from the seepage survey and flow gauging survey. The authors concluded that there was significant variation (spatially and temporally) in water fluxes along the 1km studied stretch of river.

For further information, see Keery et al (2007).

Geochemical conditions at the groundwater-surface water interface

The geochemical conditions typically differ between the aquifer and surface water, with further differences likely in the hyporheic/hypolentic zone. Conditions will vary due to a range of factors, including microbial activity and the extent of connectivity with atmosphere (e.g. increased oxygen content in surface water). These variable conditions can help to identify the transition zone from aquifer to surface water (see Example 5.2).

Example 5.2: Geochemical data as an indicator for water origin

Investigations had been undertaken at a former chemical manufacturing site in the north of England, which identified the potential for discharge of groundwater containing a range of contaminants to the adjacent river. Groundwater monitoring wells were installed close to the river bank, with the aim of characterising the flux of contaminants discharging to the river system perpendicular to groundwater flow. One monitoring well appeared to have periodic anomalous concentrations of the contaminants in comparison to the other groundwater monitoring wells, with concentrations considerably lower than expected. Whilst variability along the transect was anticipated, the data obtained did not fit the existing conceptual site model. Geochemical data had been collected at the wellhead during the sampling of groundwater (pH, ORP, dissolved oxygen, conductivity). Review of the data identified the anomalous groundwater monitoring well to have a different geochemical signature to the remaining groundwater monitoring wells on a number of monitoring visits, with a signature much closer to that of the adjacent surface water. It was concluded that surface water was “flushing” through this area of the river bank during periods of heavy precipitation when the river water level was at its highest, potentially associated with a small weir system in this location, therefore the groundwater monitoring data from this well was representing either hyporheic conditions or post-dilution surface water conditions.

CL:AIRE (2011) highlight some of the key elements to consider when designing an investigation of the hyporheic (or hypolentic zone), building upon the above factors (Practical Application 5.4).

Practical Application 5.4: Hyporheic zone investigation design

There are a range of elements which should be considered when designing an investigation of the hyporheic zone. These include, but are not limited to:

- Safety of working in, on or near waters, including safe working practices;
- The geology (including hydraulic conductivity) of the deposits underlying and adjacent to the watercourse;
- The geomorphology of the watercourse;
- The hydraulic difference between the aquifer and surface water;
- The presence of preferential flow pathways (e.g. water discharge pipes, naturally occurring preferential pathways);
- The potential for spatial and temporal variation in the groundwater-surface water interaction;
- The geochemical conditions of the adjacent aquifer, hyporheic zone and watercourse.

The selection of investigation tool, or tools, may be based on the capability of the tool to assess more than one of the elements.

Modelling of the hyporheic interface is typically performed using simplistic, one-dimensional models which are not specifically designed to simulate water or contaminant transport through the hyporheic zone, although some more sophisticated groundwater transport modelling tools (e.g. MODFLOW and associated modelling codes for contaminant transport) can be used to simulate localised discharge zones (CL:AIRE, 2011). On the basis of a limited toolkit to model the transport of water and contaminants through the hyporheic zone, the importance of collecting empirical data where a robust understanding of contaminant transport through the zone is clear.

5.2.4. Onshore to offshore system hydraulics

While there has been an increased focus on the system hydraulics associated with groundwater to surface water interaction for inland, and a toolkit of investigation techniques which can be readily applied, work is still on-going to improve understanding of onshore to offshore system dynamics. It is not the intention of this publication to reproduce information regarding this complex environment in detail (e.g. Fredsøe and Deigaard, 1992; Trenhaile, 1997; Masselink and Hughes, 2011) but to highlight specific elements which may affect the CSM development, investigation design and interpretation of findings. In particular, the following elements are discussed:

- Identifying the discharge points for groundwater to the coastal environment;
- Understanding the interaction of freshwater-brackish water-saline water in the transition from inland to marine environment;
- The migration of sediments between estuarine, coastal and marine environments.

Practical application 5.5 identifies some of the key questions which may need to be considered when developing an understanding of the on-shore to off-shore interaction in a coastal environment.

Practical Application 5.5: Elements to consider when conceptualising the on-shore to off-shore water environment

Water flow

- Where is groundwater being discharged, and through which geological unit or units?
- What is the rate of water discharge from on-shore to off-shore?
- Does the discharge of water vary (e.g. as a result of cyclical events, such as tidal activity which may include “tidal pumping” affecting dredging activities, or as a result of discrete events, such as storms)?
- Could contaminants be deposited in the zone of discharge (e.g. sorption to sediments)?
- What is the zone of mixing with receiving water body, and how could this impact upon contaminant presence in the sediment environment?
- Is the net water transport from on-shore to off-shore, or could on-shore activities need consideration (e.g. groundwater pumping resulting in saline intrusion)?

Sediment transport

- What are, and were, the sediment input sources to the coastal system?
- Is the net sediment input from on-shore to off-shore?
- What impact are anthropogenic activities having on the sediment input sources and erosion/deposition locations?
- Are there cyclical or discrete factors which play a significant role in sediment transport?
- Could future changes to the system (e.g. introduction of new coastal erosion protection schemes) significantly alter the sediment transport regime?

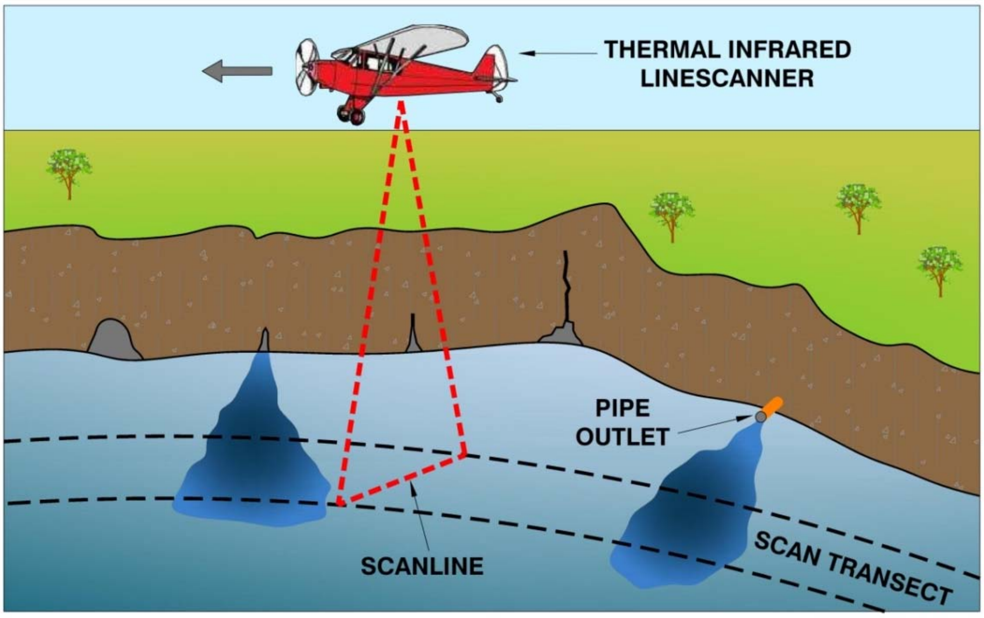
Identifying groundwater discharge locations

In the same way that there are a range of factors to consider when conceptualising and investigating the discharge of groundwater to inland surface water, there are multiple elements which may need to be considered when evaluating the interaction between freshwater, brackish water and saline water (e.g. discharge locations, mixing mechanisms. The mechanisms controlling the discharge of groundwater affected by contaminants can impact upon the potential for sorption or deposition of contaminants to the coastal and marine sediment environments. Example 5.3 highlights one approach used to identify groundwater discharge points from a fractured limestone system on the south coast of England, relying on temperature (see also Example 5.1).

Example 5.3: Monitoring groundwater discharge to Plymouth Sound using an aircraft-mounted thermal infrared line scanner

The Plymouth Limestone which outcrops along the south coast of England is known for its fracture systems and caverns (karst geology), leading to the presence of submarine springs where freshwater discharges into Plymouth Sound. The limestone has relatively low primary porosity, making prediction of the locations of discharge locations along the coast associated with the fracture systems a challenge. Review of seawater and groundwater temperature throughout the year of 1983 showed a 2°C or more difference between the two water types for eight months of the year, a difference which had been observed during previous years. As expected, the groundwater temperature remained consistent (12.0°C to 12.2°C) whereas the seawater temperature ranged from 7.2°C to 16.0°C. This temperature differential was highlighted as a method for detecting the discharge of the groundwater into the coastal environment. An aircraft-mounted thermal infrared line scanner was used to identify relative temperature changes, with the data interpreted using the GEMS system. Five "cool" anomalies (see **Figure 5.6,** dark blue water) were detected along the transect, interpreted as submarine groundwater discharge points associated with the rock fracture system (one correlating well with a known fracture system) and artificial coastal discharge points (major sewage outfall).

Figure 5.6: Schematic showing the aircraft-mounted thermal infrared line-scanner



Technology has progressed further since this study was completed in 1985, resulting in the potential to identify such temperature changes using satellite imagery, depending on the resolution of the data required. For more information relating to the 1985 study, see Roxburgh (1985).

Freshwater-brackish water-saline water interaction

The change in water density between freshwater, brackish water and saline water has important implications for the on-shore to off-shore water interaction. Saline water has a greater density than freshwater, which can lead to complex salinity gradients and zones of diffusion (e.g. Fetter, 2001). Further, the change in density can result in an increase in dissolved solids and/or a change to the physical-chemical behaviour of some organics (e.g. solubility, partitioning) moving from a freshwater to saline water environment.

An alternative to use of thermal technology to identify freshwater to saline water interaction zones is to use geochemical indicators, isotopic analysis (e.g. Moore, 1999) or to laterally and vertically profile the water salinity through collection of conductivity or resistivity data (Example 5.4). Such an approach can be used to assist in development of a system hydrodynamic model (see Section 4.4, estuarine or coastal environments), highlight changing depositional environments and varying geochemical environments which could impact upon contaminant fate and transport.

Example 5.4: Continuous-resistivity profiling to investigate submarine groundwater discharge

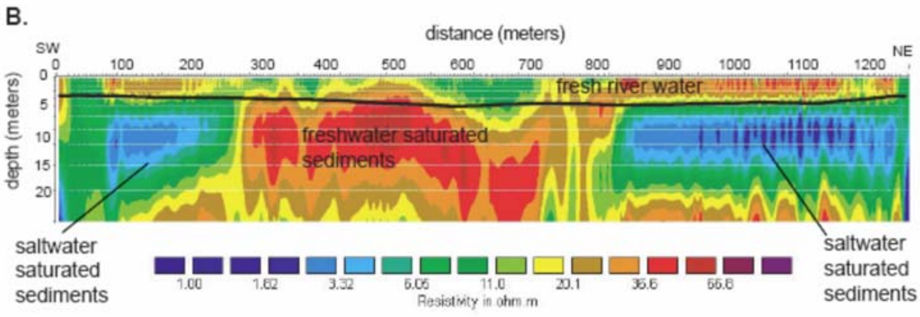
Belaval et al (2003) reported on three locations (Winyah Bay in South Carolina, Waquoit Bay in Massachusetts and Cape Cod Bay in Massachusetts) where continuous-resistivity profiling (CRP) was used to identify the location of submarine groundwater discharge points. Additional data collected including water column temperature and conductivity measurements, alongside echo sounder data used to constrain the water depth.

The survey equipment was towed on the surface of the water, collecting continuous measurement data (one data point per 2.8 seconds) which was interpreted by inverting the apparent resistivity data. This allowed generation of a model of subsurface resistivity.

The survey data was used to:

(a) identify a submarine groundwater discharge point at the location of a forest/marsh boundary in Winyah Bay (**Figure 4.7**);
(b) further mapped the extent of known seepage locations and the freshwater/saltwater boundary in Waquoit Bay (previously investigated using sea floor seepage meters); and
(c) verification of an existing model which predicted the presence of freshwater saturated sediments in Cape Cod Bay.

Figure 5.7: Example inverted resistivity section, Winyah Bay, South Carolina



Understanding the properties of freshwater, brackish water and saline water can assist with developing the CSM, both in terms of the system hydrodynamics and potential for contaminant transport on-shore to off-shore but also in terms of the differing ecosystems which could be present (see Section 5.4). What is clear from Examples 5.3 and 5.4 is that the data collection and interpretation requirements to robustly characterise the on-shore to off-shore water interaction can be onerous.

Coastal and Marine Sediment Transport

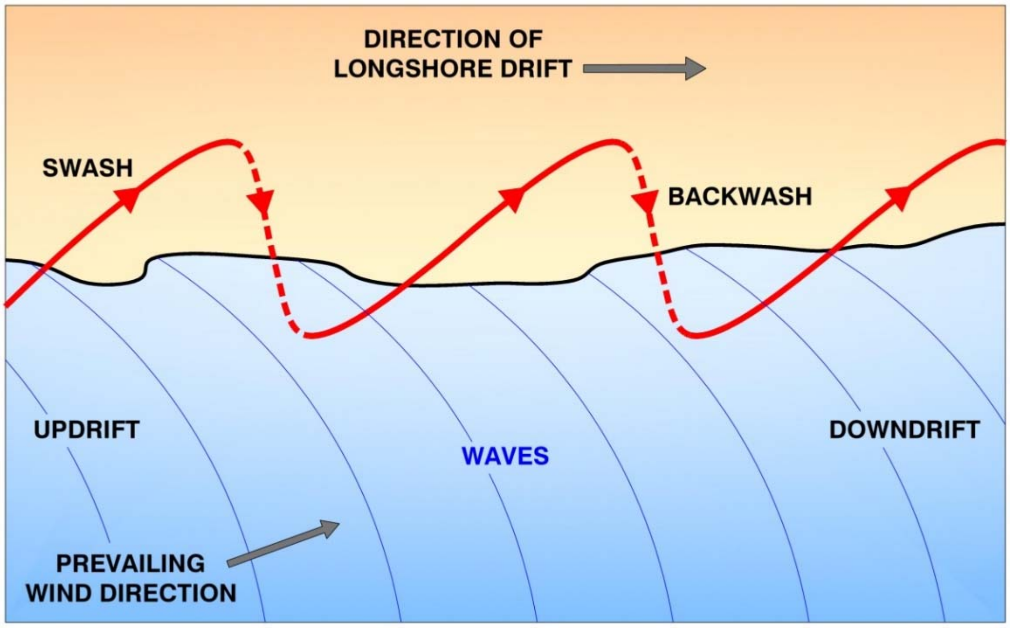
Significant research has been carried out to understand the transport of suspended particles and deposition of sediments (e.g. Fredsøe and Deigaard, 1992; Trenhaile, 1997; Masselink and Hughes, 2011; the Coastal Sediment Transport Modelling Group, Wales), primarily driven by coastal protection requirements, although many of the principles are now being cross-applied to the field of contaminant migration in the sediment environment. An understanding of sediment deposition, transport and re-deposition regimes in the coastal and marine environment is important in understanding the possible input sources to the sediments, whether contaminants have migrated as a result of sediment transport, the design of investigations and in predicting where sediments (and, therefore, contaminants) could migrate to in the future. Modelling tools can, in some cases, be used to predict or simulate the transport of sediments in the coastal and marine environments (Section 5.4).

Section 5.2 explored the transport and deposition of sediment from upland to lowland inland areas, reaching the estuarine environment. The system hydrodynamics in estuarine, coastal and marine environments mean that sediment transport can be affected by many of the same mechanisms as for inland waterways, however additional processes may need to be considered (amongst others) when predicting or modelling the transport and deposition of sediments in the coastal environment:

- tide-related processes;
- current-related;
- wind-related processes;
- wave-related processes; and
- anthropogenic processes.

Sediment transport in the coastal environment needs to consider both the net migration from (or in some cases to) inland waterways to the coastal and marine environment, but also the transport within the coastal environment (parallel to the shoreline). Tides, currents, wind and wave effects combined contribute to long-shore currents, where waves meet the shoreline at an angle. This can result in long-shore transport of particles parallel to the coastline, through cyclical process of erosion and re-deposition (the concept of “long-shore drift”, **Figure 5.8**). Suspended particles may be deposited and accumulate in one location to form beaches, bars, spits or barrier islands. This can result in previously sub-aquatic deposits (i.e. sediments) forming part of a new landmass, albeit the landmass may be ephemeral in nature, with the potential for exposure by different receptor types than those associated with sub-aquatic deposits.

Figure 5.8: Schematic illustration of long-shore drift



The impact that anthropogenic processes and activities have on the transport of sediments in the coastal environment should not be underestimated. For example, the discharge of waters containing suspended solids or coastal erosion protection structures can lead to a greater influx of material to the system (including temporal variability) and erosion/deposition environments which can be challenging to model or predict. This may affect the initial CSM development, but also impact upon remediation design; a remediation solution in such a dynamic system will need to consider the wide range of factors which could result in the erosion and re-deposition of sediments under changing conditions in the future.

5.3. CONTAMINANT FATE AND TRANSPORT

Where contaminants are present in a dynamic sediment system, the potential for migration of contaminants from the source area may need to be considered to identify all receptors which could be at risk. Both the transport mechanisms (influenced by the system hydraulics, Section 5.2) and the fate of the contaminant in the system (e.g. microbial degradation, photolysis) play a role in understanding the risk presented to different receptor types.

Empirical data relating to the fate and transport of contaminants can be collected, but for larger sites, there is typically at least a degree of reliance on prediction of contaminant transport using modelling tools (see Section 5.4) due to the large-scale empirical data requirements for measurement of contaminant fate and transport.

5.3.1. Contaminant transport

Contaminants originating from a sediment source area may be transported through the aquatic system through migration of the same environmental media found in the sediment source area (**Figure 4.2**), namely migration of sediment particles, dissolved phase, separate phase gases, liquids and solids, alongside migration of suspended particles in the overlying water column (**Table 5.3**).

