Guidelines for Assessing and Managing Contaminated Gasworks Sites in New Zealand

Part One: Users' Guide

Part Two: Supporting Technical Information (on disk)

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MINISTRY FOR THE ENVIRONMENT
MANATŪ MŌ TE TAIAO

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Guidelines for Assessing and Managing Contaminated Gasworks Sites in New Zealand

Part One: Users' Guide

Background

In December 1996 the Ministry for the Environment released the Draft Guidelines for the Management of Contaminated Gasworks Sites in New Zealand for consultation. During the submission period, workshops were held in Auckland, Wellington and Christchurch to introduce and discuss the guidelines. The structure and content of this guideline incorporates the views of submitters and workshop participants.

The guideline has been separated into two parts - this Users' Guide, and Supporting Technical Information (on disk).

This Users' Guide provides a summary of the steps involved in assessing and managing contaminated gasworks sites in New Zealand. This includes a discussion of why we are concerned about gasworks sites, site sampling and assessment processes, generic soil and water acceptance criteria, and site management.

The technical information which forms the basis for most of the guidelines, has been condensed from the original draft guidelines and can be found on the disk accompanying this document.

Acknowledgments

Input into this document has come from a number of people. Of special mention are the members of the National Steering Committee who helped the Ministry for the Environment prepare this guideline. The members were as follows:

- Martin Ward — Independent Environmental Adviser (formerly of the Natural Gas Corporation)
- John Sherriff — Wellington Regional Council
- Roger Matthews — Auckland City Council
- Stuart McLaren — Ministry of Health

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I would also like to acknowledge the help of those who provided peer review comments on the draft guidelines and the Users' Guide:

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Viv Heslop
Contaminated Sites Group

Abbreviations

ADI	Acceptable daily intake
AGA	Australian Gas Association
ANZECC	Australian and New Zealand Environment and Conservation Council
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
B(a)P	Benzo(a)pyrene
BTEX	Benzene, toluene, ethylbenzene, xylene
CCME	Council of Canadian Ministers for the Environment
CDI	Chronic daily intake
DNAPL	Dense non-aqueous phase liquid
DOE	Department of the Environment
DQI	Data quality indicators
DQO	Data quality objectives
EM	Electromagnetic
EPRI	Electric Power Research Institute
EQL	Estimated quantitation level
GRI	Gas Research Institute
HASP	Health and safety plan
HQ	Hazard quotient
K_{oc}	Partition coefficient for octanol-water, corrected for organic carbon
K_{ow}	Partition coefficient of octanol-water
LNAPL	Light non-aqueous phase liquid
LOEL	Lowest observable effect level
MAV	Maximum acceptable values
MDL	Method detection level
MfE	Ministry for the Environment
MoH	Ministry of Health
MRL	Maximum residue levels
NHMRC	National Health and Medical Research Council
NOEC	No observable effect concentration
NOEL	No observable effect level
NSW EPA	New South Wales Environment Protection Agency
NZDWG	Guidelines for Drinking Water Quality Management in New Zealand
NZDWS	New Zealand Drinking Water Standards
OSH	Occupational Safety and Health
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyls
PID	Photoionisation detector
PPM	Parts per million
PTWI	Provisional tolerable weekly intake
PVC	Poly vinyl chloride
QAP	Quality assurance plan
QA/QC	Quality assurance/quality control
RfD	Reference dose
RfDc	Chronic reference dose
RM Act	Resource Management Act 1991
RME	Reasonable maximum exposure
SF	Slope factor
TCLP	Toxicity characteristic leaching procedure
TEFs	Toxic equivalence factors
USEPA	United States Environmental Protection Agency
Vic EPA	Victoria Environment Protection Agency
WHO	World Health Organization

1

Gasworks sites - what to expect

1.1 Introduction

There are believed is be approximately 54 gasworks sites in New Zealand. Between the late 1800s and 1988 gasworks were a familiar sight in towns and cities throughout New Zealand. During this time the production of gas from coal was a major source of fuel for heating, cooking and lighting.

With the setting up of a national natural gas reticulation system during the 1970s and 1980s, these gasworks were gradually closed.

The manufacturing process generated a number of by-products and wastes, such as coal tar, spent oxide, purifier waste, ash and clinker. These wastes have a number of substances within them that are potentially hazardous to human health, for example, phenols and polycyclic aromatic hydrocarbons (PAHs) in tar, cyanide and sulphides in spent oxide, and heavy metals in ash and clinker. Many of these wastes were disposed of both on and off site. In addition, when many of the sites were closed, underground structures containing many of these contaminants were left.

The environmental legacy of gas manufacturing is now becoming apparent in New Zealand and has highlighted the importance of providing guidance to those who are involved in the management of these sites. These guidelines, and the supporting technical information, are designed to provide those with an interest in contaminated gasworks management with information on assessing and managing soil and water contaminated by gasworks waste.

A risk-based approach has been adopted in the guidelines. It is hoped that this approach, if properly implemented, will facilitate a flexible approach to site assessment and management, focusing on the issues that pose the greatest risk to human health and the environment.

This Users' Guide provides a summary of the assessment and management of contaminated gasworks sites in New Zealand. More detailed technical information can be found on the disk accompanying this guide.

This first section covers the following aspects of site assessment:

- ➔ the status of these guidelines
- ➔ the suggested layout of gasworks sites based on historical information
- ➔ the contaminants of concern
- ➔ the waste products associated with the contaminants and sources of contamination
- ➔ patterns of contamination found at gasworks sites

1.2 Status of these guidelines

These guidelines, and the accompanying supporting technical information on disk, have no statutory effect and are of an advisory nature only. The information should not be relied upon as a substitute for the wording of the relevant legislation or for detailed advice in specific cases, or, where relevant, as formal legal advice. If advice concerning specific situations or other expert assistance is required, the services of a competent professional adviser should be sought.

The sections references contained in this publication cite only the principal relevant provisions of the legislation - they are not intended to provide a comprehensive index of all the relevant sections that may have a bearing on the matters covered in the preceding text.

Additional information on the characteristics of gasworks sites and the nature of contamination can be found in Module 1 on disk, including

- ▲ historical background (Section 1.1)
- ▲ the gas production processes (Section 1.2)
- ▲ the major process units (Section 1.3)
- ▲ the fate and transport of gasworks contaminants (Section 1.4)

1.3 Suggested site layout

Many gasworks sites were located near ports, rivers and railways, as this was how the coal feedstock was delivered. They were also generally laid out in a similar way. Figure 1.1 shows the common layout for a gasworks. This layout may provide some useful information for site assessment where there are few details about a particular site.

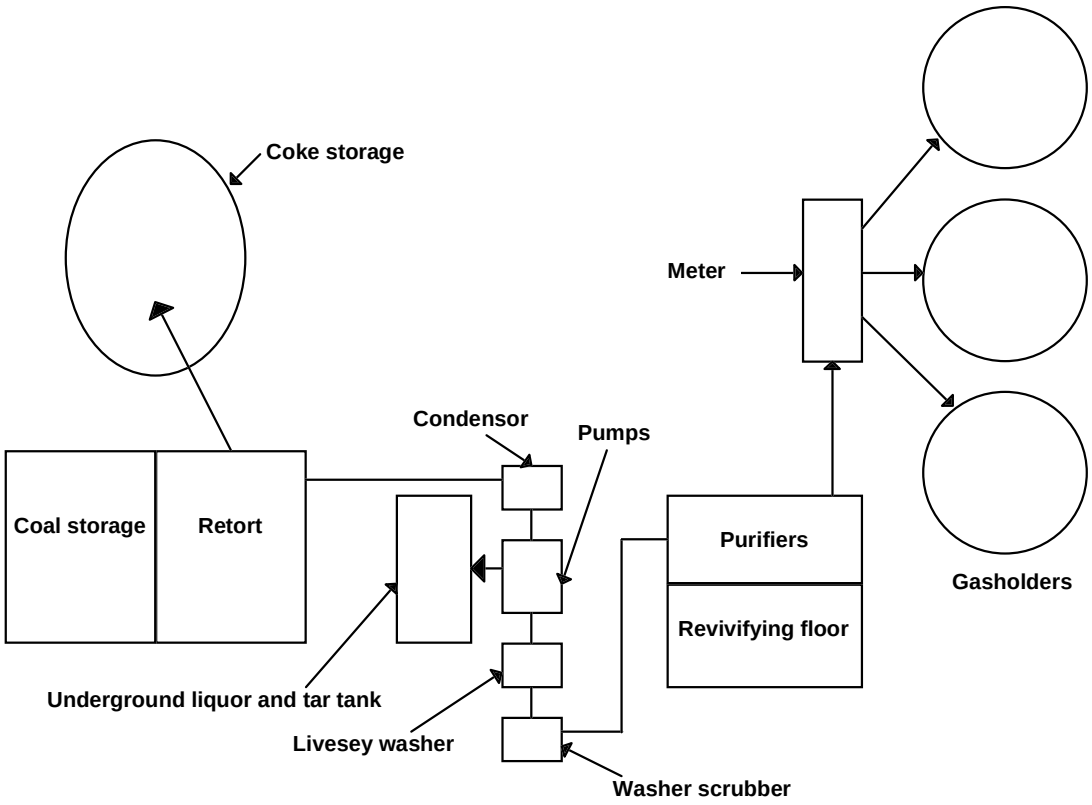

Figure 1.1 Common layout for a gasworks (adapted from Meade 1934)

Information on the processes and the major process units can be found in Module 1, Sections 1.2 and 1.3 on disk.

1.4 Contaminants of primary concern

Of the range of contaminants likely to be found at a gasworks site, several are of primary concern:

- polycyclic aromatic hydrocarbons (PAHs) - generally dominate clean-up requirements of near surface and surface soil

- benzene, toluene, ethylbenzene, xylene (BTEX) - can be significant groundwater contaminants and can be significant soil contaminants
- phenolics, i.e. phenol and cresol - can be significant groundwater contaminants. Also often present in soil but do not usually determine the remediation requirements for a site
- inorganics, including cyanide, sulphate, ammonia - can be significant groundwater contaminants.

Heavy metals are also frequently present at elevated concentrations in soils at gasworks sites. However, the overall risk to human health is usually governed by the carcinogenic PAHs. The presence of heavy metals and cyanide, while generally not defining clean-up requirements, may affect the selection of remedial techniques.

In general, the carcinogenic PAHs determine soil clean-up requirements, with phenols and some inorganics significant in groundwater contamination. Relatively small volumes of waste containing elevated concentrations of cyanide and other inorganics may also require careful consideration.

Information on the fate and transport of gasworks contaminants can be found in Module 1, Section 1.4 and Appendix 1A on disk.

1.5 Waste products associated with contaminants

The process of gas production varied between sites and not all the raw materials used were identical (e.g. coal from different sources varied in heavy metal content). As a result, contamination at the sites will differ depending on the process and residue variations, as well as the waste management practices (both on and off site).

Waste products typically included:

- organics, such as coal and oil tar, tar/oil/water emulsions and hydrocarbon sludges
- inorganics, such as coke and ash, spent oxide and lime wastes, and ammonium sulphate.

The degree to which the waste streams were treated and products recovered depended on whether there was a market for the recovered products, and whether recovery was economic. Ammonia may have been stripped from waste water and recovered as ammonium sulphate. Coal carbonisation plants often included on-site tar processing facilities. However, the market value of the by-products fluctuated significantly and the economics of recovery were at times unattractive. The recovery of by-products influenced the types of contaminants and waste products that may be found at gasworks sites.

1.5.1 Sources of potential contamination

"Normal" site operations of the time included many practices that would be very inappropriate by today's standards. Industries operating during the period of the coal industry commonly disposed of residual wastes on site. Solid wastes were often used as reclamation material where sites were uneven, marshy or low-lying (Department of the Environment 1987). Liquid wastes were sometimes poured into the ground. Several activities that were part of the production process have also resulted in contamination.

The Department for the Environment (1987) identified a number of types of contamination which could be found at gasworks sites:

- coal particles underground at coal storage areas
- coke and coke breeze may still remain in areas used for storing by-products
- spent oxide may contaminate areas of the site. Of particular importance are

  - areas around purifier boxes and towers where treated oxide may have been spilt
  - areas where oxide was ‘revivified’, that is, spread out in thin layers to allow atmospheric oxidation
  - mechanical handling plants where oxides with various sulphur contents were mixed
  - storage areas where the spent oxide was accumulated pending sulphur recovery or disposal
- contaminated areas may result from the spillage of other by-products, e.g. coal tars, ammoniacal liquors and their derivatives
- leaks from coal-gas or spills of odorants added to oil-gas may have contaminated soil
- other raw materials used which may occasionally have contributed to land contamination included lime, sodium hydroxide, sodium carbonate and various catalysts and corrosion inhibitors, such as: nickel, zinc, copper, chromium, magnesium, uranium, vanadium and their compounds. Lead was used in paint, in caulking on gasholders, in pipework and roofing, and in batteries
- additional contamination may have resulted from common industry operations. Examples include spillages of lubricating and fuel oils or paints, dumping lead-acid batteries, lead contamination from pipework and pest or weed control operations.

The gas production systems were the same in New Zealand so the above are possible sources of contamination on all gasworks in New Zealand. In addition there are a few other potential sources of contamination that have been identified during gasworks site investigations in New Zealand:

- leaks of coal tar and ammoniacal liquor from underground tar wells and associated pipework
- off-site discharge of waste ammoniacal liquors
- on-site disposal of waste materials, both during plant operation and demolition
- liquid waste material left in underground tar pits, pipework and gasholder sumps when the gasworks closed down
- residual waste materials remaining on-site and off-site in stormwater drains, gas mains, peripheral gasholders and service pipes.

1.6 Patterns of contamination at gasworks sites

Historical records showing the layout of gasworks facilities can help to identify the nature and location of contamination, and assist in designing sampling and analytical strategies for assessing the site. Historical records may include:

- site maps and surveys
- site records of regulatory controls and waste management practices
- photographs of the site, especially aerial photographs taken over a number of years
- building and engineering plans and specifications
- information from past and present owners and employees.

Historical information relating to some gasworks sites in New Zealand can be found at the Alexander Turnbull Library in Wellington.

A site inspection may provide further information on the location of contamination. Features of significance include:

- empty chemical containers, tanks, pits, pipelines, sumps and drains
- fill material, especially coke breeze, with disturbed and discoloured areas of soil
- chemical or other unusual odours
- discoloured or poor quality surface waters
- evidence of waste treatment practices
- differences in vegetative growth compared with adjacent areas may be evidence of phytotoxicity.

Table 1.1 shows the potential sources of organic and inorganic contamination at gasworks sites.

Table 1.1 Potential contaminant sources at gasworks sites

Facility	Contaminants
Retort houses	Heavy metals, coke & coal wastes, sulphides, free tars & oils, PAHs, BTEX, phenolics, catalysts (nickel, uranium oxide)
Gasholders, Tar wells/pits, Tar/water separators, Scrubbers, Effluent tanks, Sludge disposal, Pipelines	Free tars & oils, PAHs, BTEX, phenolics
Condensers	Ammoniacal liquors, free tars & oils, PAHs, BTEX, phenolics
Ammonia liquor wells	Ammoniacal liquors
Coal dump	Coal wastes, sulphides & heavy metals
Gas cooling plant	Lighter aromatics
Purifiers	Lead, oxides of iron, iron cyanide complexes, sulphates
Spent lime & oxide disposal sites	Acid formed from sulphur, oxides of iron, iron cyanide complexes, sulphates
Waste material	Free tars & oils, PAHs, BTEX, phenolics, used catalysts
Oil storage tanks	Petroleum hydrocarbons, PAHs
Building rubble	Asbestos
Engine room, electrical equipment	Polychlorinated biphenyls (PCBs)

Contaminants can be distributed around gasworks sites as follows:

- organics may have migrated through higher permeability lenses in the soil and can contaminate soils and groundwater over a large area
- tars are often oxidised and solidified into rocky masses at or near the soil surface
- tar was accumulated in the gasholders during manufacturing, and in some plants tar and emulsions from the tar/water separator were pumped to the holders. During decommissioning, non-recoverable tar and emulsions were often left in place and covered with fill or scrap
- tar ponds and tar pits were also used to receive tar/water emulsions from carburetted-water gas operations. They were sometimes unlined and may have been filled with soil, rubble or ash. A zone of contamination usually occurs beneath the pond

- spills and leaks were common at most tar handling areas. Separating tanks and pipes may have leaked contaminating the soil
- tars and oils may be present as dense non-aqueous phase liquids (DNAPLs), light non-aqueous phase liquids (LNAPLs) or as dissolved phase liquids. Tars may appear as accumulations which can be pumped directly from the ground, particularly in the case of LNAPL. However, the recovery of DNAPLs is much more difficult
- free tars may accumulate in stratigraphic traps in the ground resulting in lateral migration. This can cause significant contamination over considerable areas of gasworks sites The most important sources of free tar are the tar wells (and other components of the tar recovery and processing facilities) and, to a lesser extent, the gasholders
- sometimes tar/oil/water emulsions and sludge from the separator were used for dust control
- typically gasworks sites have had extensive surface filling, ranging in depth from less than 0.5 m to several metres
- waste materials from the site (e.g. spent oxide, sludges) may have been used as fill
- purifier wastes can consist of a variety of materials, including iron-impregnated wood chips or spent lime. Wood chips may have been disposed off-site, spread around for dust control, or dumped in mixed waste areas
- sites with large coking operations may have large volumes of decomposed purifier wastes (typically stained blue by ferrocyanides)
- purifier wastes were often disposed off site and used for roading base and fill along river banks
- leachable metals may be associated with mixed wastes and fill due to the presence of coal and process residues
- heavy metal contamination tends to be associated with surface filling and waste disposal practices
- sulphates, cyanides and ammonia are frequently found in groundwater at gasworks sites, reflecting their mobility in the soil environment
- spent catalysts may be disposed of in drums or mixed with other wastes.

2

Risk assessment

Risk assessment forms the basis of these guidelines. This section covers the following:

- ➔ the risk assessment process
- ➔ the role of risk assessment in site management
- ➔ the importance of consultation
- ➔ roles and responsibilities for contaminated sites management
- ➔ the link between the Users' Guide and the supporting technical information on disk

2.1 Risk assessment

Risk assessment is the process of estimating the potential impact of a chemical or physical agent on an ecosystem or human population under a specific set of conditions. It is a flexible tool that can be used at several stages in assessing and managing gasworks sites. The principal applications of risk assessment are to:

- assess the risk to human health and the environment of contaminants found on the site
- develop land-use based generic acceptance criteria
- assess the comparative risk of different site management options.

Risk assessment is a four-step process:

Hazard Identification	The results of sampling and analysing soil, groundwater and other environmental media are collated and assessed to determine the nature and extent of contamination at the site.
Exposure Assessment	Exposure assessment involves: • identifying exposed groups both on-site and off-site (receptors) • identifying complete pathways (from the contaminant source through to the exposed group) • estimating the concentrations to which the receptors may be exposed • estimating the degree of exposure likely to be experienced by receptors, whether human or environmental.
Toxicity Assessment	This involves assessing the possible adverse effects that may be associated with exposure to a given chemical or mixture of chemicals, and the level of exposure associated with the onset of the adverse effects. This level is characterised using dose-response factors.
Risk Characterisation	The results of the exposure assessment and toxicity assessment are combined to provide an estimate of risk to human health or the environment.

The use of a risk-based approach leads to site assessment and management actions that are appropriate for each site. Applying the risk-based approach ensures that all actions are focused to achieve the desired level of protection for human health and the environment.

2.1.1 Risk management

Risk management is the final step and involves assessing the information from the risk assessment and deciding what risk mitigation is required. When deciding on the most appropriate risk management options, consideration is usually given to scientific, legal, social, economic and political factors.

2.1.2 Risk communication

Risk communication is an important part of the risk assessment and management process. Well-managed risk communication will ensure that the messages you want to get across to the public are constructively formulated, transmitted and received, and result in meaningful action.

The risk assessment process is outlined in Figure 2.1.

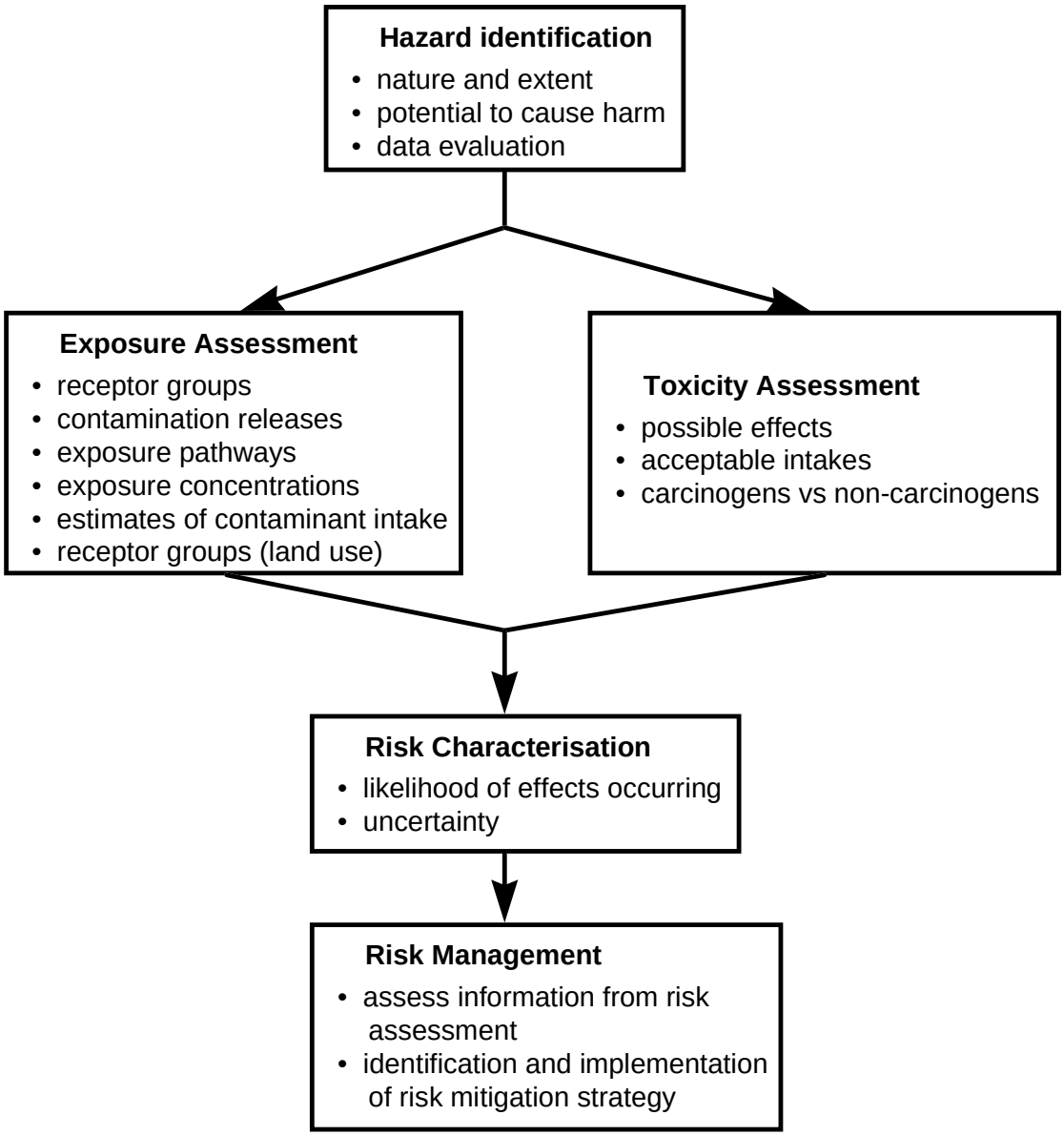

Figure 2.1 Risk assessment model

Risk assessment should not be seen as an end in itself, but rather as a tool in risk management. The objective of any site assessment programme is to manage or minimise risk rather than simply to assess the risk to human health and the environment.

2.1.3 Health risk assessment

Health risk assessment is the process of estimating the potential impact of a chemical or a physical agent on a specified human population under a specific set of conditions.

The underlying objective of health risk assessment is to effectively protect "almost all" individuals in the exposed population. This objective is demonstrated in the commonly adopted levels of acceptable cancer risk used for regulatory purposes. In New Zealand, an acceptable level cancer risk level of 1 in 100,000 per lifetime (one additional case of cancer per 100,000 people per lifetime) has been adopted by the Ministry of Health. This value is also used in these guidelines.

The aim of health risk assessment is to determine an individual's chemical intake, and whether it is less than or above a nominal dose that is considered acceptable. Exposure is estimated via a number of pathways, including ingestion of soil, inhalation of volatiles or particulates, dermal absorption and food chain exposure.

In assessing possible adverse effects on human health, consideration is given to a range of carcinogenic and non-carcinogenic effects.

2.1.4 Ecological risk assessment

Ecological risk assessment is the process of estimating the potential impact of a chemical or physical agent on a specified ecosystem under a specific set of conditions.

While the development of ecological risk assessment methods have been slower than the methods for health risk assessment (due to the complexity of ecosystems), the use of ecological risk assessment is increasing.

Ecological risk assessment focuses on protecting populations of species and ecosystems rather than individual organisms.

In April 1997, the Victoria Environment Protection Agency (Vic EPA) released a *Draft National Framework for Ecological Risk Assessment of Contaminated Sites.* The framework is part of an overall national contaminated sites policy that revises the Australian and New Zealand Environment and Conservation Council *Guidelines for the Assessment and Management of Contaminated Sites* (ANZECC/NHMRC 1992).

The aims of the document are to:

- describe a clear framework for ecological risk assessment for chemically contaminated soils that can be readily used by the various states environment agencies and risk assessors in Australia
- provide a scientifically defensible methodology for deriving generic and site specific ecological impact levels for contaminants in soils that protects ecological values identified at a contaminated site.

This framework will be a useful resource document that can be used to develop ecological risk assessment for New Zealand ecosystems.

2.2 Role of risk assessment in site management

Risk assessment allows a comparison to be made of the risk posed by a site with agreed levels of acceptable risk. This helps to determine whether action is required. It also facilitates the ranking of sites in order of the risk posed to human health and the environment, and is a tool for comparing site management options.

Risk assessment may involve, in order of increasing detail and complexity:

- a screening level risk assessment, incorporating comparison of measured contaminant concentrations in soil and water with generic, risk-based acceptance criteria or guideline values
- a qualitative or semi-quantitative risk assessment, based on generic, risk-based acceptance criteria, including site-specific consideration of the relevance of exposure pathways assumed to exist in the derivation of the generic criteria, the impact of land use controls and a range of other factors that impact on the risk to human health and the environment
- a quantitative risk assessment, drawing on the approaches used to derive the generic criteria, and on other published methodologies, and incorporating as much detailed site-specific information as possible.

