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Risk Assessment and Management of Terrestrial Ecosystems Exposed to Petroleum Contamination

M. S. Kuyukina[1,2], I. B. Ivshina[1,2], S. O. Makarov[2] and J. C. Philp[3]
[1]Institute of Ecology and Genetics of Microorganisms, Russian Academy of Sciences, Perm
[2]Perm State University, Perm
[3]Science and Technology Policy Division, Directorate for Science Technology and Industry, OECD*, Paris
[1,2]Russia
[3]France

1. Introduction

Risk assessment as part of a strategy for dealing with contaminated land is becoming the norm internationally. The term covers both human health and ecological risk assessment. Risk assessment may be defined as the "characterisation of the potential adverse health effects of human exposures to environmental hazards" (human health risk assessment) or the "process of estimating the potential impact of a chemical or physical agent on a specified ecological system under a specific set of conditions" (ecological risk assessment) (Markus & McBratney, 2001).

The risk assessment movement was probably born as a result of experiences with its forerunner, the multifunctionality approach, which was particularly prevalent in the Netherlands. The Dutch example serves as our introduction to this change of policy from multifunctionality to suitability for use, or functionality. The situation was elegantly described by Honders et al. (2003).

In the Netherlands in the early 1980's, all contaminated sites had to be fully excavated and remediated to the level of the reference values (natural contaminant concentrations in soil), in order that the land could be used for a variety of purposes. This very rigorous stance was based upon the perception that the total national remediation costs would be in the order of Euro 0.5 billion. Remediation funds were largely provided by the national government. By the end of the eighties, it had become clear that total remediation costs were going to be in the order of Euro 50 billion if all sites were to be cleaned up to this very high standard.

The Soil Protection Act in the Netherlands initiated the move towards a risk-based approach to site remediation. The concept of "multifunctionality" was replaced by the concept of

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* The opinions expressed and arguments employed herein are those of the author(s) and do not necessarily reflect the official views of the OECD or of the governments of its member countries.

"functionality", or "suitability for use", or "fitness for use". Quite clearly if a contaminated site was to be re-developed as, say, a car park that would be covered with concrete or tar, then the exorbitant cost of decontamination to reference values was unwarranted. On the other hand, if the site was to be re-developed for a purpose that would involve the exposure of humans to contaminants (for example, a housing development or kintergarden) then removal of contaminants to a higher level, and therefore higher cost, was justified.

In this way a risk assessment would determine the clean-up standard and could also be used in the selection of a remedial technology for the site (the so-called risk-based remedial design). In the eighties, *ex-situ* treatment technologies were still in their infancy. Incineration of contaminated soil, whilst controversial, ensures destruction of the contaminants and was therefore a reasonable option for sites that required to be cleaned to a very high standard. Unfortunately incineration also destroys the soil itself. There has always been concern about the destruction of soil, and the European Union has acknowledged this with the proposal for a directive for the protection of soil. The following is taken from that proposal (Commission of the European Communities, 2006).

> "*Soil is a resource of common interest to the Community, although mainly private owned, and failure to protect it will undermine sustainability and long term competitiveness in Europe. Moreover, soil degradation has strong impacts on other areas of common interest to the Community, such as water, human health, climate change, nature and biodiversity protection, and food safety*".

A common technique internationally for dealing with contaminated land at that time was landfill, which became known as "dig and dump". However, it is recognised that this is not a treatment option; rather it simply moves the problem somewhere else as the anaerobic environment of landfill is not conducive to the destruction of organic contaminants. Besides, landfill is under strong scrutiny as sites suitable for development for landfill become rarer. Even in a country like Australia, with a large land mass and low population, there are good reasons to consider the available supply of landfill to be a scarce resource that should be used conservatively (Pickin, 2009). A country with quite the opposite conditions is Japan, where there is limited space and high population density. In Japan, it is becoming increasingly difficult to obtain public acceptance to install waste disposal facilities, such as landfill sites, due to a rising pressure on land use and growing public concern over environmental and health protection (Ishizaka & Tanaka, 2003). There has been legislation developed in many countries aimed at maximising the efficiency of use of landfill sites, and dumping contaminated soil in them does not represent a good use of space.

Landfill has typically been the least expensive option, compared with, say, bioremediation and soil washing. However, with the arrival of Landfill Tax, the costs of alternatives to landfill disposal become more comparable. It was predicted in the UK that, as more experience was gained with alternative technologies, costs should fall, helping to encourage new cost-effective remediation approaches (Day et al., 1997). That prediction has come true.

The risk assessment concept favours technologies such as bioremediation. Bioremediation has had difficulty competing with other remedial technologies because of some uncertainties, such as remedial target end points and the time required (Diplock et al., 2009). It has therefore been more difficult to establish engineering parameters (Philp et al., 2005a). With risk assessment, and the inherently less rigid outcomes for remediation that may be

derived from the assessment, bioremediation technologies have become more attractive. Bioremediation technologies are now deployed internationally and are cost-competitive.

Scope of the chapter

Figure 1 shows the overall contaminated land management process (modified from DEFRA and Environment Agency, 2004, with all the steps other than risk assessment in grey for clarity). This chapter will be confined to the left column, which is the risk assessment part of the management process, although some comments will be made about risk-based remedial design i.e. remedial options appraisal. As can be seen from the flowchart, risk assessment in the context of contaminated land management is an iterative process, during which more site data may or may not be required depending on the complexity of the contamination problem. Most common problems associated with terrestrial petroleum contaminations are old petrol station sites in urban areas and accidental crude oil-spillage sites along cross-country pipelines, which are complex, with multiple contaminants, and typically require a remediation treatment train. The greater the number of pollutant linkages, the greater the requirement for iteration.

2. Drivers for contaminated site remediation

In the European context the three major drivers for contaminated site clean-up are:

1. Direct regulatory intervention;
2. The need for the development of urban industrial areas ("brownfield sites") (van Hees et al., 2008);
3. National, mainly state-funded, programmes ("orphan sites").