Table 5.3: Examples of Contaminant Transport Mechanisms in the Aquatic Environment

Environmental Medium	**Transport Mechanism**	**Contaminant Migration Mechanism**	**Example compounds**
Particles (natural and anthropogenic)	Traction and saltation (along watercourse bed – see Box 5.1)	Contaminants sorbed to sediment particles	Organic compounds (e.g. polycyclic aromatic hydrocarbons), PCBs, pesticides
		Contaminants chemically bound to sediment particles	Metals
		Solid phase particulates	Anthropogenic particles, such as coal or soot or slag solids
Suspended particles	Water flow within dynamic system (within water column), potential for re-deposition	Contaminants sorbed to sediment particles	Organic compounds (e.g. polycyclic aromatic hydrocarbons)
		Contaminants chemically bound to sediment particles	Metals
		Solid phase particulates	Anthropogenic particles, such as coal or soot
Water	Water flow in dynamic system (e.g. river flow, tidal)	Dissolved phase contaminants	Volatile organic compounds including low carbon petroleum hydrocarbons and halogenated hydrocarbons, metals, pesticides
Separate phase liquids and gases	Gravity-driven, density-driven	Liquid phase	Dense and light non aqueous phase liquids, such as petroleum hydrocarbons and halogenated hydrocarbons ("chlorinated solvents")
		Gaseous phase	Volatile organic compounds, methane, carbon dioxide

While the system hydraulics plays a critical role, the contaminant properties will in part dictate the method of transport (**Table 5.3**). Example 5.5 highlights the importance that sediment transport can play in influencing the distance over which a watercourse can become impacted by contaminants in sediments.

Example 5.5: Hexachlorobenzene release, River Rhine

A well-studied example of a contaminant entering a watercourse, with sediment transport affecting the presence of contamination a significant distance from the source area, is the discharge of hexachlorobenzene to the River Rhine. Hexachlorobenzene, one by-product from chemical production near Rheinfelden, was discharged into the Upper Rhine in 1960-1985. The relatively recalcitrant nature of the compound resulted in it persisting in the sediment environment and transporting more than 300 km down-stream of the discharge area (Heise et al, 2004).

5.3.2. Contaminant fate

During transport through the aquatic environment, contaminants may be lost (for example, through volatilisation from surface water), re-deposited in sediments (for example, deposition of suspended particles) or transformed as a result of the physical, chemical or biological conditions in the system. For example, many of the contaminant properties and system geochemical conditions which impact upon the contaminant form in sediment (Sections 4.3.1 to 4.3.7) also play a role in the fate of contaminants in the sediment environment. The different types of contaminant transformation mechanisms which can be active should be considered in development of the CSM (**Table 5.4**).

***Table 5.4*:** Examples of Contaminant Transformation Mechanisms in the Aquatic Environment

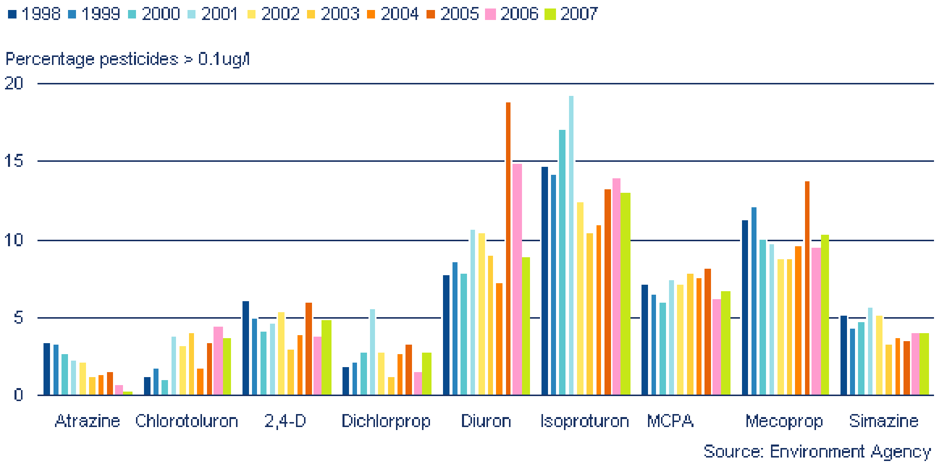
Transformation Mechanism	**Description**	**Conditions**	**Examples of Compounds**
Metabolic/transformation processes (including microbial degradation)	Changes to chemicals as a result of metabolism within a living organism or transformation within flora. Specific metabolites may be excreted by living organisms following intake and uptake of contaminants. Microbial degradation is defined as "*A process by which microbial organisms transform or alter (through metabolic or enzymatic action) the structure of chemicals introduced into the environment*" (USEPA, 2009). Degradation can take place under a wide range of geochemical conditions, which dictate the type of microbes degrading different types of contaminants. Heterotrophic microorganisms are able to use organic molecules as a carbon source, whereas chemo-lithotropic microorganisms can derive energy through the oxidation of certain inorganic contaminants (CL:AIRE, 2011).	Living organisms (e.g. benthic organisms, shellfish, and fish) exposed to contaminants which can be metabolised and excreted. Contaminants may be taken up by flora and stored within the plant or transformed into new compounds. Different conditions (e.g. "aerobic" or "anaerobic") are needed for the microbial degradation of different contaminants. The resulting daughter products may be more or less toxic and/or bioavailable than the parent product, and will have differing physic-chemical properties. Microbial degradation may occur for contaminants in all compartments of the aquatic environment.	Petroleum hydrocarbons (typically more rapid under aerobic than anaerobic conditions). Halogenated hydrocarbons (typically more rapid under reducing conditions). Metabolic/transformation products include gases (e.g. carbon dioxide) and ammonium, although a wide range potential depending on parent product and transformation mechanisms.
Photolysis	The chemical decomposition or ionic dissociation under radiation (Chambers, 1999), including sunlight. Photodegradation is another term used to describe this process.	Interaction with radiation source (i.e. sunlight), so of particular importance for contaminants in the upper parts of the water column.	Wide range, including many aromatic hydrocarbons, aliphatic hydrocarbons, sulphur and nitrogen-containing compounds
Photo-oxidation	Oxidation caused by radiation, including sunlight.	Interaction with radiation source (i.e. sunlight), so of particular importance for contaminants in the upper parts of the water column.	Wide range, including many aromatic and aliphatic hydrocarbons, sulphur and nitrogen-containing compounds
Hydrolysis	The chemical decomposition or ionic dissociation caused by water (Chambers, 1999).	Contaminants susceptible to chemical decomposition or ionic dissociation caused by water (e.g. salt of a weak acid or weak base dissolved in water)	Wide range, including many aromatic hydrocarbons, aliphatic hydrocarbons, sulphur, nitrogen-containing compounds
Chemical precipitation	The formation of a substance through separation from a solution or suspension (Chambers, 1999).	Contaminants where changing geochemical conditions (e.g. pH) can trigger a precipitate to form	Heavy metals in combination with iron, manganese and organic matter, and other inorganics (e.g. sulphur)
Decay	Typically applied to the disintegration of a radioactive substance (Chambers, 1999).	Contaminants susceptible to decay (e.g. radionuclides).	Radioactive isotopes of Pb, U, Rn, C

An understanding of contaminant behaviour is required to develop models which predict the fate of contaminants in the aquatic environment (Section 5.4). For many contaminants, their behaviour in a system can be predicted either from laboratory experiments or from empirically calculated relationships between contaminant properties (e.g. molecule size, solubility) and transformation properties. However, where there is reduced confidence in the desk-top data, for example due to limited literature information, evaluation of the behaviour of contaminants in the field may instead be required. The data requirements will be dependent upon the transformation mechanism being evaluated, and could be as simple as sampling for degradation or decay products alongside the original contaminant (Boxes 5.2 and 5.3 and Practical Application 5.6).

Box 5.2: Historical release of pesticides to river systems, England and Wales

There is a long history of use of industrially manufactured pesticides throughout Europe, resulting in the entry of compounds to watercourses, for example through surface run-off and as a result of the discharge of diffuse groundwater containing pesticides to watercourses (**Figure 5.9**, taken from the Environment Agency website). There has been an increased focus on the fate of pesticides in the water environment, in part driven by the Plant Protection Product Directive and Biocide Directive, and in part by the EU Water Framework Directive which defines statutory groundwater quality standards for pesticides as part of the Chemical Status tests for groundwater bodies.

Figure 5.9: Trends in pesticides concentrations in freshwater, England and Wales (1998-2007) (taken from the Environment Agency)



Source: Environment Agency

One of the more prevalent pesticides in the freshwater environment in England and Wales is **Diuron**, which is no longer in use.

Review of the properties and behaviour of Diuron in the water environment indicates that:

- The primary degradation mechanism once in the environment is believed to be microbial. The aerobic degradation path suggested by Tixier et al (2001) includes the potential for formation of intermediates such as **3,4 dichloroaniline**.
- It has a relatively low potential for hydrolysis
- It has some susceptibility to photolysis, potentially forming a further pesticides **mono-nuron** (Farran and Ruiz, 2003).

Mono-uron is believed to have a comparable environmental toxicity to diuron, with 3,4 dichloroaniline having a lower environmental toxicity (European Chemicals Bureau, 2006). Based on this knowledge, where there is known or suspected contamination in a watercourse by diuron, chemical analysis should also include mono-uron and 3,4 dichloroaniline.

Box 5.3: Fuel oxygenates in the environment

There is a range of ether oxygenates which have been added to petroleum fuels, and in some cases are still added to petroleum fuels, to improve the performance of petrol. These include methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME) and tert-butyl alcohol (TBA). CONCAWE (2012) provides an overview of ether oxygenate fate and transport characteristics in the environment, identifying not only the ether oxygenate added to fuels but also the potential degradation products. An understanding of which fuel oxygenates are present can not only help to distinguish sources, but also highlight the likely degradation of each oxygenate – i.e. the rate of degradation which might be expected, which constituents to analyse for and the toxicity of both the parent and daughter compounds. In general, CONCAWE (2012) concludes that ether oxygenates are highly water soluble, weakly retarded (during transport in an aquifer) but are biodegradable under favourable environmental conditions. Dependent on the conditions present (e.g. aerobic or anaerobic), differing degradation reactions can take place, making it important to consider which decay products could be present given the site conditions. Recording the presence of degradation products provides good evidence that degradation processes are active, and allows an assessment of potential risks associated with both the parent and daughter product to be evaluated.

Practical Application 5.6: Investigating the fate (transformation, degradation and transport) of contaminants in the sediment environment

There are a wide range of data sources and techniques which can be used to understand the potential fate of a contaminant in the sediment environment (**Table 5.4**). The lowest cost (financial and timescale) solutions (literature sources, model predictions) are likely to be sufficient for many sites, provided there is reasonable confidence in the literature value or modelling approach. However, in some instances it may be necessary to collect site specific data (e.g. for a contaminant poorly studied previously) or undertake bench-scale tests in a laboratory to derive information relating to the fate of contaminants while migrating towards the location of a receptor.

Literature sources

Literature sources include publications (e.g. Howard, 1991, Verschueren, 2009, Heise et al, 2004), European Union Risk Assessment Reports and website databases (e.g. SedNet, www.sednet.org, European Chemical Substances Information System, http://esis.jrc.ec.europa,eu/, European Chemicals Agency, http://echa.europea.eu/, Toxnet, http://toxnet.nlm.nih.gov/). Values can be extracted from literature sources with relative ease, although experience is needed to appropriately interpret the data before use in a site evaluation.

Model prediction

Quantitative structure activity relationships (QSAR) can be used to predict or estimate the fate of a specific contaminant in the environment, as long as the limitations with the approach are understood (as for any modelling solution). Modelling tools which can be used include the USEPA EPI Suite (which contains different modules for different fate ‘endpoints’, e.g., BIOWIN for prediction of biodegradation, HYDROWIN for prediction of hydrolysis) and the OECD QSAR toolbox (which contains a wider range of modules than EPI Suite). It is always necessary to check the applicability of the model in relationship to the contaminant under assessment, as well as the level of accuracy required for the output (e.g. to identify whether a more accurate form of assessment, such as a laboratory study, is required). A good degree of experience is needed before such models can be used with confidence.

Bench-scale experiments
Likely to incur a relatively high cost, both financial and timescale, laboratory studies can be commissioned for a contaminant to understand its fate under certain environmental conditions. There are numerous examples in literature of such studies, which have in part led to the development of the datasets described above. It is noted that without good experimental design and controls it can be challenging to distinguish between contaminant loss through adsorption and contaminant loss through degradation.

Empirical data collection
Data collected in the field is often necessary to understand the distribution and the fate of contaminants in the sediment environment, typically relying on multiple lines of evidence (e.g. geochemical conditions, decrease in contaminant concentration, increase in degradation daughter products) to draw meaningful conclusions.

Innovative methods of investigation are being employed to further improve and understand the transport of contaminants, for example use of chemical forensic testing (see Practical Application 4.2), *in situ* probing and passive sampling.

5.3.3. Attenuation in the hyporheic and hypolentic zones

The interaction of groundwater and surface water in the hyporheic and hypolentic zones has already been highlighted as an important mechanism to consider when conceptualising the system hydraulics (Section 5.2.3). These zones can also play an important role in the fate and transport of contaminants between aquifer and fluvial environments. In particular, the potential for contaminant attenuation during transport through the zones should be considered, and may play a significant role in understanding the potential for monitored natural recovery as a remediation technique. The importance attenuation of contaminants in the hyporheic zone has been well studied (e.g. Gandy et al, 2007; Smith and Lerner, 2008; Smith et al, 2009), for a wide range of contaminants under different environmental conditions. Methods of contaminant attenuation include:

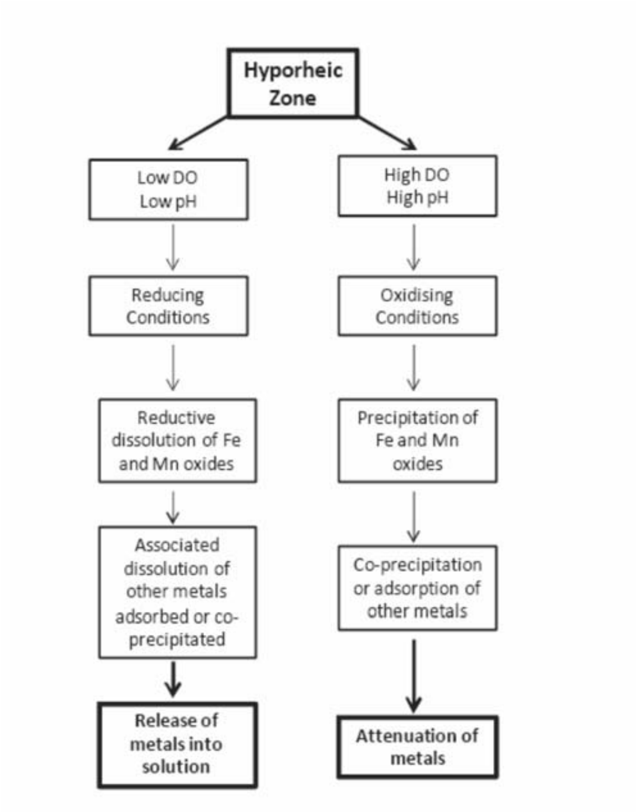
- Microbial degradation or transformation (e.g. heterotrophic and chemo-lithotrophic microorganisms);
- Retardation (“*a measure of the reduction in solute velocity relative to the velocity of groundwater caused by sorption processes”* (Carey et al, 2006));
- Contaminant “precipitation” (e.g. as a result of change in chemical speciation under variable redox conditions);
- Dispersion (“*irregular spreading of solutes due to aquifer heterogeneity at a pore-grain scale – mechanical dispersion – or at a field scale – macroscopic dispersion”* (Carey et al, 2006)); and
- Dilution due to mixing of groundwater and surface water under turbulent conditions within the shallow sediments.

The extent and nature of attenuation is dependent on the geological and hydrogeological conditions within the hyporheic zone, the geochemical conditions, microbial populations and the properties of the contaminant. Example 5.5 illustrates the importance of considering one element – the geochemical conditions – when evaluating the fate of heavy metals in the hyporheic zone.

Example 5.5: Fate of heavy metals in the hyporheic zone

CL:AIRE (2011) illustrates how the geochemical conditions within the hyporheic zone can play an important role as to whether heavy metals attenuate or are released into solution (**Figure 5.9**). Carey et al (2000) provides a detailed overview of factors influencing the microbial degradation of contaminants in the environment, highlighting that the degradation reaction of organics is largely driven by the redox potential in the system. The redox potential impacts upon which terminal electron acceptors (TEAs) are used in place of oxygen, including nitrates, Mn and Fe oxyhydroxides, sulphate and carbon dioxide (CL:AIRE, 2011). **Figure 5.10** demonstrates that reducing conditions can result in the release of other solutes associated with the oxyhydroxides, such as heavy metals or phosphate. As such, the geochemical conditions within the hyporheic zone impact upon the potential for attenuation of organics but also the potential for additional contaminants to be released into the environment as a result of microbial degradation processes associated with the organic contaminants.

Figure 5.10: The role of geochemical conditions in controlling the attenuation or release of heavy metals within the hyporheic zone (source: CL:AIRE, 2011)



Further information can be obtained from CL:AIRE (2011) and Gandy *et al.* (2007).

Contaminants may also be removed from the hyporheic zone prior to discharge to surface water as a result of intake and uptake by the community of organisms, described collectively as "hyporheos". CL:AIRE (2011) provides the following definitions for different organism types which form the hyporheos:

- Stygoxenes: *"stream organisms only entering the interface through accidental infiltration*"
- Stygophiles: "*organisms which "have a greater affinity to hyporheic environments and actively exploit resources and the available habitat (e.g. during periods of high stream flow, drought or for protection from predators*)"
- Stygobites: "*obligatory inhabitants of aquatic subsurface habitats*"

Flora (e.g. macro-algae, vascular plants and mosses) may also remove contaminants from the system, either transforming them into an (often less toxic) by-product or storing the contaminant which is subsequently released back into the aquatic environment through decay of the plant material.

Having understood the importance of contaminant attenuation within the groundwater-surface water interface, it is clear that this interaction may be affected by certain remediation techniques with the potential for adverse effects to occur if the interaction is not considered appropriately. For example, removal of sediments affected by contaminants may result in increased groundwater discharge to surface water without the same degree of attenuation within the hyporheic zone occurring, thus resulting in the potential for deterioration of the aquatic environment rather than the intended improvement to the aquatic environment.