The information required and the cost of undertaking each of the levels of risk assessment increases as the detail and complexity increases. Further, not all sites warrant a highly detailed quantitative risk assessment; a screening level risk assessment may provide sufficient information to make sound risk management or site management decisions. It is sensible therefore initially to gather only enough data for a screening level assessment. The necessity for further, more detailed risk assessment, and the associated information requirements, may be determined from that. The site assessment and management process is illustrated in Figure 2.2.

2.3 The importance of consultation

Consultation with stakeholders, including regulators, site owners and neighbours, and other potentially adversely affected parties, is an important aspect of managing contaminated gasworks sites. It is important that these stakeholders are involved in the process of site assessment and management as early as possible. Consultation with regulatory agencies is particularly important, as they can provide guidance on any resource consents requirements for assessing and managing the site.

2.4 Roles and responsibilities

There are a number of organisations with an interest in contaminated sites. In most cases more than one agency will become involved in site assessment and management.

Regional councils Regional councils are responsible for specifying controls on contaminated sites when contaminants are being discharged into or onto land, air or water. In most areas the regional council is the first point of contact for those who are concerned about a site that may be adversely affecting the environment.

Territorial authorities Territorial authorities have responsibilities under the Health Act 1956 and are involved in the control of contaminated sites when there are adverse effects on human health. They are also involved in issues relating to the use, development or protection of land, through their responsibilities under the Resource Management Act 1991.

Public health agencies Public health agencies have an interest in contaminated sites when there are adverse effects on human health.

Occupational Safety and Health Occupational safety and health are involved is the management of contaminated sites when there is a potential risk to employees working at the site.

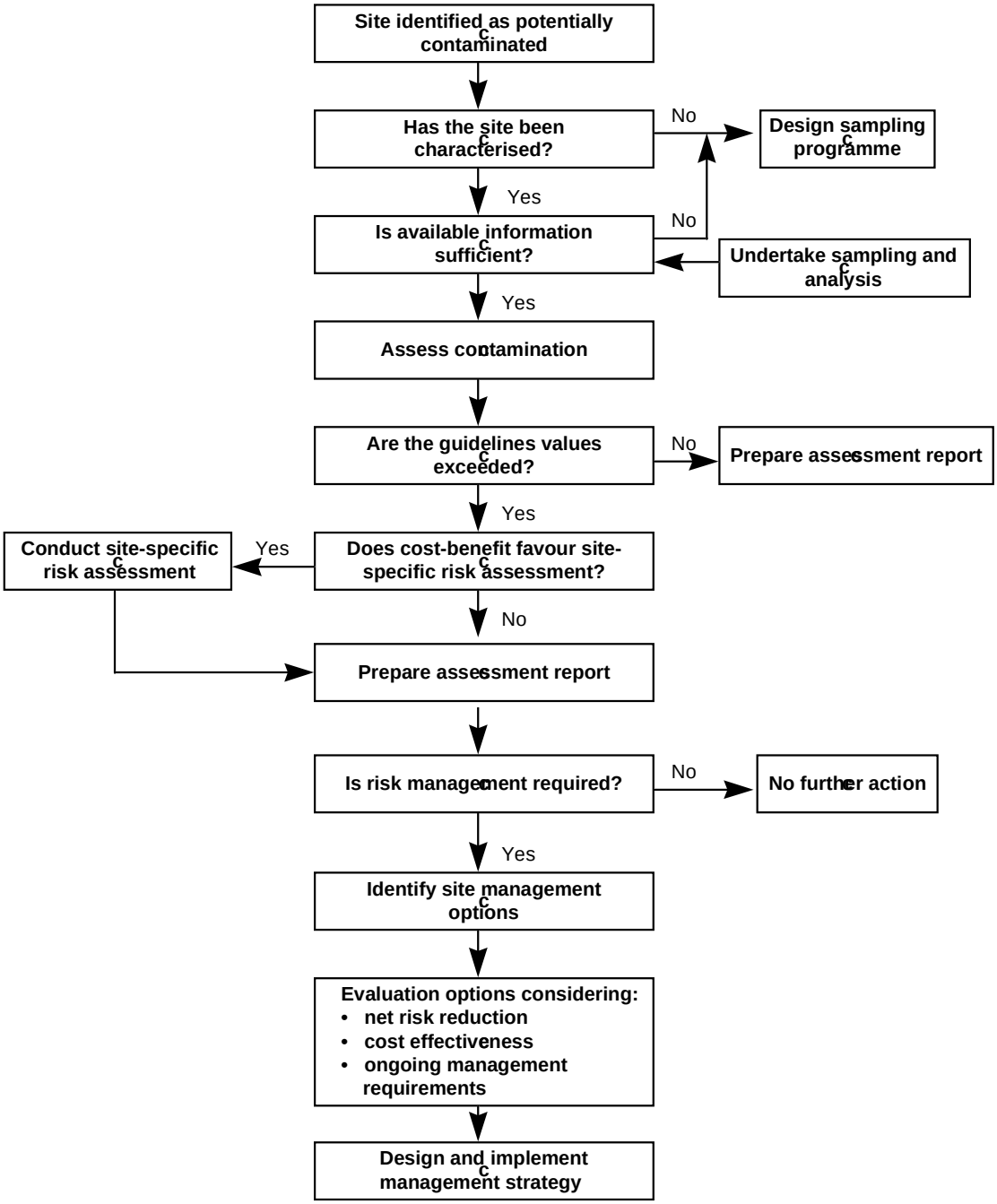

Figure 2.2 Outline of the site assessment and management process

2.8 The link between the Users' Guide and the supporting technical information on disk

The supporting technical information can be found on the disk accompanying this guideline. Figure 2.3 illustrates the links between the Users' Guide and the supporting technical information.

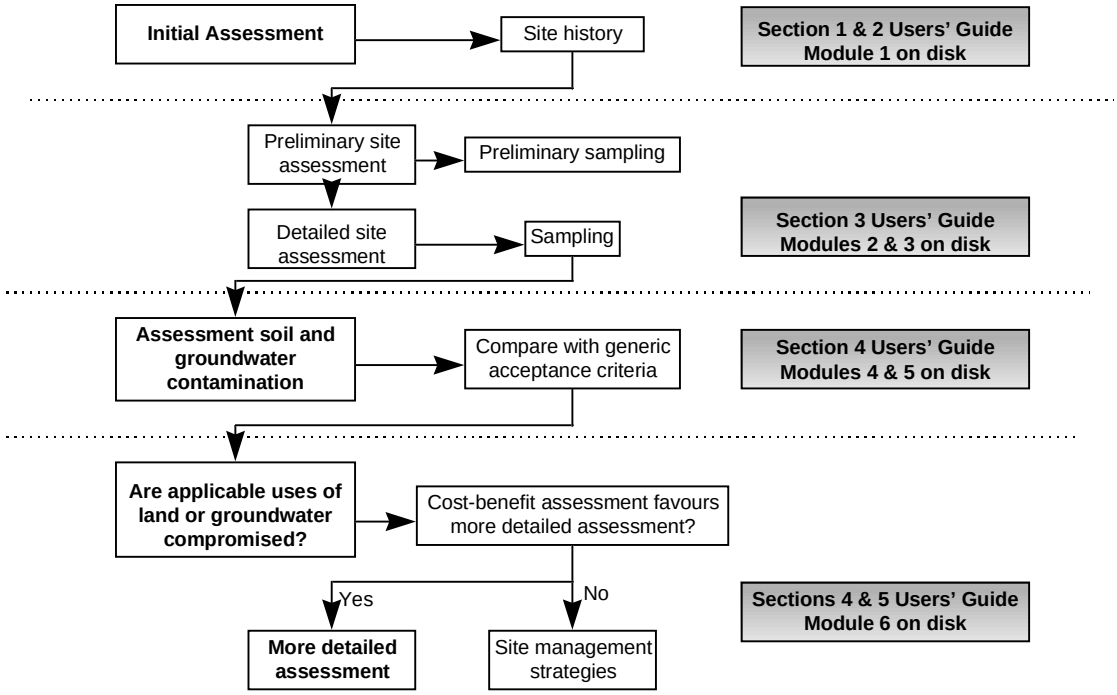

Figure 2.3 The link between the Users' Guide and the supporting technical information on disk

3

Site assessment procedures

3.1 Introduction

A site assessment must provide reliable information on the nature, distribution, and fate and transport of contamination. This section covers the following aspects of site assessment:

- ➔ the site assessment process
- ➔ what media should be sampled
- ➔ recommended approach to sampling
- ➔ site sampling techniques
- ➔ field sampling procedures
- ➔ analytical programme
- ➔ recommended approach to compositing
- ➔ reference analytical methods
- ➔ site assessment reporting
- ➔ health and safety issues
- ➔ a typical site assessment plan

Additional information on site assessment can be found in Module 2 and 3 on disk, including:

- ▲ quality assurance/quality control framework (Section 2.2)
- ▲ sampling strategies (Section 2.3)
- ▲ general sampling requirements (Section 2.4)
- ▲ site assessment techniques (Section 2.5)
- ▲ soil, groundwater and surface water and sediment sampling (Sections 2.6, 2.7 & 2.8)
- ▲ the use of blank and duplicate samples (Section 2.9)
- ▲ documentation and record keeping (Section 2.10)
- ▲ field cleaning procedures (Section 2.11)
- ▲ disposal of sampling wastes (Section 2.12)
- ▲ analytical methods for organic and inorganic contaminants (Sections 3.2 & 3.3)
- ▲ analytical field methods (Section 3.5)

3.2 Site assessment process

The initial assessment of a gasworks sites will usually consist of two phases:

Phase one - background information study

First a background study should be carried out to identify the history of activities which could have resulted in contamination. The initial work generally consists of a site visit and a review of site history records and prior uses including, if possible, interviews with the present and previous site occupiers and employees.

Phase two - field investigation programme

A programme of field work can then be planned and carried out. This may include collecting soil, groundwater and surface water samples for analysis. The extent of the investigation depends on the type of site being evaluated, the exposure pathways and exposed population or environment. It will be based on the results of the background study and will contribute to subsequent site characterisation.

3.2.1 Phase one - background information study

All pertinent background information should be reviewed to identify the potential for on-site and off-site contamination. This phase of the work should be completed before commencing phase two.

The background information study should include:

- the chronological history of previous site uses and industries
- the gasworks activities or processes carried out on the site, particularly the location of facilities such as gasholders, purifiers, and waste disposal tanks
- information on demolition procedure at the gasworks to determine facilities that may have been moved and buried
- any past investigations or remediation carried out at the site
- any changes during the history of the site
- interviews with site personnel and past workers at the site. Other sources of site history information include:
  - records of regulatory controls and waste management practices
  - past and present owners of the site
  - aerial and ground photographs, and site maps and surveys
  - local government records (e.g. history of complaints, discharge or building permits)
  - trade and street directories
  - local literature (e.g. newspapers)
  - long-term adjoining owners
- identification areas where the likelihood of contamination resulting from past or current work practices is high (e.g. accidental spillage of tars and waste disposal sites)
- source information in order to establish raw material use, products, known chemical or treatment waste release history (spills, leaks, etc.) and waste disposal practices (i.e. on-site, off-site)
- local hydrogeological data including
  - the extent, interconnection and use of aquifers in the area
  - probable direction and rate of groundwater flow in each aquifer
  - information on the site geology and soils at the site
  - local municipal drinking water supply sources, and the location of private or industrial wells or bores, especially those supplying drinking water
- location of surface water bodies (creeks, rivers, estuaries, wetlands) particularly where these may be adversely affected by contaminated groundwater or surface drainage from the site. Surface water bodies should be evaluated to determine environmental values, beneficial uses, sensitivity to change and physical, chemical and biological characteristics

- published or known information which establishes whether adjacent property owners are or have been potential sources of contamination of the soil and groundwater of the site
- available information on geological, hydrogeological and pedological characteristics of the site and surrounding areas
- location, age and construction material of above- and under-ground storage tanks on the site (including underground tar wells)
- location and construction details of underground services including the site stormwater system. These may have a impact on future remediation activities, and can act as preferential drainage pathways
- present and likely future zoning of the site
- likely future use of the site
- contour or topographic maps for locating of filling and earthmoving activities
- potential cultural issues, e.g. archaeological
- the location of any off-site underground services.

3.2.2 Phase two - field investigation programme

A field investigation programme should be developed for each site after completing the background study. Given the variability in size and complexity of gasworks sites, it is not possible, or appropriate to provide general advice on developing field investigation programmes.

3.3 What media should be sampled?

The sampling programme should include the following:

- soil sampling
- groundwater sampling
- surface water and sediment sampling at locations to be determined following assessment of site run-off patterns.

Additional sampling could include:

- soil gas sampling to define the extent of contamination by volatile contaminants
- environmental media and potentially affected ecological receptors, e.g. ambient air, plant materials, aquatic biota
- stored sludges, stockpiles, waste pits and water contained in site structures to determine disposal requirements.

Information on sampling locations can be found in Section 3.4.

A site work plan should be prepared setting out the requirements and objectives for field sampling and sample collection at the site. All field sampling and associated data collection must be supervised by an experienced person, and carried out in accordance with approved sampling procedures (Quality Assurance Plan (QAP) and an approved site Health and Safety Plan (HASP)).

3.3.1 Soil

An assessment programme for characterising soil contamination can be used to determine:

- whether human receptors on and off site (e.g. full and part time workers, maintenance workers, residents and recreational users) are at risk from contact with contaminated soil
- whether there are unsecured areas of contaminated soil which could be transported off site as contaminated sediment in run-off or dust
- whether the contamination is mobile within the soil and has potential to leach to groundwater (off site transport)
- the potential for other off site impacts.

3.3.2 Groundwater

If hydrogeological conditions indicate there is potential for impacts from site contamination on groundwater, then a groundwater investigation programme should be completed as part of the second phase investigation. If groundwater is at a depth of less than 10m, a groundwater monitoring programme should be considered. However, other site-specific factors including the nature of the overlying soils[1] need to be considered.

If shallow or perched groundwater exists at a site, migration through underground service conduits should also be considered.

The design of the groundwater investigations should be directed towards:

- determining the depth to groundwater, thickness of the near-surface aquifer, direction and rate of groundwater movement and location of possible surface waters connected to groundwater (e.g. surface drains, streams, wetlands, etc.)
- determining whether contaminants are present in the groundwater (both on and off site) and if so, at what concentrations and in what form (including light non-aqueous phase liquids (LNAPLs) and dense non-aqueous phase liquids (DNAPLs).

The groundwater monitoring programme should aim to identify the impact of contamination on current and future uses of the groundwater, the risk to groundwater users', the potential for off site impact and the impact on other receiving environments.

3.3.3 Surface water and sediment

The aim of surface water and sediment sampling is to determine contaminant concentrations of media to which human and ecological receptors may be exposed.

It is possible to extrapolate contaminant concentrations in surface water and sediments from groundwater and surface soil concentrations. However, direct measurement provides more reliable estimates of the potential human and ecological impacts.

The surface water and sediment sampling programme should provide an estimate of contaminants leaving the site via drains, surface water run-off and groundwater discharge to surface water bodies. Sediment sampling is a useful source of qualitative information about off-site transport of contaminants as some substances will partition preferentially into the sediments.

3.3.4 Air

This guideline does not specifically address sampling requirements for air. In general, vapour and gaseous phase contamination does not pose a significant risk at gasworks sites. This is mainly due to the age of the sites and subsequent degradation of volatile contaminants. However, vapour issues, such as odour, may be important during site sampling and site management, and are addressed in this context in these guidelines. The *Draft*

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1 The potential exists for contamination of groundwater at depths greater than 10m where soil or rock permeabilities are high. For example, contamination of groundwater at depths greater than 15m readily occurs in fractured rock systems and permeable unconsolidated deposits. Notwithstanding this, the nominated value of 10m represents a pragmatic guideline based on general site conditions encountered.

Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand, due for release in August 1997, have more detailed information on volatilisation.

A potential problem during the assessment and management of gasworks sites is the presence of hydrogen sulphide. Care should be taken where this is an issue.

Information on volatilisation can be found in the following guideline:

Draft Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand. This document is to be released for submissions in August 1997.

3.4 Recommended approach to sampling

The information requirements for site assessment vary according to the size and complexity of the site. For this reason it is not possible to rigorously define the required sampling and analysis programme that will provide adequate information for risk assessment purposes.

3.4.1 Sampling at gasworks sites - some specific issues

Contamination at gasworks sites is usually heterogeneous, reflecting the nature of gasworks wastes and waste disposal practices. Some of the specific issues associated with sampling as gasworks sites include:

Free tars and organic liquids	Free tars and other organic liquids (e.g. oil from gasholder seals) may be present at gasworks sites. For the purposes of this guideline it is assumed that free tars and organic liquids will always be contaminated and will therefore need to be disposed of appropriately. The focus should be on developing appropriate management options rather than sampling these wastes.
Tar clumps	Aged tar contamination in soil may be present as tar balls or clumps, resulting in uneven distribution of contaminants. Sampling of soil containing tar clumps can results in highly variable results and therefore care should be taken to note whether such material is present in a sample. These clumps may pose a risk to human health or the environment and need to be managed appropriately.
Spent oxide wastes	Spent oxide wastes are frequently found at gasworks sites, sometimes in a stockpile or used as general fill. Spent oxide waste should be managed as a waste material since the treatment options are limited.
Demolition rubble	Most gasworks sites will have been subject to several cycles of development and redevelopment, both as part of gas-making activities at the site and subsequent use. As a result concrete, bricks and other building materials frequently remain on-site as fill. Concrete building slabs may remain intact, and tar well and gasholder foundations may remain on-site. These features can make investigation of such sites more difficult, limiting the ability to sample at some locations and restricting the usefulness of some sampling techniques.

The design of sampling programs should consider:

- minimising the disturbance of contaminated material to reduce odour impact beyond the site boundary
- appropriate health and safety protocols to minimise the exposure of investigation workers to gasworks contaminants
- limiting off-site transport of contaminants by limiting exposure of contaminated soil and managing stormwater flows appropriately.

3.4.2 Soil sampling

The following general approach is suggested for a soil sampling programme:

- identify the areas likely to be contaminated based on site history and relevant information (e.g. retort house, gasholders, tar wells)
- divide the site into a number of areas based on the likelihood of contamination
- adopt a targeted or systematic sampling strategy within those areas that are expected to be contaminated to develop an understanding of the likely contaminant concentrations and distribution within the contaminated areas
- adopt a systematic sampling strategy across the general site areas where contamination is not expected or specific contaminant sources have not been identified.

Some general comments on systematic and targeted sampling follow:

Systematic Sampling

- use for identifying hot spots in areas which are not expected to be contaminated
- use for estimating mean concentrations if an area is expected to be contaminated
- grid spacing of 10 - 30 metres may be appropriate depending on the sampling objectives and site details
- must be flexible when designing systematic sampling grids for instances where obstructions may be present that prevent sampling

Targeted Sampling

- a targeted sampling programme is highly dependent on site history
- may recover samples from these sources
  - retort houses
  - gasholders
  - tar wells and other tar processing plants
  - condensors
  - purifiers
  - coal and coke storage
  - waste disposal areas
- several samples should be recovered from the area surrounding each source to assess the heterogeneity of the distribution
- usually combine targeted sampling with systematic sampling across general areas of the site
- samples should be recovered from a range of depths depending on the nature of the contaminant and the location of the source. For example
  - gasholders may extend several metres below the ground surface
  - in the vicinity of other surface facilities, samples should be recovered from depths up to 2 metres
  - in heavily contaminated areas soils in the vicinity of the groundwater may need to be sampled to assess the potential for ongoing contamination of groundwater.

Visual assessment of wastes can assist in determining which samples should be analysed. For example, if a number of obviously tarry samples are recovered from a particular area and depth, only one or two may need to be analysed. These samples are likely to return high concentrations of contaminants and the analyses of a limited number of samples would be sufficient to provide information about that particular area and depth. This visual analysis should be done by a person experienced in assessing these wastes at gasworks sites.

3.4.3 Groundwater sampling

The recovery of groundwater samples from the following locations may be warranted:

- upgradient of the site (one or more locations as background bores to assist in assessing groundwater quality and aquifer characteristics)
- adjacent to potentially major sources of groundwater contamination
- downgradient of contaminated areas
- downgradient of site boundaries.

Issues which need to be considered when designing and implementing groundwater sampling include:

- the number and location of monitoring bores depends on the complexity of the sites. However, for a simple site, at least five would be required to obtain a reasonable understanding of the groundwater conditions and the extent of contamination at the site
- where DNAPLs have been found, groundwater should be monitored at a range of depths, as the DNAPLs may be an ongoing source of dissolved phase groundwater contamination
- should consider installing nested bores at strategic locations to identify the impact of DNAPL contamination
- should also monitor for the presence of light non-aqueous phase liquids (LNAPLs) where DNAPLs have been found
- groundwater monitoring bores should be installed under the supervision[2] of suitably qualified drilling contractors
- soil samples may be recovered and analysed during bore installation to assist in assessing contaminant distribution
- during preliminary investigations, drawdown and recovery or similar tests should be carried out on selected bores to determine aquifer characteristics.

3.4.4 Surface water and sediment sampling

The surface water sampling locations should be determined following a detailed review of surface water flow patterns on site and likely groundwater flow direction and discharge. Surface water samples should be recovered from:

- at least one location upstream and one downstream of the site, and from one or more locations adjacent to the site, where the site is near to a flowing water body (e.g. stream)
- several locations at varying distances from the shore where the water discharges to a bay or other coastal or lake environment. A sample characterising the likely background conditions in the surface waterbody should also be collected.

Issues which need to be considered when designing and implementing surface water and sediment sampling include:

- at least one sample should be recovered from any potentially contaminated drain discharging from the site
- several rounds of surface water sampling may be needed to provide an estimation of water quality under wet and dry weather conditions. During wet weather the sampling regime should targeted towards characterising the first flush of run-off, and during dry weather surface water contamination from groundwater inputs should be characterised

2 Under the supervision of an experienced geologist/hydrogeologist/environmental scientist.

- a representative sediment sample should be collected from each sample location, where possible. Additional sediment samples may be recovered from drains from the site discharging to the surface water body
- sediment should be recovered during weather conditions to which aquatic species would normally be exposed.

Additional information on sampling strategies and quality control/quality assurance can be found in Module 2, Sections 2.2 and 2.3 on disk.

3.5 Site sampling techniques

3.5.1 Soil sampling techniques

Soil samples may be recovered from gasworks sites by a range of techniques. The primary consideration in selecting sampling techniques should be the integrity of the samples, so that the quality of information is adequate for the assessment. Table 3.1 shows the advantages and disadvantages of various soil sampling techniques.

Table 3.1 Soil sampling techniques

Technique	Advantages	Disadvantages
Borehole	• minor disturbances of soils • limited occupational exposure • accurate recovery of samples • ability to sample at depth as required	• cost • time • need to carefully decontaminate equipment • limited ability to observe nature of the material encountered
Hand Auger	• low cost • quick	• limited depth • impractical in difficult soil conditions • care required to ensure quality of samples recovered • limited ability to observe nature of material encountered • labour intensive
Back Hoe Test Pit	• lower cost than boreholes • relatively quick • ability to make more detailed observations about the nature of materials encountered • able to accurately recover samples	• extent of soil disturbance and the effect on odour, occupational exposure, and compaction • limited to depth of 3 to 4 metres • impractical in unstable soil conditions

Selection of a sampling technique should consider:

- depth from which samples are to be recovered
- soil conditions (e.g. stability)
- current use or development of the site (e.g. to what extent can site disturbance be tolerated)
- presence of concrete slabs or foundations at or below the surface (subsurface foundations are often found at gasworks sites, limiting sampling)
- likely level of contamination and the likely health and safety implications associated with disturbance of contaminated material.

3.5.2 Groundwater sampling techniques

A wide range of techniques are available for recovering groundwater samples, with and without the installation of permanent groundwater monitoring bores. In environmental site assessments, groundwater is most often sampled by constructing permanent groundwater monitoring bores. Preferred sampling techniques should recover a sample representative of surrounding groundwater conditions.

Some issues in the assessment of groundwater contamination are outlined as follows:

- the technique adopted must avoid the introduction of contaminants from one zone into another. Hollow stem auger techniques are frequently used for unconsolidated materials, and percussion techniques are frequently used for consolidated materials
- bore construction materials must be selected to minimise impact on groundwater quality and chemistry. Screw thread PVC standpipes are frequently used
- where nested bores, or sampling from a discrete depth interval below the water table is proposed, bores must be securely sealed, allowing sampling from the desired depth and minimising the potential for migration of DNAPLs through the space of the drilled hole and the bore casing. This is especially important where a confining layer is present
- the water column in the monitoring bores should be carefully examined for free phase organics before purging and sampling
- bores must be properly developed and purged of stagnant water before sampling
- field measurements of groundwater quality (e.g. pH, dissolved oxygen) should not occur until these parameters have stabilised in the extracted water
- groundwater samples should be recovered in a manner that minimises loss of volatiles.

3.5.3 Surface water and sediment sampling techniques

There are no particular techniques for sampling surface water and sediment.

Additional information on typical soil,, groundwater, surface water and sediment sampling can be found in Module 2, Sections 2.6, 2.7 & 2.8 on disk.

3.5.4 Subsurface techniques

3.5.4.1 Geophysical surveying

Geophysical surveying is a remote sensing tool that is able to provide a cost-effective and efficient way of better defining the subsurface conditions at an investigation site. For the most part, geophysical methods are non-destructive and non-invasive, which can be extremely important for a site where little is known of past practices or locations of subsurface structures. A preliminary geophysical survey can locate subsurface structures that may otherwise present a health and safety hazard in drilling or trenching programmes designed on a random or grid basis.

3.5.4.2 Electromagnetics

Electromagnetic (EM) fields generated above the ground are used to induce currents in the ground that, in turn, set up secondary EM fields that are detected at the surface. The strength of these secondary fields is dependent on the conductive properties of the subsurface materials and therefore help detect and map lateral variations in subsurface conditions.

3.5.4.3 Magnetics

Magnetic surveying measures variations in the magnetic field at or above the ground surface which is affected by lateral variations in the concentrations of the magnetic minerals or man-made materials, such as pipes and tanks.

3.5.4.4 Resistivity

Resistivity surveying relies on the injection of electrical current into the ground and the measurement of the induced potential differences between points at the surface.