The most widely accepted definition of brownfields is that of the US EPA (1997), where they are described as: "abandoned, idled, or under-used industrial and commercial facilities where expansion or redevelopment is complicated by real or perceived environmental contamination". The widespread problem of brownfield sites is the result of two concurrent factors (Alberini et al., 2005):

1. The 1970's saw the down-sizing of US and Western European manufacturing, with many factory closures;
2. The passage of environmental legislation, especially based on the polluter pays principle, whereby parties were identified with the responsibility for the clean-up of contaminated sites.

It has been said that the most significant driver of the regeneration of contaminated sites in the UK is the development process, especially for brownfeld sites (Luo et al., 2009). This is likely to be the case in relatively small, but densely populated countries with a high demand for housing provision. It has also been the case in the US and Canada (de Sousa, 2003).

Scarcity of land, particularly for house building, has raised the political profile of brownfield site redevelopment, and as a result contaminated land has gradually risen up the political agenda (Catney et al., 2006). The development of brownfield sites helps prevent the use of green sites for housing, and also promotes economic growth in inner cities, and is therefore a potentially important component of sustainable growth.
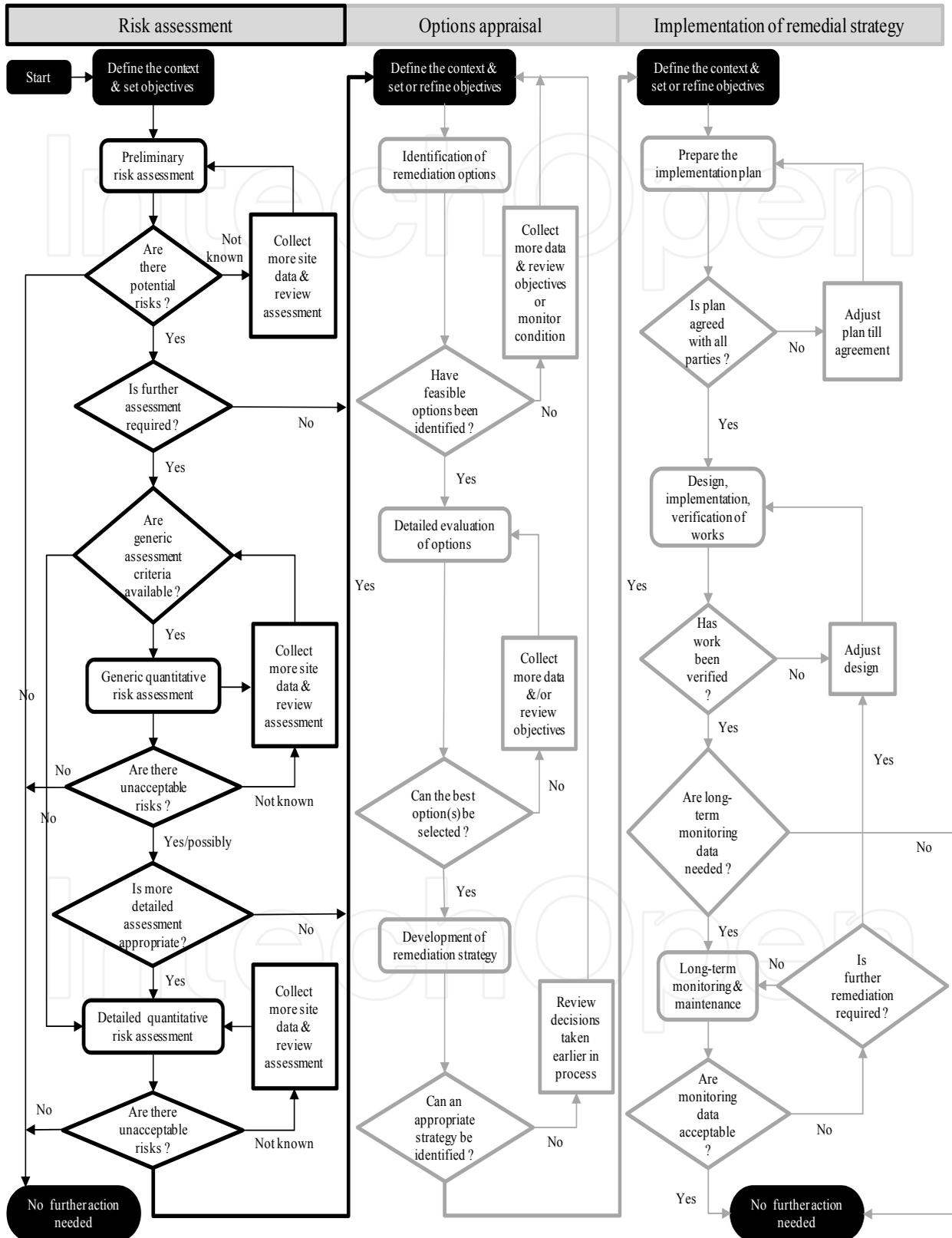
Fig. 1. The contaminated land management process (modified from DEFRA and
Environment Agency, 2004).

In the Russian Federation, fundamental economical and political changes during the last decades have reinforced the problem of sustainable remediation of brownfields, especially in city areas. The main reasons for that are:

- Large space requirements for growing offices, housing, shopping and service facilities;
- Former industrial areas, which were closed for economic and/or environmental reasons, represent a serious hazard to the population due to pollution emissions and also a potentially good investment medium due to the increasing land cost (Sojref & Weinig, 2005).

3. Principles of risk assessment

Risk assessment of contaminated land serves two general purposes:

1. It is used to determine the *significance* of contamination at a site;
2. It may be used to determine the level of clean-up required for the intended use of the site.

Risk assessment as a methodology is not limited to the assessment of contaminated land but often used for other purposes, varying from prevention of pollution from new chemicals and processess, through reliability engineering of industrial activities and new technologies, to environmental impact assessment. Risk assessment of contaminated sites is somewhat different from risk assessment in other fields. The evaluation of risk from soil contamination is not usually a preventive approach; the source is already there. In principle this makes the assessment easier because claims about exposure can be verified at the site. In practice, however, this advantage is rather limited due to the complexity of the source, the difficulties of performing experiments and the need to predict *future* exposure. This predictive element means that there is much in common with risk assessment methods used in other fields.