5.4. SIMULATING THE FATE AND TRANSPORT OF CONTAMINANTS

There is a large range of numerical modelling tools which can be used to simulate groundwater-surface water transport, system hydrodynamics (water flow), sediment transport, and contaminant fate & transport as shown in **Table 5.5**. An interactive guide has been developed by the US Geological Survey (Surface Water and Water Quality Models Information Clearinghouse, SMIC) which compares and contrasts the capabilities of different models, and has been referred to in the development of **Table 5.5**. Before any model is selected, an understanding as to why the model selected is appropriate and applicable to the scenario being modelled is required.

The models rely on the use of site specific data, literature data or laboratory data to characterise different elements of the sediment system. Model development relies upon an existing CSM, considering each of the elements described in Section 4 and Sections 5.2 and 5.3 to compile a (typically large-scale) representation of the system. Confidence in the simulation comes from the way in which the model is calibrated and tested, relying on field or site data to confirm that the model predictions are closely matching observed conditions. This is typically undertaken by comparing predicted surface water heads to measured heads, and comparison of predicted surface water flow rates to measured flow rates. It is critical that the approach which will be used to verify the model accounted for prior to modelling commencing.

It is noted that the complexity of the natural environment does mean that there are limitations with the use of any of the models listed, a heavy reliance on the expertise of the user, and in some cases, no added benefit to the assessment from use of the modelling tool given the time and cost implications. Use of site data to develop such a site specific and relatively sophisticated model would usually only be included for a Tier 2 or higher risk assessment, due to the data and time requirements, and level of expertise needed. However, a well calibrated model can be used to predict future conditions, sensitivity test the impact of differing conditions within the system (e.g. as a result of a flood event) and evaluate the likely efficacy of a remediation solution.

Table 5.5 Examples of Hydrologic Modelling Tools (Adapted from US Geological Survey Surface Water and Water Quality Models Information Clearinghouse)

Model Name	Domains	Key Components	Groundwater-Surface Water Interaction	Water Flow	Sediment Transport	Contaminant Transport	Model Systems
BRANCH	rivers, estuaries, channel networks	Dynamic, 1-dimensional model to simulate flow in streams and rivers that can be assumed to be well-mixed		✓			
CH3D-WES	rivers, lakes, estuaries, reservoirs, coastal areas	Varying three-dimensional numerical hydrodynamic, salinity, and temperature model		✓			
DAFLOW	rivers, channel networks	One dimensional model to simulate unsteady flow in well-mixed streams and rivers		✓			
DYNHYD5	rivers, estuaries	Solves the one dimensional shallow-water equations of continuity and momentum for a branching or channel-junction computational network. Capable of handling variable tidal cycles, wind, and unsteady inflows. Used with WASP		✓			
FEQ	rivers, channel networks	Dynamic, 1-dimensional model to simulate flow in streams and rivers that can be assumed to be well		✓			
FESWMS	rivers, lakes, estuaries, reservoirs, coastal areas	Hydrodynamic modelling code that simulates two-dimensional, depth-integrated, steady or unsteady surface-water flows		✓			
FourPt	rivers, channel networks	One dimensional model to simulate unsteady flow in networks of open channels		✓			
HEC-RAS	rivers, channel network	A one dimensional, steady and unsteady water flow, sediment transport and water quality analysis. Applicable for both natural and constructed channels.		✓			
RMA2	rivers, lakes, estuaries, reservoirs, coastal areas	A two dimensional depth-averaged unsteady state (finite element) hydrodynamic model		✓			
MODFLOW	rivers, lakes	A three dimensional, finite difference groundwater flow model. Can be coupled with other modules to widen the capabilities of the model.	✓				
TOPMODEL	watersheds, channel networks	Physically based watershed model that simulates hydrologic fluxes of water (infiltration-excess overland flow, saturation overland flow, infiltration, exfiltration, subsurface flow, evapotranspiration, and channel routing) through a watershed. The model simulates explicit	✓	✓			

Model Name	Domains	Key Components	Groundwater-Surface Water Interaction	Water Flow	Sediment Transport	Contaminant Transport	Model Systems
		groundwater/surface-water interactions by predicting the movement of the water table, which determines where saturated land-surface areas develop and have the potential to produce saturation overland flow					
UNET	rivers, channel networks	One dimensional Unsteady flow through a full NETwork of open channels. In addition to solving the network system, UNET provides the user with the ability to apply many external and internal boundary conditions, including: flow and stage hydrographs, rating curves, gated and uncontrolled spillways, pump stations, bridges, culverts, and levee systems		✓			
BLTM	rivers, estuaries	Dynamic, 1-dimensional Lagrangian transport model to simulate water quality in streams and rivers that can be assumed to be well-mixed. Suitable for unsteady and reversing flows				✓	
CE-QUAL-ICM	rivers, lakes, estuaries, reservoirs, coastal areas	Finite volume eutrophication model that can be used to calculate one-, two-, three-dimensional water quality variables. The model can, therefore, be applied to any surface water system, including in mixed dimensions (e.g. a river discharging to an estuary).				✓	
CE-QUAL-R1	reservoirs, lakes	Dynamic, one dimensional (areally averaged) model to simulate vertical profiles of water quality in lakes and reservoirs				✓	
OTIS	rivers	One dimensional model used to characterize the fate and transport of water quality constituents in streams and rivers that can be assumed to be well-mixed				✓	
RMA4	rivers, lakes, estuaries, reservoirs, coastal areas	Two dimensional finite element water quality transport numerical model in which the depth concentration distribution is assumed uniform. It computes concentrations for up to 6 constituents, either conservative or non-conservative (with linear decay). The model is useful for evaluation of basic advection-diffusion processes in distributing water quality constituents				✓	

Model Name	Domains	Key Components	Groundwater-Surface Water Interaction	Water Flow	Sediment Transport	Contaminant Transport	Model Systems
SED-2D	rivers, lakes, estuaries, reservoirs, coastal areas	Dynamic, two dimensional finite element models for vertically-averaged sediment transport. Non-cohesive (sand) and cohesive (clay) sediments can be simulated, but not simultaneously			✓		
WASP	rivers, lakes, estuaries, reservoirs, coastal areas	Generalized framework for modelling contaminant fate and transport in surface waters. WASP is based on the flexible compartment modelling approach, and can be applied in one, two, or three dimensions.		✓	✓	✓	
CE-QUAL-RIV1	rivers, channel networks	Dynamic, one dimensional (laterally-averaged) model to simulate flow and water quality in rivers and run-of-the-river reservoirs where variation along the axis of flow is important, but variation with depth and across the channel can be neglected		✓		✓	
CE-QUAL-W2	rivers, reservoirs, estuaries	Two dimensional, laterally averaged, finite difference hydrodynamic and water quality model		✓		✓	
EFDC/HEM3D	rivers, lakes, estuaries, reservoirs, coastal areas	Three dimensional surface water models for hydrodynamic and water quality simulations in rivers, lakes, reservoirs, wetland systems, estuaries, and the coastal ocean		✓	✓	✓	
HSPF	watersheds, channel networks	Distributed watershed model that simulates precipitation- and snowmelt-driven movement of water through the basin via overland flow, interflow, and base flow	✓	✓	✓	✓	
MIKE 11	estuaries, rivers, channel networks	System for the one dimensional, dynamic modelling of rivers, channels and irrigation systems, including rainfall-runoff, advection-dispersion, morphological, and water quality. Can be routed to additional modules that simulate the transport of cohesive and non-cohesive sediment, dissolved oxygen, nutrients, heavy metals, and eutrophication		✓	✓	✓	
MIKE 21	estuaries, coastal areas	Modelling system for two dimensional free-surface flows that can be applied in lakes, estuaries, bays, coastal areas, and seas where stratification can be neglected		✓	✓	✓	
MIKE 3	rivers, lakes, estuaries, reservoirs, coastal areas	Three dimensional modelling system for free surface flows, including advection-dispersion,		✓	✓	✓	

Model Name	Domains	Key Components	Groundwater-Surface Water Interaction	Water Flow	Sediment Transport	Contaminant Transport	Model Systems
		water quality, heat exchange with the atmosphere, heavy metals, eutrophication, flooding and drying of intertidal areas, and sediment processes					
MIKE SHE	watersheds, channel networks	Distributed, physically based hydrologic modelling system for the simulation of all major processes occurring in the land phase of the hydrologic cycle, including interception, evapotranspiration, overland and channel flow, snow melt, unsaturated and saturated zone flow, and surface water/groundwater interactions	✓	✓	✓	✓	
PRMS	watersheds, channel networks	Distributed watershed model that simulates precipitation- and snowmelt-driven movement of water through the basin via overland flow, interflow, and base flow	✓	✓	✓		
QUAL2E	rivers, channel networks	Steady-state, one dimensional model to simulate flow and water quality in streams and rivers that can be assumed to be well-mixed		✓		✓	
QUAL2K (or Q2K)	rivers	A one-dimensional river and stream water quality model, which assumes the channel is well-mixed vertically and laterally		✓		✓	
RMA10	rivers, lakes, estuaries, reservoirs, coastal areas	Dynamic three dimensional finite element hydrodynamic model for computing water surface elevations and horizontal velocity components for stratified, free-surface flow		✓	✓		
HSCTM2D	rivers, estuaries	Finite element system, simulates two-dimensional, vertically-integrated, surface water flow, sediment transport, and contaminant transport		✓	✓	✓	
Visual Plumes	rivers, estuaries, coastal areas	Can be used to simulate surface water jets and plumes, and assists in mixing zone analyses.		✓	✓	✓	
GENESIS	coastal areas	Spatial and temporal assessment of shoreline change			✓		
HEC-6	rivers, reservoirs	One dimensional sediment transport model			✓		
RMA11	rivers, lakes, estuaries, coastal areas	Three dimensional, finite element water quality model for estuaries, bays, lakes, rivers and coastal regions				✓	

Model Name	Domains	Key Components	Groundwater-Surface Water Interaction	Water Flow	Sediment Transport	Contaminant Transport	Model Systems
SBEACH	coastal areas	Cross-shore erosion for beaches, berms and dunes			✓		
UNIBEST	coastal areas	Models coastal erosion as a result of wave action			✓		
SEDCAM	rivers, lakes, estuaries, coastal areas	One dimensional sediment transport model			✓	✓	
DELFT3D	rivers, lakes, estuaries, coastal areas	Numerical modelling of flows, sediment transport, waves, water quality, and morphological developments		✓	✓		
GenScn	watersheds, rivers, channel networks	An interactive hydrologic modelling system that supports model setup and data management, model calibration, and analysis of alternatives. Models are incorporated into the system by compiling existing model codes into Dynamic Link Libraries, which allows model codes to be incorporated into the system without rewriting them in a different language.					✓
MMS	watersheds, channel networks	Modelling framework that enables a user to selectively couple the most appropriate process algorithms from applicable models to create an "optimal" model for the desired application. Models that have been incorporated into MMS include PRMS and TOPMODEL.					✓
SMS	rivers, lakes, estuaries, reservoirs, coastal areas	Graphical user interface for two dimensional hydrodynamic modelling					✓

Notes:

While the table provides an overview of many available models, and the environmental media which they are designed to model, a review of the model applicability for the scenario being modelled is needed to ensure the model is fit for purpose.

It is critical that the approach which will be used to verify the model is considered and accounted for prior to modelling commencing

6. EXPOSURE SCENARIO ASSESSMENT

6.1. INTRODUCTION

An exposure assessment estimates qualitatively (Tier 0 assessment) or quantitatively (Tier 1 or higher assessment) the dose of each substance to which ecological or human health receptors are exposed. This section explores the elements comprising exposure scenario assessment, which starts with identification of the receptors potentially at risk from contaminants in sediments. **Figure 2.2** illustrated a number of potential receptor exposure scenarios for a site with sediments containing contaminants.

It is noted that what constitutes a "receptor" may vary from country to country, depending on the regional or national legislation. This is particularly the case for ecological receptors, where different habitats and species may be offered protection depending on the national legislation. Historically, the focus of risks to the environment (including ecology) in the European Union has been on water quality (groundwater and surface water) rather than evaluation of risks to specific organisms.

6.2. EXPOSURE POINT CONCENTRATIONS

For human and ecological receptors, the contaminant concentration and form at the point of exposure is critical. For receptors exposed directly to contaminants in the source area, the exposure point concentration (e.g. sorbed to organic material in sediments or present as dissolved phase within the sediment pore water) may be readily measurable. However, for receptors which are indirectly exposed to the contaminants originating from the source area, a greater degree of uncertainty can arise as a result of reliance on prediction rather than measurement of contaminant concentrations at the point of exposure. Indirect exposure to contaminants in the source may be as a result of one or more of the following:

- A receptor being exposed to the contaminant only after it has entered a lower trophic level of the food chain (see Sections 6.2.1 and 6.2.2);
- A receptor being exposed to the contaminant after it has migrated some distance from the source area (see Section 5.3, contaminant fate and transport); and
- A receptor being potentially exposed at some time in the future and reliance on predictive modelling in the absence of any current measureable exposure to the receptor.

The greater the reliance on modelling the transfer of contaminant to the point of exposure (whether as a result of contaminant fate and transport, or transfer through the food chain), the higher the degree of uncertainty with the exposure assessment is likely to be. This is because of the often complex chemical, physical and biological mechanisms which impact upon contaminant fate and transport. For example, simple bioaccumulation factors are frequently used to estimate contaminant concentrations in fish for the purpose of Tier 1 (screening) assessments. However, when fish are collected and analysed, the measured concentrations are often different (generally lower) than predicted for a variety of reasons such as:

- the generic bioaccumulation factors used in initial assessments are deliberately conservative;

- the bioaccumulation factors used do not account for all chemical and physical factors controlling bioavailability;
- the fish species evaluated may be relatively mobile and therefore exposed to a wide range of concentrations;
- the bioaccumulation factor may not account for metabolism or depuration; and
- available sediment data may not reflect the true heterogeneity of the sediment concentrations.

Conservatism can therefore often be introduced into the assessment with reliance on model predictions. Even where data are collected at the point of exposure, conservatism is often present in the assessment based on the need to rely on theoretical (predicted) effects rather than observed effects in the field.

6.2.1. Contaminant intake versus uptake

Where the receptor exposure is assessed, a distinction between the intake of the contaminant and the uptake should be considered. The intake can be defined as the concentration or dose of a contaminant to which a receptor is exposed, whereas the uptake is the concentration or dose of contaminant which is taken into the receptor and reaches the organs at risk (e.g. via blood flow in mammals). As described in Section 4.4, understanding the contaminant intake and uptake means that the contaminant bioavailability (including bio-accessibility) needs to be considered.

The first element to understanding the potential bioavailability of a contaminant is to measure or predict the concentration of contaminant that is in a form which allows exposure through oral, dermal or inhalation intake routes (Box 4.3). There are a wide range of investigation techniques and chemical/physical data which can be used to answer this question. However, typically the more challenging data to collect relates to the interaction between the contaminant and organism once intake has occurred, as this relies on *in vitro* or *in vivo* studies to simulate the uptake of different contaminants by different organisms.

The Bioaccessibility Research Group in Europe (BARGE) has been collating and carrying out research on the human bio-accessibility of priority contaminants in soils (e.g. arsenic, lead and cadmium) *via* the gastrointestinal tract, recognising that appropriate consideration of both bio-accessibility and bioavailability (as defined by BARGE, see Box 4.3) could have significant implications on risk-based decision making. For example, if bioavailability (and bio-accessibility) testing can be used to show that only a small percentage of the contaminant present in sediment actually reaches the target organ within an organism, the risk-based screening criteria for that contaminant in the sediment system could be increased accordingly. The challenge associated with *in vitro* and *in vivo* testing has historically included:

- Variability between test organisms and receptors in the field;
- A variation in testing methods used by different laboratories;
- A variation in testing results depending on the laboratory undertaking the analysis, due to differing protocols;
- The timescale involved in completing the tests;
- The costs involved in completing the tests; and,
- Ethical considerations, including the use of animal testing.

As a result, wider acceptance as to the use of bioavailability (and bio-accessibility) testing has occurred relatively recently, in part due to the work undertaken by BARGE. Costs for testing, as it becomes used more widely, are starting to decrease and a focused effort on improving consistency in approach (e.g. the Unified Bioaccessibility Method) means that more certainty can be placed on the findings and subsequent use in risk evaluations. It is still likely that, while collection of data relating to contaminant concentrations in different environmental media at the point of exposure may be undertaken as part of a Tier 1 assessment, the commissioning of *in vitro* or *in vivo* studies would usually be undertaken as part of a Tier 2 or 3 assessment, and used to support a more robust exposure calculation.

6.2.2. Contaminant storage in flora and fauna

Contaminants may be metabolised once they have entered the food chain or broken down/transformed (e.g. through photosynthesis) following uptake by flora, reducing the contaminant mass available for exposure. However, contaminants may also bioaccumulate or biomagnify. The potential for contaminant bioaccumulation or biomagnification is dependent on the contaminant properties and the nature of the organism or flora.

The US Geological Survey (2007) defines bioaccumulation as "*The biological sequestering of a substance at a higher concentration than that at which it occurs in the surrounding environment or medium".* Bioaccumulation accounts for intake as a result of direct partitioning and dietary intake. This is in contrast to bioconcentration which can be defined as "*the biological sequestering of a substance at a higher concentration than that at which it occurs in the surrounding environment or medium, as a result of non-dietary intake"* (USEPA, 2010). The USEPA (2009) defines biomagnification as a "*Result of the process of bioaccumulation and biotransfer by which tissue concentrations of chemicals in organisms at one trophic level exceed tissue concentrations in organisms at the next lower trophic level in a food chain".* There are only limited organic compounds used historically or currently which have been detected in food chains, and are defined as bioaccumulative. For example, fuel constituents such as petroleum hydrocarbons and oxygenates are not considered bioaccumulative. However, perfluoro-octane sulfonate (PFOS) is one such example of an organic compound which has been detected in a wide range of food chains, as a result of bioaccumulation (Example 6.1).