The four methods outlined above are generally employed in conjunction with a well-designed drilling or trenching programme to provide ground truth for the geophysical observations.

Additional information on subsurface assessment techniques can be found in Module 2, Section 2.5 on disk, or refer to the following publication:

Subsurface Assessment Handbook for Contaminated Sites, CCME, Report CCME EPC-NCSRP-48E, March 1994.

3.6 Field sampling procedures

Field sampling procedures need to be followed to ensure that the appropriate level of detail and care are taken while collecting environmental samples from a gasworks site. An important part of these field sampling procedures is quality assurance/quality control requirements.

Information on the field sampling procedures can be found in Module 2 on disk, including:

- ▲ general sampling requirements (Section 2.4)
- ▲ site assessment techniques (Section 2.5)
- ▲ typical soil, groundwater, surface water and sediment sampling procedures (Sections 2.6, 2.7 & 2.8)
- ▲ the use of blank and duplicate samples as quality assurance and quality control measures (Section 2.9)
- ▲ documentation and record keeping (Section 2.10)
- ▲ field cleaning procedures (Section 2.11)
- ▲ disposal of sampling wastes (Section 2.12)

3.7 Analytical programme

The analytical programme is based on the contaminants that are likely to be found at gasworks sites. Table 3.2 outlines the possible analytes for the various media.

Table 3.2 Possible analytes

Analytes	Soil	Groundwater	Surface Water and Sediment
PAHs	✓	✓	✓
BTEX	✓	✓	✓
phenols and cresols	✓	✓	✓
petroleum hydrocarbons	✓	✓	✓
copper	✓	✓	✓
chromium	✓	✓	✓
cadmium	✓	✓	✓
lead	✓	✓	✓
nickel	✓	✓	✓
zinc	✓	✓	✓

ammonia	✓	✓	✓
sulphate, sulphide, total sulphur	✓	✓	✓
cyanide	✓	✓	✓
pH	✓	✓	✓
Electrical conductivity		✓	
Total suspended solids			✓

3.7.1 Soil

Samples should be analysed for those contaminants identified in the background information study.

3.7.2 Groundwater

When analysing groundwater samples, emphasis should be placed on the more soluble parameters, such as BTEX, light-end PAHs, such as naphthalene, ammonia, and soluble heavy metals. These are contaminants that tend to be more mobile and may migrate some distance from the site, depending on the sites hydrogeological conditions. Where floating layers of separate phase liquids/hydrocarbons or hydrocarbon sheens are detected in groundwater, samples collected from these wells should not be analysed for organic parameters.

Selected groundwater samples should be analysed for pH, total dissolved solids and other general characteristics to assist in determining the potential impact on current or likely future uses. This may require recovery of additional samples in conjunction with samples for chemical contaminant analysis.

Where non-aqueous phase liquids are detected in a bore the sample should not be analysed for dissolved phase contaminants as the analysis is unlikely to be reliable.

3.7.3 Surface water and sediment

The analysis of surface water samples includes the same parameters specified for groundwater. For sediments, particular attention should be paid to the analysis of samples for constituents that are likely to bind strongly to particulate matter (e.g. heavier PAHs, heavy metals).

3.8 Recommended approach to compositing

Generally it is not appropriate to composite soil samples from gasworks sites.

Compositing soil samples assumes that a valid estimate of the contaminant concentration of the composited sample can be obtained from a single sub-sample analysis of the composite sample. A sub-sample containing a high concentration of contaminant may remain undetected due to dilution in compositing.

Where a site is heavily contaminated and the extent of contamination needs to be defined, the use of composite sampling is not appropriate as sub-samples will have to be reanalysed where contaminant concentrations exceed the acceptance criteria. Composite sampling is also not appropriate where samples are to be analysed for volatile chemicals, such as BTEX, due to the possible losses during compositing.

In areas where contamination is expected, samples may be composited provided there is some basis for expecting similar contaminant concentrations in each sample (e.g. at the base of a sludge tank), or where an average contaminant concentration is specifically sought (e.g.

estimating the average exposure of site users). In areas where contamination is not expected, samples may be composited to reduce analytical costs.

Some general rules for compositing are as follows:

- compositing should be limited to no more than four sub-samples so that any sub-sample can be detected if it exceeds the guidelines
- composites should only be comprised of samples from immediately adjacent locations
- composites should only comprise samples from the same depth and of similar soil type
- samples should be homogenised prior to forming the composites. Samples that are not readily homogenised (e.g. clays) should not be used to form composites
- equal masses from each sub-sample should be used to form the composite.

3.9 Reference analytical methods[3]

Recommended methods for analysing each of the possible gasworks contaminants are given in the tables below. The tables include the method detection levels (MDLs). Laboratories wishing to use alternative methods should confirm for themselves (or their clients) that an equivalent level of performance, or MDL, is achieved. This should include selectivity of the method towards the analytes of interest, and recovery efficiencies in any extraction and clean-up steps.

Recommended methods for clean-up and extraction steps are also listed where applicable. The extraction and clean-up methods used should be chosen carefully to ensure that they are appropriate for the contamination concerned.

Contamination concentrations in soil samples should be reported in mg/kg on a dry weight basis, with the moisture content included in the report. Results from water samples should be reported in g/m^3.

Field methods are also discussed, but no reference methods have been proposed as the available methods are mainly suitable for investigation and screening purposes, rather than testing against any 'acceptance' criteria. It is recommended that results from 'screening' methods should be within at least 80% of the accuracy obtainable with a more thorough 'reference' method.

Tables 3.3 and 3.4 show the reference methods for the analysis of organic and inorganic contaminants.

Additional information on the analyses of contaminants can be found in Module 3 on disk, including:

- ▲ analytical methods for organic contaminants (Section 3.2)
- ▲ analytical methods for inorganic contaminants (Section 3.3)
- ▲ sampling and sample preservation (Section 3.4)
- ▲ quality assurance requirements (Section 3.6)

Table 3.3 Reference methods for the analysis of organic contaminants

Analyte and Matrix	Clean-up Step	Extraction Step	Determination Step	Method Detection Limit

3 The analytical method selected should be one that provides the greatest accuracy and reproducibility at concentrations close to the generic acceptance criteria. Where the detection limit of the method is close to the generic acceptance criteria it may be appropriate to develop site-specific acceptance criteria.

PAHs and Semi-volatile Organics				
Soil/Sediment (low level contamination)	EPA 3630	EPA 3540 or EPA 3550	EPA 8270[4]	1 mg/kg
Water - contaminated	EPA 3630	EPA 3510 or EPA 3520	EPA 8270	10 µg/l
Water - drinking	EPA 525.1	EPA 525.1	EPA 525.1	
Volatile Organic Compounds (BTEX)[5]				
Soil/Sediment	n/a	EPA 5030	EPA 8260	1 µg/kg
Water - contaminated	n/a	EPA 5030	EPA 8260	0.03-0.1 µg/l
Water - drinking	n/a	EPA 524.2	EPA 524.2	0.03-0.1 µg/l
Phenols				
Soil	EPA 3650	EPA 3540 or EPA 3550	EPA 8270 or EPA 8041	1 mg/kg
Water-contaminated	EPA 3650	EPA 3510 or EPA 3520	EPA 8270 or EPA 8041	10 µg/l 0.15-0.3 µg/l[6]
Water - drinking	EPA 525.1	EPA 525.1	EPA 525.1	
Total Petroleum Hydrocarbons (TPH)				
Soil			RJ Hill Method	

Table 3.4 Reference methods for the analysis of inorganic contaminants

Analyte and Matrix	Clean-up Step	Extraction Step	Determination Step	Method Detection Limit
Total Cyanide				
Soil	APHA 4500 CN (C)	APHA 4500-CN (A2)	APHA 4500-CN (E) or EPA 9013	0.1 mg/kg
Water		APHA 4500 CN (C)	APHA 4500 CN (E) or EPA 9012	1 µg/l
Free Cyanide				
Soil	APHA 4500 CN (I)	APHA 4500 CN (A2)	APHA 4500-CN (E)	0.1 mg/kg
Water		APHA 4500 CN (I)	APHA 4500 CN (E)	1 µg/l
Metals[7]				

4 Estimated quantitation level (EQL) of Method 8270. EQL for wastes are from 1-200 mg/kg, dependent on sample matrix and method of preparation. EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the MS detector. Sample EQLs are highly matrix dependent . The EQLs listed above are provided for guidance and may not always be achievable. Documentation for Method 8270 indicates that EQLs for high concentration soil may be 7.5 times greater, while those for non-water miscible waste may be 75 times greater. (EQL is generally 5 to 10 times the MDL).

5 EQL for groundwater is 1µg/l for all BTEX. EQL for low-level contaminated soil is 5 µg/kg. For other matrices, the EQLs may be greater than the value for low-level soil by 50 times for water miscible liquid waste, 125 times for high concentration soil and sludge and 500 times for non-water miscible waste.

6 EQLs can range from 10 to 10^5 times the MDL depending on the sample matrix.

Soil		EPA 3050, EPA 3051 or APHA 3030	EPA 6020 or APHA 3111-3	0.02-2 mg/kg[7]
Water		EPA 200.2 or APHA 3030	EPA 6020 or EPA 200 series APHA3111-3	0.02 - 0.4 µg/l[7]
Elemental Sulphur				
Soil			Method 31 ANZECC	
Sulphate				
Soil		Method 29 ANZECC	APHA 4110 or APHA 4500-SO_4	
Water			APHA 4110 or APHA 4500-SO_4	1 mg/l
Sulphide				
Soil			EPA 9030 or EPA 9031	
Water			APHA 4500-S^{2-} (D or G)	0.02 mg/l
Ammonia				
Soil		Method 10 ANZECC	APHA 4500-NH_3 (D or E)	
Water			APHA 4500-NH_3 (D or E)	0.01 mg/l
Acidity				
Soil			EPA 9045 or Method 6 ANZECC	
Water			APHA 2310	

3.9.1 Analytical field methods

Field testing may be required for several reasons:

- to ensure health and safety requirements are met
- to analyse unstable or very volatile contaminants
- where immediate analytical response is required, for example, for making on-site decisions on the progress of remediation activities.

A range of field analytical equipment is available, from simple colorimetric test kits to sophisticated portable versions of laboratory instrumentation. Many of these are now based on standard methods such as those in the APHA manual, and will be perfectly acceptable, provided the required levels of performance are achieved.

It is recommended that unstable or volatile contaminants not be analysed in the field.

Test kits can be based on colorimetric chemical tests, used with either a visual colour comparator or a photometer, or on electronic chemical sensors, usually based on an electrochemical principle. Examples of parameters that can be measured by such field test kits are:

- ammonia

7 MDLs are dependent on the individual metal elements. These values are for samples of "clean" matrices and are subject to variation.

- nitrate, nitrite
- sulphate, sulphide, sulphite
- aluminium, copper, iron, chromate, manganese, molybdate, zinc
- pH, acidity, alkalinity, conductivity
- phosphate
- phenols (total)
- hydrocarbons (total), PAHs, BTEX

Additional information on the analytical field methods can be found in Module 3, Section 3.5 on disk.

3.10 Site assessment reporting

At the conclusion of the sampling and analytical programme, a formal report should be prepared. The report should include:

- a statement of the objectives, scope and limitations of the assessment and report
- a detailed description of the land, including ownership and occupier details, certificate of title etc
- a detailed history of the uses of the site. This should include a list that specifies the identities and locations of any known or suspected chemicals or any other substances which could be a hazard whether imminent or otherwise
- sources and validation of information
- current and likely future use of the land
- recording of any visual inspections of the site
- details of the geology and hydrology of the area, including physical characteristics of the soil (for example: type, porosity and sorptivity, transmissivity, areas of fill, variation of such characteristics with depth) and groundwater (depth, rate of flow), regional groundwater quality, use of the groundwater in the area. Copies of all bore logs, soil profiles and other records of field observations and measurements should also be provided
- details of the condition and location of buildings, sewer and drainage systems, natural water courses, underground storage tanks, waste disposal areas and other activities on the site
- a detailed site plan including scale, dimensions of site, north point, relationship to streets and other properties, and all relevant site features and sampling locations
- details about the services on and off-site (since these are potential routes for contamination to spread)
- the sampling and analysis programme used to determine the extent and distribution of contamination, including:
  - basis for selecting the chemicals included in the analytical programme
  - rationale for sample locations and depths in each medium of concern (air, soil, groundwater, surface water)
  - sampling methods
  - detection limits (levels chosen and their derivation)
  - quality assurance procedures

  - quality control details
  - laboratory and analytical methods used.
- results of the sampling and analysis programme on which a conceptual model is based of how contaminants are moving on the site and their fate and transport characteristics in each media of concern
- information about any contaminants of concern, selected on the basis of the results of the sampling programme. This information should include an evaluation of:
  - the fate and transport of each chemical
  - the form or species present
  - physical characteristics
  - potential harm to humans, plants, animals, and structures
  - aesthetic impairment
  - any detriment to possible beneficial uses of the site
  - potential for adverse off-site effects
  - potential exposure pathways
- the results of the field investigations should be discussed with reference to the guideline values nominated for various site uses. Particular attention should be given to site-specific factors which may require modifying the nominated values
- recommendations, including further activities required at the site to mitigate contamination, if necessary.

3.11 Health and safety issues

Under the Health and Safety in Employment Act 1992, a place of work must be investigated to identify the hazards present, these hazards must be assessed for their significance, and those identified as significant must be eliminated, isolated or minimised as appropriate. Existing documentation regarding safety practices, such as oil industry hot work and confined space permitting procedures and the codes of practice for petroleum sites, should be reviewed thoroughly before investigating site contamination.

Workers may be exposed to hazardous substances during the assessment and management of contaminated gasworks sites. The occupational health and safety hazards associated with this exposure may present a danger to human health and safety. Appropriate protection should be given to workers involved in site assessment and management.

The Occupational Safety and Health Service and the Department of Labour have published *Health and Safety Guidelines on the Cleanup of Contaminated Sites*. The guidelines, published in 1994, provide a general framework for employers, contractors, local authorities and others, for controlling exposure to hazardous substances which may be present at contaminated sites. These guidelines should be consulted prior to the assessment and management of a contaminated gasworks site.

Refer to the Occupational Safety and Health Service/Department of Labour document - *Health and Safety Guidelines on the Cleanup of Contaminated Sites* (1994). Copies of this document are available from the Department of Labour.

3.12 Example of a typical site assessment plan

3.12.1 Introduction

The objectives of this typical site assessment are to:

- develop a general understanding of the nature and extent of contamination at a fictitious site
- determine whether the potential for off-site transport of contamination is significant
- identify the main areas and sources of contamination.

The proposed investigation is not designed to determine the full extent of contamination (for example, there are no off-site sampling locations), but rather to identify areas of contamination associated with known sources and to screen for contamination across general site areas.

3.12.2 Background to the site

- a small disused gasworks site
- no buildings or other aboveground structures remain
- holder pits were filled although not destroyed
- alluvial soils (sands and clays) are expected to be present in with groundwater to a depth of approximately 4 - 6 metres.

A review of site history suggests general filling across the site although no specific waste disposal/fill areas were identified.

3.12.3 Sampling plan design

3.12.3.1 Soils

A combination of grid and targeted sampling is proposed to screen general site areas for contamination and to focus on the contamination associated with known sources of contamination (see Figure 3.1).

- ***Grid sampling***

  The site are is approximately 0.5ha. A minimum of 13 sample locations are required to provide 95% confidence of identifying a "hot spot" of 23.1m diameter. Samples are to be recovered from a depth of 0.3m and 1m, or at 0.5m intervals to the base of the fill (whichever is the greater depth). They are to be analysed for PAHs, heavy metals, cyanide, and phenolics. The samples should be screened using a PID and those that report significantly elevated PID readings should be analysed for BTEX.

- ***Targeted sampling***

  Limited targeted sampling is proposed to address specific areas of concern at the site, including:

  - gasholders
  - tar well or tank
  - liquor pit
  - purifier boxes
  - laboratory and workshop
  - retort house.

  Unless the identified source is below ground, samples should be recovered as for the grid sampling above or to a depth below obvious signs of contamination (e.g. odour, discolouration). In areas where the source of contamination is below ground (e.g. gasholders, tar wells, and liquor wells) samples should be recovered from a depth greater than the base of the source. For example, if a gasholder

foundation extends to a depth of 4m, samples should be recovered at 2m intervals to a depth of 6m. The proposed targeted sampling locations are shown in Figure 3.1. In total, eight targeted locations are proposed. Soil samples would also be recovered from the groundwater monitoring well locations during installation.

Targeted samples should be analysed for a range of samples consistent with the nature of the possible source of contamination.

3.12.3.2 Groundwater

Groundwater at the site is expected at a depth of four to six metres, with regional flow to the south. A total of five groundwater monitoring bores are proposed as follows (see Figure 3.1):

- upgradient/background bore
- downgradient of the holders and liquor well
- downgradient of the tar tank
- downgradient of the retort house
- downgradient of the purifier boxes.

Groundwater samples should be analysed for a range of contaminants including PAHs, phenolics, BTEX, ammonia, cyanides, and sulphate. In addition, general water quality parameters such as pH, total dissolved solids, temperature, redox potential and dissolved oxygen should be measured.

3.12.3.3 Soil sampling technique

A range of soil sampling techniques may be used to determine the nature and extent of contamination. Fill test pit sampling is particularly useful. Extended test pits or trenches may also be useful to find the extent of contamination, particularly near the holder pits. However, care must be taken to avoid penetrating subsurface structures that may still hold free tars. Soil sampling below a depth of 4m and installing groundwater monitoring bores requires the use of a drill rig.

3.12.3.4 Analytical programme

The analytical requirements for soil and groundwater samples are set out above. In practice the PAHs are expected to be limiting under most circumstances (with the exception of spent oxide and metals in the vicinity of workshops). Initially, a broad range of analytes should be screened with any follow-up work focussing on the specific contaminants of concern identified as part of the original investigations.

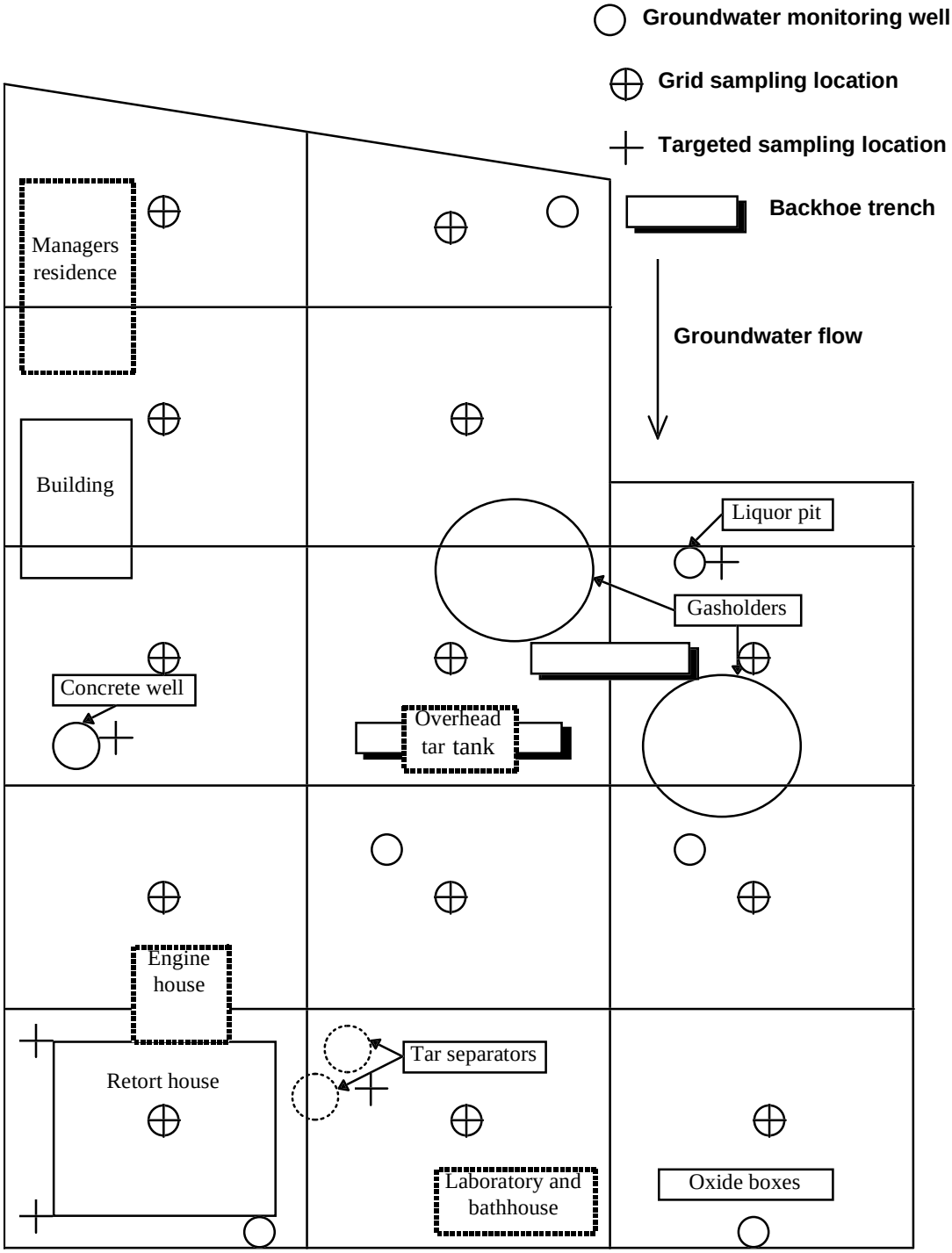


Figure 3.1 Sampling plan design

4

Generic acceptance criteria

4.1 Introduction

The development of risk-based acceptance criteria requires the risk assessment process to be operated in reverse, starting at the target risk level and making assumptions regarding site conditions and land use. Risk assessment can then be used to determine the contaminant concentrations in various media corresponding to the target risk levels - these are termed the '**generic acceptance criteria**'.

This section describes the basis for developing generic soil and groundwater acceptance criteria for gasworks sites in New Zealand. This section covers:

- ➔ development of generic soil acceptance criteria
- ➔ application of the generic soil acceptance criteria
- ➔ development of generic water acceptance criteria
- ➔ application of the generic water acceptance criteria
- ➔ development of site-specific acceptance criteria

Detailed information on the development of the generic acceptance criteria can be found in Modules 3 and 4 on disk.

4.2 Health-based generic soil acceptance criteria

4.2.1 Land uses

Land use is the key determinant of the extent to which site users may be exposed to soil contamination. The land uses selected for these guidelines are as follows:

Agricultural/ Horticultural	Agricultural/horticultural land use is deemed to include all agriculture and horticulture, particularly those related to food production. The general public is protected by ensuring that soil contamination does not give rise to a concentration in produce that exceeds a published Maximum Residue Level (MRL). However, MRLs have not been nominated for most contaminants of concern. Therefore consideration is given to the risk associated with consuming 100% of produce from a contaminated source. Consideration is also given to protecting the health of residents at any farm property, assuming that residents may be exposed by consuming homegrown livestock and produce, and through direct contact with contaminated soil. It is assumed that residences do not incorporate basements.
Standard Residential	This is based on a low density residential use, including rural residential use, where a considerable proportion of the total amount of produce consumed is grown at the site. No consideration is given to livestock uptake of contaminants. It is assumed that residences do not incorporate basements.
High Density Residential	For high density residential areas it is assumed there are limited soil access opportunities, therefore there is significantly less soil and dust exposure by ingestion compared with a standard residential site. This scenario does not include consuming of produce grown at the site.

Commercial/ Industrial	This scenario is based on exposure conditions at a largely unpaved industrial site where workers may come in direct contact with contaminated soil. This scenario does not consider workers actively involved in excavation or similar activities. Where a site is largely paved, higher contaminant concentrations may be acceptable based on site specific criteria.
Parkland/ Recreational	This land use reflects shorter exposure times but potentially on a regular basis. Opportunities for contact with soil will arise and children are the key concern in these areas.

4.2.2 Hazard identification

As discussed in Section 2.1, hazard identification is the first step in the risk assessment process, and involves collecting information about the nature and extent of contamination at the site.

4.2.2.1 Contaminants of concern

Gasworks site wastes are complex mixtures of hydrocarbons and other compounds. It is therefore impractical to rigorously assess the concentration of, and risk associated with, each of the specific contaminants. A group of compounds that are likely to pose the greatest risk to human health have been selected as indicators for assessing the overall level of contamination at a site. Table 4.1 summarises the contaminants of concern, and those which have been used for deriving the generic soil acceptance criteria.

Table 4.1 Contaminants of concern

Contaminant	Contaminants for Criteria Derivation
Carcinogenic PAHs • benzo(a)pyrene • benzo(a)anthracene • benzo(b)fluoroanthene • benzo(k)fluoroanthene • chrysene • dibenzo(a,h)anthracene • indeno(1,2,3-cd)pyrene **Non-carcinogenic PAHs** • naphthalene • fluorene • fluoranthene • acenaphthene • pyrene • anthracene • acenaphthylene • phenanthrene • benzo(g,h,i)perylene	benzo(a)pyrene[8] and non-carcinogenic PAHs
BTEX • benzene • ethylbenzene • toluene • xylene	benzene ethylbenzene toluene xylene
Phenolics	phenol cresol
Inorganics	free cyanide[9] complex cyanides
Heavy metals	none[10]

8 Carcinogenic PAHs may be considered in terms of a benzo(a)pyrene equivalent concentration, based on published Toxicity Equivalence Factors.

9 Cyanides are of most concern to human health.

10 Heavy metals concentrations are not the limiting consideration so generic acceptance criteria have not been developed for heavy metals.

4.2.2.2 Receptors

The key human receptors considered in developing soil screening criteria are presented in Table 4.2.

Table 4.2 Key human receptors

Site Use	Receptor Group
Agricultural/Horticultural	Child residents Adult residents/on-site workers Maintenance workers
Residential - Standard and High Density	Child residents Adult residents/workers Maintenance workers
Commercial/Industrial	Adult workers Maintenance workers
Parkland/Recreational	Children Adults Maintenance workers

4.2.3 Exposure assessment

Exposure assessment is a measure of the likely exposure of the receptors. It involves identifying complete exposure pathways, measuring contaminant concentrations and estimating the dose likely to be experienced by each receptor.

More information on exposure assessment can be found in Module 4, Section 4.2.3 on disk.

4.2.3.1 Exposure pathways

Soil contamination poses a risk to a receptor where there is potential for the receptor to come into contact with the contaminants i.e., an exposure pathway. There are a number of elements that make up an exposure pathway:

- source
- transport mechanism
- point of exposure
- exposure route.