The assessment of soil quality in general is based on the determination of the concentration of pollutants in soils. The estimated concentration is compared with specific threshold values and the degree of contamination is evaluated. An assessment of health risks from a soil contaminant may consider whether total exposure from several pathways exceeds a critical (tolerable or acceptable) intake level. The total intake is compared with an appropriate health criterion (tolerable daily intake, etc.) that represents the maximum acceptable level of exposure because of a critical effect on a target organ or metabolic pathway. Exposure in excess of this threshold is then considered to indicate that the soil contaminant poses a significant risk to human health. Thus, many regulatory bodies all over the world have developed or are considering the development of soil quality values.

Before proceeding there are some terms that require definition (some taken from Barlow & Philp, 2005). *Toxicity* is the potential of a material to produce injury in biological systems (usually human in contaminated land risk assessment, but not necessarily so). A *hazard* is the nature of the adverse effect posed by the toxic material. *Risk* is a combination of the hazardous properties of a material with the likelihood of it coming into contact with sensitive *receptors* under specific circumstances. Risk is therefore a statistical entity, and the term significance is important. In the UK, Part IIA of the Environment Act, 1995 (routinely called "Part 2A") defines contaminated land as land where it appears, by reason of substances in, on or under the land, that:

1. Significant harm is being caused or there is a significant possibility of such harm being caused (e.g. Evans et al., 2006), or;
2. Pollution of controlled waters is being, or is likely to be, caused (DETR, 2000).

Significance in this context is linked to (Cole & Jeffries, 2009):

• The margin of exceedance;
• The duration and frequency of exposure;
• Other site-specific factors that the enforcing authority may wish to take into account.

A *receptor* is the biological entity which may be at risk, and is usually humans in contaminated land investigations. Children are normally identified as the most sensitive receptor (Jeffries & Martin, 2009) because their intakes of food, water, air and soil are greater per unit body weight than in adults. A *source* is the source of the contamination, and a *pathway* is the means by which the source contaminants reach the receptor, which is described by the *source-pathway-receptor* approach to risk assessment.

The underlying principle of site remediation is to eliminate or modify one or more of the above factors such that the risk is reduced to meet site-specific requirements. Under the current regime in the UK, a site is only designated contaminated if a significant *pollutant linkage* is established. That is, there must be present a source, a pathway and a receptor. If a source cannot be connected to a receptor, in the UK legal definition the site does not constitute contaminated land (Clifton et al., 1999). Some sites may have several such pollutant linkages (DEFRA and Environment Agency, 2004), and it is this type of linkage analysis that allows remedial design strategies to be defined that are realistic and cost-effective. This often results in a strategy less conservative than one based on multifunctionality.

4. The risk assessment process

There are four key steps in the process of assessing the risks associated with pollutant linkages.

1. *Hazard identification*. This is the stage at which the chemicals present on a site are anticipated, along with their characteristics, e.g. their concentrations, water solubility and toxicity. Due to the likelihood of many tens or even hundreds of potential contaminants being present at a site, the hazard identification stage usually focuses on known contaminants of concern.This would be typical of an oil-contaminated site, where the oil itself is composed of perhaps hundreds of individual compounds.
2. *Exposure assessment.* This is the estimation of pollutant dosages to receptors, based upon the use of the site and the conditions therein. There are multiple facets to these calculations. Among the factors to be considered are exposure duration and frequency, mean body weight and future population growth or decline.
3. *Toxicity assessment*. This is the acquisition of toxicity data, such as dose-response, and its evaluation for each contaminant for both carcinogens and non-carcinogens.
4. *Risk characterisation*. This is an assignment of the level of risk to each pollutant linkage. For many contaminated sites the best that can be reasonably expected at an initial desk-based stage is a qualitative risk estimate, such as insignificant, low, medium or high. The amount of data required for quantitative risk characterisation may be beyond all but the most rigorously characterised sites, such as national high priority sites.

4.1 Qualitative and quantitative risk assessment

The purpose of the qualitative risk assessment is to assign the significance or degree of real risk, as opposed to perceived risk. It is based on a systematic assessment of site-specific critical factors using professional judgement and expertise in addition to guidelines and standards. The causal chain of source-pathway-receptor is the basis. Formulation of the remedial objectives and strategy will essentially identify whether the source and/or pathway should be the focus of remedial objectives, or whether protection of the receptor is a more viable option.

In quantitative risk assessment the aim is to assign values for existing and future deleterious effects associated with exposure. It requires high quality data and is often applied when a site is suspected to pose an unacceptably high risk to human health. One of the reasons that quantified risk assessments are so data-intensive is that not only direct pathways need to be considered. Indirect contact can occur when contaminants are transported through soil, groundwater, surface water, uptake or adsorption by plants, dusts or aerosols. Current understanding of the complex interactions between chemicals in the subsurface is low. Also, most contaminated ground has previously been used for industrial or chemical works, and the presence of made ground and foundations usually causes large uncertainty in the various fate, attenuation and transport processes that affect the movement of contaminants (US EPA, 1996). Figure 2 gives an overview of the steps involved in quantitative risk assessment (adopted from DEFRA, 2002).

It should also be noted that for petrochemical- and crude oil-contaminated sites, quantitative risk assessment is made more challenging by the complexity of the contaminant mixture (Kuyukina et al., 2009) and the effects of weathering on the bioavailability of risk-critical compounds. It is common for high heterogeneity to exist in the distribution of hydrocarbon contaminants which impacts risk assessment results and the success of remediation actions. For heavier fraction hydrocarbons such as paraffines and polycyclic aromatic compounds (PAHs), losses due to biotic and abiotic weathering processes may result in compounds with increased hydrophobicity and recalcitrance (Pollard et al., 2004). These compositional changes dramatically affect the affinity of the weathered hydrocarbon pool for risk-critical compounds such as prior to, during and following a cleanup treatment.