Example 6.1: Perfluoro-octane Sulfonate (PFOS)
Perfluoro-chemicals have been used by a wide range of industries, including as repellents for dirt and grease, hydraulics fluids, fire fighting foams and photographic coatings. Perfluoro-octane sulfonate, or PFOS, is one chemical within the group which is no longer manufactured, but is persistent in the environment, toxic, and bioaccumulation has been documented. PFOS has been detected in different environmental media across the world, including drinking water (e.g. Environment Agency, 2007), surface water (e.g. Hansen et al, 2002), waste water (Boulanger et al, 2005) and aquatic mammals (e.g. Kannan et al, 2005).

Both concepts can play an important role in the evaluation of risk to human health and ecological receptors, as receptors may be exposed directly (e.g. direct contact with sediments) and indirectly (e.g. predation on a lower trophic level organism) to contaminants, and potentially at higher concentrations in the food chain than in the sediment itself. Alongside the potential for bioaccumulation and biomagnification, the potential for contaminant metabolism both within the receptor and the organisms in the food chain need to be considered to fully understand the degree of receptor exposure. Thus, evaluations of risks to human health and ecological receptors not only need a robust understanding of the food chain and exposure scenarios (Sections 6.3 and 6.4), but also an understanding of the fate of the contaminant once it has entered the food chain.

The bioaccumulation and biomagnification potential of contaminants can either be measured directly through collection of specimens for laboratory analysis (e.g. analysis of fish tissue) from a system where contaminants are known to be present, or through experimentation on identified members of the ecosystem (typically the benthic community filter feeders) by exposure within a laboratory setting (e.g. 28-day bioaccumulation tests) (USEPA, 2000 a,b). For many contaminants, literature datasets are readily available based on pre-existing experimentation data or QSAR relationships (see Practical Application 5.6). The data are typically reported as a:

- Bioaccumulation factor (BAF), defined as "*The ratio of the contaminant in an organism to the concentration in the ambient environment at a steady state, where the organism can take in the contaminant through ingestion with its food as well as through direct content*" (USEPA, 2009); and/or
- Bioconcentration factor (BCF), defined as the ratio of the contaminant concentration in the organism to that in water.

An even more specific factor, for which increasing datasets are being derived (e.g. http://www.epa.gov/med/prods_pubs.htm), is the Biota-Sediment Accumulation Factor (BSAF). BSAF has been defined as "*a parameter describing bioaccumulation of sediment-associated organic compounds or metals into tissues of ecological receptors*" (Burkhard, 2009). These are targeted at understanding the potential for accumulation of contaminants originating in sediments, rather than contaminants in water.

The factors are then incorporated into risk-based exposure calculations, either increasing or decreasing the predicted dose received by a higher trophic level receptor.

It is noted that, while much focus has been placed on estimation of BAF and BCF in recent years, the potential for alternative contaminant transport or loss mechanisms within the system must not be overlooked, to avoid development of an over-conservative exposure assessment.

6.3. EXPOSURE ROUTES

There are three primary potential exposure routes for ecological and human health receptors to contaminants in the sediment system (**Table 6.1**):

- Ingestion;
- Dermal contact; and
- Food chain or food web transfer.

Exposure may be to contaminants in the sediments themselves or to contaminants in other environmental media such as suspended particles or surface water as a result of contaminant release from the source. There are depth-limiting factors in all sediment contaminant exposure assessments which need to be considered to understand what potential, if any, contaminants present beneath the surficial sediment layer (the Biologically Active Zone, BAZ) may play in the exposure by different receptor types:

1. What is the depth of sediment, and therefore contaminants in sediments, to which benthic organisms are exposed?
2. Could higher trophic level organisms be exposed to contaminants at a greater depth than benthic organisms, for example as a result of foraging?
3. Is there a plausible route for deeper sediment layers containing contaminants to become exposed in the future, for example as a result of natural (e.g. storm events) or anthropogenic activities (e.g. dredging activities)?

In many cases, the potential for exposure to contaminants in sediment is limited to the BAZ (typically the upper 15-20cm of sediment), which is determined based on concentrations of dissolved oxygen, bioturbation, and other biological processes (USEPA, 2005).

***Table 6.1*:** Three primary exposure routes for contaminants in sediments

Exposure route	**Ecological Receptors**	**Human Health Receptors**
Ingestion	• Direct exposure may occur for contaminants in surficial sediments. Receptors resident in the benthic zone thus vulnerable to exposure via ingestion include invertebrates and certain fish. • Upper trophic level ecological receptors, such as birds and mammals may incidentally ingest sediment during foraging, or ingest suspended particles or surface water. • Exposure may vary significantly throughout the year (e.g. hibernation, migration) • Exposure may include ingestion of sediments, pore water or the overlying surface water • Following intake, consideration must be given as to the uptake percentage of contaminant (Section 6.2.2).	• Human health receptors may incidentally ingest surficial sediment during shore-based activities (e.g. fishing along shallow shorelines) and water-based activities (e.g. swimming or wading in shallow waters, canoeing), or may ingest suspended particles or surface water. • Following intake, consideration must be given as to the uptake percentage of contaminant (Section 6.2.2).
Dermal contact	• May occur for contaminants in surficial sediments. Potential receptors include benthic invertebrates, benthic fish, and aquatic plants. • Contaminants bound or sorbed to sediments and those dissolved in the sediment pore-water can enter an aquatic organism through dermal contact and partitioning of the compounds from the sediment into tissues. • Upper trophic level ecological receptors, such as birds and mammals may come into dermal contact with sediment during foraging, or come into dermal contact with contaminants in suspended particles or surface water • Exposure may vary significantly throughout the year (e.g. hibernation, migration)	• May occur for contaminants in surficial sediments for the same activity-types as for ingestion exposure.
Food chain/web transfer	• Contaminants can accumulate in benthic organisms (bioaccumulation and bio-magnification, see Section 6.2.2), which comprise a portion of the diet of fish and, as a result, serve as an exposure route to benthic-feeding fish or shellfish. • Contaminants that may accumulate in fish or shellfish can subsequently provide a source for exposure to higher trophic level wildlife. • Contaminants taken up by plants present a potential exposure pathway for herbivorous wildlife. • As for ingestion, following intake, consideration must be given as to the uptake percentage of contaminant (Section 6.2.2).	• Contaminants can accumulate in lower trophic level organisms (bioaccumulation and biomagnification, see Section 6.2.2), including fish and shellfish. • Human exposure to the contaminants occurs through ingestion of the fish or shellfish.

6.4. ECOLOGICAL RECEPTOR EXPOSURE SCENARIOS

The potential for both direct exposure to contaminants in sediments (ingestion and dermal contact) and indirect exposure (food chain transfer) means that all trophic levels in an ecosystem may need consideration when developing the ecological receptor CSM and investigating a site, to minimise the potential for uncertainties in the assessment. This can include vegetation, benthic invertebrates, fish, aquatic mammals and upper trophic level wildlife (e.g. birds). However, the risks will not need to be evaluated for every potential receptor, instead appropriate indicator receptors representative of each trophic level under consideration can often be identified and used as a proxy.

The USEPA (1998) highlights a number of questions to ask when conceptualising an ecosystem (focused on inland, estuarine and coastal environments), which assist both in identification of receptor-types and also receptor exposure scenarios (Practical Application 6.1). Considering these questions when the CSM is first developed will help to guide the assessment process (see Section 3).

Practical Application 6.1: Conceptualisation of an ecosystem

The following are example questions which may need to be answered when conceptualising and assessing an ecosystem (adapted from USEPA, 1998):

1. What are the geographic boundaries to the ecosystem?
2. What abiotic features (e.g. climate, water quality, and sediment type) could be influencing the ecosystem?
3. What are the functional characteristics (e.g. energy source and processing, nutritional cycling) driving the ecosystem?
4. What are the key structural characteristics of the ecosystem (e.g. species numbers and abundance, trophic relationships)?
5. What habitat types are present?
6. What impact do the characteristics have on receptor susceptibility, such as sensitivity to exposure and likelihood of exposure?
7. Is there anything unique about the ecosystem, or are there legally protected habitats or species within the ecosystem?

6.4.1. Guidance for conceptualising and modelling ecological exposure scenarios

There are a wide range of modelling approaches and tools available to assess the exposure of ecological receptors to contaminants in the sediment system. In some countries, specific toolkits are recommended for use by the regulatory authorities (e.g. the Netherlands, Norway, US) targeted at ecological risk assessments for sediments. In some countries (e.g. the UK) there is guidance provided by the regulatory authorities relating to ecological risk assessments targeted to terrestrial sites, the principles of which can often be cross-applied to sediment sites. In other countries, no methodology has been defined by the regulatory authorities, allowing flexibility in risk assessment approach. Examples of regulatory-approved modelling approaches and toolkits are outlined in **Table 6.2**. A more comprehensive overview is provided by den Besten et al (2003), although noted that new and revised methods have been introduced since 2003 to some European Member States.

Table 6.2: Examples of Regulatory-Approved Ecological Exposure Modelling Approaches

Country	**Key Guidance Documents**	**Applicable for Sediment Ecological Risk Assessment?**	**Applicable for Terrestrial Ecological Risk Assessment?**	**Modelling Tools**
England and Wales	Environment Agency (2008a-f)	(Many concepts are cross-applicable)	Yes	None
Germany	Set criteria rather than guidance on how to complete modelling, but guidance on data collection (HABAB, 2000, GÜBAK, 2009) and data validation.	Yes	No	None
Netherlands	Multiple, the most important for ecological exposure assessment (site specific) being Messman et al, (2011)	Yes	Yes	SEDIAS (focused on re-deposition of material in water bodies)
Norway	SFT (1999) KLIF (2011)	Yes (SFT, 1999)	Yes (KLIF, 2011)	None (algorithms provided within guidance)
US	USEPA (1988), USEPA (1992b), USEPA (1997), USEPA (1998)	Yes	Yes	No specific model, but algorithms recommended for use

6.4.2. Ecological Assessment (Receptor) End-Points

Ecological receptor assessment end-points are explicit expressions of the actual environmental values (i.e. ecological resources) that are to be protected at a site (USEPA, 1997). Valuable ecological resources are those resources that if adversely affected could impair overall ecosystem functioning from either a biological, economic or social perspective. Appropriate and timely selection and definition of assessment (receptor) end-points is critical because they focus the overall site risk assessment design and analysis. It is important to note that an “end-point” in this context refers to a specific receptor, rather than an end-point to the risk assessment process (see Section 7.5.1, Quantifying potential risks to ecological receptors, for evaluation of risk significance). Assessment end-points are generally populations, communities, or trophic guilds (e.g. insectivorous birds). Populations or trophic guilds may be deemed at risk if reproduction or survival of individuals is determined to be significantly impaired. The general types of adverse effects include:

- Mortality, growth, or reproductive effects resulting from direct exposure to contaminants that affect a significant proportion of a receptor population;
- Potential mortality, growth, or reproductive effects resulting from exposure to contaminants that have bio-accumulated in the ecological food chain that affect a significant proportion of a (higher trophic level) receptor population unable to transform and/or excrete the contaminant; or
- Indirect effects associated with a substantial reduction in abundance of prey populations.

Measurement end-points are quantifiable ecological characteristics that are related to the valued characteristic chosen as the assessment end-point (USEPA, 1992b; 1998). The measurement end-point is sensitive and has to represent the same exposure pathway and mechanisms of toxicity as the assessment end-point that it represents. Types of measurement endpoints that can be used in the ecological risk assessment process at a Tier 1 or 2 level of assessment generally fall into three categories:

1. Comparison of estimated or measured contaminant doses to doses known to cause adverse effects,
2. Bioassay testing of site media; and
3. Comparison of observed population- and community-level effects in areas downstream of the source area with those observed at background or reference areas.

6.4.3. Ecological exposure parameters

In a Tier 1 or 2 risk assessment, exposure by lower-trophic level organisms (plants, benthic invertebrates, and fish) is typically modelled using concentrations in site-collected media. Exposure by upper-trophic level wildlife (fish, birds and mammals) is more often defined by a “wildlife dose model” that incorporates estimated concentrations of prey tissue items to estimate the exposure point concentration.

Exposure parameters can be sourced from a number of literature sources, the selection of which may be dictated by the local or country-specific regulations or guidance for undertaking ecological risk assessments. Example sources include KLIF (2011), Messman et al (2011), USEPA (1993), Sample and Suter (1994), Nagy (2001) and Beyer et al (1994).

Exposure parameters for ecological receptors need to consider the frequency and magnitude of exposure, requiring a good understanding of receptor behaviour. For example, it may be necessary to include a Site Use Factor (SUF), a term used to represent the portion of a wildlife receptor’s foraging range or variable exposure throughout the year (for example, due to hibernation, migration patterns). Using a default setting of 1 for an SUF is the worst-case scenario that when not applicable to the receptor under evaluation might introduce conservatism into the evaluation process.

6.4.4. Ecological toxicological reference values

Exposure can be assessed through comparison to existing screening levels which match the exposure scenarios modelled (Tier 1 assessment), or use of modelling tools to derive a predicted dose for comparison with a toxicological end point (e.g. wildlife toxicity reference values, Tier 2 assessment). A good understanding and accounting for how the toxicological data has been derived is important (Practical Application 6.2).

Practical Application 6.2: Understanding uncertainty in ecotoxicological data

The uncertainties which arise in an ecological exposure assessment in part relate to the selection of toxicological data. Points to consider when understanding the significance of this uncertainty include:

- The taxonomic relationship between the test animal and the indicator species;
- Use of laboratory animals or domesticated species, with preference for wildlife species;
- A preference for toxicological studies where the contaminant was administered through diet to studies using other dosing methods, such as oral gavage or intraperitoneal injection;

- The ecological relevance of the study end-points (e.g. studies with toxicity end-points such as reproduction, growth, behaviour, and development) and selection of the study end-points which are most closely related to the selected assessment end-points; and
- Selection of long-term studies representing chronic exposure in preference to short-term, acute studies.

6.5. HUMAN HEALTH EXPOSURE SCENARIOS

For human health receptors, the depth of sediments to which exposure can occur and the exposure route(s) is dependent on the scenario under consideration. Exposure may occur as a result of land-based activities (e.g. contact with sediment, suspended particles or water during fishing activities), inter-tidal activities (e.g. walking) and waterway activities (e.g. swimming, boating, house-boats, dredging activities, investigations etc.). The same uncertainties associated with terrestrial (soil and groundwater) exposure assessments apply to sediment exposure assessments (Practical Application 6.3).

Practical Application 6.3: Human health exposure scenario development

Points to consider when developing the human health exposure scenario, to assist in reducing uncertainty, include:

- How plausible is each exposure route under consideration? (i.e. can exposure scenarios which are theoretically possible but in practice implausible be excluded?)
- What is a reasonable rather than worst-case exposure scenario (Example 6.2)?
- What is the margin of error associated with recommended input exposure input parameters?
- How can bioavailability be taken into account (see Section 6.2.1)?
- Does bioaccumulation or biomagnification need to be considered, if fish or shellfish are being consumed (see Section 6.2.2)?
- How can uptake potential be estimated rather than purely intake potential (e.g. see Section 6.2.1)?
- What confidence can be placed on the toxicological reference values?
- What data can be collected to reduce potential conservatism in the exposure assessment? (e.g. decision to collect empirical data on exposure point concentrations rather than rely on model prediction)?

The greater familiarity and experience in assessing risks from soil and groundwater, combined with the requirement to consider a single species (i.e. humans), means that the assessments may be less complex than ecological exposure assessments. However, there is the same need to carefully interpret the findings of the assessment, and understand and limit the uncertainties introduced within the evaluation.

Example 6.2: Reasonable versus worst-case exposure conceptualisation
Conceptualising direct or indirect exposure by humans to contaminants present in sediments typically relies on the use of literature studies to support selection of input parameters for exposure modelling (e.g. frequency of swimming events, average daily ingestion of fish). Selection of the worst-case or upper 95th percentile values from each study can result in a combination of parameters which do not represent a reasonable, realistic exposure scenario. A study by Chin et al (2011) reviewed the Reasonable Maximum Exposure (RME) recommended by regulatory authorities in the US for modelling the consumption of fish exposure route at lake settings. By back-calculating the fish stock which would be required to support the level of fish consumption recommended for use in the exposure modelling, it was shown that the RME was not appropriate for the system under evaluation. Use of such "reality checks" can help to reduce conservatism in human health exposure assessments.

6.5.1. Guidance for conceptualising and modelling human exposure scenarios

Interestingly, there appears to be a smaller range of modelling approaches and tools available than for ecological receptors to assess the exposure by human receptors to contaminants in the sediment system, even though the concepts are familiar to land contamination risk assessors. As for ecological assessments, in some countries, specific toolkits are recommended for use by the regulatory authorities (e.g. the Netherlands, Norway, US) targeted at human health risk assessments for sediments. In some countries (e.g. the UK, Belgium, France, Italy) there is an expectation that the exposure would be evaluated if potential risks were highlighted within the CSM. Examples of regulatory-approved modelling approaches and toolkits are outlined in **Table 6.3**.

Table 6.3: Examples of Regulatory-Approved Human Exposure Modelling Approaches

Country	Example Guidance Documents	Example Modelling Tools
US	USEPA (2011) for exposure factors pertinent to the sediment/aquatic environment.	No specific tool, but existing proprietary models (e.g. Risk Based Corrective Action for Chemical Releases) modified based on exposure factors recommended by USEPA (2011) to evaluate human exposure.
Netherlands	Multiple, including van Elswijk et al (2001), Lijzen et al (2001), and Verbruggen et al (2001).	SEDISOIL
Norway	KLIF (2011)	None (algorithms within guidance)

No matter the approach or tool used, it may be necessary to consider not only current exposure scenarios but also future plausible exposure scenarios.

6.5.2. Human health exposure parameters

In a Tier 1 or 2 risk assessment, exposure to human receptors is typically modelled by estimating the exposure doses from concentrations in site-collected media, which may comprise sediment, sediment pore-water or organism-specific measurements (e.g. fish or shellfish sampling, see Section 7.5.2).

Exposure parameters can be sourced from a number of literature sources, the selection of which may be dictated by the local or country-specific regulations or guidance for undertaking human health risk assessments. Example sources include KLIF (2011), van Elswijk et al (2001), and USEPA (2011).