The exposure pathways considered in developing the soil screening criteria are summarised in Table 4.3.

Table 4.3 Exposure pathways

Exposure Pathway	Agricultural/ Horticultural		Standard Residential		High Density Residential	
	Surface	Subsurface	Surface	Subsurface	Surface	Subsurface
Ingestion of contaminated soil	✖		✖		✖	
Consumption of produce	✖		✖			
Dermal absorption	✖		✖		✖	
Inhalation of volatiles (indoors)	✖	✖	✖	✖	✖	✖
Inhalation of volatiles (outdoors)	✖	✖	✖	✖	✖	✖
Inhalation of particulates	✖		✖		✖	

Exposure Pathway	Commercial/ Industrial		Parkland/ Recreational	
	Surface	Subsurface	Surface	Subsurface
Ingestion of contaminated soil	✖		✖	
Consumption of produce				
Dermal absorption	✖		✖	
Inhalation of volatiles (indoors)	✖			
Inhalation of volatiles (outdoors)	✖	✖	✖	✖
Inhalation of particulates	✖		✖	

More information on exposure pathways can be found in Module 4, Section 4.2.3.1 on disk.

4.2.3.2 Exposure concentration

To derive acceptance criteria, it is necessary to find the relationship between contaminant concentrations in soil and those in other media to which site users may be exposed. Estimating contaminant concentrations at the point of exposure is one of the most critical elements of the risk assessment. For most initial site assessments, it is assumed that contaminant concentrations will be measured in soil and groundwater.

Additional information on exposure concentration can be found in Module 4, Section 4.2.3.2 on disk.

4.2.3.3 Exposure estimation

Generic acceptance criteria for protecting human health, have been based on the Reasonable Maximum Exposure (RME) for a particular scenario (USEPA 1989). Detailed information on this scenario can be found in Module 4 on disk.

Additional information on exposure estimation can be found in Module 4, Section 4.2.3.3 on disk.

4.2.3.4 Exposure factors

The exposure factors adopted developing the soil acceptance criteria are consistent with those adopted for other New Zealand guidelines (for example, the Health and Environmental Guidelines for Selected Timber Treatment Chemicals). Table 4.4 presents the exposure factors used on the development of the soil acceptance criteria.

Table 4.4 Exposure factors

Exposure Factor	Units	Agricultural		Standard Residential		High Density Residential	
		Child	Adult	Child	Adult	Child	Adult
Body Weight	kg	**15**	**70**	**15**	**70**	**15**	**70**
Exposure Duration	years	**6**	**24**[11]	**6**	**24**[12]	**6**	**24**[13]
Exposure Frequency	days/year	**350**	**350**	**350**	**350**	**350**	**350**
Soil Ingestion Rate	mg/day	**100**	**25**	**100**	**25**	**25**	**5**
Area of Exposed Skin	cm^2	**2625**	**4700**	**2625**	**4700**	**2625**	**4700**

11 A total of 30 years if the adult has lived on site since birth
12 A total of 30 years if the adult has lived on site since birth
13 A total of 30 years if the adult has lived on site since birth

Soil Adherence	mg/cm^2	**1**	**1**	**0.5**	**035**	**0.1**	**0.1**
Produce Ingestion Rate	kg/day	**0.13**	**0.45**	**0.13**	**0.45**	**NA**	**NA**
Proportion of Produce Grown On site	%	**100**	**100**	**50**	**50**	**NA**	**NA**
Indoor Inhalation Rate[14]	m^3/day	**3.8**	**15**	**3.8**	**15**	**3.8**	**15**
Outdoor Inhalation Rate[15]	m^3/day	**3.8**	**20**	**3.8**	**20**	**3.8**	**20**

Exposure Factor	Units	Commercial/ Industrial	Maintenance	Parkland/ Recreational	
		Adult	Adult	Child	Adult
Body Weight	kg	**70**	**70**	**15**	**70**
Exposure Duration	years	**20**	**20**	**6**	**24**[16]
Exposure Frequency	days/year	**240**	**50**	**350**	**350**
Soil Ingestion Rate	mg/day	**25**	**100**	**50**	**10**
Area of Exposed Skin	cm^2	**4700**	**4700**	**2625**	**4700**
Soil Adherence	mg/cm^2	**1**	**1.5**	**1**	**1**
Produce Ingestion Rate	kg/day	**NA**	**NA**	**NA**	**NA**
Proportion of Produce Grown On site	%	**NA**	**NA**	**NA**	**NA**
Indoor Inhalation Rate[17]	m^3/day	**10**	**10**	**0**	**0**
Outdoor Inhalation Rate[18]	m^3/day	**10**	**10**	**1.1**[19]	**2.4**[20]

Additional information on exposure factors can be found in Module 4, Section 4.2.3.4 on disk.

4.2.4 Toxicity assessment

Toxicity assessment involves analysing the possible effects, and acceptable intakes of the contaminants. This information has been sourced from a number of references.

Information on the health effects summaries for gasworks contaminants can be found on in Module 4, Appendix 4A on disk.

4.2.5 Risk characterisation

Risk characterisation involves combining the outputs of the exposure assessment and the toxicity assessment to obtain an overall estimate of risk.

Calculating the level of risk that is acceptable or tolerable, in a regulatory sense, is essential to the risk assessment process. To further define the level of acceptable risk, chemical contaminants are divided into two broad groups according to their effects on human health - carcinogens and non-carcinogens.

4.2.5.1 Carcinogens (non-threshold[21])

14 Based on a 24 hour period
15 Based on a 24 hour period
16 A total of 30 years if the adult has lived on-site since birth
17 Based on a 24 hour period
18 Based on a 24 hour period
19 Average or 10 year old child and 1 year old child
20 Average or 10 year old child and 1 year old child

For carcinogenic contaminants an incremental lifetime risk of cancer, associated with exposure to a given chemical, is defined as follows (USEPA 1989):

Risk = CDI x SF

Where **CDI** = Chronic Daily Intake

SF = Slope Factor

The Ministry of Health has adopted an incremental cancer risk level of 1 in 100,000 per lifetime (1 additional case of cancer per lifetime) for the derivation of similar guideline values. For the derivation of the soil screening criteria for non-threshold carcinogens a cancer risk level of 1 in 100,000 per lifetime has been adopted in these guidelines.

4.2.5.2 Non-carcinogens

It is common practice to consider the exposure to each substance separately. For non-carcinogens this is done using the hazard quotient (HQ). A chronic hazard quotient is defined as follows (USEPA, 1989):

$$\mathbf{HQ} = \frac{\mathbf{CDI}}{\mathbf{RfDc}}$$

Where: **HQ** = Hazard Quotient

CDI = Chronic Daily Intake

RfDc = Chronic Reference Dose

Where sensitive population groups may be exposed, a HQ of 1 is appropriate to protect human health.

More information on non-carcinogens can be found in Module 4, Section 4.2.4.2 on disk.

4.2.6 Derivation of generic soil acceptance criteria

Contaminant concentrations corresponding to the target risk level have been estimated for each exposure route. The soil acceptance criteria developed are health based and are presented for each of the contaminants used for the derivation of the criteria, for specific exposure routes.

The generic health-based soil acceptance criteria are presented overleaf.

Details of the calculations underlying the health-based soil acceptance criteria can be found in Module 4, Appendix 4C on disk.

21 Non-threshold carcinogen - where the carcinogenic effects associated with the contaminant are evident from the lowest of doses, rather than from some threshold dose.

4.2.7 Summary of generic soil acceptance criteria

4.2.7.1 Agricultural/horticultural

Contaminant	Exposure Route					Protection of Plant Life[22]	Adopted
	Ingestion of Soil	Inhalation of Volatiles		Dermal Absorption	Produce Consumption		
		Surface	Sub-surface				
Phenolics							
Phenol	NA[23]			NA	33	(40)	**30**[24]
Cresol (o,m)	3900			3000	5	(5)	**5**
BTEX							
Benzene	520	2.3	2.4	190	0.3	(1)	**1**
Toluene	NA	200	210	NA	59	(130)	**60**
Ethylbenzene	7800	1000	1000	6000	51	(50)	**50**
Xylene	NA	150	160	NA	110	(25)	**100**
Non-carcinogenic PAHs							
Naphthalene	310	67	70	1200	1.7		**2**
Acenaphthene	4700			NA	86		**90**
Anthracene	NA			NA	870		**800**
Fluorene	3100			NA	81		**80**
Phenanthrene	2300			8900	88		**90**
Pyrene	2300			8900	150		**150**
Fluoranthene	3100			NA	320		**320**
Acenaphthylene	2300			8900	53		**50**
Carcinogenic PAHs							
Benzo(a)pyrene	2.1			3.8	0.2		**0.2**
PAH (Total)						(40)	**80**[25]
Inorganics							
Cyanide (free)	390			-	-	(20)	**400**
(complex)	980			-	-		**1000**

22 Dutch Intervention Values are presented for comparison only.
23 NA denotes calculated criterion exceeds 10000 mg/kg.
24 Lower concentrations of phenols may cause tainting of water in plastic pipes.
25 Based on estimated criteria for individual non-carcinogenic PAHs.

4.2.7.2 Standard residential (50% of produce homegrown)

Contaminant	Exposure Route					Protection of Plant Life[26]	Adopted
	Ingestion of Soil	Inhalation of Volatiles		Dermal Absorption	Produce Consumption		
		Surface	Sub-surface				
Phenolics							
Phenol	NA[27]			NA	65	(40)	**60**[28]
Cresol (o,m)	3900			6000	10	(5)	**10**
BTEX							
Benzene	520	2.3	2.4	380	0.5	(1)	**1**
Toluene	NA	200	210	NA	120	(130)	**130**
Ethylbenzene	7800	1000	1000	NA	100	(50)	**100**
Xylene	NA	150	160	NA	210	(25)	**150**
Non-carcinogenic PAHs							
Naphthalene	310	67	70	2400	3.4		**3**
Acenaphthene	4700			NA	170		**170**
Anthracene	NA			NA	1700		**1700**
Fluorene	3100			NA	160		**160**
Phenanthrene	2300			NA	180		**180**
Pyrene	2300			NA	310		**300**
Fluoranthene	3100			NA	650		**650**
Acenaphthylene	2300			NA	110		**100**
Carcinogenic PAHs							
Benzo(a)pyrene	2.1			7.5	0.4		**0.4**
PAH (Total)						(40)	**160**
Inorganics							
Cyanide (free)	390			-	-	(20)	**400**
(complex)	980			-	-		**1000**

26 Dutch Intervention Values presented for comparison only.
27 NA denotes calculated criterion exceeds 10000 mg/kg.
28 Lower concentrations of phenols may cause tainting of water in plastic pipes.

4.2.7.3 Standard residential (10% of produce home grown)

Contaminant	Exposure Route					Protection of Plant Life[29]	Adopted
	Ingestion of Soil	Inhalation of Volatiles		Dermal Absorption	Produce Consumption		
		Surface	Sub-surface				
Phenolics							
Phenol	NA[30]			NA	330	(40)	**300**[31]
Cresol (o,m)	3900			6000	52	(5)	**50**
BTEX							
Benzene	520	2.3	2.4	380	2.7	(1)	**1**
Toluene	NA	200	210	NA	590	(130)	**200**
Ethylbenzene	7800	1000	1000	NA	510	(50)	**500**
Xylene	NA	150	160	NA	1100	(25)	**150**
Non-carcinogenic PAHs							
Naphthalene	310	67	70	2400	17		**17**
Acenaphthene	4700			NA	860		**800**
Anthracene	NA			NA	8700		**9000**
Fluorene	3100			NA	810		**800**
Phenanthrene	2300			NA	880		**900**
Pyrene	2300			NA	1500		**1500**
Fluoranthene	3100			NA	3200		**3200**
Acenaphthylene	2300				525		**500**
Carcinogenic PAHs							
Benzo(a)pyrene	2.1			7.5	1.8		**1**
PAH (Total)						(40)	**800**
Inorganics							
Cyanide (free)	390			-	-	(20)	**400**
(complex)	980			-	-		**1000**

29 Dutch Intervention Values are presented for comparison only.
30 NA denotes calculated criterion exceeds 10000 mg/kg.
31 Lower concentrations of phenols may cause tainting of water in plastic pipes.

4.2.7.4 High density residential

Contaminant	Exposure Route					Protection of Plant Life[32]	Adopted
	Ingestion of Soil	Inhalation of Volatiles		Dermal Absorption	Produce Consumption		
		Surface	Sub-surface				
Phenolics							
Phenol	NA[33]			NA		(40)	**NA**
Cresol (o,m)	NA			NA		(5)	**NA**
BTEX							
Benzene	2100	2.3	2.4	1900		(1)	**2**
Toluene	NA	200	210	NA		(130)	**200**
Ethylbenzene	NA	1000	1000	NA		(50)	**1000**
Xylene	NA	150	160	NA		(25)	**150**
Non-carcinogenic PAHs							
Naphthalene	1300	67	70	NA			**70**
Acenaphthene	NA			NA			**NA**
Anthracene	NA			NA			**NA**
Fluorene	NA			NA			**NA**
Phenanthrene	9400			NA			**NA**
Pyrene	9400			NA			**NA**
Fluoranthene	NA			NA			**NA**
Acenaphthylene	9400						**NA**
Carcinogenic PAHs							
Benzo(a)pyrene	8.5			38			**7**
PAH (Total)						(40)	**9000**
Inorganics							
Cyanide (free)	1600			-		(20)	**1600**
(complex)	3900			-			**3900**

32 Dutch Intervention Values are presented for comparison only.
33 NA denotes calculated criterion exceeds 10000 mg/kg.

4.2.7.5 Commercial/industrial[4]

Contaminant	Exposure Route					Protection of Plant Life[34]	Adopted
	Ingestion of Soil	Inhalation of Volatiles		Dermal Absorption	Produce Consumption		
		Surface	Sub-surface				
Phenolics							
Phenol	NA[35]			NA			**-**
Cresol (o,m)	NA			NA			**-**
BTEX							
Benzene	5100	8.6	8.8	910			**8**
Toluene	NA	660	690	NA			**600**
Ethylbenzene	NA	3300	3400	NA			**-**
Xylene	NA	500	520	NA			**500**
Non-carcinogenic PAHs							
Naphthalene	8500	220	230	7600			**200**
Acenaphthene	NA			NA			**-**
Anthracene	NA			NA			**-**
Fluorene	NA			NA			**-**
Phenanthrene	NA			NA			**-**
Pyrene	NA			NA			**-**
Fluoranthene	NA			NA			**-**
Acenaphthylene	NA			NA			**-**
Carcinogenic PAHs							
Benzo(a)pyrene	20			18			**10**
PAH (Total)							
Inorganics							
Cyanide (free)	NA			NA			**NA**
(complex)	NA			NA			**NA**

34 Dutch Intervention Values are presented for comparison only.
35 NA denotes calculated criterion exceeds 10000 mg/kg.

4.2.7.6 Parkland/Recreational

Contaminant	Exposure Route					Protection of Plant Life[36]	Adopted
	Ingestion of Soil	Inhalation of Volatiles		Dermal Absorption	Produce Consumption		
		Surface	Sub-surface				
Phenolics							
Phenol	NA[37]			NA			
Cresol (o,m)	7800			6000			**600**
BTEX							
Benzene	1100	8.6	8.8	380			**8**
Toluene	NA	6600	690	NA			**600**
Ethylbenzene	NA	3300	3400	NA			**3300**
Xylene	NA	500	520	NA			**500**
Non-carcinogenic PAHs							
Naphthalene	6300	220	230	2400			**200**
Acenaphthene	9400			NA			**N/A**
Anthracene	NA			NA			**N/A**
Fluorene	6300			NA			**N/A**
Phenanthrene	4700			NA			**N/A**
Pyrene	4700			NA			**N/A**
Fluoranthene	6300			NA			**N/A**
Acenaphthylene	4700						**N/A**
Carcinogenic PAHs							
Benzo(a)pyrene	4.3			7.5			**2.7**
PAH (Total)							**4700**
Inorganics							
Cyanide (free)	780			-	-		**780**[38]
(complex)	2000			-	-		**2000**[39]

36 Dutch Intervention Values are presented for comparison only.
37 NA denotes calculated criterion exceeds 10000 mg/kg.
38 Includes consideration of maintenance workers.
39 Includes consideration of maintenance workers.

4.2.8 Ecological considerations

Ecological considerations are an essential part in assessing the impact of contamination at gasworks sites. However currently there is limited information on the impact of gasworks contaminants on ecosystems.

As discussed in Section 2.1.4. the Victoria EPA have released a *Draft National Framework for Ecological Risk Assessment of Contaminated Sites*. The framework is part of an overall national contaminated sites policy that revises the Australian and New Zealand Environment and Conservation Council *Guidelines for the Assessment and Management of Contaminated Sites* (ANZECC/NHMRC 1992). When more information on New Zealand species is available, this framework may be used to develop ecologically based generic acceptance criteria for New Zealand.

Where a site is ecologically significant it may be necessary to use published data on environmental soil quality guidelines. The Environmental Quality Objectives for the Netherlands, and the ANZECC Environmental Investigation Levels are presented in Appendix 4B of Module 4 on disk. Discretion should be exercised when using these numbers as they have not been developed for New Zealand conditions or species.

More information on ecological considerations can be found in Module 4, Section 4.3 on disk.

International ecologically based environmental quality objectives can be found on in Module 4, Appendix 4B on disk.

4.2.9 Aesthetic considerations

Some of the primary aesthetic concerns associated with contaminated soil include:

- odour
- discolouration
- changes in soil structure
- adverse effects on plant growth in a residential context.

Aesthetic impact is readily assessed on a site-specific basis, therefore generic acceptance criteria based on aesthetic impacts have not been developed.

More information on the impact of aesthetic considerations on gasworks sites can be found in Module 4, Section 4.4 on disk.

4.2.10 Application of generic soil acceptance criteria

Contaminated sites vary greatly in their characteristics, and in the risk they may pose to human health and the environment. Therefore it is important to adopt an approach which can be tailored to a particular site.

The use of generic acceptance criteria help and the following approach is proposed:

- The generic acceptance criteria provide an initial measure to compare with the site soil and water contamination
- This comparison will help determine the significance of the contamination, and may be sufficient to decide a preferred course of action, particularly if the contamination is minor or easily dealt with
- If the initial assessment indicates that the site contamination exceeds the generic acceptance criteria which could lead to a costly clean-up, more detailed field investigations and/or risk assessment may be justified (including incorporation of site-specific information in the risk assessment framework).

Generic acceptance criteria should not be regarded as fixed criteria that are not be exceeded. Frequently, site-specific considerations mean that the actual risk to human health and the environment as a specific site is substantially less than indicated by the preliminary criteria.

However, generic criteria can streamline the assessment process, so that resources are not wasted in rigorously assessing contamination that is likely to pose only a very low risk. Where the preliminary criteria are exceeded, consideration should be given to completing a more detailed, site-specific assessment of the risk.

When generic acceptance criteria are used to assess the significance of soil contamination judgement must be applied, giving consideration to issues such as:

- the uncertainty in derivation of investigation levels and in sampling and analysis, so that there is not necessarily cause for concern if the investigation level is exceeded slightly
- the exact nature of the land use
- the natural barriers to exposure (e.g. paving)
- the depth of contamination
- the potential for off-site transport of contaminants
- the distribution of contamination
- whether single or multiple contaminants are involved
- the form of the contaminant and its bioavailability, and
- the likely duration of exposure given activity patterns at the site and the likely fate of the contaminants
- the uncertainties associated with the sampling design and any errors associated with sampling methodologies.

Primarily the soil acceptance criteria presented in this section are based on protecting human health. Other considerations that must be addressed include:

- ecological impacts
- aesthetic impact (e.g. odour)
- protection of groundwater quality.

Each of these considerations depends on site-specific factors and is best addressed on a site by site basis.

In applying the generic soil acceptance criteria it is important to understand how to deal with exposure to multiple contaminants, variable contamination, contamination at depth, and protection of groundwater quality. These are discussed in detail below.

4.2.10.1 Exposure to multiple contaminants

Gasworks wastes include complex mixtures of contaminants, and site users may be exposed to multiple contaminants simultaneously. Where exposure to several contaminants occurs, there may be additive, synergistic or antagonistic effects. For most of the contaminants of concern, quantitative information on exposure to multiple contaminants is limited.

The following conventions may be useful in assessing exposure to multiple chemicals:

- ***Carcinogens***

  Assume cancer risks are additive (for assumed non-threshold carcinogens consider as per non-carcinogens).

- ***Non-carcinogens***

  If the site of the impact and mechanism of action are similar, assume effects are additive - otherwise effects are assumed not to be additive.

At gasworks sites, the primary concern is exposure to a complex mixture of PAHs. The additive effects associated with exposure to the carcinogenic PAHs is addressed by using Toxicity Equivalency Factors (TEFs) as follows:

- develop risk-based criteria for benzo(a)pyrene, then
- measure carcinogenic PAH concentrations in the soil, then
- estimate the benzo(a)pyrene equivalent concentration based on the measured carcinogenic PAH concentrations in soils and the published TEFs (refer Table 4.5), then
- compare the benzo(a)pyrene equivalent concentration with the generic soil acceptance criteria for benzo(a)pyrene.

Some of the non-carcinogenic PAHs also act in a similar way and therefore exposure should be considered to be additive as follows:

$$\frac{C_1}{T_1} + \frac{C_2}{C_2} + \frac{C_i}{T_i} < 1$$

where C_i = measured concentration of species '*i*'
T_i = acceptance criterion for species '*i*'

In practice the non-carcinogenic PAHs are not usually limiting in terms of health risk and therefore the requirement to consider additive exposure for these chemicals is lessened.

Table 4.5 Toxic Equivalence Factors (TEFs) For Carcinogenic PAHs

Chemical	Adopted[40] TEFs
Benzo(a)pyrene	1.0
Benzo(a)anthracene	0.1
Benzo(a)fluoranthene	0.1
Benzo(k)fluoranthene	0.1
Chrysene	0.01
Dibenzo(a,h)anthracene	1.0
Indeno(1,2,3-cd)pyrene	0.1

4.2.10.2 Variable contamination

The pattern of soil contamination for some contaminants, such as PAHs, can be highly variable. For example, when PAHs are present in a discrete phase as particles in the soil, analysis may indicate a highly variable soil concentration. It may then be appropriate to consider the average concentration when estimating exposure, and thereby accept some higher values in localised areas. Where sampling had targeted a small patch of contamination (e.g. a visibly stained area), the contamination measurements may not be typical of the wider area of interest.

In assessing the impact of contamination on human health, consideration may be given to:

- long-term chronic effects, for which the long-term average exposure to contamination is important
- acute effects, for which short-term (hours to days) exposure may be important.

Generally chronic effects occur at much lower rates of exposure than acute effects, and therefore chronic effects and long-term average exposure are usually the limiting considerations. Hence, the risk should be assessed on the average soil (or water) concentrations across the area site users may occupy, after allowance for the uncertainty associated with the measurement of contaminant concentrations (e.g. use 95% upper confidence interval on the mean, rather than a simple mean). Concern about acute effects provides an upper limit on soil concentrations with localised areas, or 'hot spots'.

40 USEPA (1993) "Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons.

The following principles may be used to apply the health-based preliminary soil acceptance criteria:

- The average concentration for exposure estimation should be the reasonable maximum average concentration (e.g. as the 95 percentile upper bound of the mean)
- The area over which the averaging takes place should be based on the proposed land use
- For example, for residential land use an averaging area corresponding to the area of a residential backyard may be appropriate
- For other uses, such as for playing fields, a larger averaging area may be appropriate, such as 50m x 50m. Use of land for a railway yard may involve an even larger averaging area
- Averaging should be used only where it can be expected that extreme concentrations of contaminants will not be present
- Situations where a large averaging area can be responsibly applied have the potential to save considerable remediation costs, especially for larger sites where contamination is patchy, and it becomes costly to identify all of the areas of localised contamination and clean them up
- The maximum contaminant concentration should not exceed a limit based on avoiding acute health effects, or chronic health effects should site activity patterns change so that site users spend a greater portion of their time in one section of the area over which contaminant concentrations were averaged. The National Environmental Health Forum (1996) indicates the maximum contaminant concentration should not exceed 250% of the acceptance criteria.

4.2.10.3 Contamination at depth

It is common for contamination to be present to considerable depth at gasworks sites (e.g. 3 to 8 metres). There is no formal policy in New Zealand on the depth to which clean-up may be required. Maximum depths of concern (with regard to the impact of soil contamination on surface use of the site) in the range of 2 to 5 metres have been nominated on different sites. The following principles for contamination at depth are drawn from current practice in the assessment and auditing of contaminated land:

- the depth of clean-up should be sufficient to avoid exposure or adverse effects to the site users under the range of activities which can be expected on the site, given the current land use and possible future land use (based on consideration of the surrounding land use and zoning of the site)
- the residual contamination will not affect persons or the environment off site (e.g. through groundwater contamination).

By way of illustration, activities involving excavation to depth on residential land, which is within a predominantly residential area may be restricted to one or more of the following:

- excavation for services (typically to 2m)
- excavation for sewers (to 3m - may vary depending on the location)
- excavation for a swimming pool (to 3m)
- excavation for single-level basement (to 3.5m), if such basements occur in the area.

These various activities can involve digging up material from a depth and spreading it over the site, and thus there is potential for future exposure to the contamination present at depth.

Based on the above depths it may be possible to allow significant contamination on a particular residential property to remain at or below 3 to 3.5 metres, especially if the nature, extent and concentration of the contamination would not pose a major concern in the future if the material were to be dug up unexpectedly.

An approach to assessing the significance of contamination at depth is outlined as follows:

- contamination in near surface soils (i.e. within the range typically encountered in day-to-day activities, say, 0 to 1.0 metres) should comply with criteria based on direct contact by humans, and a range of other considerations (e.g. plant life, aesthetics)
- contamination of soil between the depth commonly encountered (1.0m) and the reasonable maximum depth likely to be disturbed by excavation (3.5m) is assessed using criteria based on direct contact with contaminated soil in conjunction with an adjustment factor to reflect the probability that the soil would be excavated and spread around (may typically range from 2 to 10 metres, on a conservative basis depending on depth)
- contamination at depths greater than that likely to be disturbed by excavation should be assessed on the basis of protecting groundwater quality and protecting deep foundations from chemical attack.