As previously stated, the receptor is usually human and therefore the ultimate purpose of quantitative risk assessment is the protection of human health. The risk to human health posed by contaminants on a site is dependent on the concentration of the contaminant and the means of exposure, e.g. skin contact, inhalation, ingestion. Essentially, the exposure from a certain contaminant can be quantified from the following equation or permutations of it (Ferguson, 1996).

$$\textbf{Exposure} = \frac{(\textbf{Soil Intake Rate})(\textbf{Exposure Time})(\textbf{Resorption Rate})(\textbf{Contaminan t Concentrat ion})}{\textbf{Body Weight}}$$

Where:

- Exposure or Absorbed Dose = Daily mass of contaminant absorbed per day, divided by the body weight of the receptor (mg per kg body weight per day);
- Soil Intake Rate = Daily amount of soil a receptor is exposed to (grams);

- Exposure Time = Number of days of exposure to the contaminant;
- Resorption rate = Toxicokinetics-based, empirical value quantifying the daily transfer of contaminants from the intake medium into the systemic circulation;
- Contaminant Concentration = Concentration of contaminant in the uptake medium (mg per gram of soil);
- Body Weight = Mass of receptor (kg).

An understanding of the fate and transport of contaminants is crucial if a meaningful risk assessment is to be obtained. This analysis can be very complicated, since the number and types of processes affecting contaminants during transport is governed by both inherent contaminant characteristics and environmental conditions. Understanding these complex dynamic processes requires a best approximation of the environmental chemistry of contaminants (e.g. biodegradability, hydrophobicity,) and the environment at the site (e.g. geology, geochemistry). At the heart of such matters is the concept of bioavailability.

Step 1

> Define conceptual exposure model

Step 2

> Collect human exposure characteristics and contaminant fate and transport data

Step 3

> Select contaminant concentration in soil from review of site investigation data

Step 4

> Quantitative modelling of exposure

Step 5

> Compare predicted human exposure with health criteria values

Step 6

> Evaluate significance of risk to human health where exposure is close to or exceeds health-based reference values

Fig. 2. Overview of the steps in quantitative site-specific risk assessment.

4.2 The conceptual model

A desk study should be undertaken for any given contaminated site to decide if enough information already exits to carry out a satisfactory risk assessment to a required degree of confidence. Such desk studies vary in investigative depth, but there are certain components that should be considered mandatory:

- The history of the site, including previous owners, occupiers and uses;

- A site visit, during which any visual evidence of potential contamination, site conditions and nearby features are recorded;
- Local geology and hydrogeology, including the presence and quality of groundwater and surface waters;
- The above and below ground layout of the site and its historical development;
- Any history of mining, including shafts and worked seams;
- Nearby waste disposal tips, abandoned pits and quarries;
- Information on previous investigations at the site;
- Processes used on the site including their locations, raw materials, products, waste and methods of disposal;
- Nearby sensitive receptors, e.g. water courses, houses, parks, areas of ecological sensitivity.

An interpretative desk study, i.e. one that not only provides factual data but also professional interpretation, will normally include a conceptual site model. This is a key component of the overall risk assessment process and is used as a tool to consider potential sources, pathways and potential receptors.

4.2.1 Generic conceptual model 1: Petrol station with operational spills and leaking underground storage tank

The following conceptual model (Fig. 3) and source-pathway-receptor matrix (Table 1) are from the Institute of Petroleum (1998). In the analysis of a petrol station with regular operational spills and leaking underground fuel storage tank (an exceedingly common occurrence; the US EPA estimated at one time over 200,000 in the US), there are many pathways by which the pollutants can reach receptors, and naturally there are several possible receptors. For example, an annual loss of petroleum products from operating petrol stations on the territory of Russia exceeds 160,000 tonnes, from which about 130,000 tonnes are lost during tank refuelling and fuel delivery. The impact of petrol stations on total air, soil and groundwater pollution of the world's large cities is estimated to be significant, causing a dramatic increase in health risks (Karakitsios et al., 2007). Estimated impacts of different sources in total evaporative emissions from petrol station operations are: filling underground fuel tank – 58%, underground fuel tank breathing and emptying – 3%, vehicle refuel operations – 37%, operational spillages – 2%.

A guide to good practice for development of conceptual models is available (McMahon et al., 2001). In the conceptual model, all possible combinations should be identified, but the matrix can be used to delineate which are the critical pathways and receptors, and which ones pose insignificant risk. The example is a great simplification. Each case will be site-specific with respect to geology, hydrogeology, geography (human population density is critical) and other factors. As a result, the source-pathway-receptor matrix can become complex. Once complete, the matrix saves time and effort as a number of insignificant risks can be identified and ignored.

Sufficient numbers of soil and groundwater samples should be collected in on-site and off-site areas affected by contamination originating from the petrol station. Laboratory analyses must be performed to provide the sample concentrations of individual contaminants, volatile organic compounds (VOCs): benzene, toluene, ethylbenzene, xylenes and methyl

tert-butyl ether, semiVOCs: PAHs, which would be used as the bases for subsequent uniform and site-specific risk evaluations. The main chemicals of concern in the conceptual model of petrol station risk assessment are usually include benzene, toluene, ethylbenzene and methyl tert-butyl ether, among those benzene represents a highest hazard due to its toxic and cancerogenic effects. A comprehensive user guide for the human health risk assessment of petroleum releases at petrol stations is available (Joy & VanCantfort, 1999).
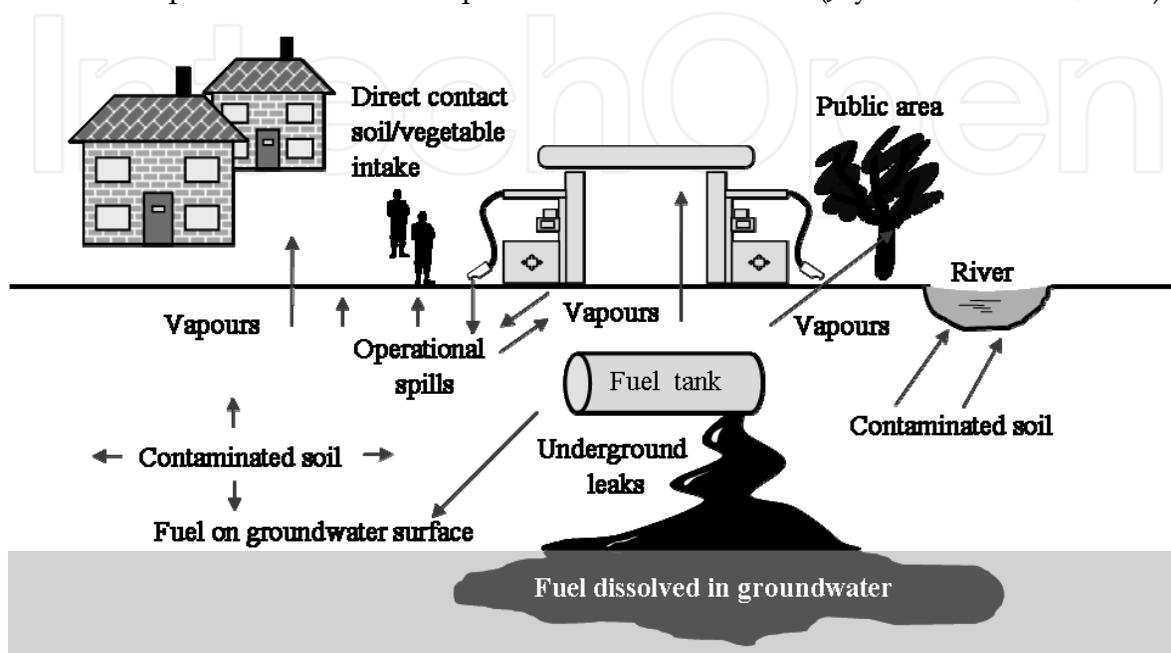
Fig. 3. Risk assessment for a petrol station with operational fuel spills and leaking underground storage tank.