6.5.3. Human health assessment end-points

The end-point for a human health exposure assessment is measured either through use of a hazard quotient or index (ratio of predicted dose to an acceptable dose) or a cancer risk level (predicted increased risk of developing cancer as a result of exposure compared to the risk if the exposure had not occurred). The method applied is dependent on the contaminant toxicological properties (e.g. cancer versus non-cancer effects) and the regional or national recommended approach. There is no internationally agreed end-point, or agreement as to whether an assessment should be focused on the target organ. For example, “acceptable risk levels” for cancer effects range from an increased risk of developing cancer of 1 in 10,000 to 1 in 1,000,000. Regional or national policy should be followed where assessment end-points are defined.

6.5.4. Human health toxicological reference values

As for ecological exposure scenarios, human exposure can be assessed through comparison to existing screening levels which match the exposure scenarios modelled (Tier 1 assessment), or use of modelling tools to derive a predicted dose for comparison to a toxicological reference value (Tier 2 assessment). Where toxicological data are not provided by the regional or national regulatory, good practice in selection of toxicological reference values includes understanding and accounting for:

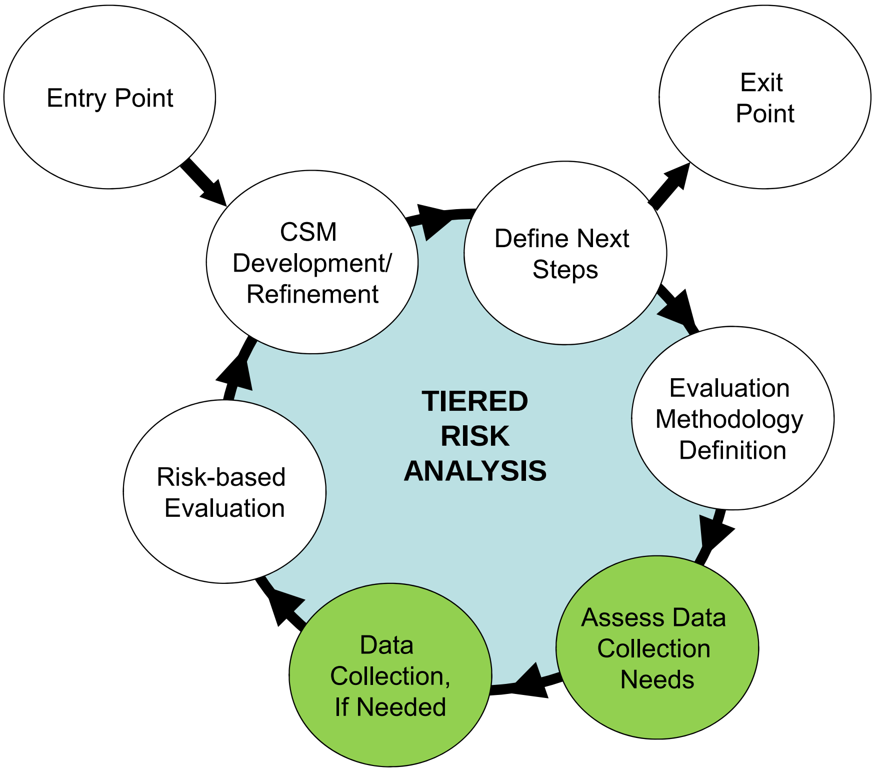
- The validity of uncertainty factors introduced to account for inter-species and sensitive population translations;
- Selection of long-term studies representing chronic exposure in preference to short-term, acute studies;
- Selection of studies based on low-dose/low-response rather than reliance on extrapolation from high-dose/high-response studies.

7. DATA COLLECTION AND RISK EVALUATION

7.1. DATA COLLECTION FOR RISK ANALYSIS

Assessment of data collection needs (investigation design, Section 7.1.1) followed by collection of the data (Sections 7.1.2 to 7.1.4) forms an integral part of the tiered risk analysis approach (**Figure 7.1**). The CSM should inform the data collection process, and be revisited and, if appropriate, refined based on the findings of the investigation.

Figure 7.1 Risk analysis – investigation design and data collection (adapted from Report E1001)



The planning and implementation of an investigation should always take account of the plausible outcomes of the data collection process, and make allowances in the project planning where appropriate. For example, analysis of concentrations of contaminants in sediments will be undertaken for comparison to sediment screening levels. But is there any other data which could be collected (e.g. organic matter content) that would allow a site specific assessment to be completed if the concentrations fail the sediment screening levels? Identifying potential outcomes before an investigation is carried out helps setting Data Quality Objectives (DQOs) and may help reduce the number of times a field investigation has to be undertaken, thereby reducing project timescales and financial costs.

Data collection can be in the field (e.g. sample collection, field inventories), which is followed by external laboratory testing in many cases (e.g. chemical analysis, physical analysis of the sediment structure), to support a Tier 1 to 3 risk assessment. Data collection may also take place in a laboratory setting, to support a Tier 2 or 3 risk assessment (e.g. bioassays, bioaccumulation tests).

7.1.1. Challenges with Field Data Collection

Report E1001 highlighted a number of elements to consider when planning and carrying out a sediment investigation, from the health and safety considerations of working in, on or near water to the difficulties of collecting sub-aquatic samples. A number of the challenges faced can impact on the overall quality of an assessment, including:

- **Sampling of aquatic organisms**. The sampling of aquatic organisms provides an additional challenge to the sampling of other media, such as sediment of water, in that it may not be possible to:
  - Locate the target species
  - Collect sufficient organisms for analysis (noting that the organisms have to be exposed to the contamination)
  - Collect organisms within the target age range
  - Identify an appropriate analysis technique for the target organism.
- **Accounting for temporal variability in the** system. In many sediment systems, there may be a desire to collect data which allows a time series to be developed accounting for seasonal variation. However, this is not always possible, potentially influenced by the stakeholders involved or timescale/financial implications.
- **Accounting for spatial variability in the system**. It may not be possible to investigate all of the locations planned to understand the spatial variability in a system, either because of stakeholder issue (e.g. denied access) or access/safety issues (e.g. service routes, bridges etc.).

The potential limitations introduced as a result of not being able to overcome these challenges should be taken into account during the risk evaluation process (Section 7.6).

The potential challenges associated with undertaking field work in the aquatic environment should be raised and understood when a decision regarding the viability of the assessment is being made (Section 2). There needs to be clarity as to what constitutes a reasonable timescale for the investigation and the appropriate tools to undertake an investigation. For example, an investigation in an estuary or deep river environment may need specialist barges and drilling tools which can only be operated under certain conditions, dictating at what point in the year the investigation can take place. A sediment investigation may take months or longer to plan and implement, which may not be acceptable to all relevant stakeholders.

7.1.2. Uncertainties in Field Data Collection

Uncertainty will always be present in the evaluation of risks presented by a site, due to the heterogeneity natural systems, differing receptor behaviour and variable responses by individual organisms within the same species to the same stressor. This does not mean that there cannot be confidence in the risk-based decision making process, but that such uncertainties should be recognised in the risk evaluation process. In some cases, the predicted uncertainties associated with investigation of sediment and subsequent Tier 1 or 2 risk assessment may be unacceptably high to the stakeholders, triggering instead a data collection to undertake a Tier 3 assessment. Report E1001 provides guidance on developing an investigation strategy and investigation and analysis techniques. The guidance showed clearly that a well-considered investigation design requires the setting of clear data quality objectives (DQOs), robust planning of data collection activities and selection of investigation techniques most appropriate to answer the DQOs. Defining and agreeing these as well as how the data are going to be used will dictate what level of uncertainty introduced as a result of the data collection activities is acceptable (Practical Application 7.1).

Practical Application 7.1: Understanding and reducing uncertainty in investigation design
1. Is there a clear hypothesis(es) or question(s), based on an existing CSM, driving the investigation design? 2. Where could errors occur in the investigation? (e.g. sample labelling errors, loss of volatiles during sampling, limits of detection for analysis tools) 3. What degree level of confidence is needed in the investigation, given the DQOs and how the data will be used? 4. Which investigation approach, tools or techniques are most appropriate the DQOs?

Table 7.1 provides examples of where uncertainty or errors may be introduced, and recommendations on how the uncertainties can be reduced and errors eliminated.

Table 7.1: Examples of Uncertainties and Errors, and Potential Solutions, for Sediment Investigations

Stage of Investigation	Example of Uncertainty or Errors	Potential Solutions
Planning	Objectives not clearly set	Set DQOs (e.g. USEPA, 2005) and agree with team
	Inadequate desk top information regarding underwater structures, including potential preferential pathways	Carry out an appropriate survey prior to investigation commencing to allow design to take account of conditions present
	Poor source characterisation leading to inappropriate investigation area and/or contaminant suites being selected	Requirement for robust source characterisation, including definition of likely reference area and contaminants (historical and current sources) which could be present
Data collection	Unacceptable level of accuracy in identifying location where sediment (or other environmental media) samples were collected (e.g. as a result of visual location compared to riverbank features)	Use of a Geographical Positioning System (GIS) to locate each sample point, recognising the margin of error for the system used
	Low quality logging of sediments	Training of involved staff, clear indication of scale to which sediment cores should be logged
	Sediment sample loss during transport above water	Selection of appropriate sampling tools and sample preservation techniques, clear indication of degree of acceptable sample loss (accept/reject criteria)
	Systematic measurement bias	Training, equipment calibration, robust QA/QC procedures

	Errors introduced during sample labelling	Robust work plan/method statements, training, use of automated labelling system
	Loss of volatiles from sample	Use of appropriate sampling tools and sample preservation techniques, quick transference to sampling container, robust QA/QC procedure for sample storage and transport to laboratory
Data collation	Apparent erroneous or unexpected laboratory analysis	Robust field QA/QC procedures (e.g. trip blanks, duplicates, standards, clear work plans/standard operating procedures), clear DQOs for all stakeholders
	Unacceptable margin of error in laboratory analysis	Clear communication of DQOs to all stakeholders, careful selection of analysis technique
	Reported method detection limit too high	Clear communication of DQOs to all stakeholders, careful selection of analysis technique
	Transcription errors introduced during data collation	Use of automated systems, robust QA/QC procedures even for automated systems, training, review of data throughout the collation process rather than just at end

7.1.3. Field sampling strategies

The selection of a sampling strategy is linked to the DQOs, with the assessor having to decide which environmental media to sample, where to sample, how often to sample and how many samples to collect (Report E1001).

The environmental media which are sampled is largely dependent on the planned method of data analysis and whether there will be more than one opportunity to collect environmental samples. There is a balance between collecting sufficient information at an early stage in the investigation to allow more than just a screening assessment to be carried out in comparison to the timescale and costs associated with carrying out a multi-environmental media sampling exercise. For example, it is unlikely that an initial investigation will include direct sampling of aquatic organisms, unless there is a clear reason why this should be completed, whereas sampling sediment, pore water and surface water is routinely undertaken at an early stage of investigation.

Where environmental samples should be collected relates in part to the reference area (7.1.4) and how often to sample depends on the DQOs and the CSM. For example, there is no minimum number of times surface water should be sampled, instead the focus is on ensuring that sufficient data are collected to characterise the site such that a robust evaluation can be made.

The location and number of samples impact upon how the data can be interpreted once collected. In many cases, it is desirable to use statistical testing to help understand how well the sample set reflects the underlying population being evaluated (e.g. concentrations of contaminants in sediments, water, aquatic organisms, vegetation etc.). The statistical analysis techniques (see Section 7.3) which will be used should ideally be identified prior to designing the investigation, to ensure that appropriate data are collected (e.g. targeted vs. non-targeted investigations, number of samples required etc.).

7.1.4. Reference areas

A site affected by contaminants in sediments rarely exists in isolation, as it is always part of a wider hydro-geologic and/or hydrologic system. In addition, these sites are often located in or downstream of heavily developed industrial or urbanized areas. Therefore, there can be numerous chemical and physical stressors completely unrelated to the site that can influence the potential risks associated with sediments defined as being part of the site. This needs considering when defining the reference area for a site, which helps to describe the lateral and vertical extent of the system which could impact upon decision-making regarding contaminants in the system (Report E1001). The identification of an appropriate reference area for investigation relies on good characterisation of potential sources (Section 4), fate and transport pathways (Section 5) and exposure routes (Section 6). A reference area may be considered analogous to a “control site” which helps the assessor in understanding and differentiating potentially wide-ranging stressors on the sediment system. This can allow reference conditions (or “background levels”) to be defined for the system.

When selecting a reference area, the intent is not to identify a pristine area against which to compare the site, but to match the physical, biological and chemical conditions of the reference area against the site under evaluation as closely as possible. For non-tidal areas, the ideal reference area may be an upstream location with similar physical characteristics (e.g. substrate, width, depth, flow rate, etc.) and that is subject to similar non-site related stressors. In more complex systems, it may be beneficial to consider having multiple reference areas to address different aspects of the project site, and the potential impact of the system hydrodynamics. Another option is to consider regional information. However, care needs to be taken to ensure that the regional data has been collected from areas that may be similar to - but not impacted by - the project site itself. The key point in selecting the reference area is to remember that it should, to the extent possible, represent all chemical and physical stressors that are present in the system.

7.1.5. Selection of field sampling techniques

There is a large range of investigation tools which can be used to collect and assess environmental media. Report E1001 provides an overview of many of the available tools, and promotes the selection of tools which best meet the DQOs. When selecting the investigation tool, or tools, it may be necessary to consider operational and commercial factors, alongside the technical requirements (Practical Application 7.2).

Practical Application 7.2: Selection of investigation tool(s)
Using a similar approach to that which may be used to select an appropriate remediation technique, investigation tools can be selected on the basis of technical, operational and commercial factors. **Technical** The tool must be able to meet the agreed DQOs rather than the DQOs being adjusted to match the tool capability. For example, if the vertical distribution of contaminants in sediments needs delineation, “careful” use of a surface sampler to try to collect an undisturbed sample is not appropriate. Instead, the range of different sub-surface samplers should be considered and ones most appropriate for the site conditions highlighted.

Commercial
There are always commercial factors which play a role in investigation design, which include the timescale over which the investigation must take place and the financial implications of different approaches. Different stakeholders may also have views which affect the choice of toolkit, for example a desire to use a tool which causes the least disturbance to the sediment system.

Operational
Operational factors can range from familiarity and expertise with use of different toolkits through to physical constraints of the system under investigation. For example, there may be a desire to collect a sub-surface core from a specific location, but health and safety factors may mean that only a surface sample can be collected.

If needed, each toolkit can be given a score as to its technical applicability, and then those which are deemed technically suitable can then be scored against commercial and operational considerations, to guide the selection of investigation tool(s). Weighting can be applied as needed to the factors which are most critical for the site. For example, where time is a key factor, could a real-time screening tool or an innovative investigation technique be used to reduce investigation timescales (improve efficiency), acknowledging that the financial costs may be higher?

7.1.6. Innovation in field investigation techniques

Progress continues to be made in expanding the investigation toolkit, moving from the more traditional approach of sediment and surface water sampling to a more holistic characterisation of the sediment system. This includes use of samplers to assess pore water quality (Section 4.3.5), collection of real-time data using *in situ* probes (Section 4.3.6), suspended particle quality (Section 4.3.7), forensic testing (Section 4.2.3) and groundwater-surface water flux (**Table 5.2**). Multiple tools may be used to investigate a site, during a single or multiple phases of investigation, building up a more complete CSM. This can reduce the incorporation of conservatism within the assessment, replacing assumptions with site data. For example, a carefully planned investigation of a riverbank to understand the groundwater-surface water flux can be used to identify actual zones of contaminated groundwater discharge, rather than assuming that a continuous discharge occurs along the length of a riverbank adjacent to a terrestrial site affected by contamination.

For some sites, especially shallow watercourses, there is still often a reliance on divers to collect data (e.g. underwater photography, sampling of shellfish). However, as technology progresses further, and the need for innovative investigation tools becomes more widespread, there is likely to be a larger reliance on submersibles (e.g. to survey the watercourse base or to collect environmental samples). This should reduce the need for humans to enter the water body, potentially increase investigation flexibility and reduce the potential risks associated with undertaking a sediment investigation.

More recent forms of investigation techniques introduced to assist in robust site conceptualisation include:

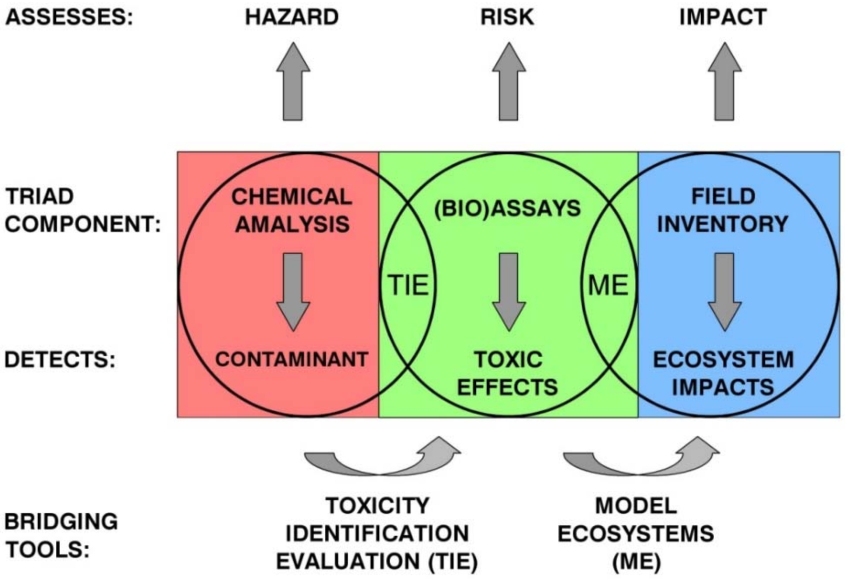
- mapping of sediment and fluid mud layers using a parametric multi-frequency sounding technique combined with an echo-sound waver (e.g. the Admodus-USP probe);
- characterisation of groundwater discharge using fibre optic technology; and

- use of remote sensing and geophysical techniques to characterise physical conditions and features.

7.1.7. Understanding laboratory-based investigation techniques

Alongside the broadening of potential field investigation tools, there has been an increased focus on laboratory-based investigation techniques which can be used to better understand the potential relationship between stressor and receptor than comparison to chemical screening levels alone. Report E1001 describes the Sediment Quality Triad approach (**Figure 7.2**), which brings together knowledge gained from three lines of assessment - chemical analysis, bioassays and field inventories - to develop a more robust CSM (focused on risk to ecological receptors).