The following considerations should be applied in addition to those outlined above:

- no soil within the zone where excavation is possible should pose an immediate (acute) concern to human health
- the depth of groundwater and geological characteristics of the site will dictate whether soil contamination at depth will affect groundwater quality
- where volatile contaminants may be of concern, the impact of volatilisation of contamination at depth and migration to indoor or outdoor air, and the consequent impact on human health or site amenity (odour) should be considered.

4.2.10.4 Protection of groundwater quality

The protection of groundwater quality, consistent with the current and likely future uses of the groundwater, must be considered when assessing the significance of soil contamination at a site. The relationship between soil contamination and groundwater quality is complex. Some of the considerations include:

- nature of the chemical (solubility, K_{oc})
- unsaturated zone characteristics (organic carbon content, permeability)
- recharge characteristics (e.g. net infiltration rate)
- aquifer properties (e.g. salinity, yield, hydraulic conductivity, hydraulic gradient)
- discharge characteristics (distance to point of discharge, nature of receiving water).

The soil acceptance criteria presented in this section do not consider the protection of groundwater quality. Rather, it is preferable to measure the groundwater quality directly when assessing the impact of soil contamination.

4.3 Generic water acceptance criteria

4.3.1 Groundwater and surface water uses

The significance of water contamination depends on the uses and values of the water resources which are to be protected. Defining the potential uses of the water is an integral step in assessing water contamination. The following uses have been adopted for developing generic water acceptance criteria:

- potable
- stock watering
- irrigation

- aquatic ecosystem protection
- primary contact recreation.

4.3.1.1 Potable use

Guidelines for potable water generally consider:

- the protection of public health
- the aesthetics, including taste and odour
- the protection of the water supply assets (for example, corrosion of pipework).

The New Zealand Drinking Water Standards (NZDWS) are used for most contaminants. However, in the absence of NZDWS values for any of the gasworks site contaminants, the risk assessment approach is used. The assumptions used in deriving the water acceptance criteria (Table 4.6) are the same as those used for deriving the NZDWS.

Table 4.6 Assumptions

	Assumption
Water consumption rate	2 L/day
Body weight	70 kg
Proportion of RfD[41] assigned to drinking water	0.1

More information on potable use can be found in Module 5, Section 5.3 on disk.

4.3.1.2 Stock watering use

Development of acceptance criteria for stock water use may include:

- protection of stock health via the consumption of livestock products
- protection of human health
- palatability of water for stock.

The derivation of the criteria for stock water used is based on protecting stock health. The derivation is similar to that provided for potable use.

Protection of stock health

Cattle have been selected as representative of livestock since they exhibit a relatively high water consumption per unit body weight.

The following are assumed in deriving the stock water criteria:

- cancer is not a relevant end point for cattle given their relatively short lifespan compared with humans
- full protection of sensitive sub-populations is not required.

More information on stock watering use can be found in Module 5, Section 5.4 and Appendix 5A on disk.

4.3.1.3 Irrigation use

41 For information on the reference doses (RfDs) for gasworks contaminants, refer to Appendix 3 of Section 5 on disk.

Water acceptance criteria for irrigation use are based on spray irrigation in a domestic setting. In this case, dermal absorption by children is considered to be the limiting factor. The following processes have been considered in deriving irrigation water criteria:

- contaminant loss by volatilisation due to spray irrigation
- inhalation of vapours and aerosols by site users
- dermal absorption and ingestion of water by children playing under sprinklers
- uptake of contaminants applied in irrigation water by plants, and consumption of homegrown produce (assume 100% of produce would be homegrown to protect the general public in the absence of Maximum Residue Levels (MRLs).

In deriving the criteria, the following conservative assumptions have been made:

- no leaching or volatile losses of contaminants once they have entered the soil
- no metabolism or degradation of contaminants within the plant.

More information on irrigation use can be found in Module 5, Section 5.5 and Appendix 5B on disk.

4.3.1.4 Aquatic ecosystem protection

Currently in New Zealand there is no definitive guidance on the protection of ecosystems. For this reason the ANZECC guidelines (ANZECC/NHMRC 1992) are used.

More information on aquatic ecosystem use can be found in Module 5, Section 5.6 on disk.

4.3.1.5 Primary contact recreation

There is limited published information on acceptable concentrations of contaminants in water to be used for primary contact recreation, such as swimming. The primary contact recreation criteria developed are based on a commercial swimming pool scenario assuming regular usage. Other values may be acceptable in the context of recreational bathing in a domestic swimming pool or bathing in surface waters, such as lakes, the sea etc.

More information on primary contact recreation can be found in Module 5, Section 5.7 and Appendix 5C on disk.

4.3.2 Summary of generic water acceptance criteria

Table 4.7 Acceptance criteria for water (mg/l)

Contaminant	Potable	Stock Watering	Irrigation[42]	Aquatic Ecosystem	Primary Contact Recreation
PAHs total		**3**		**0.03**	
Non-carcinogenic PAHs					
Naphthalene	**0.01**	**0.4**	**0.2**		**0.3**
Acenaphthene	**0.2**		**2.3**		**1.8**
Anthracene	**1**		**7.9**		**5.6**
Fluorene	**0.1**		**1.3**		**1.0**
Phenanthrene	**0.1**		**0.8**		**0.5**
Pyrene	**0.1**		**0.4**		**0.4**
Fluoranthene	**0.1**		**0.7**		**0.3**
Acenaphthylene	**0.1**		**1.0**		**0.7**

42 Based on domestic irrigation scenario. Dermal absorption by children playing is estimated to be limiting. Higher values may be acceptable in the context of use of water for agricultural irrigation.

Carcinogenic PAHs					
Benzo(a)pyrene	**0.0007**		**0.0002**		**0.00003**
BTEX					
Benzene	**0.01**	**10**	**0.3**		**0.3**
Toluene	**0.8 (0.024)**[43]	**20**	**13**		**15**
Ethylbenzene	**0.3 (0.002)**	**10**	**5.2**		**5**
Xylene	**0.6 (0.02)**	**18**	**8.8**		**8**
Phenolics					
Phenol	**2.1**	**60**	**44**		**150**
Cresol (o,m)	**0.18**	**5**	**4**		**10**
Cresol (p)	**0.0175**	**0.5**	**3.3**		**1.0**
Inorganics					
Ammonia	**1.5**				**1.8**
Cyanide as CN-					**5**
Free cyanide	**0.08**	**1**	**0.5**		
Complex cyanide	**0.07**	**2.5**	**1.2**		
Nitrate	**50**				
Nitrite	**3**				
Sulphate	**250**				

4.3.3 Application of generic water acceptance criteria

The water acceptance criteria have been developed principally on the basis of use. Water quality criteria may be sub-divided into direct uses (potable, stock watering) and indirect uses (ecosystem support) of groundwater.

4.3.3.1 Direct use of groundwater

If the aquifer is useable, groundwater contamination should be assessed on the impact on the potential use of the groundwater. Criteria pertaining to direct uses may be applied:

- to groundwater at the site boundary, or
- at some point further downgradient on the site, if use of groundwater in the immediate vicinity of the site is unlikely.

When assessing the risk consideration needs to be given to:

- assessing contaminant concentrations at the nearest current point of use of groundwater or
- assessing contaminant concentrations at the nearest point at which the water is likely to be used, and
- attenuation, degradation and dilution between the source and the point of use or potential use which may reduce the risk.

If groundwater use is probable and the acceptance criteria are exceeded at the point of use, groundwater clean-up, or removal of the source of contamination, could be required.

43 Values in brackets indicate aesthetic based limits.

4.3.3.2 Indirect use of groundwater

Aquifers that are not of sufficient quality or yield to be used directly may discharge into a river or other body of surface water affecting its quality. Where this happens, the water quality should be assessed against preliminary acceptance criteria for the protection of aquatic ecosystems, or for other uses of the river.

When assessing the risk consideration needs to be given to:

- dilution which may prevent the criteria being exceeded in the water column
- groundwater clean-up or interception and treatment if river flow is small compared with the groundwater flow
- localised mixing zones, if the groundwater discharges to a river or lake through defined seeps at or above the water surface
- if the groundwater discharges into a water body, turbulence will usually mix the water body rapidly and completely
- protecting benthic organisms in sediments
- dilution and attenuation between the point of measurement and point of impact.

4.4 Developing site-specific soil and water acceptance criteria

Where contaminant concentrations at a gasworks site exceed the generic acceptance criteria, more detailed consideration of the significance of contamination on a site-specific basis, including the development of site-specific acceptance, may be warranted.

The health and environmental impacts of soil and groundwater contamination depend heavily on site-specific conditions that affect the exposure of human and ecological receptors to contamination.

The development of site-specific soil acceptance criteria focuses primarily on the exposure assessment component of risk assessment. This step has the greatest potential for variation between sites. The toxicological assessment of contaminants is site independent, with the possible exception of synergistic and antagonistic effects, and the bioavailability effect (although this can be included in the exposure assessment component).

In developing site-specific acceptance criteria, the risk assessment procedures may be used in conjunction with site-specific exposure factors. Alternative site-specific exposure factors should be clearly documented and justified.

4.4.1 Refining exposure assessment

Site-specific information may be incorporated as follows:

- revising default exposure factors such as exposure duration, time spent outdoors, and soil ingestion rate, to reflect the conditions, receptors and activity patterns at the site being assessed, given the land use to be considered
- refined assessment of the fate and transport of contaminants, taking into account information regarding conditions at the site (e.g. soil type, depth to groundwater).

The significance of soil and groundwater contamination depends on contaminant concentrations in environmental media to which receptors (both human and ecological) may be exposed. The development of generic soil acceptance criteria involves simplified, conservative modelling of the volatilisation of contaminants and plant uptake of contaminants. Exposure estimates may be refined by directly measuring contaminant concentrations in relevant exposure media, including:

- indoor and outdoor air
- homegrown fruit and vegetables

- surface water and sediments (where discharge of contaminated groundwater is suspected).

Site-specific groundwater acceptance criteria may be developed by estimating attenuation between the site and the point of impact. Groundwater fate and transport modelling can be used to predict such attenuation. Groundwater fate and transport can be modelled at varying levels from simple analytical one-dimensional models accounting for advection and dispersion only, to detailed two- and three- dimensional numerical models including advection, dispersion, biodegradation, adsorption and separate phase organic liquids. Groundwater fate and transport modelling should be:

- undertaken at a level consistent with the available input data
- directed towards addressing specific issues of concern in the overall decision-making process for the site
- consistent with observations at the site over time (if possible).

5

Site management

5.1 Introduction

The objective in managing gasworks sites is to minimise the risk to human health and the environment. The range of site management options include:

- land use controls - controlling the use of land to avoid or limit the exposure to contaminants
- management controls - preventing activities that may result in unacceptable exposure
- intrinsic remediation - leaving the contamination in place and letting it degrade over time
- containment - placing a barrier between the contamination and receptors
- remedial treatment systems - removing the contaminants
- disposal to landfill - removing the contaminants from the site and placing in a secure landfill
- monitoring - monitoring the movement of contamination to determine whether migration could lead to unacceptable risk.

5.2 Site management issues

When managing a gasworks site the following factors need to be considered:

- underground structures, such as foundations, backfilled gasometers, tar wells etc., may be present on site
- backfill materials from the gasholders may need to be removed and replaced with engineered fill. Removing the backfill may pose a health and safety risk for site workers, as well as endangering the stability of the gasometer sidewalls
- most gasworks will be covered with a layer of uncontrolled fill that may be several metres thick. This fill may have to be removed because of its poor founding characteristics
- several gasworks contaminants will attack and degrade building materials if appropriate protection measures are not taken. These issues need to be discussed with the territorial authority
- dust and odours may be generated from work on site that could pose a human health risk and be a nuisance off-site.

5.3 Evaluation, selection and implementation of site management options

5.3.1 Evaluation

Site management options should be evaluated primarily on their ability to reduce risk, and then on their cost-effectiveness and the future site utility. The risks include those to site users, the general public, and the environment, during and after implementation of the management strategy.

Also important in evaluating site management options are:

- timing - if a site management option could take a long time to reduce contaminant concentrations, what are the risks to human health and the environment in the intervening period?
- failure - if the contamination is contained in situ, what will happen if the containment system fails?
- off-site disposal - if the contaminants are to be disposed of off-site what risks are associated with moving the contaminants?

5.3.2 Selection

The most appropriate management and remedial option(s) for a particular site should only be selected after the following have been determined:

- type and nature of contamination
- chemical and physical properties of the contaminants
- site-specific geology and hydrogeology
- lateral extent and depth of contamination
- potential for off-site migration, identification of migration pathways and receptors
- likely future use of the site and clean-up levels required
- resource consent requirements
- anticipated remediation project cost and project timing
- regional or national remediation and disposal infrastructure.

The site management options should also consider:

- workers
- the surrounding environment and neighbouring populations during and after implementation of the site management or remediation strategy
- future users of the site
- risks to human health and the environment when wastes are disposed off site.

No one single remedy represents the optimal selection for all sites or all gasworks contaminant waste streams. The various waste streams, including contaminated soil, tar waste, building rubble, and contaminated groundwater, may require different waste treatment or management strategies.

At each site, the remedial system design must:

- evaluate the practicality of using a specific remedial option
- attempt to evaluate the cost
- assess the problems that may be associated with that option
- assess the timeframe for the treatment.

5.3.3 Implementation

Some of the concerns associated with implementing site remediation or containment options include:

- generating odours and volatile emissions from excavated soil. Such releases would only be a health risk in the immediate vicinity of the works (i.e. primarily an occupational issue) but odour impacts may extend further off site

- generating contaminated dust through earthworks and traffic within the site area. Such dust releases may affect the public around the site
- air emissions resulting from soil or groundwater treatment systems such as thermal desorption, vapour extraction, and groundwater stripping
- transporting contaminated soils, tars and other waste materials through populated areas en route to landfill disposal or off-site treatment
- treatment of the wash water from truck movement off site
- occupational exposure to high level gasworks wastes.

A range of strategies is available to minimise some of these concerns, and any remediation strategy should aim to minimise the risks.

5.4 Legislation

5.4.1 The Resource Management Act 1991

The purpose of the Resource Management Act 1991(RM Act) is to promote the sustainable management of natural and physical resources. The RM Act is the principal statute for the management of land, air, water, soil resources, subdivision of land, the coast, and pollution control. It clearly sets out the resource management responsibilities of individuals, territorial authorities, regional councils and the Government. It sets up a system of policy and plan preparation and administration, including the granting of resource consents, which allows the balancing of a wide range of interests and values.

The provisions of the RM Act relating to discharges to land, air and water, and the control of the use of land, are of most relevance in managing contaminated sites. Section 30 of the RM Act requires regional councils to control discharges of contaminants into or onto land, air or water. They must also control the use of land in order to prevent or mitigate the adverse effects of the storage, use, disposal, or transportation of hazardous substances.

Section 31 of the RM Act requires territorial authorities to control any actual or potential effects of the use, development, or protection of land, which includes preventing or mitigating any adverse effects of the storage, use, disposal, or transportation of hazardous substances.

5.4.1.1 Resource consent requirements

A number of resource consents may be required for managing a contaminated site. They include:

- a discharge consent from the regional council for discharges into or onto land, air or water
- a land use consent from the territorial authority

Resource consents may be necessary at various stages in the site assessment and management process. It is important to contact the regional council and the territorial authority to determine what their particular requirements are, since these may vary throughout the country.

5.4.2 The Health Act 1956

Sections 29 to 35 of the Health Act provide that in certain cases where a nuisance is being caused within the meaning of the Act, an owner or occupier of the premises can be required to abate the nuisance. The primary responsibility for enforcing these provisions rests with the territorial local authority. In the event that the person creating the nuisance fails to comply with an abatement request there are legal remedies available.

A prosecution may be taken for failing to abate a nuisance. The prosecution may result in an order from a District Court judge requiring an owner or occupier of the premises to abate the nuisance effectively; prohibit the recurrence of the nuisance; both abate and prohibit the

recurrence of the nuisance; or to carry out specified works to abate or prevent a recurrence of the nuisance.

If there is default in complying with an order, the territorial local authority, or the Medical Officer of Health on behalf of the territorial local authority, may carry out any works at the expense of the owner and occupier. The costs are deemed to be a charge on the land.

In instances where, in the opinion of the Engineer or Environmental Health Officer of a territorial local authority, immediate action for the abatement of a nuisance is necessary, those officers may, without notice to the occupier, enter the premises and abate the nuisance. Any costs incurred are recoverable as a debt from the owner or occupier.

5.4.3 The Building Act 1991

The Building Act also addresses site contamination but only where there is an intention to carry out building work. The purpose of the Act is to provide controls relating to the building work and the use of buildings to ensure that buildings are safe and sanitary. Under the associated Building Code F1 "Hazardous Agents on Site", the objective is to safeguard people from injury or illness caused by hazardous agents or contaminants on a site. The Act requires that buildings shall be constructed to avoid the likelihood of people within being adversely affected by hazardous agents or contaminants on site. Code F1 requires that sites be assessed to determine the presence and potential threat of any hazardous agents or contaminants. The likely effect of these is to be determined taking account of:

- the intended use of the building
- the nature, potency or toxicity of the hazardous agent or contaminant, and
- the protection provided by the building envelope and building systems.

5.4.4 The Health and Safety in Employment Act 1992

The purpose of this Act is to prevent harm to employees and other people (e.g. visitors, contractors) while they are at work. All organisations are required to comply with the minimum standards outlined in the Act. To do this, employers need to take all practicable steps to maintain a safe working environment. These include:

- minimising, isolating, or eliminating the hazards (or potential hazards)
- training staff in safe work practices
- ensuring employees are not exposed to hazards in the course of their work
- informing staff of what to do in an emergency.

Employees are also encouraged to be responsible and look after their own, and others, safety and health at work. Ways of doing this include:

- observing safe work practices
- following instructions given to them by their managers
- taking responsibility for their own and others safety and health at work.

5.5 Site management options

The site management options considered in these guidelines include:

- land use controls
- management controls
- intrinsic remediation
- containment
- remedial treatment systems
- disposal to landfill

- monitoring

It is important to note that the regional council and territorial authority should be involved in the site management process as early as possible. They will be able to provide guidance and advice on regulatory requirements.

5.5.1 Land use controls

Controlling the future use of a site to permit only less sensitive uses is one way of avoiding or reducing exposure to contaminants, and therefore enables higher contaminant concentrations to remain on site e.g. redevelopment of a site for commercial use rather than residential use. If significant contamination is allowed to remain on site, it must be shown that the contamination will not cause an unacceptable risk to human health and the environment. The land use controls available include:

Land Information Memoranda & Project Information Memoranda	Land Information Memoranda, issued under the Local Government Official Information and Meetings Act 1987, and Project Information Memoranda, issued under the Building Act 1991, can be used to release information on site contamination to interested parties.
District plan	Structures or activities such as basements or pools, or their construction, can be controlled using the district plan.
Regional plan	Activities on a contaminated site could be controlled through a regional plan.
Memorandum of encumbrance	The memorandum creates a nominal mortgage in favour of the local authority and can be made binding on successors in title. It acts as a notification to those searching the title prior to purchase. The memorandum can be used as a condition of a resource consent.
Notation on a district plan	A notation can be placed on the district plan identifying a site as being contaminated. This can be initiated by an individual, company or council.

Another mechanism which is being considered is the use of notation on title, where a notation could be placed against the land title to identify the presence of contamination or to restrict the land use. No decision had been made by the Government on this issue at July 1997.

5.5.2 Management controls

Management controls are usually required where contamination is to be left on site at depth or under structures or paving. Controls are necessary to avoid uncontrolled excavation in the future which could result in the contamination being exposed. Imposing management controls acknowledges that the land is not suitable for uncontrolled use.

An example of a management control may be the requirement that any subsurface maintenance work that involves penetrating the pavement in a contaminated area is conducted in accordance with a designated protocol and that appropriate health and safety precautions are implemented. For example, any excavations and re-use or disposal of material must be done in accordance with management protocols.

Management controls will usually be placed on a site by a local authority.

5.5.3 Intrinsic remediation

Intrinsic remediation relies on natural processes to reduce the levels of contamination including:

- biological degradation of organic contaminants by indigenous bacterial populations
- volatilisation of volatile organic compounds and passive dispersion to the atmosphere

- dispersion and dilution of contaminants
- photodegradation of contaminants at the ground surface.

Intrinsic remediation is generally only applicable where human health and environmental risks are low and natural site conditions and processes result in the reduction of contaminants.

The key issues associated with the use of intrinsic remediation can be found in Module 6, Section 6.2 on disk.

5.5.4 Containment options

Setting up barriers to prevent migration of contaminants is widely used in the management of gasworks sites in the United States and Europe. Containment focuses on mitigating risk by placing a barrier between the source of contamination and the receptor, and avoiding further migration of the contamination.

Containment systems should have the following characteristics to be effective:

- provide sufficient separation of receptors and contamination to ensure risk reduction
- have sufficient durability to ensure the required performance
- control movement of contaminants
- reduce or prevent rainfall infiltration, which might otherwise increase contaminant leaching and off-site migration
- be resistant to erosion or slope instability
- be resistant to subsidence
- include appropriate management and monitoring systems.

Containment systems include:

- capping systems to reduce infiltration and direct contact between site users and the contaminated materials
- cut-off walls to prevent further lateral migration of contaminants
- interception trenches to reduce migration of contaminated groundwater
- construction of an on-site repository.

Module 6 on disk discusses the key issues associated with the use of

▲ capping systems (Section 6.3.1)

▲ cut-off walls (Section 6.3.2)

▲ groundwater interception (Section 6.3.3)

▲ on-site repositories (Section 6.3.4)

5.5.5 Remedial treatment systems

Remedial treatment systems include the following:

- off-site disposal, where the contaminants are removed from the site and disposed of in a appropriately designed landfill
- stabilisation and solidification, where both the mobility of the contaminants and the exposure pathways through which adverse effects can occur are reduced. This can be done either in situ or ex situ
- bioremediation, where the contaminant degradation is stimulated by the naturally occurring microorganisms in the soil and groundwater. Oxygen and nutrients are often added to stimulate biodegradation. This can be done either in situ or ex situ

- thermal desorption, where the soil is heated to approximately 450C in a rotary kiln or retort. The volatile contaminants are then destroyed in an afterburner
- incineration using mobile on-site incineration or cement kilns.
- soil washing, where a wash solution is injected into the soil to mobilise the contaminants. This can be done either in situ or ex situ.
- groundwater treatment either in situ or ex situ.

Module 6 on disk discusses the key issues associated with the use of

▲ stabilisation and solidification (Section 6.4.1)

▲ bioremediation (Section 6.4.2)

▲ thermal desorption (Section 6.4.3)

▲ incineration (Section 6.4.4)

▲ soil washing (Section 6.4.5)

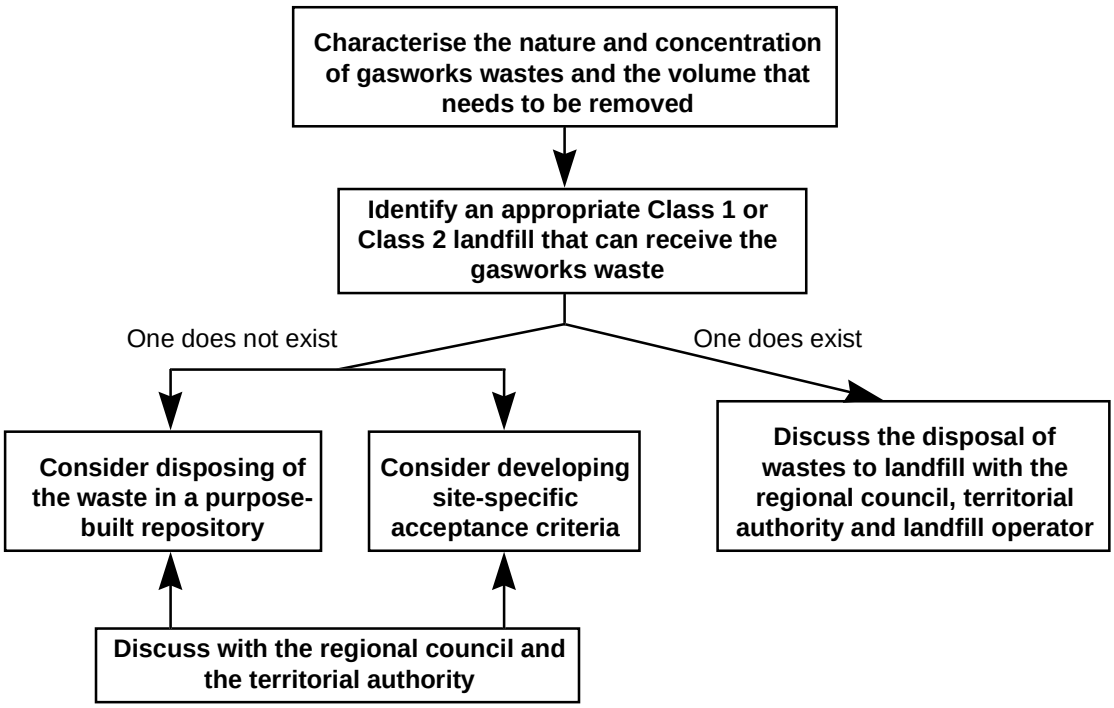
▲ groundwater treatment (Section 6.4.6)

5.5.6 Disposal of contaminants to landfill

The interim landfill acceptance criteria presented in the draft guidelines were based on preliminary leaching data from the US Electric Power Research Institute (EPRI). The Ministry for the Environment is currently trying to obtain the full data-set to develop a more robust set of numbers for landfill acceptance criteria. For this reason the preliminary landfill acceptance criteria are not provided in this document. These will be provided once the updated criteria from the full data set have been obtained.

5.5.6.1 General philosophy

Determining whether a particular gasworks waste can be landfilled, with minimal adverse effects, can be assessed using the simple steps as follows:



Additional information on the landfilling of gasworks contaminants can be found in Module 6 on disk, including:

▲ gasworks waste types, composition and nature (Section 6.5.1)

▲ landfill type and processes (Section 6.5.2)

▲ leachability testing (Section 6.5.3)

▲ landfilling of low-level gasworks wastes (Section 6.5.4)

▲ landfilling of high-level gasworks wastes in repositories (Section 6.5.5)

5.5.7 Monitoring

Monitoring programmes may be implemented at various stages of site management and for a number of reasons, for example:

- to establish seasonal variations in groundwater flow and quality and to assist in deciding whether remedial works are necessary, and to determine the most appropriate method of remediation
- to determine remediation progress, and to demonstrate that remedial works have been effective and there are no adverse effects
- to monitor dust prior, during and after remediation to ensure that adverse effects are not occuring.