4.2.2 Generic conceptual model 2: Crude oil spillage from a disrupted pipeline

Crude oil and petroleum products are widespread soil and groundwater pollutants resulting from spillage from the storage tanks and damaged pipelines. There are thousands of sites that have been seriously contaminated by petroleum products in oil-producing regions around the world (Etkin, 2001). In the US (Restrepo et al., 2009) crude oil is far and away the most frequently spilled hazardous liquid (39.4% of all cases, compared to gasoline, in second place, with 10.6%). Also the most frequent cause is easily demonstrated (a recent example – the Yellowstone River oil spill in Montana from the disrupted crude oil pipeline on July 1, 2011, when 1,000 barrels of crude oil went into the flood-swollen river); external and internal corrosion is the cause of 13.4% of all hazardous liquid spills, over three times higher than the next highest cause.

For Russia and the former Soviet Union (FSU), reliable data are difficult to find. In 2003, the World Bank published a report on pipeline failures in the countries of the former Soviet Union. The data search identified 113 major crude oil spill accidents during the period 1986–96 (inclusive). Just under 90% of these occurred in Russia. Whilst corrosion was still a major cause, there were double the number of spills caused by mechanical failure (UNDP/World Bank Energy Sector Management Assistance Programme, 2003). According to the Russian Federation State Environment Report, in 2003 losses of Russian oil and gas companies were approximately 3% from the product transported (Epifantsev & Shelupanov, 2011).

Primary source	Secondary source	Hazard	Transport mechanism	Pathway	Exposure medium	Receptor
Fuel tank	None	Dizziness, CNS depression potential carcinogenicity	Vapour, through air	Vapour inhalation	Air	Humans
Fuel tank	None	Vegetative die- back, leaf function damage	Vapour, through unsaturated zone	Vapour absorption	Air	Vegetation, adjacent trees
Fuel tank	None	Derogation of groundwater quality	Product loss and vertical migration to water table	Groundwater dissolution	Water	Groundwater aquifer
Fuel tank	None	Derogation of surface water quality	Product loss and dissolution in groundwater	Base flow and discharge to adjacent surface water body	Water	Adjacent river
Fuel tank	Contaminated soils	Dizziness, CNS depression	Vapour, through unsaturated zone	Vapour inhalation	Air	Humans (recreation)
Fuel tank	Contaminated soils	Skin irritation, contact dermatitis when extreme	Contact with contaminated soil	Dermal contact at surface	Soil	Humans (recreation)
Fuel tank	Contaminated soils	Flammability	Vapour, through unsaturated zone	Vapour build-up in basement	Air	Humans (residential)
Fuel tank	Contaminated soils	Flammability	Vapour, through unsaturated zone	Vapour build-up in basement	Air	Property
Fuel tank	Contaminated soils	CNS depression asphyxiation	Vapour, through unsaturated zone	Vapour build-up in basement	Air	Humans (residential)
Fuel tank	Contaminated soils	Derogation of surface water quality	Bulk fluid, through unsaturated zone	Free product flow to adjacent river	Water	Adjacent river
Fuel tank	Free product on water table	Derogation of soil quality	Evaporation to overlying soils	Vapour phase	Soil vapour	Soil
Fuel pump	None	Derogation of soil quality	Spillage and percolation through cracked hardstanding	Leaching	Soil	Soil
Fuel pump	None	Various, potential carcinogenicity	Vapour, through air	Inhalation	Air	Humans (customers)
Operational spills	None	Vegetative die-back	Vapour, through unsaturated zone	Vapour absorption	Soil gases	Home grown produce
Operational spills	None	Various, potential carcinogenicity	Vapour, through unsaturated zone	Consumption of contaminated produce	Vegetable produce	Humans (residential)
Operational spills	None	Various, potential carcinogenicity	Vapour, through air	Inhalation	Air	Humans (customers)
Operational spills	Contaminated soils	Dizziness, CNS depression	Vapour, through unsaturated zone	Vapour inhalation	Air	Humans (customers)

Table 1. Source-pathway-receptor for the petrol station with leaking underground storage tank

A conceptual model (Fig. 4) for the terrestrial oil-spillage from a disrupted pipeline occurring near a river can be used in the source-pathway-receptor risk assessments. It

should be noted that the risk assessment of terrestrial oil-spills is much less explored compared to marine oil spills. However, it is an important field for development, especially if the pipelines are situated near, or are planned to cross rivers, lakes or other water bodies (Yang et al., 2010).

Oil types can differ in viscosity, volatility and toxicity. These three characteristics are very important when oil spills are being evaluated, because these parameters can influence the risk assessment results. For example, river water has a density of 1.0 g/cm³ (compared to sea water having a density between 1.02 and 1.03 g/cm³, depending on the salt concentration). This means that a heavy oil, with a density of 1.01 g/cm³, would float in ocean water, but sink in a river, causing a severe problem of sediment oil contamination (Muijs & Jonker, 2011). Also, the oil can be moved with the current and, thus, spread a long distance from its origin. Some oil will evaporate, up to 50 percent of the volume. Natural physical, chemical and biological processes can cause the oil to weather, changing its characteristics (Malmquist et al., 2007). For example, emulsification leads to water-in-oil or oil-in-water stable mixtures that can persist for years.