Figure 7.2 The Sediment Quality Triad approach (adapted from SedNet, 2004)



For the highest tier assessments, the three elements of the triad are bridged using two tools, namely the use of Toxicity Identification Evaluation (TIE) and Model Ecosystems, each of which has uncertainties which need to be considered during investigation design (Practical Application 7.3).

Practical Application 7.3: Understanding uncertainties with the Sediment Quality Triad investigation process

DEFRA (2010) highlights that each element of the Sediment Quality Triad has associated draw backs and uncertainties. This should not preclude the triad from being used, but does mean that the limitations with the approach should be considered during the investigation design and risk evaluation process. Report E1001 highlights a number of challenges associated with each element, outlined below alongside additional areas where uncertainty can arise.

Triad Element - Chemical Analysis

The uncertainties associated with chemical analysis of sediment sites are consistent with those for terrestrial sites, such as:

- How well the testing data reflects the true conditions, due to sampling bias, system heterogeneity, sample heterogeneity, margins of error for each analysis etc. The potential for errors in the analysis can be reduced (see **Table 7.1**) but the natural system heterogeneity will always be present.
- How reliable the chemical analysis is as an indicator for the potential for an adverse effect to occur to a receptor (e.g. can sediment chemical analysis be used as a reliable indicator for the bioavailability of contaminants? See Section 4.3.5).
- Whether the laboratory can undertake reliable analysis, given the variable matrix content and potential for brackish or saline water (Report E1001).

Triad Element – Bioassays

The EA (2002) defines a bioassay as "*a laboratory test in which the toxicity of a contaminant or environmental sample is measured by exposing a specific organism and measuring a lifecycle parameter (for example, survival, reproduction, development, growth). In general, bioassays are conducted under controlled conditions so that the effects of environmental factors that could confound interpretation of results are avoided".* Inappropriate decision-making can be introduced into the assessment as a result of:

- Inappropriate bioassay selection. The bioassay must be reproducible, representative, responsive, robust, and most importantly relevant for the CSM.
- Measurement limitations. There is a limit to what a bioassay can be used to test, and not all environments can be simulated.
- Interpretation of a laboratory study in the context of a natural, complex system. Perhaps the greatest challenge, as a laboratory-based study will only give an indication of potential response in the real world, where multiple stressors, which can include multiple chemicals of concern, could also be present.

Triad Element – Field Inventory

The field inventory aims to collect empirical data looking for evidence of stressor-receptor response, or the long term impact on sediment biota. For a historically contaminated site, it may be possible to collect such data although it can be difficult to distinguish a response linked to a certain contaminant in the sediment system versus a response from an unrelated stressor. Uncertainties can be introduced into the assessment as a result of:

- Incorrect identification of receptor stress. A robust field inventory relies on the expertise of the person undertaking the evaluation, ensuring that receptor stress can be accurately determined.
- Field inventory undertaken at an inappropriate time. If the field inventory is undertaken during the wrong time of the year, or is not repeated as appropriate, there is a risk that uncertainties will be introduced into the assessment (e.g. completing a survey of population numbers for a migrationary species and concluding that the population is reduced as a result).
- Undertaking a field inventory before harm has occurred to a receptor. If the impact of exposure to a contaminant is a chronic, or long-term, health effect, undertaking a field inventory for a recent contaminant release may not identify the potential for harm to occur.

Bridging Element – Toxicity Identification Evaluation

The TIE bridges the gap between the sediment chemistry (chemical analysis) and sediment toxicity elements (bioassays). The testing aims to identify which contaminant is causing the observed response (e.g. in the bioassay). Toxicity identification evaluation is not always successful (SedNet, 2004), and it is debatable whether an approach looking to identify single toxicants is advisable where a complex mixture of constituents are present or whether an assessment of the whole system is more appropriate.

Bridging Element – Model Ecosystems
A replication of field conditions is setup within a laboratory giving the opportunity to use the replicated systems to test the response of perturbations. Uncertainties introduced as a result of setting up a model ecosystem are focused on how accurately a model ecosystem can replicate the true site, which will have multiple additional inputs and outputs which cannot be modelled in a laboratory setting.

The Sediment Quality Triad is increasingly being used by European Member States (e.g. Netherlands, Belgium) to evaluate sediment sites affected by contaminants. The increased focus on this approach in Europe has partly been driven by a need to implement the Water Framework Directive using a risk-based, proportionate approach, but also driven by the data needs under the Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation.

7.2. DATA INTERPRETATION

A wide range and volume of data may be generated as a result of characterising a sediment site (e.g. intrusive investigation data, laboratory bench-scale studies, land use surveys). It is important that the data are compiled and interpreted with respect to the existing CSM before the quantitative risk evaluation is undertaken. This allows appropriate data quality checks to be completed, and refinement to the CSM if require (Practical Application 7.4). Use of a database to store information gathered from site characterisation activities helps to reduce the potential for data loss or errors during the interpretation process (**Table 7.1**), and can often be linked to spatial analysis and statistical analysis toolkits to improve data evaluation and identification of next steps.

Practical Application 7.4: Data interpretation prior to quantitative risk evaluation

There are multiple questions which can be asked following collection of site specific data from a site affected by contaminants in sediment, which may include:

1. Have the data quality objectives been met, and are the data appropriate to carry out the planned quantitative risk assessment?
2. Does the data support the existing CSM, or does the CSM need refining?
3. Is further data needed to understand the spatial variability and transient nature of the system?
4. Do the investigation findings indicate specific elements (e.g. collection of fish for analysis) which need further investigation?
5. Is any statistical (Section 7.3) or other analysis needed to interpret the data?
6. How can the data best be documented and presented to allow the clearest interpretation?

A number of data interpretation tools have been discussed in previous sections, including data analysis to account for the heterogeneities in the sediment system (e.g. normalisation to organic matter content, particle size, AVS; Sections 4.3.1 to 4.3.3).

The tier of risk assessment which is subsequently completed in order to understand the potential significance of the investigation findings will have been decided prior to carrying out the investigation, during development of the data quality objectives. While a single CSM may have been developed, different forms of quantitative risk assessment may need to be employed to evaluate risks to:

- Ecological receptors (Section 7.5.1);
- Human health receptors (Section 7.5.2); and
- Other receptors, namely water quality and management activities (Section 7.5.3).

7.3. DATA ANALYSIS TECHNIQUES

There are multiple forms of data analysis techniques which can be used to evaluate the findings of a sediment assessment, typically in the form of statistical testing. Two of the simplest forms of data analysis are the calculation of the upper 95th percentile of the dataset and the calculation of the population mean value at a 95th percentile confidence level, for comparison against the assessment criteria in place of the maximum concentration. A number of more sophisticated statistical tests which may be employed are described in **Table 7.2**, which includes a number of examples of multivariate analysis (e.g. principal components analysis, cluster analysis). These are designed to identify relationships between different parameters. Statistical tests can be split into parametric tests (which are underpinned by assumptions that the data originate from a specific probability distribution) and non-parametric tests (which do not incorporate the same assumption). However, before any testing can be applied, the assessor must understand whether the data are appropriate for the testing to be carried out (e.g. have sufficient data points been collected, do the data represent a single population or multiple populations). It is also important to clearly define the hypothesis, or hypotheses, underpinning the statistical testing.

Table 7.2: Examples of Data Analysis and Statistical Testing Tools

Test	**Description**
Mean comparison analysis (Analysis of variance)	An inferential method for comparing the means of different datasets to evaluate for a potential relationship or correlation.
Discriminatory analysis	A statistical tool to identify which population a data point relates to (e.g. background population or alternative population).
Correlation analysis	Evaluating the degree of similarity between test responses using correlation analyses
Cluster analysis	Used to identify data clusters (groups) and evaluate the relationships, if any, between groups of data.
Principal components analysis	The evaluation of correlations between multiple datasets to identify if a relationship can be identified which best expresses the datasets.
Multi-dimensional scaling	Another statistical tool for evaluating relationships between datasets to aid data visualisation.

Many software models are available which might be used to assist in completing the calculations, but should only be used if the assessor has the right level of expertise, is known to be applicable to the analysis being undertaken and an understanding as to what the limitations of the test are.

7.4. EVALUATING RISKS

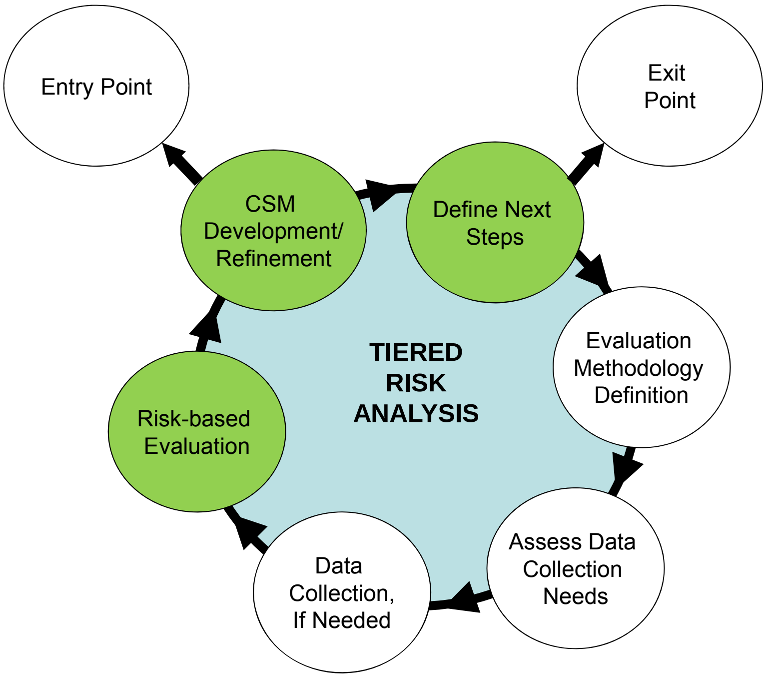
Robust risk evaluation includes revisiting (and if necessary refining) the CSM to define whether the site assessment process can be exited (for example, based on the conclusion that contaminated sediments are not present, or that remediation works should be considered), or whether further data collection and/or risk assessment is required (**Figure 7.3**).

The risk-based evaluation process should have been considered, and ideally documented, prior to the assessment commences, clearly setting out the “exit strategy”, or the point at which no further risk management activities will be deemed necessary.

A qualitative risk evaluation performed at a Tier 0 level of assessment will in many cases support a robust conclusion that contaminated sediments are not present (exiting the assessment process), but is highly unlikely to result in a conclusion that contaminated sediments as defined within this publication are present. Quantitative analysis is likely to be required to draw such a conclusion, typically with the most robust conclusion drawn only after a Tier 3 level of assessment. For many sites it may never be possible to definitely conclude that contaminated sediments are present. Instead, multiple lines of evidence will be needed to provide a final evaluation based on a balance of probabilities (Section 7.7).

Where a quantitative risk assessment has been undertaken (Tier 1 to 3, Section 7.5), and it is concluded that (a) contaminated sediments, as defined within this publication, are present, or (b) there is still uncertainty as to whether contaminated sediments are present, the decision may be taken to implement remediation. However, the reasons for exiting the assessment process should be documented (e.g. socio-economic reasons, legislative requirement) to provide clarity to all stakeholders as to the driver for remediation and associated remediation objectives.

Figure 7.3 Risk analysis – risk-based evaluation and next steps (adapted from Report E1001)



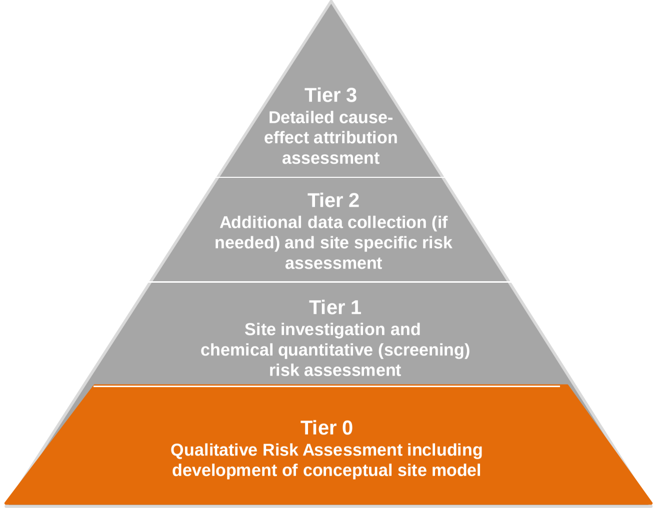
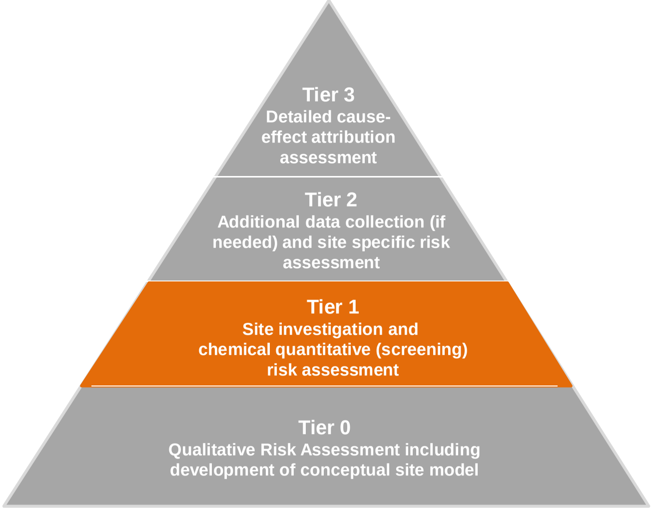
The following sections explore the elements which may need considering during a risk-based evaluation alongside data interpretation (Section 7.2), namely:

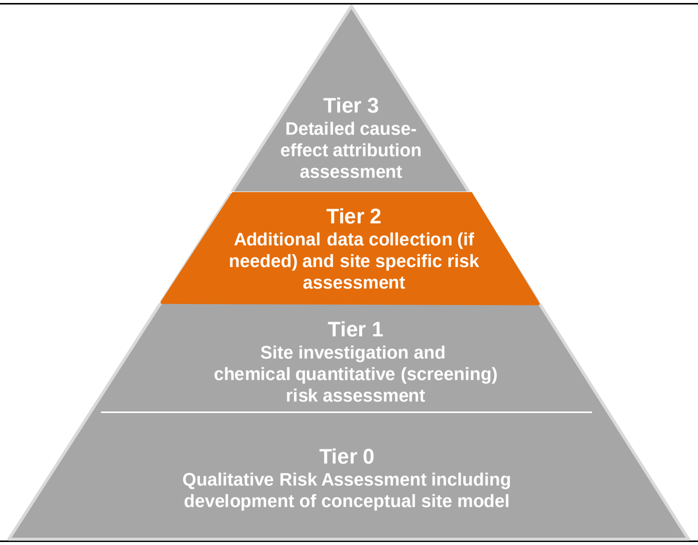
- Quantification of potential risks to ecological receptors (Section 7.5.1);
- Quantification of potential risks to human health (Section 7.5.2);
- Quantification of potential risks to other receptors (Section 7.5.3);
- Uncertainty in quantitative risk assessments (Section 7.6);
- Balance of probabilities (Section 7.7); and
- Sustainable decision-making (Section 7.8).

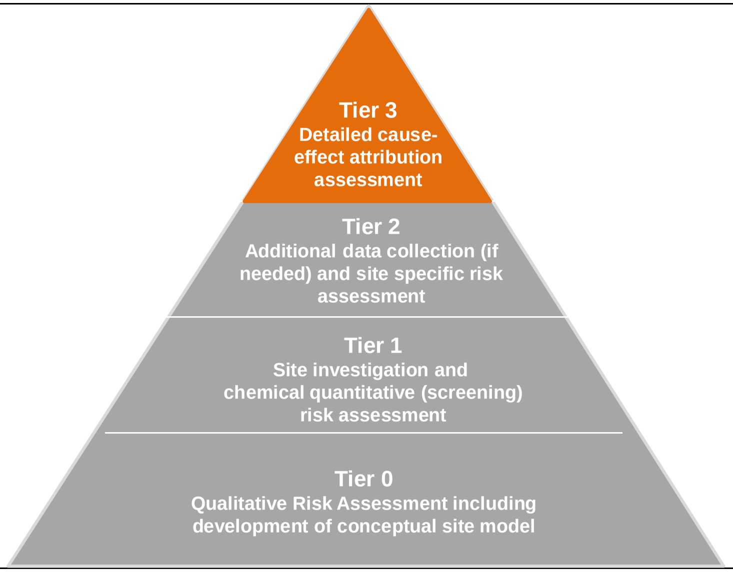
7.5. RISK QUANTIFICATION

The Tier of assessment typically determines the method used to quantify potential risk to a receptor (Box 7.1, adapted from Report E1001).

The higher the tier of assessment, typically the higher the degree of certainty in the assessment output and the greater the chance for measuring, rather than predicting, a dose-response (human and ecological receptors). For example, Report E1001 describes a number of techniques for collecting site specific data to support a Tier 2 or 3 ecological risk assessment, which include eco-surveys that can help to evaluate a real rather than theoretical dose-response. However, for ecological assessments, the focus of data collection (e.g. bioassays, toxicity testing) tends to be on the lower trophic level, requiring significant assumptions to be made regarding the potential for contaminant bioaccumulation in the higher trophic levels and toxic effects.