The details of monitoring can be found in Module 6 on disk, including:

▲ post-investigation/pre-remediation monitoring (Section 6.6.1)

▲ remediation monitoring (Section 6.6.2)

▲ post-remediation monitoring (Section 6.6.3)

▲ monitoring determinands and frequency (Section 6.6.4)

5.6 Site management plan

The site management plan is a summary, operational document designed to focus attention on the key issues associated with site management. The site management plan should provide statements on the following:

- site history
- the condition of the site, including contaminants of concern
- impact on on-site and off-site receptors (both human and environmental)
- current restrictions regarding use of the site
- site management controls necessary in the context of the current or proposed site use
- deficiencies in the current information and the need for additional investigation to facilitate decision-making
- risk mitigation or management requirements for site redevelopment
- requirements for ongoing monitoring
- any ongoing regulatory controls and reporting requirements
- the definition of the responsibilities for implementing and auditing ongoing management controls and monitoring.

5.6.1 Ongoing site management

One of the most important functions of the site management plan is the definition of responsibilities for future management of the site. This may range from responsibility for the

design and implementation of further investigation or site remediation works, to responsibility for implementing an ongoing risk management strategy. Some of the important considerations in defining responsibilities include:

- responsibility for maintaining restrictions on site use, particularly following a number of sequential property transfers
- responsibility for ensuring controls on site activities are maintained (e.g. paving is maintained indefinitely as part of a medium or high density residential use, or personal protective equipment is worn by workers involved in sub-surface works)
- responsibility for maintaining and operating containment systems (e.g. capping, groundwater interception trenches)
- responsibility for conducting and reporting monitoring results.

6

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2. CCME (1994). Subsurface Assessment Handbook for Contaminated Sites. Report CCME EOC-NCSRP-48E, March.
3. Department of the Environment (1987). Problems Arising from the Redevelopment of Gas Works and Similar Sites (Second Edition). Prepared by Environmental Resources Limited.
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Guidelines for Assessing and Managing Contaminated Gasworks Sites in New Zealand

Part Two: Supporting Technical Information (on disk)

Part two: Table of contents

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1

An introduction to gasworks sites

Appendix

An introduction to gasworks sites

1.1 Introduction

The gas manufacturing industry is almost two hundred years old, having initially commenced in the UK in the early 1800s and subsequently spreading to Europe and North America. In the UK and US in excess of 1000 gasworks sites manufactured gas from coke, coal and oil up until the 1960s (Turczynowicz 1993), but only approximately 54 sites existed in New Zealand. The first of these gasworks began supplying gas in Auckland in 1865, and the last gasworks closed in 1988 in Hastings.

This module covers the following:

- ➔ gasworks processes
- ➔ major process units
- ➔ fate and transport or gasworks contaminants

Additional information on the characteristics of gasworks sites and the nature of contamination can be found in Section 1 of the Users' Guide, including:

- ▲ the suggested layout of gasworks sites (Section 1.3)
- ▲ the contaminants of concern (Section 1.4)
- ▲ the waste products associated with the contaminants (Section 1.5)
- ▲ patterns of contamination (Section 1.6)

1.2 Gasworks processes

There were three principal processes used for the manufacture of gas:

- coal carbonisation
- water gas or carburetted water gasification
- oil gasification.

1.2.1 Coal carbonisation

Coal gas was produced by heating coal in a closed vessel, known as a coal-carbonisation retort, until all the volatile materials were removed. The evolved gases were collected and purified prior to use, and the remaining coke was removed from the retort.

1.2.2 Carburetted water gas production

Carburetted water gas, or 'blue gas' was produced by passing steam through a bed of incandescent carbon. The resultant gas was then further reacted with liquid hydrocarbons to produce a gas of higher calorific value.

Carburetted water gas (CWG) production was often integrated with coal gas production, using coke from the coal-carbonisation process. The CWG process was useful as it was relatively quick to start up and shut down and produced a gas useful for blending with gas from other sources to obtain a consistent calorific value.

Carburetted water gas was introduced into most of the large gasworks in New Zealand by the 1950s but their use was generally confined to meeting peak loads by augmenting the normal stream of coal gas (John Pollard pers comm).

1.2.3 Oil-gas production

Carbon and oil were used in the production of oil-gas in either a one-shell or two-shell apparatus. The steps in a one-shell apparatus were:

- blow with air to burn off carbon
- heat carbon with air and oil

- steam generation of blue gas
- oil and steam generation of a mixture of gaseous hydrocarbons
- steam purging to remove the final product.

Oil gasification came into use in New Zealand in the early 1960s. This process progressively augmented coal carbonisation as the source of gas until the production of Maui gas in the late 1970s. The feedstocks for this process included naphtha, light distillate spirit and natural gas. Approximately six sites in New Zealand are known to have used oil gasification to supplement the production of coal-gas.

Table 1.1 outlines the residues resulting from the different gasmaking processes (Luthy et al 1994):

Table 1.1 Process residuals from the manufacture of gas from coal, coke, and oil

		Gas Manufacturing Process		
Process Residuals	**Physical form and principal chemical content**	**Coal Carbonisation**	**Carburreted Water Gas**	**Oil-Gas**
Ammonia liquors	Aqueous liquid: inorganics, phenolics	✓[a]	-	-
Ash and clinker	Solid: metals (and unburned coke or coal)	✓	✓	-
Carburetted water gas	Organic liquid: PAHs, BTEX[b]	-	✓	-
Coal tar	Organic liquid: PAHs, BTEX and phenolics	✓	-	-
Coke and coke breeze	Solid: pyrolysed coal	✓	-	-
Lampblack	Sludge: elemental carbon and oil tar	-	-	✓
Light oils	Organic liquid: BTEX	✓	✓	✓
Oil tar	Organic liquid: PAHs, BTEX	-	-	✓
Spent oxide or lime, wood chips (support media)	Solid: metals, cyanide, sulphur, tar	✓	✓	-
Tar sludges	Solid liquid: PAHs, BTEX	✓	✓	✓
Tar-oil-water emulsions	Aqueous and organic liquids: PAHs, BTEX	✓	✓	✓
Wastewater treatment sludges	Solids, aqueous, and organic liquid: inorganics, phenolics, PAHs, BTEX	✓	✓	✓

a "✓" indicates that residual was produced; "-" indicates that residual was not produced in substantial amounts

b PAH = polycyclic aromatic hydrocarbons; BTEX = benzene, toluene, ethylbenzene, and xylene

1.3 Major process units

1.3.1 Coal and coke production

Coal may have been stockpiled on site for considerable lengths of time during periods of low demand. The coke from the retort was stored either for use in a carburetted water gas plant (where such a plant was installed on site) or prior to being sold. Leachate from these sources contained heavy metals, sulphides and some hydrocarbons. Surface contamination by coal and coke may also be expected.

1.3.2 Retort houses

The retorts were loaded with coal and heated for several hours to drive off all volatile material, resulting in coke which was removed from the retort. The coal was usually heated with producer gas, developed on site by heating coal or coke with air. Coal gas and coal tar

condensed from the coal gas were also used for heating if markets were not available for these by-products. Solid process residuals included ash, clinker and coke.

1.3.3 Carburetted water gas plant

Carburetted water gas was produced cyclically by first blowing air through the coke bed, burning the coke and heating the bed, then cutting the air flow and blowing steam through the bed. The steam reacted with the carbon to produce a mixture of carbon monoxide and hydrogen which was of low calorific value. Thermal cracking of liquid hydrocarbons in the mixture, using heat recovered from the air blow, produced carburetted water gas which had a higher calorific value. Process residuals included clinker and waste water.

1.3.4 Oil-gas

The process of oil-gas production varied but generally consisted of catalytic cracking and steam reforming of a particular fraction from the distillation of crude oil, e.g. light distillate spirit, naphtha, or LPG, followed by another catalytic reaction to increase the H_2/CO ratio Blending with LPG or natural gas enriched the calorific value of the product gas. Purification was usually simpler than for coal gas, but sometimes carbon dioxide was removed by washing with potassium carbonate solution containing arsenic trioxide. Depleted nickel, uranium and vanadium catalysts were often left on sites where oil-gas production took place.

1.3.5 Gas purification processes

Purification was required to ensure that impurities did not foul the manufacturing and distribution systems. These impurities included:

- water and tars removed by condensation and separation
- naphthalene, light oils and ammonia removed by scrubbing
- hydrogen sulphide and cyanide.

1.3.5.1 Condensation and separation

Condensers were used to remove water and tars from the raw coal gas. Separation of the water and tar used a variety of procedures including tar extractors, electrostatic precipitators, steam distillation, centrifugation and dehydration. The tar may have been stored in a tar pit or tank prior to being further distilled into other products.

1.3.5.2 Scrubbing

Scrubbers removed naphthalene and light oils using other oil types for the process. Ammonia removal was usually by scrubbing with water, condensate or sulphuric acid. Phenol was recovered from the ammonia waste by washing with benzene or light oil, and then washing the benzene with sodium hydroxide resulting in a waste ammoniacal liquor. This process also recovered tar acids from the ammonia waste.

1.3.5.3 Oxide beds

Hydrogen sulphide and cyanide were removed either by the use of lime in the form of calcium hydroxide or by the use of iron oxide to produce ferric sulphide and ferric ferrocyanide complexes. Spent oxides formed a significant part of the waste stream and may have been used as fill around the site.

1.3.6 Gasholders

Gas was stored prior to distribution in gasholders or gasometers. These were set in large pits, filled with water to provide a seal, and were able to rise and fall with the change in volume of gas stored. Relief gasholders also stored raw gas from the retort house or the carburetted water gas plant prior to purification. The base of the gasholder accumulated tar and contaminated water over time. Tar was used as a lubricant for the gasholders, so it may be found spread around beyond the perimeter of the concrete bases. Gasholders were often located on the perimeter of the gas distribution system.

1.3.7 Other facilities

Tanks and pipework left on site after decommissioning may contain residual material. On site, old gas mains were sometimes used as convenient receptacles for waste holder oil and water during decommissioning. Off-site facilities such as mains, syphons and peripheral gasholders may also contain residual material. These are generally less significant sources of contamination and generally environmental assessments are confined to the actual site. However, such sources still need to be considered.

1.4 Fate and transport of gasworks contaminants

The processes affecting the fate and transport of contaminants associated with gasworks sites depend heavily on their chemical and physical properties, and the soil and groundwater characteristics of each site.

In the context of former gasworks sites, some of the important issues include:

- the potential for leaching of contaminants from soil to groundwater, which is highly dependent on soil type, depth to groundwater and the physical and chemical properties of the specific contaminant
- the presence and movement of free-phase organics (either as DNAPL or LNAPL)
- the erosion of surface contamination and its transport to adjacent surface water bodies, which is highly dependent on the nature of surface soils, proximity to surface water bodies, the nature of site drainage and the topography of the site.

Aging of contaminants will produce changes in the composition of contamination through loss of volatiles, separation of lighter and heavier fractions, biodegradation, and off-site transport of more water-soluble compounds (Turczynowicz, 1993).

The factors affecting the environmental fate and transport of gasworks contaminants are highly complex and involve a variety of both physico-chemical and biological processes. Physico-chemical processes include convective transport, dispersion, dilution and adsorption of the contaminants. Physical and chemical reactions, for example hydrolysis and oxidation/reduction, may affect the contaminant. Contaminants may be transferred between media via volatilisation, erosion, sedimentation and similar activities. Biological processes involve uptake, transformation and degradation by plants, aquatic species, microorganisms and other biota (Turczynowicz, 1993).

In soils, pH influences the chemical specification and mobility of contaminants. Acidification of soils can often occur at gasworks sites where soil pH can drop to less than 4, which is generally considered by soil chemists to be strongly acidic. This is due to the high concentration of elemental sulphur which can be associated with former sulphur purification processes and the effect of natural microbial action resulting in the formation of sulphuric acid in the soil.

General background information on fate and transport processes affecting gasworks contaminants is presented in Appendix 1A.

1.4.1 Volatile aromatics

Benzene and other volatile aromatics are amongst the most mobile of the organic contaminants found at gasworks. The high solubility of BTEX compounds often result in significant contamination of groundwater beneath former gasworks sites. (Turczynowicz, 1993).

Volatile contaminants, such as benzene, are generally found in soil samples in areas of heavy contamination, but in relatively low concentrations compared with inorganic and PAH levels. However, groundwater samples often contain proportionally higher concentrations of BTEX relative to PAHs. Groundwater samples taken off-site may also have elevated levels of the volatile components, (often when PAHs are not detected) indicating migration of these more soluble contaminants from a source on site.

Volatile aromatics are readily lost by volatilisation and therefore are not usually found at high concentrations in surface soils. Volatilisation from heavily contaminated soil at depth can result in the accumulation of volatiles in enclosed spaces.

Most of the volatile aromatics are readily degraded where conditions favour biological activity. For example, in aerobic aquifers benzene plumes arising from gasoline spills have been found to rarely exceed 100m in length.

1.4.2 Phenolics

Phenolics (phenol and cresols) are highly mobile in the soil environment, reflecting the relatively high solubility of these compounds compared to many other organic contaminants at gasworks sites. They are frequently detected as contaminants of concern in groundwater associated with former gasworks sites. At low to moderate concentrations phenolics are readily degraded in soils and groundwater where conditions favour biological activity.

Phenolics have a tendency to migrate through plastic pipework and have been associated with tainting potable water supplies where water passes through polyvinyl chloride (PVC) or polyethylene pipes installed in contaminated soil. Cresols, although not highly volatile, are odorous compounds and may be significant contributors to the odour encountered during excavations at former gasworks sites.

1.4.3 Polycyclic aromatic hydrocarbons

The polycyclic aromatic hydrocarbons (PAHS), with their higher molecular weight, are hydrophobic, and bind strongly to soil particles and have low solubility. These heavier PAHs are therefore generally found at higher concentrations near the source of contamination, particularly in surface soils. The lighter, more soluble PAHs, e.g. naphthalene, are frequently detected in groundwater, although volatilisation and leaching losses reduce their concentrations in surface soils (compared to the heavier PAHs).

PAH concentrations and the pattern of individual PAH compounds detected in stormwater and sediments tend to reflect the contamination in the surface soils, i.e. higher concentrations of the heavier PAHs than the lighter PAHs.

The heavier PAHs resist natural biological degradation and are consequently more persistent in the environment. Lighter PAHs such as naphthalene are readily degraded where conditions favour biological activity. The biodegradation of PAHs is heavily influenced by the extent to which they bind to the soil particles. Heavier PAHs move slowly through soils with high organic content, but the presence of surfactants or dissolved organic matter can increase their solubility and hence mobility and tendency to biodegrade (Turczynowicz, 1993).

Volatilisation can be a significant fate and transport mechanism for the lighter PAHs, accounting for considerable loss of naphthalene and methylnaphthalene (Turczynowicz, 1993).

1.4.4 Inorganics

Inorganic contamination at former gasworks sites usually occurs at or near the ground surface. The mobility of inorganic contaminants depends heavily on their solubility and factors such as pH, and the presence of other chemical species, which affect solubility and binding of contaminants to the soil.

Shallow soil contamination by inorganics can be extensive at former gasworks sites, however deeper contamination can be more variable, depending on the volume and mobility of the source and the presence of preferential migration pathways.

Cyanide, ammonia and sulphate are frequently detected in groundwater reflecting the mobility of these contaminants. Complex cyanides are not particularly mobile in the soil, however complex cyanides may break down to form free cyanide in the presence of UV light. Low-level free cyanide does not persist in the soil environment, due to chemical and biological reactions, although higher-level free cyanide can inhibit biological processes. Anaerobic conditions favour the formation of cyanide complexes.

Catalysts are inert and non-radioactive and may be buried on site.

1.5 References

1. Department of the Environment (1987). Problems Arising from the Redevelopment of Gas Works and Similar Sites (Second Edition). Prepared by Environmental Resources Limited.
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Appendix 1A

Fate and transport of organic contaminants in the subsurface environment

Forms of hydrocarbon contamination

Liquid phase

In the subsurface, hydrocarbons in liquid phase can occur in the following forms:

- mobile or free (free product) liquids moving down through the unsaturated zone or migrating near the top of the capillary fringe
- immobile residual liquids in the unsaturated zone
- immobile residual liquids trapped in the saturated zone
- free product on top of the water table (LNAPLs)
- free product below the surface of the water table (DNAPLs).

The particular form taken or the distribution between forms is dependent on the extent to which saturation of the pore spaces by hydrocarbons is possible and on the wetting characteristics of the geologic materials. Further, the degree of adsorption or absorption affects the contaminant plume and the extent to which the liquid is retarded and becomes immobile.

The amount of hydrocarbon product that can be sorbed is dependent on the residual saturation of the geologic formation, that is the amount of liquid the soil can hold. The residual saturation is dependent on:

- aquifer materials
- product viscosity
- the degree of water saturation
- the spill history
- rate and timing of the spill
- temporal and spatial extent of spill.

The degree of adsorption is dependent on:

- chemical equilibria
- soil organic carbon content
- product and soil chemical composition
- the existence of preferential pathways.

In the unsaturated zone the exposed surfaces of most geologic materials will be coated with a thin film of water, which acts as a wetting fluid. Liquid hydrocarbons can also act as a wetting fluid coating water film and soil particles as they migrate through the soil-water, intermediate vadose, and capillary fringe zones occur.

Dissolved phase

Dissolved phase hydrocarbons exist in the following areas:

- in water infiltrating through the saturated zone

- in the residual films of water covering solid surfaces or filling pore spaces (water subject to sorption) in the soil water, intermediate vadose, and capillary fringe zones
- in groundwater within the saturated zone.

Vapour phase

Hydrocarbon vapours in the subsurface can be present in:

- pore spaces in the unsaturated zone not already occupied by liquids. This is the predominant area of distribution for vapours and in these zones they are potentially highly mobile
- the free liquid hydrocarbon plume
- water in the underlying capillary fringe and saturated zone.

Vapour may become entrained in the liquids (either groundwater or free organics) as small bubbles. The bubbles are relatively immobile, but may move slowly with liquid flow, dissolve into the groundwater, or be released into the soil air.

Subsurface hydrocarbon migration

The mechanisms for migration of hydrocarbon contaminants (including tars and PAHs) within the subsurface is central to assessing the fate and transport of the contaminant. This section provides information on migration processes that should be considered in the assessment of gasworks sites.

A spill or leak of hydrocarbons will exist in the subsurface as free product, dissolved in groundwater and/or as a vapour. Some of the main processes affecting hydrocarbons in the hydrogeological environment include sorption (adsorption, absorption), chemical degradation, diffusion (dilution, dispersion), solvation, volatilisation, and biodegradation. These processes affect the rate at which the hydrocarbon contamination migrates through the subsurface by dispersing or retarding the hydrocarbon compounds.

Physical and chemical processes

The following are definitions of chemical and physical processes which will have an impact on hydrocarbon fate and transport.

Absorption is the physical filling of pore space by a fluid.

Adsorption involves surface to surface chemical bonding with organic compounds (organic carbon) and inorganic compounds (e.g. clay particles). It is affected by reaction equilibrium, the organic carbon content of the soil, chemical composition, and preferential pathways. Non-adsorbed compounds move with groundwater. A plume of adsorptive compounds will move more slowly than the groundwater.

The migration and adsorption potentials of various compounds can be compared through the use of K_{oc} (organic carbon / water partition coefficient) values. A K_{oc} value is a measure of the tendency of an organic compound to be adsorbed by the soil. The higher the K_{oc}, the higher its potential to be adsorbed and the lower its potential to migrate.

Diffusion is the process in which molecular or ionic constituents move under their kinetic activity with or without a concentration gradient. If there is a gradient, the rate of diffusion will be greater and will be from higher towards lower areas of concentration. Characteristics such as temperature or density can also drive diffusion.

Advection is the transportation of chemical constituents by groundwater movement and is dependent on geologic material hydraulic conductivity, and groundwater flow rates.

Dispersion is the spread of chemical constituents in directions other than those that would be expected from advection, such as sideways spreading due to flow divergence around particles

or formations, i.e. it occurs due to mechanical mixing during advection, and attractive forces between fluids and soil particles. Diffusion is a dispersive process.

Chemical degradation through abiotic transformations due to naturally occurring chemical reactions may result in degradation of a chemical. BTEX compounds seldom chemically degrade, but several halogenated compounds undergo hydrolysis and dehydrohalogenation reactions in groundwater.

Volatilisation is the change of a compound from a liquid state into a vapour or gaseous phase. This is one process by which compounds are transported away from the soluble groundwater plume, through the capillary fringe, and into the soil gas of the vadose zone. Under hydrogeological conditions the mass of a contaminant like benzene removed through this mechanism is expected to be very low (of the order of a few percent). Optimum conditions for volatilisation would be in shallow groundwater and at high temperature. Volatilisation can be very significant in the removal of hydrocarbons from shallow or exposed soils. Light hydrocarbons tend to be more volatile than heavier ones.

Biological processes

Biological processes which result in the degradation of hydrocarbon compounds can have a significant effect on these contaminants in the ground. They can therefore be an important consideration when assessing sites and remediation options.

Subsurface microorganisms are generally present in the form of a fixed biofilm on the surface of geologic material, and in some circumstances these organisms can use carbon and energy in organic chemical pollutants as a food source. This results in the biodegradation or biotransformation of the organic chemical.

Many microorganisms such as bacteria and fungi can metabolise the hydrocarbons from petroleum, either completely or partially. Microbial oxidation is dominated by bacterial action which appears to be species dependent.

Degradation of gasworks contaminants varies considerably. The lighter contaminants (including MAHs and lighter PAHs) are readily degraded and eventually converted to carbon dioxide and water. PAHs are degraded more slowly.

Biodegradation is dependent on the correct conditions being available for the growth of microorganisms. Some of the factors affecting biodegradation rates include:

- the composition and size of the soil microbial population
- the presence of a suitable and bioavailable source of energy (carbon)
- the presence of oxygen
- the presence of heavy metals and complex cyanides
- soil conditions, i.e. a pH between 6 and 9; warm temperatures; and high moisture content
- the presence of essential elements including: N, P, K, Ca, Mg, S, Fe, Mn, Cu, and Zn.

If any of these factors is missing or deficient it will limit microbial activity and significant biodegradation will not proceed.

At some sites, biodegradation of the BTEX constituents by indigenous microorganisms appears to be the primary mechanism of natural attenuation.

Biodegradation of aromatic compounds under aerobic conditions (> 1 to 2 mg/l dissolved oxygen) is a significant mechanism for the natural attenuation of BTEX compounds. Biodegradation half-lives for benzene can range from 15 to 160 days or more for varying conditions when modelled as a first order process.

Anaerobic biodegradation rates are much slower than aerobic rates and hydrocarbons may be degraded under anaerobic conditions. For this reason contamination may occur in areas where the available oxygen is depleted.

Liquid phase migration

To assess hydrocarbon contamination, an understanding of the transport mechanisms of the various hydrocarbon phases is required. Following a release, free liquid product will move, under the force of gravity, down through the unsaturated zone towards the water table. A significant proportion of the free liquid will be absorbed into, or become adsorbed to, geologic particles as the vertical (and lateral) migration continues. Lateral or horizontal spreading occurs within the unsaturated zone due to the divergence of flow around grains and because of the attractive forces between liquid hydrocarbons and solid granular surfaces.

Downward and lateral migration of the free liquid hydrocarbons will occur at different rates depending on:

- the rate and volume of the release
- the density of the hydrocarbons
- soil and rock porosities
- the attractive forces between soil particles and hydrocarbons
- the attractive forces between the water and the hydrocarbons.

Layers with low hydraulic conductivity will slow or stop downwards migration and promote lateral dispersion of hydrocarbon liquids. Water or hydrocarbons moving downwards can become perched above these layers. If there is sufficient volume of liquid, or the impermeable layer is tilted, the liquid will migrate around laterally discontinuous impervious layers, and continue downwards migration.

The volume of the release, the depth to the water table, and the sorptive capacities of the geologic materials will determine whether the release reaches the capillary zone.

When the free organic liquids that are less dense than water first reach the capillary fringe the organic liquid piles up on the capillary fringe, not the water table. This compresses the capillary rise, displaces water, and creates a free organic liquid plume. Lateral spreading of the plume near the top of the capillary fringe can occur more rapidly than the movement of groundwater below the water table. That is, the hydrocarbons spread more quickly than the rate of groundwater flow. This happens because the initial rate of migration is controlled by the pressure head of the free liquid and not by groundwater.

After reaching the capillary zone, the plume begins to migrate down gradient under the influence of gravity and groundwater flow. If the plume is small relative to the depth of the capillary zone, migration can be inhibited by the capillaries. The plume is the lateral extension of the original subsurface hydrocarbon release. The rate of downgradient movement varies depending on the volume of the spill, groundwater flow velocity, product lost from the plume due to phase transformation and retardation processes, and the hydraulic conductivity as the plume proceeds.

The size of the plume is affected by:

- release volume and rate
- porosities of soils and rocks
- hydraulic conductivity
- water table gradient
- the depth to the water table

Fine grained materials have larger surface areas which tend to retain more of the liquid, reducing the volume of free product. Coarse grained materials and formations containing

fractures and other secondary porosity features have smaller surface areas. Free organic liquids migrating through these materials are less likely to be immobilised by sorptive forces.

The water table gradient (and other factors affecting flow, such as permeability) also affects the shape of the plume. The steeper the gradient, the narrower the plume.

Fluctuations in the water table level promote vertical spreading of the plume. When the water table drops, free product associated with the capillary zone will descend leaving hydrocarbon liquid in the expanded unsaturated zone above the water table. This is known as smearing. Subsequent rises of the water table will cause the capillary fringe and associated product to move upwards. This may result in lateral spreading at a different level.

The water table fluctuations can affect the amount of product detectable, and available for removal, in monitoring and recovery wells by altering the quantity of liquid hydrocarbons that are mobile and can flow into a well. This leads to seasonal fluctuations in detectable organic liquid thicknesses in wells. Smearing will also result in a continuing source of dissolved phase contamination.

Free organic liquids can migrate into underground structures such as wells, underground service trenches and ducts, foundations, basements, and natural groundwater discharge areas like springs, creeks and rivers.

Dissolved phase migration

Free organic liquids are transformed into the dissolved phase when the liquid hydrocarbons contact subsurface water. This contact can happen when:

- water infiltrates through an unsaturated zone which contains residual adsorbed organics
- groundwater contacts a free organic's plume.