Harmful effects of oil spills on natural environments have been extensively studied. However, only few studies so far have focused on the effect of oil exposure on human health (Aguilera et al., 2010). This supports the need for appropriate risk assessment methodology for human populations exposed to spilled oils, including the workers involved in the cleanup, in order to evaluate not only possible immediate consequences for their health but also the medium- and long-term effects, and the effectiveness of the protective devices used.
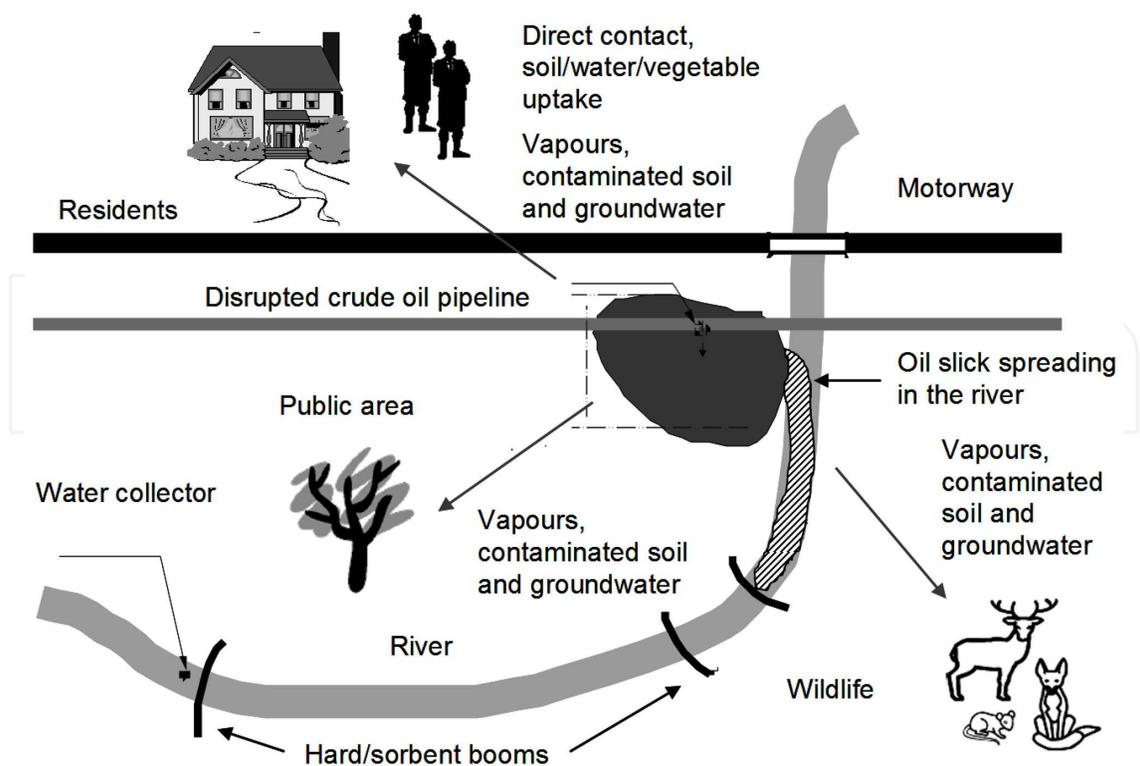
Fig. 4. Risk assessment for crude oil spillage from a disrupted pipeline.

5. The key role of soil guideline values and human health risk assessment

Soil Guideline Values (SGVs) are scientifically based generic assessment criteria that can be used to simplify the assessment of human health risks arising from long-term and on-site exposure to chemical contamination in soil. SGVs are guidelines on the level of long-term human exposure to individual chemicals in soil that, unless stated otherwise, are tolerable or pose a minimal risk to human health. They represent trigger, or intervention values – indicators that soil concentrations above this level are unacceptable.

Where representative soil concentrations of contaminants on a site are at or below the SGV, it can be assumed that it is very unlikely that a *significant possibility of significant harm* exists (DEFRA, 2008). Where representative soil concentrations of chemicals on a site exceed an SGV, further evaluation and assessment of the human health risks will normally be required to determine if a *significant possibility of significant harm* exists (Cole and Jeffries, 2009).

The situation in the US is similar. The US EPA Soil Screening Guidance (US EPA, 1996) is a tool to help standardise soil remediation at sites on the National Priority List (NPL). The outcome is soil screening levels (SSLs) for contaminants in soil that may be used for guidance purposes. SSLs are not national clean-up standards. At sites where contaminant concentrations fall below SSLs, no further action is warranted under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Generally, where contaminant concentrations exceed the SSLs, further investigation, but not necessarily clean-up, is warranted.

This resembles the 'trigger-action' approach and SSLs are risk-based concentrations derived from risk assessment procedures. However, the US EPA lists generic SSLs for 110 chemicals using default values that are conservative and likely to be protective for the majority of site conditions. It is noted that generic SSLs are not necessarily protective of all known human exposure pathways, reasonable land uses, or ecological threats.

The US soil screening is a seven-stage process:

1. Develop a Conceptual Site Model (CSM) based on historical records and available background;
2. Compare soil component of CSM to soil screening scenario;
3. Define data collection needs for soils to determine which site areas exceed SSLs;
4. Sample and analyse soil at site;
5. Derive site-specific SSLs if needed;
6. Compare site soil contaminant concentrations to calculate SSLs;
7. Decide how to address areas identified for further study.

Essentially, SSLs are risk-based concentrations derived from equations combining exposure assumptions with EPA toxicity data.

6. Risk assessment models

The nature of risk assessment i.e. gathering data, setting thresholds, statistical decision making and movement between different sections of a flow chart (see Fig. 1) make risk assessment procedures eminently suited to software modeling. Seventeen such human health risk assessment models (Table 2) have been identified recently in the literature (Cheng & Nathanail, 2009).