Box 7.1: Understanding the Risk Assessment Tiers (adapted from Report E1001)		
Qualitative Assessment (Tier 0)		• The use of desk-top information combined, where possible, with site reconnaissance information to develop a conceptual site model, highlighting potential source-pathway-receptor linkages which may be active. • A Tier 0 risk assessment can be used to conclude that only specific linkages (if any) may require further assessment. • It is possible to conclude that contaminated sediments are not present based on a robust conceptual site model developed as part of a Tier 0 risk assessment (see Section 3).
Chemical Quantitative Assessment (Tier 1)		• The use of pre-existing chemical screening levels to evaluate measured concentrations of contaminants in sediment (or, where available and allowed) other environmental media. • Chemical screening or guideline values (Tier 1 assessment) should be used where required by national or local legislation or regulatory framework, but the assumptions inherent in their derivation should be understood and the limitations of using the screening criteria for robust decision-making identified. The issues associated with use of generic guideline values (Report E1001) include: o Whether sediment type used to derive the guideline values is appropriate. o Whether the guideline values can be used in freshwater, brackish or saltwater environments. o Whether the sensitive receptors used to derive the

		guideline values are present, or representative, of those at the site. o Whether all potential receptors (e.g. humans, aquatic organisms, water quality) have been used to derive the guideline values. o Whether the partitioning and the bioavailability of the contaminants has been appropriately accounted for. • Whether background or reference conditions have been accounted for.
Site Specific Risk Assessment (Tier 2)		• The Tier 2 site specific risk assessment is typically the first time that the potential risks to each of the different receptors can be quantified, incorporating site-specific data. • A Tier 2 assessment may not differ significantly from a Tier 1 assessment, if the same software tool is used to derive site specific assessment criteria but with more site specific input parameters. However, a Tier 2 assessment introduces a higher degree of flexibility into the approach, should be underpinned by stronger scientific principles and may draw on a wider toolkit to enable the risks to be evaluated. • At this tier of assessment, the focus is still likely to be on a theoretical prediction of risk, as opposed to collection of empirical data which provide evidence for the presence or absence of source-pathway-receptor links.
Detailed Cause-Attribution Assessment (Tier 3)		• Rather than relying on predictive tools to model individual components of a system, a Tier 3 assessment instead aims to consider the wider system including interactions between different components. • Multiple lines of evidence, or a weight of evidence approach, are used to draw conclusions from the data collected. • Data collection and analysis may include bench-scale laboratory studies, or may rely on surveys completed in the

		field. • Examples of data which might be collected to support a Tier 3 risk assessment include: o Toxicity identification evaluation; o Model ecosystem testing; o Organism sampling; and o Detailed ecosystem, trophic level or species surveys.

7.5.1. Quantifying Potential Risks to Ecological Receptors

There is a wide range of modelling tools which can be used to evaluate the transport of contaminants in the sediment system and subsequent exposure by ecological receptors (Section 6.4). The toolkit is wider than that available for human health receptors, in part because aquatic organisms are often exposed to higher contaminant doses than human receptors and cause-effect can be studied in the field and in the laboratory. However, even when site specific data is incorporated into the modelling, models should only ever be seen as tools which as used to predict dose-response based on theoretical dose-response. Therefore, the output from a model may be used to indicate a *potential* for contaminated sediments to be present, but can rarely be used in isolation to conclude that contaminated sediments are present. For example, if a model predicts that an ecological receptor will have an adverse health effect, the assessor should consider factors such as what the effect could be or what percentage of the population could be affected and whether the effect is long term.

USEPA (1998) highlights that the potential for an effect or change to an ecosystem function or individual species should not automatically be assumed to be negative. When the potential for a change to ecosystem function or individual species is identified, or such change is observed, USEPA (1998) recommends "*the next step is to interpret whether these changes are considered adverse. Adverse ecological effects, in this context, represent changes that are undesirable because they alter valued structural or functional attributes of the ecological entities under consideration. The risk assessor evaluates the degree of adversity, which is often a difficult task and is frequently based on the risk assessor's professional judgment*". In some cases, a change to the ecosystem structure may have occurred, or predicted, but again this should not automatically be seen as a negative effect; the structure of an ecosystem changes with time. An assumption that a change to the ecosystem structure is always negative would result in a difficulty with implementing any remediation strategy, as changes to ecosystem structure will occur as a result of anthropogenic intervention or natural processes. Thus it is important to understand what constitutes natural variation versus an underlying change to the ecosystem structure with associated adverse consequences.

Agreeing as to what constitutes an adverse ecological effect between all stakeholders may be a challenge. Practical Application 7.5, taken from USEPA (1998), identifies factors to consider when deciding whether a change represents an adverse ecological effect.

Practical Application 7.5: Deciding between a change and adverse ecological effect

The USEPA highlights the potential difficulties with deciding whether or not a change to an ecosystem or species represents an adverse ecological effect. To help the decision-making process, the following factors should be considered:

1. What is the nature of the effects?
2. What is the intensity of the effects?
3. What is the spatial and temporal scale of the effects?
4. What potential is there for recovery, and over what timescale?
5. What is the statistical significance of the effect?

Ultimately, for many ecological assessments, there may be no definitive evidence that an adverse effect is occurring, only that a change has, or could occur. However, there is likely to be greater chance of collecting evidence of adverse effects, and therefore concluding that contaminated sediments (as defined within this publication) are present, than for a human health risk assessment.

Where ecological receptors are being assessed, what is deemed an acceptable effect may be a regional or national policy decision (e.g. no predicted average daily dose to exceed the acceptable daily dose), but in some cases the decision will be dependent on the system under evaluation with more flexibility in the assessment process.

7.5.2. Quantifying Potential Risks to Human Health

As for ecological receptors, there are tools available which allow the potential risk to human health from a range of exposure pathways to be evaluated (Section 6.5.1). The greatest certainty in the risk quantification process comes from use of site specific data to characterise the exposure point concentration and also the subsequent exposure. For example, a risk evaluation based on measurements of a contaminant concentration in a fish population is likely to have lower uncertainty than a risk evaluation based on model prediction of contaminant concentrations in the same species. Similarly, an exposure assessment based on the behaviour of the local population rather than a population from a literature study is likely to better represent the real potential for exposure. Report E1001 describes a number of techniques for collecting site specific data to support a Tier 2 or 3 risk assessment. However, even use of site specific data within Tier 2 or 3 assessment will typically not provide a definitive answer as to whether contaminated sediments are present. This is partly as a result of the additional areas of uncertainty which will be present, notably those associated with the toxicological properties of contaminants and mixtures of contaminants (See Section 7.6). However, it is also based on the low level of risk accepted in human health QRAs. Where risk-based evaluation is promoted regionally or nationally, there is typically a recommended level at which the risks are deemed “acceptable” (See Section 6.5.3, “acceptable risk levels”). The risk levels are sufficiently low that, in the absence of a large-scale epidemiological study, the potential for observing an effect in the population is minimal.

As such, quantification of risks to humans is at best likely to conclude that source-pathway-receptor linkages have a significant potential to cause harm, but not that harm is occurring or can be measured. This is unless evidence for harm has actually been observed, which has occurred on rare occasions (e.g. mercury poisoning observed in local residents of Minamata Bay, Japan in the 1950s, Sinderman, 2006). Therefore, drawing a conclusion as to whether contaminated sediments are present is likely to be on a balance of probabilities approach, using multiple lines of evidence to support the conclusion and, if necessary, taking socio-economic factors into account (Section 7.7).

7.5.3. Quantifying Potential Risks to Other Receptors

Reliably quantifying the potential risks to receptors other than ecological or human health (i.e. water resources, water management activities) is often a more simple process. This is because the endpoint of the assessment is typically acceptable or unacceptable water or suspended particle quality, rather than a predicted or observed adverse effect on health or a species population. The risks are more often related to non-compliance (e.g. breach of European water quality legislation) or financial/timescale concerns (e.g. increased cost of dredging a watercourse as a result of added disposal costs). Where possible, efforts should be made to ensure that decision-making regarding next steps takes sustainability considerations into account (Section 7.8). For example, if water quality in one location is in breach of water quality legislation, is it, or could it have an adverse effect on other receptors, and what are the costs and benefits of reaching a compliance situation?

7.6. UNCERTAINTIES IN QUANTITATIVE RISK ASSESSMENTS (QRAS)

The outcome of a QRA undertaken at a Tier 1 or Tier 2 level of assessment using predictive models need careful interpretation before a conclusion is reached as to whether the risks are acceptable or unacceptable (i.e. whether contaminated sediments are present). Where a QRA indicates that the risks are acceptable, provided the modelling has been undertaken using appropriate (and if necessary, conservative) assumptions and there are other lines of evidence to support the findings, the assessor should have confidence in concluding that contaminated sediments are not present. However, a QRA outcome that the risks could be unacceptable rarely equates to a real risk of adverse harm to the receptor. Instead it may highlight the need for further, more detailed considerations (e.g. a Tier 3 assessment) before a more robust conclusion can be reached. Even at a Tier 3 level of assessment, the uncertainties, and often conservatism, inherent in the evaluation process means that the data can only be evaluated on the balance of probabilities. Understanding the different components of the QRA where uncertainties can be introduced, in particular focusing on risks to human health and ecological receptors, helps to target further data collection and risk evaluation.

7.6.1. Complexity of natural systems

Natural systems are complex and involve the interaction of a number of physical, chemical and biological systems. Quantitative risk assessments (Tier 1 to 3 assessments) attempt to model these interactions to the extent possible, but have to use simplifying assumptions to do so. The assumptions made and models used, and how well or poorly these assumptions and models reproduce the interactions taking place in the natural system, introduce uncertainty (and often conservatism) in the QRA. These can be reduced through use of site specific data, contaminant measurements which negate the need to predict exposure point concentrations using conservative assumptions (e.g. laboratory analysis of fish lipids in place of theoretical modelling of contaminant uptake) and sensitivity testing to identify the more critical parameters in the evaluation.

7.6.2. Consideration of bioavailability

The increased focus on collection of data to support bioavailability analysis for inclusion in QRAs will help to reduce potentially undue conservatism within exposure modelling for human health and ecological receptors. However, there is still potential for significant conservatism to be introduced into the assessment process where the default to 100% bioavailability is made in the absence of literature or site data to suggest otherwise.

7.6.3. Exposure parameters for receptors

Quantitative exposure modelling typically requires assumptions regarding the extent to which organisms are exposed to contaminants in the system. Exposure parameters used to conduct food chain models for benthic organisms, fish/shellfish, birds and mammals (including humans) are often selected to represent conservative feeding or activity patterns of each of the selected receptors, in the absence of site specific data. For example, it may be assumed that “mobile” or transient wildlife receptors consume food from the ecosystem throughout the entire year in the absence of information regarding feeding, hibernation or migration patterns. For human receptors, research into the activity patterns and dietary intake of one particular group of individuals (e.g. fisherman) from one part of a country may be cross-applied to another part of the country where activity patterns and dietary intake are different. The use of conservative literature estimates, in particular within Tier 1 and Tier 2 QRAs, may result in over-estimation of the risks presented.

7.6.4. Exposure point concentrations

An important contributor to uncertainty is the data or information upon which a QRA is based. Use of maximum measured contaminant concentrations or upper 95th percentile concentrations – provided the site has been well characterised – should provide a worst-case estimate of the potential risk. For small datasets, uncertainty is introduced through the development of a single point concentration to which the receptors are likely to be exposed. For a Tier 1 or Tier 2 evaluation, alternatives include use of statistical testing to generate an upper confidence level in the average concentration of contaminants present (see also Section 7.4) where the dataset allows such a calculation to be performed, or a greater reliance on measurement rather than prediction of exposure point concentrations.

7.6.5. Intake versus uptake

Quantitative risk assessments at Tier 1 or 2 typically use literature-derived BAFs and BSAFs to estimate tissue concentrations for sediment invertebrates, plants, and fish tissue. Appreciating that there is often no plausible alternative to use of literature-derived values, modelled accumulation factors can introduce a high degree of conservatism into QRAs.

7.6.6. Laboratory toxicological data

Quantitative risk assessments typically use toxicological data that are collected on an individual receptor basis, rather than at the population level. This results in the estimation of risks to single species of organisms, not to a population or community. However, the risks are commonly extrapolated to include an entire population.

The majority of toxicity data used in Tier 1 or Tier 2 QRAs are derived from laboratory studies conducted in settings that do not mimic true field conditions (ecological or human exposure). Laboratory studies typically control various factors in order to isolate one particular parameter. Although such controlled experiments make it simpler to interpret isolated parameters or relationships, uncertainty is associated with assuming that laboratory exposure conditions are equivalent to in-field exposure conditions. The direction, magnitude, and effects of such uncertainties are always quantifiable, resulting in the use of conservative safety factors in derivation of acceptable doses for either human health or ecological receptors.

In many cases (ecological assessments) a more detailed cause-attribution evaluation, in place of reliance on a predictive model, improves confidence in the assessment outcome. However, predictive models used within QRAs often have value in identifying which receptors within the ecosystem should be targeted for a higher tier risk assessment.

7.6.7. Synergistic effects

There is continued debate as to whether there is potential for mixtures of contaminants to result in either a positive synergistic effect (greater dose-response than for exposure to the individual contaminants) or antagonistic effect (lower dose-response than for exposure to the individual contaminants). A review carried out by

European Union (2012) concluded that there is no evidence for synergistic effects in human health. However, this research does not extend to ecological receptors. Common consensus still appears to be not to account for potential synergistic effects, based on the absence of good evidence to suggest these are either active or important in the risk assessment process.

7.7. BALANCE OF PROBABILITIES

As described in Sections 7.6, the uncertainties which are inherent in the assessment of a complex natural system means that, even if a Tier 3 assessment is completed, it is commonly not possible to conclude with certainty that risks are present, although such examples do exist (Example 7.1).

Example 7.1: Exposure to organo-chlorines by bald eagles, the Great Lakes
One of the better studied examples of contaminants in the aquatic environment, including sediments, adversely affecting a receptor, is the bald eagle (*Haliaeetus leucocephalus*). A range of adverse health effects were identified in bald eagles resident in the Great Lakes, US and Canada, from the 1950s, based on the presence of organo-chlorines in the sediment and water environment. Effects included increased embryonic mortality, wasting syndromes for hatchlings, adult deformities and shell thinning. This led to the definition of the term GLEMEDS, describing the **G**reat **L**akes **E**mbryo **M**ortality, **E**dema and **D**eformities **S**yndrome. The end result of GLEMEDS was a significant decline in the population of bald eagles through the 1950s, close to extinction by the 1970s. The primary cause of the decline was attributed to exposure to organo-chlorine compounds such as DDT and polychlorinated biphenyls (PCBs). With data collected to monitor the status of the populations since that time, the USEPA report an increase in bald eagle reproductive parameters which correlate with the decline in global output of organo-chlorine compounds (including the banning of the use of DDT in the 1970s). There is general consensus that there is a direct relationship between the presence of the contaminants and the population decline. However, even for this extremely well studied example, there is acknowledgement that other factors may also have played a role, including loss of habitat and poaching. Further information is provided by a range of authors, including Colborn (1991) and Bowerman et al (1995, 1998, 2003).

It has to be recognised that there is a point at which the benefits of further data collection in terms of improving the site evaluation are outweighed by the timescale and cost implications of undertaking such work. In the absence of legislation or regulatory guidance on what constitutes acceptable or unacceptable, there is a need for multiple lines of evidence to decide, based on a balance of probabilities, whether contaminated sediments, as defined within this guidance, are present. Such a decision may need the input from multiple stakeholders, and take into consideration not only environmental but also social and economic factors (Section 8).

8. SUSTAINABLE RISK MANAGEMENT

8.1. DECISION TO IMPLEMENT A RISK MANAGEMENT STRATEGY

In many cases, the criteria which trigger the decision to design and implement and risk management strategy will be clearly defined prior to commencing a potentially contaminated sediment assessment. Clearly, where the outcome of a risk evaluation at a Tier 3 level is that contaminated sediments are present (i.e. there is evidence that harm is occurring, or there is a significant possibility it could, occur), a detailed evaluation will typically be made as to how the risks could be mitigated. However, balancing the costs of undertaking a higher tier assessment with the costs of implementing a risk management solution may lead to the decision to undertake remedial activities based on the conclusions of a Tier 1 or 2 risk assessment.

Whatever the technical or commercial trigger for exiting the assessment process (**Figure 8.1**), consideration should already have been given to the viability of different risk management techniques. Section 2 explained the importance of identifying whether there are viable risk management solutions before commencing the potentially contaminated sediment assessment, as this can be a critical factor in deciding whether to carry out the investigation.

8.2. COST-BENEFIT ANALYSIS

Where a risk management strategy is being evaluated, a financial-environmental cost-benefit analysis should be considered to help understand (a) whether the environmental betterment arising from remediation activities is warranted given the financial costs, and (b) whether one strategy is more appropriate when the costs and benefits of different techniques are cross-compared. Typically, such an assessment comprises identification of the environmental costs and benefits associated with different risk management solutions compared against the financial costs, and an evaluation as to which risk management strategy is more appropriate. For example, if a particular risk management strategy will provide a small percentage increase in environmental betterment or protection, but with a large percentage increase in financial cost, than another alternative strategy, this is used to help decide which strategy is more appropriate.

8.3. SUSTAINABLE DECISION-MAKING

The concept of cost-benefit analysis as described in Section 8.2 has broadened over time. A growing theme within risk management frameworks, sustainable decision-making should be a core consideration throughout the risk assessment process (e.g. Mulligan et al, 2009; Sustainable Management of Sediment Resources Series: Barcelo and Petrovic (2006), Bortone (2007), Heise (2007) and Owens (2007)). Sustainability factors can also be used to guide the development and implementation of the risk mitigation strategy. In particular, where the end-point of the risk assessment is less conclusive, i.e. there is the potential for risks to exist but on the balance of probabilities these are not considered significant, sustainability considerations may be critical in deciding whether remediation action is warranted. This form of assessment typically comprises a broader benefits-impacts analysis than a financial cost-benefit analysis.

As highlighted in Report E1001, general consensus globally is that sustainable decision-making needs to consider three factors:

- Environmental factors
- Economic factors; and
- Social factors.

There is a growing list of frameworks to evaluate sustainable decision-making as it relates to the sediment environment, alongside toolkits being developed to aid assessment. The Sustainable Remediation Forum (SuRF), and SuRF-UK, are two of the first groups providing and collating guidance for practitioners wishing to undertake a sustainability appraisal that considers each of the three factors. A differentiation is made between "Green Remediation" which focuses on the environmental impacts and benefits of remediation, and "Sustainable Remediation" which also considers the economic and social factors (e.g. CL:AIRE 2011; ITRC, 2011b and c). In general, a sustainable remediation assessment can comprise a qualitative analysis, or a quantitative analysis. For a quantitative analysis, each indicator is given a site specific scoring and the importance or weightings applied to each indicator may be dependent on regional or national legislation, regulatory guidance, stakeholder concerns and site specific conditions. This allows cross-comparison between different risk management solutions, which may include remediation.