The concentration of dissolved organic compounds in water and the rates of transfer to the groundwater system are determined by:

- the depth to the water table
- soil and rock hydraulic conductivities
- recharge rates
- water table fluctuations
- groundwater velocity
- water temperature
- residual hydrocarbon concentrations
- the blend of hydrocarbon compounds in the free product liquid.

The processes of advection, dispersion, and diffusion control the movement of dissolved phase hydrocarbons. The effect of dispersion and diffusion is to dilute the contaminant concentrations in the dissolved hydrocarbon plume. Mechanical mixing is the main dispersive mechanism, chemical diffusion has minimal effect except in cases of very low hydraulic conductivity or very low flow velocities.

Dispersion increases in heterogeneous material due to changing groundwater velocities which result in greater mixing.

Vapour phase migration

Vapour phase migration is particularly important with respect to accumulation of organics in indoor air. Vapour phase organics in the subsurface result from the volatilisation of organics from:

- free liquid and residual liquid organics in the unsaturated zone
- dissolved organics downgradient from the release site.

The migration of vapour is controlled by many parameters including:

- Chemical and physical properties of the organic product:
  - Vapour pressure
  - Solubility
  - Concentration
  - Density
  - Viscosity
- Hydrogeologic properties:
  - Hydraulic conductivity
  - Depth to groundwater
  - Groundwater flow direction
  - Water temperature
  - Porosity
  - Moisture content
- Miscellaneous:
  - Barometric pressure
  - Rainfall duration and intensity
  - Man-made structures

In general, vapour tends to follow the most conductive pathways and travel from areas of greater to lesser pressure. Because organic vapours are generally more dense than air, they can accumulate in low areas such as buildings, sewers, underground service trenches and ducts, and other structures open to the atmosphere.

2

Site sampling procedures

Appendices

Site sampling procedures

2.1 Introduction

The section explains the design of sampling plans, sampling strategies that can be used at a gasworks sites, and the level of detail and care required for the collection of samples during the environmental sampling programme at former gasworks sites.

This module covers the following:

- ➔ sampling plan design
- ➔ sampling strategies
- ➔ general sampling requirements
- ➔ site assessment techniques
- ➔ typical soil sampling procedures
- ➔ typical groundwater sampling procedures
- ➔ typical surface water and sediment sampling procedures
- ➔ the use of blank and duplicate samples as quality assurance and quality control measures
- ➔ documentation and record keeping
- ➔ field cleaning procedures
- ➔ disposal of sampling wastes

Additional information site assessment can be found in Section 3 of the Users Guide, including:

- ▲ the site assessment process (Section 3.2)
- ▲ what media should be sampled for? (Section 3.3)
- ▲ the recommended approach to sampling (Section 3.4)
- ▲ site assessment techniques (Section 3.5)
- ▲ field sampling procedures (Section 3.6)
- ▲ the analytical programme (Section 3.7)
- ▲ the recommended approach to compositing (Section 3.8)
- ▲ reference analytical methods (Section 3.9)
- ▲ site assessment reporting (Section 3.10)
- ▲ health and safety issues (Section 3.11)
- ▲ example of a typical sampling plan (Section 3.12)

2.2 Sampling plan design

The sampling strategy should be developed on a site-specific basis depending on sampling objectives and site characteristics.

2.2.1 Risk-based sampling plan design

Risk-based sampling design focuses the investigation effort on the collection of information aimed to assess risk to human health and the environment. This may be undertaken at a range of levels, with associated degrees of uncertainty.

In addition to the usual sampling of soil and groundwater, consideration may be given to:

- increased sampling of surface soils, as these usually govern the risk to human health
- collection of information that allows for more accurate modelling of fate and transport of contaminants (e.g. soil and aquifer properties)
- sampling from adjacent surface water bodies
- sampling of biota (either terrestrial or aquatic) to assess uptake, and the risk to both human consumers and the local ecosystem
- sampling of indoor air or soil gas where emission of volatiles is of concern.

The direct sampling of media to which site users or ecological receptors may be exposed (e.g. ambient air, biota) rather than only soil and groundwater improves the reliability of risk estimates. Similarly, information that assists in fate and transport predictions is useful in refining exposure estimates.

2.2.2 Quality assurance/quality control framework

The quality assurance/quality control (QA/QC) framework for site assessment is designed to ensure that appropriate planning is undertaken before the assessment begins and that the information gathered as part of the assessment answers the correct questions. The essence of the QA/QC framework for site assessment may be summarised as follows:

- determine the objectives of the study, e.g. to determine whether a site is suitable for its intended use, or whether a site is contaminated or not
- identify the questions that need to be answered in addressing the objective of the study. For example, does the risk to human health exceed a nominated threshold?
- determine what information is required to answer the question and the accuracy and reliability required in the information to make reliable decisions regarding the overall study objective
- define the basis on which decisions are to be made.

Once the information has been collected it should be reviewed to make sure it complies with the requirements for quality (e.g. accuracy and reliability) and then used to make the required decisions. See Appendix 2A for more guidance on the quality assurance/quality control approach to site assessment.

2.3 Sampling strategies

The objective of sampling must be clearly identified before a sampling strategy is adopted. Sampling patterns can be:

- targeted or judgemental
- systematic
- stratified

As mentioned in the Users' Guide, a targeted sampling programme is useful where the site history and site features can be clearly identified for targeted sampling. Where site history is limited, the requirement for systematic sampling is increased so unknown areas of contamination can be identified.

2.3.1 Systematic sampling

- sampling points are usually regularly spaced in a square grid pattern (herringbone or triangular grids may also be used)
- where contamination points are known, the sampling pattern can be oriented to avoid over- or under- representation of these points

- systematic sampling should be used when the investigator has limited knowledge about the site
- systematic sampling is easily statistically analysed, increasing the confidence of locating a hot spot of a given size.

2.3.2 Targeted sampling

- sampling points are selected on the basis of the investigator's knowledge of the probable distribution of contaminants at the site
- the quality of the sampling depends on the skill and experience of the investigator and the amount of information available
- can be used for preliminary site investigations, and for detailed investigations in conjunction with the systematic sampling programme.

A targeted sampling strategy is only as good as the review of the site history on which it is based. If an area of potential contamination is not identified as part of the site history review, then it will not be addressed as part of a targeted sampling programme. Therefore, a targeted sampling programme should not be used where there is little or no site history to support the selection of sampling locations.

2.3.3 Stratified sampling

- site is divided into sub-areas based on factors including geological or geographical features, the likely spatial distribution of the contamination, former use patterns and intended future use
- each sub-area is considered as an individual site and sampling strategies for each sub-area are selected as appropriate
- targeted sampling may be used within the areas known to be a contamination source with systematic sampling across the general site area.

Additional information on statistical estimates can be found in the following document:

Draft Australian Standard (1996) Sampling of Soils, Part 1: Guide to the Sampling and Investigation of Potentially Contaminated Soil. (CH/28/96-6). August.

2.4 General sampling requirements

Some general requirements related to preserving the integrity of the samples, irrespective of the media being sampled, include:

- the sampling area should be isolated to minimise potential for cross contamination. An area should be established on which sampling equipment and containers can be placed without risk of contamination
- field personnel must wear clean PVC/latex gloves whilst handling sampling equipment and taking samples. Every member of field staff who will come into direct contact with the medium being sampled must change to a clean pair of gloves for collecting each sample
- care should be taken to avoid excess aeration of samples of soil, water or sediment
- to minimise the degradation of samples between the field and laboratory every effort should be made to keep the sample cool without having to freeze (keep under $<4^{o}C$ if possible) They should be transferred to the analytical laboratory as soon as practicable
- samples which are to be analysed for BTEX, should placed in a sealed head space vial, taking care to minimise the loss of volatiles (e.g. sampling to be

completed quickly, groundwater samples recovered using techniques that limit the aeration of samples)

- all samples should be transported to the laboratories by the field engineer, or a designated courier who must be documented in the chain-of-custody documentation.

2.5 Site assessment techniques

Information on soil, groundwater, and surface water and sediment sampling techniques can be found in Section 3.5 of the Users' Guide.

2.5.1 Subsurface techniques

2.5.1.1 Geophysical surveying

Geophysical surveying is a remote sensing tool that is able to provide a cost effective and efficient way of better defining the subsurface conditions at an investigation site. Geophysical methods are, for the most part, non-destructive and non-invasive, which can be extremely important for a site where little is known of past practices or locations of subsurface structures. A preliminary geophysical survey can locate subsurface structures that may otherwise present a health and safety hazard in drilling or trenching programmes designed on random or grid basis.

Advantages	Disadvantages
• rapid surveying over wide areas	• strong clay concentrations at or near the ground surface may significantly reduce penetration depth and signal clarity
• no ground disturbance, greatly reduces chances of occupational exposure	
• very detailed interpretation possible in the near surface zone generally of interest in gasworks investigations (0 to 10 metres below the surface)	
• ability to define the locations of important subsurface structures such as pits, tanks and pipes	
• direct detection of subsurface contaminants possible	
• initial interpretation possible in the field from continuous subsurface profiles, allowing modification of the survey to provide more detail on areas of interest	
• reprocessing of data may improve the location and interpretation of subsurface features	
• areas of interest can be located for targeted drilling thereby improving drilling efficiency and allowing for precautions to be taken when possible tanks/pits are to be drilled	

2.5.1.2 Electromagnetics

Electromagnetic (EM) fields generated above the ground are used to induce currents in the ground that, in turn, set up secondary EM fields that are detected at the surface. The strength of these secondary fields is dependent on the conductive properties of the subsurface materials and therefore allow the detection and mapping of lateral variations in subsurface conditions.

Advantages	Disadvantages
• relatively fast surveying over wide areas	• limited depth sounding ability
• relatively inexpensive	• instrument alignment during field surveys may be critical to interpretation
• no ground disturbance, greatly reduces chances of occupational exposure	• poor response in low conductivity ground
• targets near surface zone generally of interest in gasworks investigations (0.75 to 1.5m for EM38 and 3 to 6m for EM31	• plotting and contouring of data required for full interpretation
• ability to locate important subsurface structures such as pits, tanks and pipes	• may be reflected by cultural noise[1]
• direct detection of subsurface contaminants possible	
• initial interpretation possible in the field from continuous subsurface profiles, allowing modification of the survey to provide more detail on areas of interest	
• reprocessing of data may improve the location and interpretation of subsurface features	
• areas of interest can be located for targeted drilling thereby improving drilling efficiency and allowing for precautions to be taken when possible tanks/pits are to be drilled	

2.5.1.3 Magnetics

Magnetic surveying measures variations in the magnetic field at or above the ground surface which is affected by lateral variations in the concentrations of the magnetic minerals or man-made materials (pipes and tanks).

Advantages	Disadvantages
• good detection of ferro-magnetic (e.g. metallic) objects	• no depth sounding ability
• may detect lateral changes relating to varying amounts of magnetic minerals in the subsurface (i.e. differences from natural ground)	• data quality may be badly affected by natural magnetic storms
• no ground disturbance, greatly reduces chances of occupational exposure	
• may be used in conjunction with other methods to clarify nature of subsurface features	

2.5.1.4 Resistivity

Resistivity surveying relies on the injection of electrical current into the ground and the measurement of the induced potential differences between points at the surface.

The four methods outlined above are generally employed in conjunction with a well designed drilling or trenching programme to provide ground truth for the geophysical observations. An advantage in carrying out a geophysical survey is that the need for invasive testing can be greatly reduced by targeting anomalous features. Geophysical surveys also allow more confidence in the interpolation of drilling and trenching results across an entire site and reduce the possibility of missing discrete features such as buried tanks or pits.

[1] Geophysical noise caused by anthropogenic sources (e.g. car and pumps) as well as wind and moving trees

Advantages	Disadvantages
• very limited disturbance, greatly reduces changes of occupational exposure	• relatively slow and labour intensive surveying
• may be used in either profiling or sounding modes to detect lateral variations or depth structure respectively	• ground contact required by electrodes, necessitating some site disturbance
• ability to locate important subsurface structures such as pits or tanks	• processing of data required for interpretation
• direct detection of subsurface soil and water contamination possible	• may be affected by cultural noise

2.6 Typical soil sampling procedures

The number of samples required as part of any site investigation must be determined for each site, reflecting the objectives underlying the information collection (e.g. assessment of risk, or estimation of volumes). Notwithstanding this, in some cases it may be appropriate to design the investigations with a view to collecting information that may be of use in answering questions that may follow on from the current work.

The following points should be noted:

- the objective of the soil sampling should be to provide an estimate of the mean contaminant concentration in soil to which site users will be exposed. The programme should be designed taking into account the area in which site users may spend their time. (Averaging contaminant concentration across the entire site may over- or under-estimate the risk depending on whether site users spend more or less time in the contaminated areas)
- an estimate of the contaminant concentrations in surface soil is also needed to determine the risk associated with erosion and off-site transport of contaminated soil. Although sampling at a range of depths is required, greater attention should be paid to the surface and near surface soils.[2]
- the risk to site users is governed by contaminant concentrations in the near-surface soils and therefore attention may be focussed on assessing the average contaminant concentrations in these. Less information is needed on contaminant concentrations at depth, but sufficient information must be available to determine whether deep contaminated soil will continue to be an ongoing source of groundwater contamination, and what the risk will be if more highly contaminated material is excavated
- the soil sampling programme should also identify contaminant hot spots which have the potential to cause adverse health effects in the short term (e.g. acute health effects).

2.6.1 Outline of field investigation

- soil samples should be collected in accordance with a documented field sampling plan, and a health and safety plan
- drilling or excavation using a backhoe may be necessary if ground conditions make hand augering difficult, or where deep sampling is required
- the analytical programme must be developed to suit the site and should be documented in the field sampling plan. Many of these compounds may be present in trace quantities which require very sensitive laboratory analytical procedures. Consequently it is important that soil sampling procedures assume the quality of the samples

[2] Historically many soil sampling programs recover the first sample at a depth of 0.5 to 1.0 m which does not necessarily reflect the conditions to which site users are exposed. However in the context of site redevelopment, the surface soils are frequently removed or replaced or overlain with clean material.

- samples should not be composited in the field
- logs of soil conditions should be prepared on standard log sheets. The soil will be recorded using the Unified Method of Classification, using standard abbreviations. Particular note will be taken of the appearance, discolouration and odour. If contamination by volatile organic compounds is suspected, field screening of samples using an organic vapour analyser (e.g. photoionisation detector (PID)) may be warranted.

2.6.2 Hand auger sampling

The following procedures should be used when collecting shallow samples. If samples are collected from several positions within a given test location for later compositing by the laboratory, the same sampling tool and tray can be used, provided all loose dirt is removed from the tools. This does, however, reduce the integrity of individual samples, and limit the extent to which the sub-samples can be used as independent samples.

The following is an indicative procedure for recovery of soil samples by hand augering.

2.6.2.1 Shallow samples

- remove grass and other material from the area to be sampled by hand or with a clean trowel. Always rest the trowel on its wrapping
- remove soil from the sampling area with a trowel to a depth specified in the field sampling plan and place it directly in pre-cleaned glass sample jar
- depending on the analytical requirements, it may be appropriate to recover samples in more than one sample container, particularly where the analyses are to be completed by different laboratories
- if no further samples are to be taken at the location, replace any surface soil removed from the hole.

2.6.2.2 Deep samples

- unwrap a pre-cleaned auger or a pre-cleaned shovel or crowbar. Always rest the equipment on the wrapping whilst sampling
- remove the deeper samples by hand auger, taking care to minimise the possibility for cross-contamination. In order to minimise the likelihood of smearing or cross-contamination between sampling depths, recover the initial sample using a sampling spoon or auger. Advance the hole using the auger, then use a smaller diameter auger to recover the second sample
- backfill the hole. If the hand auger hole approaches the water table or passes through an aquitard (a soil horizon with low permeability) the hole should be sealed (e.g. using bentonite pellets) to minimise contaminant migration.

Recovery of samples by hand auger is difficult below a depth of approximately 2m, depending on soil type. The risk of cross-contamination also increases with sample depth when using a hand auger.

2.6.3 Boreholes

Boreholes may be drilled to sample soil and groundwater where hand auger techniques are not appropriate. The hollow auger drilling technique, with sample recovery using a split barrel sampler, is commonly used for sampling unconsolidated formations. Other drilling techniques include cable tool, solid auger, air rotary and air hammer. With the exception of cable tool, each of the techniques relies on the use of a separate sampling device (e.g. split spoon sampler) for recovery of the sample.

Techniques that involve the use of drilling fluids, or other substances that may contaminate the bore are not suitable for soil sampling. Care should be taken to reduce cross contamination from the oil often present as a mist in compressed air supplies.

Solid auger drilling may be acceptable where ground conditions are stable, but the risk of cross contamination is greater than with hollow auger drilling.

2.6.3.1 Drilling

- the drilling rig to be used must be in sound working order and free of oil leaks
- the drill string should be steam cleaned prior to commencing each borehole
- samples of sub-surface material are usually taken from the following depths (although samples may be recovered from other depths as required):

  0.5 metres

  1.0 metres

  2.0 metres or as listed in the sampling schedule
- samples of sub-surface material are recovered by driving a split barrel sampler or other similar sampling device into undisturbed material
- samples collected from air circulation or auger returns must be selected carefully to minimise the possibility of cross contamination. Results from such samples must be treated as indicative only, but it may be necessary to use them where other sampling methods are not possible (for example, in gravelly soils)
- where boreholes intersect the water table they must be sealed with cement grout or bentonite at the completion of drilling, unless they are used to establish a groundwater monitoring well
- a cleaning pad should be established on the site, where the drilling rig and other large equipment can be cleaned without risk of contamination to sampling locations. Power and water will need to be located nearby to enable use of a steam-cleaning unit
- the drilling rig should be decontaminated by steam cleaning on or, preferably, before arrival at the site. This should include all drilling equipment which will go into or be used near the borehole. The drilling rig and all drilling equipment will also be cleaned between boreholes according to the procedure outlined in Section 2.11.

2.6.4 Backhoe testpits

A backhoe may be used to recover soil samples where ground conditions make the use of a hand auger impractical. The following precautions will apply:

- the backhoe bucket and boom must be steam cleaned before each test pit and at the end of each day's work. All grease , oil and liquid tar must be removed
- the backhoe must be in good condition and free of oil or hydraulic fluid leaks
- all loose dirt will be removed from the backhoe bucket, following excavation to the target depth, and a sample representative of the material at the target depth will be recovered using the backhoe. Field staff must not enter a test pit greater than approximately 1.0 m deep under any circumstances, unless it has been made safe in accordance with relevant occupational health and safety regulations
- samples should be recovered at depths as specified in the sampling plan. Additional samples may be recovered at the discretion of the field engineer
- a sample should be recovered from the backhoe bucket using a cleaned sample spoon or trowel, taking care to select material that has not contacted the sides of the bucket. The sample should be placed in a cleaned glass jar with a Teflon lined cap where required. In some circumstances samples may be recovered directly, using a scoop rather than from the backhoe bucket

- all holes should be backfilled and reinstated near possible to original condition.

2.7 Typical groundwater sampling procedures

Particular consideration should be given to the specific hydrogeological conditions at the site when designing the groundwater investigation programme. The possibility of contaminant migration along preferential flow paths and the need to use techniques other than conventional groundwater monitoring bores should be considered for each site.

The potential for DNAPLs to be present at gasworks means there is need for:

- care in developing a conceptual model for the fate and transport of contamination. The model must take into account features such as confining layers and higher permeability lenses in the unsaturated and saturated zones which may influence the direction and rate of migration of DNAPLs
- care in undertaking field investigations to ensure that confining layers retarding the movement of DNAPL are not damaged during drilling, allowing contamination to migrate into previously uncontaminated zones
- monitoring of contaminant concentrations at various depths in the saturated zone, using a system of nested monitoring bores.

The presence of DNAPLs greatly complicates the assessment of groundwater contamination at gasworks sites, emphasising the need to develop a detailed understanding of the groundwater systems, and to avoid creating preferential pathways for transport of the contaminant through confining layers.

2.7.1 Outline of field investigations

The field investigations are designed to obtain representative groundwater information for the site in order to:

- define the geological profile and aquifer characteristics at the site
- assess the current nature and level of soil and groundwater contamination
- identify principal sources of contamination
- estimate rate and direction of contaminant flow, on and off site
- evaluate remediation requirements for the site
- identify likely zones of discharge
- identify vertical contaminant distribution/stratification.

The field investigations may involve the following:

- installing groundwater monitoring bores as indicated in the site-specific sampling plan
- recovering groundwater samples and measuring the depth to groundwater and separate phase hydrocarbons (if present) in all groundwater monitoring bores. If a separate phase is detected in a bore, groundwater samples are unlikely to be representative of the aquifer conditions, and therefore groundwater samples should not be taken
- measuring rising head permeability at the groundwater bores
- recovering soil samples from selected depths during drilling (refer soil sampling requirements).

Where dense non-aqueous phase liquids (DNAPLs) may be present, it may be necessary to measure the vertical migration of contaminants. Nested bores or several bores installed at the same location but screened across different aquifer intervals may be used to assess the

vertical extent and/or vertical stratification due to hydraulic characteristics of the aquifer as well as density effects.

2.7.2 Drilling

Material handling and quality control measures must be implemented to ensure clean drilling conditions and minimise down-hole contamination. Specific measures include:

- a cleaning pad should be established on the site, where the drilling rig and other large equipment can be cleaned without risk of contamination to sampling locations. Power and water will need to be located nearby to enable use of a steam-cleaning unit
- the drilling rig should be decontaminated by steam-cleaning on or, preferably, before arrival at the site. This should include all drilling equipment which will go into or be used near the borehole. The drilling rig and all drilling equipment will also be cleaned between boreholes according to the procedure outlined in Section 2.11.

Logs of the soil encountered must be prepared on standard borehole log sheets. The soil should be logged using the Unified Method of Classification and standard abbreviations.

Note the nature of possible soil contamination, including an assessment of appearance, discolouration and odour. Where contamination by volatile organic compounds is suspected, field screening of samples using an organic vapour analyser (e.g. PID) may be warranted. All information is to be recorded on log sheets.

All drill cuttings should be placed in sealable containers or a covered waste disposal skip on site for subsequent storage or disposal.

Preference should be given to techniques that do not introduce drilling fluids (including air). Although hollow auger drilling techniques are frequently employed, the selection of a technique should be based on the expected ground conditions and the requirements for bore construction. On those sites covered by concrete paving, drilling will be preceded by concrete coring of a size to accommodate both drilling activities and subsequent borehole completion, including installation of borehead protectors.

Accumulated drill cuttings should be removed from the borehead area as drilling progresses in order to prevent fallback.

The background monitoring bore(s) should be drilled first where possible.

2.7.3 Standpipe installation

- records should be kept on the standard record sheets. These should include all procedures used, materials used and the timing of the various stages of bore construction. Well completion reports may be used, containing information on borehole configuration, piezometer configuration (e.g. screen location, casing length, diameter etc.), placement of screen filter pack and borehole seals, and bore development and completion details. All data will be recorded directly in the field
- all materials placed in the hole must be free of any of the target contaminants
- before installation, standpipe materials should be steam cleaned with phosphate-free detergent, followed by a rinse in potable quality water and a final rinse with deionised water. After this the standpipe materials should be handled only by field personnel wearing clean PVC/latex gloves
- conventional solvent glues must not be used. Instead, mechanical screw fittings should be used on all casing and screen joints
- the length and placement of the screened section should be as documented in the field sampling plan. Excessively long (i.e. >3m) screens should not be used so the averaging affect of vertical groundwater quality entering the bore is minimised. If

significantly stratified groundwater quality is suspected or known to be present, nests of multiple short screened piezometers or piezometer bundles should be used

- groundwater monitoring bores are generally screened across the water table, allowing detection of floating product. The screen placement should account for anticipated fluctuations in the water table. Monitoring bores may be screened at discrete intervals beneath the water table where DNAPLs are suspected, or where the investigation objectives include the assessment of vertical migration of contamination
- following screen and casing installation, graded sand or gravel sized to match the aquifer materials, should be placed around the screen and to a height of approximately 200 mm above the uppermost screen slots. The bentonite seal should be placed directly above the filter pack and extend for a thickness of 1.0 m or more where possible. Where multiple (nested) piezometers are installed in the one hole, bentonite, or other low permeability seals, should be installed between each screened interval
- the filter material should be pre-washed and screened to eliminate foreign material and should be appropriately graded to the aquifer material wherever possible. Sand or gravel should be brought on site in bags and transferred directly from bag to hole
- holes should be backfilled above the bentonite seals to approximately 0.25 m below ground level. At the surface a concrete collar seal and steel protective covers will provide well-head security and prevent accidental damage. In most cases these covers will comprise cylindrical steel upstands fitted with lockable lids
- where vehicular traffic poses a problem, the installation should be fitted flush with the ground surface using a Gatic cover for protection. In this event, a sump should be provided around the top of the casing with subsurface drainage to prevent build up of drainage water around the borehead. All loose material should be removed from the borehead working area before the standpipe is installed to avoid it being dislodged into the open hole
- final levels of both screen filter packs and bentonite seals should be verified by lowering a probe down the space between borehole wall and casing
- monitoring bore basin and screens would typically be constructed from PVC pressure pipe of a nominal 50 mm diameter, but the size and material for the standpipe should suit the site conditions and the investigation objectives. Note that volatile organics are readily absorbed by polymeric material
- screen lengths should be determined on site after drilling has established preferred screen zones. Typically, slot sizes should be nominal 0.5 mm width with at least two rows of slots per screen length and average spacing of 1 cm between slots. Approximately 0.5 m of unslotted casing may be provided below each screen, to act as a sump to collect any fines that may pass through the screens. Monitoring bores should be terminated with a fitted end cap at the lower end and with a cap at the surface
- the precise diameter, material and configuration of monitoring bores should be adjusted to suit the site by a qualified professional. The above guidance is an indication of a typical installation.

2.7.4 Bore development and aquifer testing

- compressed air pumping, mechanical surging or other pumping should be used to develop the bore, depending on the aquifer characteristics. A gentle surging will help removal of any residual fines. Development pumping should continue until water clears of residual sediment and yields stabilise. Adequate development will

be verified by the stabilisation of water chemistry parameters including electrical conductivity and temperature. Records of the above should be maintained

- the selection of an appropriate pumping system for bore development depends on the nature of the aquifer. Care should be exercised, however, to ensure the aquifer is not aerated. Some alternative pumping systems include compressed air with 'U' tube system to avoid aeration, foot valve or ball valve pumps, bladder pumps, air driven displacement pumps, submersible pumps or similar mechanical pumping systems
- pumping systems that avoid aeration of the samples are preferred. Most mechanical systems will not aerate samples. Compressed air systems should be avoided, although some gas displacement systems are available which cause no gas/liquid contact
- when development pumping is completed, water levels will be depressed in the borehole. The groundwater recovery should be monitored by recording the rate of water level rise when pumping stops, and empirical analysis may be used to estimate permeability
- all items inserted into the bore should be decontaminated using high pressure hot water with phosphate-free detergent, followed by final rinse in potable quality water and distilled water.