Many of the models have comparable approaches to assess health hazards arising from polluted soils. However, the input parameters and scenarios considered are different (Poggio et al., 2008). Results obtained with different methods are therefore often not comparable (European Commission, 2006). The Netherlands National Institute for Public Health and Environment (2002) recommended a toolbox on the European level including:

- Standardisation of the common elements;
- Definition of flexible elements to account for country/region specific (geographical, ethnological and political) peculiarities;
- Documentation on the sensitivity of calculated human exposure to the input parameters and guidelines on when and how to measure concentrations in the contact media;
- Information on the uncertainty/reliability of calculated human exposure.

Model name	Developer
CETOX-human	DHI Water and Environment and Danish Toxicological Centre, Denmark

CLEA 2002
    • CLEA UK beta 2006
    • CLEA UK 1.04
	DEFRA and Environment Agency of England and Wales

CSOIL	RIVM, the Netherlands
JAGG	Denmark
LUR	LABEIN Technological Centre, Spain
No name given	INERIS, France
No name given	Kemarkta Konsult AB, Sweden
RBCA toolkit	ASTM, US
Report 4639	Sweden
RISC	Spence Engineering, US and BP, UK
RISC-HUMAN	Van Hall Instituut, the Netherlands
Risk Assistant	Hampshire Research Institute, US
ROME	ANPA, Italy
SFT 99:06	Norway
SNIFFER (1ST) SNIFFER (updated)	Land Quality Management, UK
UMS	Germany
Vlier-Humaan	VITO, Belgium

Table 2. Human health risk assessment models identified in the literature (Cheng & Nathanail, 2009)

7. Ecological risk assessment

Whilst human health protection is overwhelmingly the main objective of a risk assessment, the protection of ecosystems as a concept for risk assessment is a growing area. Ecosystem protection is based on the potential ecological risk to soils. It is intimately linked to the philosophy of soil protection, which derives from the realisation that soil is largely non-renewable, taking centuries to build a mere centimetre (European Commission, 2007), and yet it provides us with 95% of all human sustenance, and it can be destroyed very quickly. It is subject to erosion, loss of organic matter, salinisation, landslides, as well as contamination. Soil degradation is accelerating, with negative effects on human health, natural ecosystems

and climate change, and the economy. In this context it is hardly surprising that the need to re-develop brownfield sites has acquired high priority. These concerns are also the drivers for the proposed Soil Framework Directive (Commission of the European Communities, 2006). If adopted, it would be the first pan-European, soil-specific legislation.

Although ecological risk assessment is a growth area, it is inherently more complex than human health risk assessment as it requires multispecies analysis (Smith et al., 2005). Equally the identification and assessment of the significant possibility of ecological harm is hard to diagnose, and subject to interpretation. Ecological risk assessments are still therefore at a development stage (Latawiec et al., 2011).

Soil protection values have been derived for different regulatory applications by different authorities. Criteria can be developed for three main applications (Fernández et al., 2006):

*   *Screening values*: representing soil concentration levels that may cause potential ecological dysfunction and, therefore, if exceeded, will require a site-specific assessment;
*   *Clean-up targets*: representing the objectives to be achieved in restoration processes. In some cases, these values represent a similar level of protection as the screening values, but in other regulations the decision is a balance of the restoration cost and the ecological benefit;
*   *Intervention values*: representing concentrations which are indicative of seriously contaminated sites that require immediate clean-up or control actions.

Fernández et al. (2006) offered an overall process for characterisation of contaminated soils based on ecological risk assessment principles, which is based on both chemical and biological tools in the decision-making scheme to arrive at a classification of soils as low-risk or high-risk. The chemical and biological techniques involved, however, are not routine. They propose direct toxicity assessment on terrestrial plants, soil-dwelling invertebrates and soil microorganisms, and also toxicity of leachates to algae, *Daphnia* and fish. The approach also allows setting of Generic Soil Quality (GSQ) values for chemicals independently of the amount of available information.

8. Bioavailability, bioaccessibility and risk assessment

The concept of bioavailability fits perfectly with risk assessment. If a pollutant is present in soil or water but is not available to the biota, then it presents minimum risk (unless chemical conditions change that can subsequently increase the bioavailability). However, measurement of bioavailability is often a difficult task. For more than a decade regulators have directed concerted effort towards rationalisation of risk-based contaminated land policies recognizing bioavailability and bioaccessibility as concepts to be incorporated into risk assessments (Latawiec & Reid, 2009).

As soon as a pollutant reaches soil, the level that is biologically available may start to decline as the chemical becomes sequestered in the soil by sorbtion (Chung & Alexander, 1998). The current approach to exposure assessment commonly relies on the total concentration, but it will be clear that the level that is biologically available might not be related to this number (Tang et al., 1999). Bioavailability also has consequences for partitioning phenomena, biodegradability and toxicity that are described in some detail by Philp et al. (2005b). In addition, this bioavailable fraction is also dependent on the organism considered and the properties of the matrix in which the organism is exposed, and the effective exposure time. Indeed, there is no universally agreed definition of bioavailability (Peijnenburg et al., 2007).

Within the context of bioremediation, bioavailability can be regarded as the fraction of a given analyte that is in a form making it biodegradable (Semple et al., 2003). The bioaccessible fraction provides a reference not only to the amount of a substance readily available to an organism at a given instant (bioavailability) but also to the fraction potentially available over time (Semple et al., 2004). With respect to human health risk assessment, the bioaccessible fraction is defined as the fraction of a substance that is released from the soil, during such processes as digestion into solution making it available for absorption (measured *in vitro*), whilst bioavailability relates to the fraction that reaches the blood system via the gastrointestinal tract (Wragg and Cave, 2002).

Lack of statutory guidance has been cited as the main factor hampering the use of bioavailability and bioaccessibility data in regulatory decision-making (Latawiec et al., 2010). However progress is being made. The International Standards Organisation (ISO) has been working on guidance for the selection and application of methods to measure bioavailability in soil (ISO 17402, 2008). The draft was created as a response to an increasing demand for a validated pool of methods to be used in soil assessments and promotes the development and the introduction of the bioavailability concept in the context of specific site circumstances. The ISO guidance aims to specify boundary conditions and principles for the methods and is still under international panel consultation (Latawiec et al., 2011).