In Europe NICOLE (2010, 2012) presented a roadmap for sustainable remediation, while SuRF-UK (CL:AIRE, 2011) presented an assessment framework. Others, such as the ITRC (2011c), describe methods for undertaking a sustainable remediation evaluation:

- Life-cycle assessment (LCA)
- Net environmental benefit analysis (NEBA)

8.3.1. Life-cycle assessment

Life-cycle assessment, or LCA – has historically been more focused on the assessment of green remediation, comprising an evaluation which looks to:

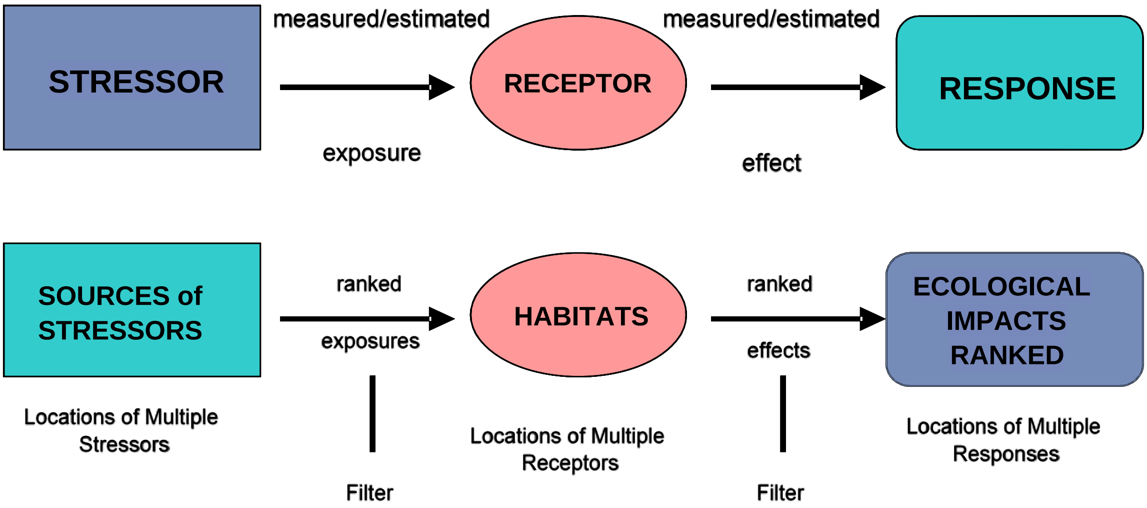
- Minimise natural resource use and promotion of use of renewable resources
- Reduce the generation of solid and liquid wastes and air pollutants
- Evaluate and reduce costs and
- Evaluate and reduce time
- Promote remediation of land fit for purpose (useful land use)
- Promote habitat and ecosystem restoration.

The process requires an inventory analysis to be completed, to identify each step within the process and understand the boundary conditions (typically a cradle-to-grave understanding of all materials used), an assessment of the overall impacts from each step in the process, and an assessment as to the potential for improvement. A LCA can take the form of a relatively simple assessment through to a detailed, quantitative evaluation. The process is described in further detail by Favara et al (2011), showing how the process of LCA is being expanded to consider wider socioeconomic factors.

8.3.2. Net environmental benefit analysis

As described in Report E1001, the underlying principle behind Net Environmental Benefit Analysis (NEBA) is the assessment of all sources which could have an impact and the associated ecological impact (**Figure 8.1**, taken from Landis, 2005).

Figure 8.1 Schematic illustrating Net Environmental Benefit Analysis – NEBA (taken from Landis, 2005)



The NEBA framework is used to guide decision-making regarding how, where and what to investigate, assess and, ultimately, remediate. It is intended that, rather than remediation focusing on improving the condition of a single site and/or contaminant, the likelihood of measurable environmental benefit to the whole ecosystem when all "stressors" in the system are considered is used to develop the strategy. The NEBA framework can be applied to develop a high level risk assessment and management strategy at sediment contamination sites, but it is recognised that there may be real difficulties when multiple stakeholders are involved, and may not be a practicable solution in many cases.

8.4. SUMMARY

Where there is clear evidence which indicates that risk management activities are warranted, it is critical that the potential effect of implementing remediation (whether to manage the source, pathway or receptor) are well considered. This helps to avoid remediation strategies which are high in cost but low in benefit to the environment, or worse, result in unintentional deterioration or adverse effect on a receptor. Sustainable decision-making, promoted through the work of organisations such as SuRF, can be used to identify risk mitigation strategies which are proportionate, effective, long-lasting and have the lowest impact on the system biodiversity.

9. CONCLUSIONS

This report, a technical companion document to Energy Institute / CONCAWE Report E1001 focuses on potential uncertainties associated with the investigation and assessment of sediments containing contaminants, and how these can be overcome. There will always be uncertainties inherent in the assessment of a sediment system, as even the most complex and sophisticated modelling tools cannot accurately replicate the natural environment. However, identifying areas of uncertainty and then working to reduce uncertainties associated with the most sensitive parameters help to provide an assessment which is reasonable, proportionate and fit-for-purpose and risk-management solutions that are effective, durable and reasonable. This process starts with the development of a robust conceptual site model, which is revisited and refined as more data are gathered.

The document highlights many ways in which the collection of focused site investigation data can contribute to a better understanding of the real - rather than theoretical - risks to ecological receptors, human health receptors, water resources and waterway management activities. Multiple examples of investigation and data analysis techniques have been described, providing the assessor with a large toolbox from which to select the most appropriate techniques for the site under assessment.

Site data can subsequently be used to undertake quantitative, risk-based analysis of the risks, using statistical testing where appropriate, to draw meaningful conclusions as to whether risk mitigation works are required. Where regional or national legislation or regulatory guidance dictates, it may be that comparison to chemical screening values (Tier 1 assessment) is required to highlight a need for remediation activities. However, there is a growing recognition that this can lead to remediation being carried out on the basis of poor site characterisation and understanding, and triggers concerns regarding the sustainability of such decision making. Instead, a more site specific level of assessment is recommended, which may culminate in a Tier 3 assessment which aims to identify if there is a real risk of harm occurring, and whether that risk is unacceptable.

Use of this evidence-driven risk-based approach to sediment site management should help to overcome at least some of the challenges associated with contaminants in sediment sites in Europe. These include multiple sources in the sediment environment and the long history of permitted discharge to European waterways and coasts, meaning that the remediation of every site, purely on the basis of contaminants being present in sediments, is not a sustainable approach to sediment site management.

10. GLOSSARY

Abiotic	Non-living, devoid of life (Allaby and Allaby, 1996)
Abrasion	Erosion of a stream/river bed
Acid volatile sulphides	An indicative measurement of the amorphous iron sulphide (FeS) present within sediments
Anthropogenic	Applied to substances, processes etc. of human origin or that result from human activities (Allaby and Allaby, 1996)
Attenuation	Reduction in mass or concentration of a chemical or substance in groundwater or surface water with time or distance from the source
Attrition	Reduction in particle size caused by collisions during transport
Background conditions	Constituents or locations that are not influenced by the release from a site, usually described as naturally occurring or anthropogenic (USEPA, 2002)
Bathymetric survey	Surveying the topography of the sediment, which can be undertaken using a range of investigation tools (e.g. underwater photography, side scan sonar)
Bed-load	The coarser fraction of a river's total sediment load, which is carried along the bed by sliding, rolling and saltation (Allaby and Allaby, 1996)
Benthic organisms	Benthic organisms are the community of organisms which live on, in, or near the seabed, also known as the benthic zone
Bio-accessibility (oral)	The fraction of the contaminant released from the environmental medium (in this case, sediments) into solution during processes such as digestion, making it available for absorption (Bio-accessibility Research Group of Europe)
Bioaccumulation	The biological sequestering of a substance at a higher concentration than that at which it occurs in the surrounding environment or medium (USGS, 2007). As a result of direct partitioning and dietary intake
Bioaccumulation factor (BAF)	The ratio of the contaminant in an organism to the concentration in the ambient environment at a steady state, where the organism can take in the contaminant through ingestion with its food as well as through direct content (USEPA, 2009)
Bioassay	a laboratory test in which the toxicity of a contaminant or environmental sample is measured by exposing a specific organism and measuring a lifecycle parameter (for example, survival, reproduction, development, growth). In general, bioassays are conducted under controlled conditions so that the effects of environmental factors that could confound interpretation of results are avoided (Environment Agency, 2002)
Bioavailability	The state of being capable of being absorbed and available to interact with the metabolic processes of an organism (USEPA, 1992a), or the fraction of a contaminant that can be absorbed by the organism – a ratio of absorbed to administered dose – through the gastrointestinal system, pulmonary system and the skin (Bio accessibility Research Group of Europe)
Bioavailability processes	Individual physical, chemical, and biological interactions that determine the exposure of plants and animals to chemicals associated with soils and sediments (NRC 2003)
Bioconcentration	The biological sequestering of a substance at a higher concentration than that at which it occurs in the surrounding environment or medium, as a result of non-dietary intake (USEPA, 2010)

Bioconcentration factor (BCF)	The ratio of the contaminant concentration in the organism to that in water
Biologically active zone	Sediment where the population of organisms is greatest, typically the top few centimetres in inland and estuarine sediments but potentially a greater depth in marine sediments
Biomagnification	Result of the process of bioaccumulation and biotransfer by which tissue concentrations of chemicals in organisms at one trophic level exceed tissue concentrations in organisms at the next lower trophic level in a food chain (USEPA, 2009)
Biota	The living organisms occupying a place together (Allaby and Allaby, 1996)
Biota-Sediment Accumulation Factor (BSAF)	A measure of bioaccumulation of sediment-associated organic compounds or metals into tissues of ecological receptors (Burkhard, 2009)
Biotic	Applied to the living components of an ecosystem, distinct from non-living, abiotic, physical and chemical components (Allaby and Allaby, 1996)
Bioturbation	The disruption of sediment by organisms (Allaby and Allaby, 1996)
Black carbon	Used to describe anthropogenically-derived particles of carbon, example of which include coke, charcoal and soot
Capping	A risk management solution which involves covering or enclosing sediments affected by contaminants to prevent or minimise potential for release to water or exposure by organisms
Chemical fingerprinting	Laboratory testing methods which provide information to distinguish between different sources of chemicals or substances (also known as “source fingerprinting”, Stout et al, 2003)
Chemical precipitation	The formation of a substance through separation from a solution or suspension (Allaby and Allaby, 1996).
Chemolithotrophic	An organism is described as chemo-lithotrophic if it can use chemicals (e.g. contaminants) for aerobic or anaerobic respiration
Conceptual site model	A representation of the characteristics of the site in diagrammatic or written form that shows the possible relationships between contaminants, pathways and receptors (DEFRA and Environment Agency, 2004)
Congener	For polychlorinated biphenyls, used to describe one of the 209 different PCB compounds; a congener may have between 1 and 10 chlorine atoms, which may be located at various positions on the PCB molecule (USEPA, 2012a)
Contaminated sediment	Sediment which contains substances, derived from anthropogenic activities, at concentrations that are causing environmental damage or a significant threat of environmental damage.
Darcy’s Law	Equation describing the flow of liquid through a porous medium
Desorption	The release of a chemical sorbed to sediment particles
Diffusive gradient thin film sampler	*In situ* water sampling device for dissolved free metal ions and labile metal complexes (representing bioavailable metals) which uses a poly-acrlyamide gel; metal species are able to diffuse into the sampling device via the exposure window
Direct source	Term used in this publication to refer to contaminants in sediments acting as a source to which receptors may become exposed and/or affected by
Disassociation	The release of ionic compounds (complexes or salts) bound within a sediment to pore water
Dispersion	Irregular spreading of solutes due to aquifer heterogeneity at a pore-grain scale – mechanical dispersion – or at a field scale – macroscopic dispersion” (Carey et al., 2006)
Dredging	The process of underwater excavation of sediment

Dynamic input	Contaminant input to the sediment system which is variable over time
Ebullition	Used to refer to the generation and migration (“bubbling”) of gas bubbles through a sediment
Ecosystem	The sum of all the living plants and animals, their interactions, and the physical components in a particular area (USEPA, 2012b)
Geomorphology	The description of the structure and topography of the sediment system
Habitat	The place where a population of plants or animals and its surroundings are located, including both living and non-living components (USEPA, 2012b)
Heterotrophic	Organism reliant on organic substances for nutrition
HydroCarbon Block Method	A method which assigns similar behaving hydrocarbons to the same blocks and then relates release rates of petroleum products to environmental concentrations and human intake rates by means of so-called environmental fate factors and human intake fractions of the hydrocarbon blocks (King et al, 1996)
Hydrolysis	The chemical decomposition or ionic dissociation caused by water (Chambers, 1999)
Hypolentic zone	The portion of lake sediments in which there is exchange of water from the lake into the lake-bed sediments, and then returning to the lake, within timescale of days to months (modified from Environment Agency, 2009a)
Hyporheic zone	The portion of the fluvial sediments in which there is exchange of water from the stream into the riverbed sediments and then returning to the stream, within timescales of days to months (Environment Agency, 2009a)
Hyporheos	Community of organisms within the hyporheic or hypolentic zone
Indirect source	Term used in the publication to describe the source of contaminants in sediment (e.g. discharges into surface water, contaminated site run-off)
Intraperitonal injection	The injection of a substance into the peritoneum, i.e. the body cavity
In vitro	Used to refer to test methods which take place outside of an organisms
In vivo	Used to refer to test methods which take place within an organism
Isomer	A compound which has the same chemical formula but different atomic arrangement in the molecule (and therefore differing properties) to one or more compounds
Isotope	One of two or more varieties of a chemical element whose atoms have a common number of protons and electrons (i.e. their atomic number is the same) but which vary in the number of neutrons in their nucleus (i.e. their atomic weight, signified by their mass number, is different) (Allaby and Allaby, 1996)
Isotopic testing	Process of laboratory analysis which identifies which isotopes, and relative concentrations, are present
Long-shore drift	long-shore transport of particles parallel to the coastline, through cyclical process of erosion and re-deposition
Metabolic process	Changes to chemicals as a result of metabolism within a living organism or transformation within flora. Specific metabolites may be excreted by living organisms following intake and uptake of contaminants
Microbial degradation	A process by which microbial organisms transform or alter (through metabolic or enzymatic action) the structure of chemicals introduced into the environment (USEPA, 2009)

Multivariate analysis	Term used to describe a statistical analysis technique which assesses data associated with more than one variable
Net Environmental Benefit Analysis (NEBA)	A net environmental benefit analysis is a methodology for comparing and ranking the net environmental benefit associated with multiple management alternatives. Net environmental benefits are the gains in environmental services or other ecological properties attained by remediation or ecological restoration, minus the environmental injuries caused by those actions
Oxidation reduction potential (Redox)	The energy change , measured in volts, required to add or remove electrons to or from an element or compound (Allaby and Allaby, 1996)
Peeper	Peepers are rigid structures, which can hold volumes of water separated from the environment by porous membranes to monitor constituents in saturated environments. They rely on diffusion of the analytes to reach equilibrium between the sampler and the pore water (ITRC, 2006)
Petrogenic PAH	A term used to describe PAH that are formed slowly and under low to moderate temperatures (often related to a natural source, such as coal deposits)
Photolysis	The chemical decomposition or ionic dissociation under radiation (Chambers, 1999), including sunlight. Photodegradation is another term used to describe this process
Photo-oxidation	Oxidation caused by radiation, including sunlight
Pollution	The direct or indirect introduction, as a result of human activity, of substances, vibrations, heat or noise into air, water or land which may be harmful to human health or the quality of the environment, result in damage to material property, or impair or interfere with amenities and other legitimate uses of the environment (Industrial Emissions Directive 2010/75/EU
Polycyclic Aromatic Hydrocarbons (PAH)	Organic compounds comprised of fused aromatic rings (hydrogen and carbon)
Pore water	The interstitial water present in sediment
Pyrogenic PAH	A term used to describe PAH that are related to higher temperature events, such as combustion of fuels (e.g. from automotive or power plants, or incomplete combustion of wood or charcoal burning) or from processing of coal to form coal tars and coal tar products
Reference area	Analogous to a “control site”, the reference area is affected by the same background stressors to the site under assessment, helping to distinguish between effects as a result of background conditions and effects due to site specific conditions
Reference conditions	Constituents or locations that are not influenced by the release from a site, usually described as naturally occurring or anthropogenic (USEPA, 2002)
Retardation	A measure of the reduction in solute velocity relative to the velocity of groundwater caused by sorption processes (Carey et al, 2006)
Saltation	Major process of particle transport in water which involves an initial steep lift followed by travel then a gentle descent to the sediment bed. An essential requirement for the process is turbulent flow that can lift particles into the zone of relatively high downstream velocity (Allaby and Allaby, 1996)
Sediment	Material which has been eroded, transported and deposited on the bottom of a water body (lake, river / estuary, marine), resulting from natural processes that can also be affected by human activities
Solid phase microextraction fibres	Sampling tool which can be used *in situ* in sediments, relying on the partitioning of a constituent between a polymeric phase and aqueous or gaseous phase

Stygobites	Obligatory inhabitants of aquatic subsurface habitats (CL:AIRE, 2011)
Stygophiles	Organisms which have a greater affinity to hyporheic environments and actively exploit resources and the available habitat (e.g. during periods of high stream flow, drought or for protection from predators) (CL:AIRE, 2011)
Stygoxenes	Stream organisms only entering the interface through accidental infiltration (CL:AIRE, 2011)
Suspended particles	Defined in this publication as suspended mineral and organic components in the surface water column
Synergistic effect	The potential for mixtures of contaminants to result in either a positive synergistic effect (greater dose-response than for exposure to the individual contaminants) or antagonistic effect (lower dose-response than for exposure to the individual contaminants)
System hydrodynamics	A qualitative or quantitative description of the interactions and motion of fluids (including water) and sediments throughout a sediment system
Traction	Movement of sediment particles in water by rolling or sliding along the stream/river bed
Trophic guild	A group of species within the same trophic level which exploit the same resources
Trophic level	The position of a species (or in some cases, types of species with similar feeding habitats) within a food chain or food web (USEPA, 2012b)

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