9. Risk based remedial design

SGVs are not derived explicitly to be used as remediation standards. The process for setting remedial objectives and standards for remediation is outlined in CLR 11 (DEFRA and Environment Agency, 2004). If risk assessment demonstrates unacceptable risks are associated with a site, then these need to be managed. At this stage Options Appraisal comes into play (see Fig. 1). There are three main stages of Options Appraisal (DEFRA and Environment Agency, 2004):

1. Identifying feasible remediation options for each relevant pollutant linkage;
2. Carrying out a detailed evaluation of feasible remediation options to identify the most appropriate option for any particular linkage;
3. Producing a remediation strategy that addresses all relevant pollutant linkages, where appropriate by combining remediation options.

The scope of this chapter is limited to the identification of feasible remediation options. The process starts with the setting of remediation objectives. The objectives will be site-specific, but general considerations are:

*   Degree to which risks have to be reduced or controlled;
*   Time frame for remediation. Often for developers, speed is of the essence to manage cash flow;
*   Technical efficacy of the proposed technology(ies) used for remediation;
*   Cost of the strategy;
*   Public opinion;
*   In future, sustainability issues are likely to become more important e.g. environmental impacts of the technologies.

Once the objectives are set, it is necessary to determine remediation criteria. Some of the quantitative measures that can be used are:

- SGVs;
- Site-specific assessment criteria resulting from the risk assessment;
- Engineering-based criteria e.g. the size and design of on-site biopiles in a bioremediation strategy.

An objective assessment of the advantages, limitations and costs of different remediation options should be done. The full range of legal, technical, stakeholder and commercial issues has to be taken into account.

In complicated cases, such as former gas works, petrol stations or oil-spill sites, no one remediation technique is likely to work over the whole site, and then a strategy involving a treatment train is required. At gas works, typically the site specific risk assessment process will identify PAHs, phenolics, ammonia and complex cyanides as the main drivers for remediation. But there will often be buried chemical storage tanks to be dealt with, concrete needing to be crushed, perhaps selective landfilling of untreatable waste and filling of excavated voids, as well as strategies for protection of controlled waters. Careful planning is required to make sure that each component activity is carried out smoothly, in the corrected sequence and effectively. A detailed account of the clean-up of the former gas works site at the location of the Millenium Dome is given by Barry (1999).

9.1 Eco-efficiency of remediation technologies

The application of eco-efficiency measures of remedial technologies is not common-place currently, but may become so in the future. Sending contaminated soil to landfill, for example, is incompatible with modern views on recycling, and is an inefficient way to use limited landfill availability. Landfill taxation is making this option more expensive, and a range of other treatment technologies has flourished. Some initial work on eco-efficiency of remedial technologies has been done by Sorvari et al. (2009) (Table 3).

Remediation method	Positive factors	Negative factors
Reactive barrier	Generally no need for removal of the barrier	Long-term operating costs, suitable only for some contaminants
Soil stabilisation, isolation	No need for soil removal; quick; can be economical	No removal of contaminants from environment; can be energy-intensive
Soil vapour extraction (SVE)	Generally cost-effective; low uncertainties in risk reduction	Suitable only for volatile contaminants; exhaust air needs to be treated
Incineration (mobile)	Effective contaminant removal	Flue gas treatment needed; energy-intensive; often needs fuel
Composting	Low cost; treated soil may be used for landscaping; no emissions requiring treatment	Suitable only for some organic contaminants; can be long duration; depends on contaminant concentrations
Landfill	Effective control of risks; soil can be used in daily cover	Not treatment; not suitable for re-use; becoming more expensive; not efficient use of landfill sites

Table 3. Eco-efficiency of selected land remediation technologies (modified from Sorvari et al., 2009)

10. Conclusion

The pollution of soil and groundwater caused by accidental petroleum bydrocarbon releases is a complex environmental problem in all industrialised countries. Early strategies for clean-up based on highly stringent standards resulted in unsustainable cost burdens. The shift to risk assessment and suitability for use decreases the cost burdens, and has also been a factor in the development of new remedial technologies, including bioremediation. Many countries have developed or are currently developing frameworks and procedures for assessing and managing the risks posed by contaminated sites. The objective of this chapter is to review the principles and procedures of risk assessment for terrestrial ecosystems exposed to petroleum contamination. Focus is made on the effects of petroleum hydrocarbon contamination on human health rather than on ecological risk evaluation.

Two examples of the generic conceptual model concidering a potential source-pathway-receptor chain are given for exceedingly common cases: a petrol station with regular operational spills and accidental crude oil spillage from a disrupted pipeline. These models can be used in *site-specific risk assessment* when local environmental conditions (e.g. geology, hydrogeology, geography, human population) are used to calibrate the model. It is widely accepted that models are powerful tools for integrating various elements in risk assessment such as site characterisation, contaminant fate and transport, exposure assessment and risk calculation. They are, however, abstract and simplified representations of complex systems and are based on numerous assumptions and approximations. It is therefore important that models are validated and tested in real-world situations, either as part of contaminated land risk assessments or in research projects.

The chapter also identifies a number of problems at a general methodological level, especially concerning bioavailability and bioaccessibility as concepts to be incorporated into risk assessments. Indeed, lack of fully appropriate assessment methods for these complex environmental processes clearly indicates further research needs in the context of current approaches for contaminated land risk assessment. In this way, further developing the risk assessment approach would provide a rational and objective basis for ecological priority setting and decision making, particularly for the selection of eco-efficient remedial technologies.

11. Acknowlegements

12. References

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Environmental Contamination

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Nature minimizes the hazards, while man maximizes them. This is not an assumption, but a basic idea of the findings of scientists from all over the world. The last two centuries have witnessed the indiscriminate development and overexploitation of natural resources by man causing alterations and impairment of our own environment. Environmental contamination is the result of the irrational use of resources at the wrong place and at the wrong time. Environmental contamination has changed the lifestyle of people virtually all over the world, and has reduced the extent of life on earth. Today, we are bound to compromises with such environmental conditions, which was not anticipated for the sustenance of humanity and other life forms. Let us find out the problem and its management within this book.

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