Data recording should include:

- daily record of progress sheets, which should include details of all activities, equipment installed, times and durations
- pumping schedule, detailing pump operating periods and measurements or estimates of discharge volumes
- water level recovery data, detailing time, elapsed period since pumping ceased and water level. Water levels should also be recorded before starting pumping.

2.7.5 Groundwater sampling

- groundwater samples must be collected several days after the development pumping and recovery test phase. The borehole should be purged before taking any samples for analysis. During the purging process, check temperature, pH and electrical conductivity and continue pumping until these parameters stabilise. Parameters will be considered to have stabilised when the difference between three consecutive monitoring periods is less than 10%
- a minimum of three bore volumes should always be purged from each bore, however stabilisation of field monitored parameters should be the primary factor determining when the sample shall be taken. Records of temperature, pH and electrical conductivity measurements shall be maintained. Where the potential for intrinsic biodegradation is to be evaluated, dissolved oxygen should also be measured
- samples should be collected in a stainless steel or Teflon downhole bailer, or with an appropriate sampling pump (where disturbance of suspended solids must be minimised). The sampling pump should be decontaminated between sampling sites by cleaning as set out in Section 2.11
- hoses and other fittings that come into contact with the bore fluid need to be of the correct type to ensure adsorption is minimised. If these are not the correct type, residual contamination in sampling hoses may lead to false positive results. Alternatively, a disposable bailer may be used for each sample, provided the bailer material is compatible with the suspected contaminants

- care should be taken when sampling to avoid any opportunity for excess aeration of the sample.

Additional requirements are as follows:

- if a bailer is used, it should be lowered gently to avoid disturbance of any sediment that may still be in the bore and to avoid damage to the bailer or the rope. Samples should be recovered from beside the slotted section of the standpipe
- during sampling, measures should be taken to avoid contamination of sampling equipment. For example, before the commencement of sampling, a clean piece of plastic should be placed on the ground beside the well. All equipment should be placed on this sheet when not in use, and all cleaning should be carried out on the plastic sheet. As the bailer is removed from the well, take care to place the rope on the plastic sheet.
- water samples should be placed in screw capped containers which will be supplied by the laboratory. Bottles supplied should be polythene for metals and inorganics, and glass for organics
- water samples to be analysed for heavy metals may require filtration on site to remove particles that could affect the metal concentration. Water samples should be filtered before they are added to the container with the preservative. Take care to minimise aeration of the sample during filtration. Alternatively, if relatively clear and low turbidity samples can be collected, the sample may be recovered without filtration and preservation, provided it is recovered without aeration (e.g. place outlet of pump directly into the base of the sample container and fill, allowing the container to overflow for several volume changes before sealing).

2.7.6 Water level determination

Following well development, the standing water level should be measured. Allow sufficient time for stabilisation of water levels following development or other disturbance of the bore. The time required for stabilisation depends on the aquifer characteristics, and may range from hours to days.

A cleaned dipper should be lowered down the well to ascertain the water level. The depth to the top of separate phase hydrocarbon can be determined using either a mechanical or electrical measuring device. The depth to top of groundwater can be measured with a cleaned electrical dipper. The difference between the two is the thickness of a separate phase hydrocarbon. This thickness will be verified by bailing with a transparent bailer.

These instruments should be washed copiously with tap water and then rinsed with deionised water. If oil or grease is picked up on the bailer, additional washing with phosphate-free detergent will be required. The bailer may be rinsed with acetone to assist in removal of oil or grease, followed by rigorous rinsing with potable, then deionised water. Alternatively, a disposable bailer may be used.

Water levels should be referenced to ground surface and recorded to the nearest centimetre.

2.8 Typical surface water and sediment procedure

The surface water and sediment sampling programme should provide an estimate of contaminants leaving the site via drains, surface water run-off and groundwater discharge to surface water bodies.

2.8.1 Outline of field investigations

The field investigations are designed to obtain representative samples of water from waters receiving contaminants (receiving waters) in the vicinity of the site.

The field investigations may involve:

- recovery of water samples from selected locations in the receiving water body
- recovery of sediment samples from selected locations within surface water bodies in the vicinity of the site.

2.8.2 Stream sampling

- samples should be recovered from the stream at locations designated in the sampling plan
- stream samples should be recovered from below the stream surface in order to prevent accidental sampling of surface slicks. A suitable sampling device, able to recover samples from a designated depth and prevent entry of surface water, should be employed. Such devices are readily available. If possible, the sample should be taken directly into the sample container prepared by the laboratory
- sampling should commence at the location furthest downstream, working back upstream in turn, with the exception that background samples should be recovered first
- care should be taken when sampling to avoid excess aeration of the sample.

Additional requirements are as follows:

- the sampling equipment should be lowered gently to avoid disturbance of any sediment
- contamination of equipment should be avoided during sampling. For example, before the start of sampling a clean piece of plastic should be placed on the ground beside the sampling location. All equipment should be placed on this sheet when not in use and all cleaning shall be carried out on the plastic sheet
- water samples should be placed in screw capped containers prepared by the laboratory. Polythene bottles should be used for samples to be analysed for metals and inorganic constituents, and glass bottles should be used for samples to be analysed for organic compounds
- only those samples which do not have preservatives in the bottles should be filled to overflowing; those bottles with preservatives should be filled to maximum capacity but not to overflowing
- sample containers should be placed in clean polyethylene bags to minimise the potential for cross-contamination.

2.8.3 Sediment sampling

Sediment samples should be recovered from selected locations within streams, drains and other surface water bodies in the vicinity of the site, as designated in the sampling plan. Samples should usually be recovered from locations where sediment, associated with run-off from the site, is likely to collect, i.e. areas of lower flow velocity adjacent to, or downstream from the site.

Sediment samples may be recovered using an appropriate scoop or other sampling tool in the case of shallow water bodies, or using purpose designed sediment core sampling equipment for recovery of samples from deeper water bodies and where a vertical profile of the sediment is required.

Sediment samples should be placed in clean glass sample jars, as for soil samples. Where samples are recovered using core sampling equipment the sample may be retained in the coring equipment (e.g. plastic or aluminium tube), sealed and transferred to the laboratory for analysis.

- observations such as river gauge levels, colour, etc. must be recorded in the field book. In particular information on how the sample relates to the general stream or drain bed should be recorded
- with the exception of background samples (which should be recovered first where practical) sampling shall start at the furthest downstream location, and work back upstream.

2.9 The use of blank and duplicate samples as quality assurance and quality control measures

The quality assurance framework for site assessment includes the development of Data Quality Objectives (DQOs), the establishment of procedures to ensure compliance with the DQOs and the establishment of data quality indicators which measure compliance with the DQOs. The DQOs may address issues such as:

- sample location and frequency
- sample collection procedures
- sample handling procedures
- constituents to be measured
- analytical methods used to measure the constituents.

The two data quality indicators most often used in field sampling to measure compliance with DQOs are bias and precision.

Bias is defined as a systematic deviation (error) in data. Precision is defined as a measure of random variation in data. Bias can be assessed using a variety of blank sample types, discussed in Section 2.9.1. Precision is typically estimated using duplicate samples, discussed in Section 2.9.2.

2.9.1 Blank samples used to estimate sampling bias

Various types of blank samples can be used to assess the following sources of bias:

- the possibility that extraneous material has been introduced to the samples
- whether the site of interest is truly different from surrounding sites
- whether the sample matrix affects the sampling and analytical process.

Blank samples often used in site assessment are outlined as follows:

Field blanks samples are samples of analyte-free media similar to the sample matrix. They are transferred from one vessel to another or exposed to the sampling environment at the sampling site. They measure incidental or accidental sample contamination during the whole sampling and analytical process (sample collection, transportation, or storage at the laboratory).

Equipment blanks (or rinsate blanks) are samples of analyte-free media (usually high purity distilled water collected in a suitable container) that have been used to rinse the sampling equipment. These blanks are collected after equipment decontamination and prior to re-sampling to assess potential cross contamination between samples as a result of poor decontamination procedures.

Material blanks are samples of construction materials such as those used in groundwater wells. They are used to assess the potential contamination of samples by these materials.

Trip blanks (or transport blanks) are test samples of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. They are

used to measure cross-contamination from the container and preservative during transport, field handling and storage.

Background samples (or matrix blanks or field control samples) are samples of the media similar to the test sample matrix (soil, surface water, sediment etc.). They are taken near the time of sampling, and from a site where the analytes may be present at background levels. The background sample measures the background concentration of analytes of interest. Background samples assist in demonstrating whether the site of interest is contaminated or whether the elevated concentrations reported are occurring naturally.

Background samples can be taken from two different kinds of sites, "local control sites" and "area control sites".

Local control sites are usually adjacent to or very near the test sample sites. The following principles apply to their use:

- local control sites should be upwind or upstream of the sampling site
- when possible, local control site samples should be taken first to avoid contamination from the sample site
- travel between local control sites and sampling areas should be minimised to reduce contamination caused by people, equipment and/or vehicles.

Area control sites are in the same area, e.g. city or district as the sampling site, but are not adjacent to it. They are chosen where a suitable local control site cannot be found. All possible efforts should be made to make the sites identical except for the presence of the analytes of interest at the site under investigation. The principles applying to local control sites are relevant to area control sites.

2.9.2 Number and frequency of blank samples

It is advisable to take a range of the blank sample types described above. The number and frequency of blank samples to be collected depends largely on the data quality objectives (DQOs) developed in the planning phase of the site assessment (refer to Appendix 2B). For example, if only a general indication of the level of contamination is needed then fewer blank samples will be needed than for a highly reliable, quantitative estimate of the level of contamination.

Costs of analysis are determined by the number of blank samples analysed from the pool of those collected. Where these costs are high it may be possible to minimise the number of blank samples that require analysis. For instance, if the field blanks show no sign of contamination, then trip blanks can be discarded or stored as necessary. Similarly, if the primary samples show analyte levels below the limit of detection or below levels considered significant, then there is less need to run all blank types. This approach is especially relevant for groundwater samples where there are likely to be several types of blank samples.

It is recommended that the following be collected per day or per 10 samples (whichever is more frequent) per collection apparatus:

- one field blank[3]
- one equipment blank
- one trip blank
- one duplicate sample.

Background samples of every matrix type should be taken during sampling.

The following additional blank samples are suggested for groundwater samples:

- one standpipe material blank per batch of standpipe material

[3] A field blank is not usually taken for soil or sediment samples

- one filter pack (sand or gravel) material blank per batch of filter pack material
- one drilling equipment blank per day
- one sampling equipment (e.g. pump, bailer, etc.) blank per day or every 10 wells (whichever is the more frequent).

Although collection of a range of blank samples is needed to assess the potential for cross contamination of samples, it may be necessary to analyse only a proportion of the blank samples collected. Blank samples that give the best indication of whether any cross contamination may have occurred should be analysed, and other samples may be held for follow-up analysis should a problem be identified.

2.9.3 Duplicate sampling to estimate precision

Duplicate samples are independent samples which are collected as close as possible to the same point in space, and at the same time. They are two separate samples taken from the same source, stored in separate containers and analysed independently. The laboratory should have no indication of the association between the two samples. These duplicates are useful in assessing the consistency of the sampling technique and the precision of the analytical laboratory.

2.10 Documentation and record keeping

2.10.1 Documentation

The following documentation should be prepared before starting the field investigations:

- **Work plan or site sampling plan**
  Used to define the exact work requirements for a given site, including sample locations, depths, analytes, etc. Also used to document variations from the standard quality assurance procedures
- **Health and safety plan**
  Used to inform workers of potential physical and chemical hazards, health and safety responsibilities, normal work precautions, monitoring requirements and action plans. An example table of contents for a Health and Safety Plan is included as Appendix 2E.

These documents can be used to set out site-specific requirements regarding procedures, sampling and analysis of soils and other environmental media.

2.10.2 Record keeping

A field log book must be maintained by each investigation work group. The log book must be used to record general progress, any deviation from the QA, Work Plan or Site Sampling Plan, and Health and Safety Plans, any changed conditions, health and safety incidents and any other notable observations. These may include a record of unusual or unexpected sub-surface conditions, the presence of perched groundwater, odours or significant Photo Ionisation Detector (PID) readings. Photographing of material removed from bores and pits can be a useful way of recording information. This information should be recorded on the log sheets where relevant.

- Sampling Locations will be located with reference to the site plan and by measuring distances from permanent features identified on the site plan. All sampling locations will be referenced by using a system of unique numbers, for example, a location number and one of the following prefixes:

HA	Hand Auger
BH	Borehole
TP	Backhoe Test pit
GW	Groundwater Monitoring Bore

All sampling locations must be recorded. Testpits should be photographed with a measuring tape and the test pit number in the photo, where practical.

Groundwater monitoring bores may need to be professionally surveyed and marked on a base map using an appropriate co-ordinate system, particularly where bore locations cannot be reasonably defined by reference to site features.

- Sub-surface conditions at every borehole, test pit or auger hole must be logged on standard field log sheets. An example of the field log sheet is included in Appendix 2F.
- All depths must be referenced to the ground surface and recorded in metric units (metres). The elevation of each sample location, relative to an appropriate height datum, should be determined by suitably experienced field personnel taking levels.
- A record of all samples collected must be kept by the field supervisor. This record should incorporate the following information:
  - Job Number
  - Client/Job/Project Name
  - Sampling Location Number
  - Sample Number (as defined in work plan. The Sampling Location Number and Sample Number may be combined).
  - Sampling Depth (where appropriate)
  - Date of sampling
  - Initials of sampling personnel
  - Weather conditions if odour is likely to be problem.
- Each sample will be labelled with the following information, which should correlate with the record of sampling to be kept by the field supervisor:
  - Job Number
  - Client/Job/Project Name
  - Sampling Location Number
  - Sample Number (as defined in work plan. May be combined with Sample Location Number)
  - Sampling Depth
  - Date of sampling
  - Weather conditions if odour is likely to be problem.

    For duplicate samples (if the sample is a duplicate sample) and triplicate samples (if the sample is a triplicate sample), do not label the sample for lab as such but make sure this is recorded in the record of sampling to be kept by the field supervisor.

    The primary objective of labelling is to give each sample a unique and clearly understood identifier.
- Chain-of-Custody Documentation shall be prepared on site by the field supervisor before the samples are delivered to the laboratory. Its purpose is to trace sample possession from the time of collection through analysis. It is especially important in cases when court litigation might be necessary. A copy of a standard Chain-of-Custody form is included in Appendix 2F. A copy is retained by the field supervisor and a copy is delivered to the laboratory with the samples.

  Information to be recorded in the Chain-of-Custody will include:
  - Job Number
  - Client/Job/Project Name
  - Date of Sample Collection
  - Chemical Analysis Required
  - Preservation requirements and maximum holding times
  - Sample Numbers (as defined in work plan)

- Person/organisation delivering samples
- Person/organisation receiving samples
- Waste type

When the samples have been submitted to the laboratory, and the relevant sections have been signed by the person relinquishing and the person receiving the samples, a copy of the Chain-of-Custody form will be sent to the site assessor and the original Chain-of-Custody form will be returned with the certified results sheet.

If the Chain of Custody is extended to include the appropriate information it may also be used as the record of samples collected outlined above.

Record-of-Progress documentation should itemise all activities carried out, including details of equipment placed into the holes, decontamination procedures and sampling episodes. The Record-of-Progress documentation is particularly useful in tracing the installation and sampling of groundwater monitoring bores.

2.11 Field cleaning procedures

An area must be established on site where all sampling equipment can be cleaned without risk of contaminating areas to be sampled, or spreading contamination around or off the site. All field tools which are used for sampling and which come into direct contact with the material to be sampled, must be cleaned and stored as described in this section.

The following field cleaning procedures should be used for cleaning field sampling equipment (e.g. hand augers, trowels, split barrel samplers, bailers, sampling pumps):

- all field tools that cannot be washed in detergent solution should be steam cleaned before starting field sampling and before sampling at each location. It is not practical or safe to steam clean small items of equipment using commonly available steam cleaning equipment
- all smaller sampling equipment should be washed in laboratory grade phosphate-free detergent, rinsed with tap water, rinsed with analytical grade acetone, then rinse in high purity analytical grade deionised water
- all sampling tools should be stored in such a way as to prevent recontamination.

If a drilling rig or backhoe is used for soil sampling or groundwater bore construction, the drill string or backhoe bucket should be steam cleaned and the sampling equipment, e.g. split barrel sampler, cleaned as above. Wastes from equipment cleaning may be sent to the site waste treatment and disposal system, or put into drums for off-site disposal as appropriate. Where tools such as crowbars and shovels do not come into contact with the material to be sampled, a less rigorous cleaning procedure, such as that used for a backhoe (i.e. steam cleaning), may be used.

Where steam cleaning equipment is not available, suitable equipment may be hired. Steam cleaner and high pressure hot water washers are synonymous for the purposes of this document.

2.12 Disposal of sampling wastes

A range of wastes may be generated as part of any sampling programme. Examples of such wastes include:

- washwater and solid residues from cleaning procedures
- waste foil, cloth pads, plastic sheeting, etc. from cleaning and wrapping tools
- excess spoil from sampling locations
- groundwater from bore development and purging.

Each of these wastes may be contaminated and should be packaged and disposed of in accordance with health and safety, dangerous goods and landfill disposal regulations.

Contaminated wastewaters may be disposed of via the site wastewater treatment system, if available, subject to the necessary approvals. Planning for a field sampling programme should include planning for the disposal of waste materials.

2.13 References

1. CCME (1991) "Guidance Manual on Sampling, Analysis and Data Management for Contaminated Sites. Volume 1: Main Report". Canadian Council of Ministers of the Environment, Report CCME EPC-NCS62E, Winnipeg, December.
2. Gilbert, R.L. (1987) "Statistical Methods for Environmental Pollution Monitoring" Van Nostrand Reinhold, New York.
3. NSW/EPA (1995) “Contaminated Sites, Sampling Design Guidelines”. NSW Environment Protection Authority, EPA 95/59, September.
4. Smith F. et al. (1988) "Chapter 10: Evaluating and Presenting Quality Assurance Sampling Data" in Principles of Environmental Sampling , L.H. Keith ed., American Chemical Society.
5. Standards Australia (1996). “Draft Australian Standard, Sampling of Soils, Part 1: The sampling and investigation of potentially contaminated soil”.
6. USEPA (1991) "Description and Sampling of Contaminated Soils: A Field Pocket Guide" EPA/625/12-91/002.
7. USEPA (1991b) "Risk Assessment Guidance for Superfund, Volume 1, HHEM, Supplemental Guidance, Standard Default Exposure Factors".

Appendix 2A

Quality assurance/quality control approach to site assessment

Overview

Site assessment planning should be based on quality assurance/quality control (QA/QC) principles. This appendix shows the amount of planning needed, and focuses on the way decisions should be made. It presents a formal QA/QC process with defined steps and documents. Although this formal process may not be necessary for every site assessment, a similar level of planning and information collection is essential.

Regardless of the size or complexity of the site contamination or waste evaluation problem, management decisions must be based on information of known quality. Quality assurance must be an integral part of the site assessment process. The basis of a quality assurance/quality control (QA/QC)[1] programme is ensuring that data produced from any part of a study designed to evaluate the problem, is sufficient to support the decision-making process. Every "problem" evaluation should follow a pattern of development similar to that shown in Table 1.

Table 1 Steps followed to ensure the decisions made to solve a problem are based on data of known quality

	Step
1	Define the goal or purpose of the study and how it will be achieved
2	Define the data quality objectives that specify the quality of the data that is acceptable
3	Design a QA plan defining overall QA policy
4	Design a QA plan detailing specific QA and QC requirements for the study
5	Undertake study based on the stipulations established in the previous steps
6	Evaluate data and make decisions

Decision-making may not always require information of the best possible quality. For example, a preliminary investigation of a potentially contaminated site might use a low-cost screening analytical technique, which although sensitive, might respond simultaneously to a number of different species, including the one of immediate interest. This technique would have lower specificity and accuracy, with a tendency for over-estimation of results (have a positive bias). From the outset of the study the investigator should be aware of the limitations of the technique. Its application should be appropriate to the objectives of the study, (e.g. the rapid, cost-effective assessment of a potentially contaminated site to establish if contaminant levels are likely to give rise to an unacceptable human health risk).

For a preliminary screening study, data quality objectives should be defined to overestimate risks. The QA/QC plans would evaluate the techniques' bias by comparing the results with those of a reference method or the analyses of a standard material. Consequently the final evaluation of the study results would be based on a defined set of objectives and on data of known quality.

[1] Quality assurance (QA) and quality control (QC) are concepts which have some degree of overlap. Quality assurance is a system of activities that assures the producer or user of a product or a service that defined standards of quality are met with a stated level of confidence. Quality control differs in that it is an overall system of activities that controls the quality or a product or service so that it meets the needs of users. Quality control consists of the internal day to day control and assessment of measurement, whereas quality assurance is the management system that ensures that an effective quality control system is in place and working as intended.

Similar considerations can be applied to sampling strategies, allowing site investigations to achieve defined objectives cost effectively.

The individual steps shown in Table 1 are discussed in more detail in the following sections.

Defining the goal or purpose of the study

The study goal will usually be defined in terms of a response to a regulatory requirement or potential regulatory requirement (e.g. clean-up notice), commercial or business decisions (sale of land), or assessment of liability for due diligence or accounting purposes.

Before the study starts, its goal or purpose should be defined concisely, but with sufficient detail to allow all parties to understand it clearly. An example goal may be to determine the suitability of a particular site for redevelopment for unrestricted residential use, the requirements for which are defined under local legislation, regulation or guidance.

In Australia, the Australian and New Zealand Environment and Conservation Council (ANZECC) Guidelines set out the general requirements for the assessment and management of contaminated land, however more detailed requirements are established on a State level (e.g. Victorian Environment Protection Authority auditing system). In New Zealand most studies will be directed towards fulfilling the requirements of the Resource Management Act (1991) and to a lesser extent, the Health Act (1956). The Resource Management Act is based on the philosophy of sustainable management and is an effects-based legislation. The Resource Management Act requires that processes (current or historical) shall not cause an actual or likely adverse effect on human health or on the environment downstream of the operation[4].

Guideline levels, where applicable, are an essential component of any study and must be incorporated into study goal statements at an early stage. Studies which are part of due diligence audits, transfer of land or in quantifying liability, (whilst initiated in a legal, commercial context), must be designed with reference to the relevant local legislation or regulations.

Data Quality Objectives

Data Quality Objectives (DQOs) describe the level of uncertainty that a decision-maker is willing to accept in results derived from environmental data. DQOs then allow for data of known quality to be generated as part of the study.

DQOs may be qualitative or quantitative. Quantitative DQOs contain quantitative terms such as standard deviations, percent recoveries and concentrations whereas qualitative DQOs are descriptive and may refer to specific actions that would be taken in a particular instance.

DQOs are developed for a study by stepwise consideration of relevant issues. They might involve the following decision-making stages:

- state the problem to be resolved
- identify the decisions that need to be made
- identify the inputs to the decision
- narrow the boundaries of the study
- develop a decision rule
- develop uncertainty constraints
- optimise design for obtaining data

One advantage of the DQO approach is clear communication at the beginning of the study between the teams involved with study management, sampling, analysis and data interpretation. The development of DQOs may involve completion of a mental checklist for a relatively simple site, or preparation of a separate scoping document for a large and complex investigation. They are a part of good project management and become part of the record of due diligence.

[4] Note also, the RM Act S.107(g) refers to “Any significant adverse effects” on aquatic life.

Once programme goals and DQOs have been appropriately defined, a programme must be designed to meet them. QA and QC measures should be used to monitor the programme and to ensure that all data generated are suitable for their intended use.

A useful approach for developing a manageable structure for appropriate QA/QC measures is the preparation of separate QA programme and QA project plans. Example DQOs are presented in Appendix 2B. Where possible reference has been made to later sections in this document which illustrate aspects related to specific points in the QA project plan.

Data quality indicators

A data quality indicator is a property that can be used to assess the quality of data acquired in a sampling programme and may be used to assess whether data quality objectives have been met. Quantifying or describing data quality indicators dictates many of the quality assurance procedures that will be adopted during the sample design, collection and analysis programme. Data quality indicators therefore provide the conceptual bridge between specifying the data quality required and measuring it through quality assurance practices (such as the acquisition of blank samples, field replicate samples etc.).

The United States Environment Protection Agency (USEPA) lists five data quality indicators that it considers important in contaminated site assessment: precision, bias, representativeness, completeness and comparability.

Precision - can be described as a "measure of mutual agreement among individual measurements of the same property". More simply, it can be thought of as a measure of how greatly an analytical result varies on repeated analysis of a sample. It is best expressed as a standard deviation or variance. In contaminated site sampling components associated with sampling design, sample collection and analysis will contribute to the overall estimate of precision. It is not possible to estimate the contribution from sampling design. Combined sampling and analytical precision can be estimated by collection and analysis of duplicate (i.e. co-located) samples. Analytical precision alone can be measured by repeated analysis of laboratory replicated samples.

Bias - can be defined as "the degree of agreement of a measurement (or an average of measurements) with an accepted reference or true value". If "X" is the measurement value and "T" the true value then bias is often expressed as the difference between the two values (X-T), or a difference as a percentage of the reference or true value (100 [X-T]/T), or as a ratio (X/T).

For contaminated site evaluation, as with variance, the bias parameter may contain components from sample design, collection and analysis phases. Again the contribution from sampling design cannot be estimated. However, combined sampling and analytical steps bias can be estimated by using collected samples spiked in the field. In this process the field sample is sub-divided in the field, at least one fraction is spiked with a known quantity of the target analyte and each fraction is analysed. The percent recovery of the spike is calculated. By combining several such results an average percent recovery or bias is obtained (i.e. average percent recovery - 100%).

Representativeness - expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point or an environmental condition.

When estimating an average concentration over some region, representativeness of a sample is assured by random sampling from the target population. Maximum concentration estimates over the same region require scientific judgement to choose sampling locations at or near the maximum.

Completeness - is a measure of the amount of valid data obtained from a measurement system, compared to the amount that was expected to be obtained under correct normal conditions.

Use of the completeness parameter acknowledges that data may be lost by a number of different routes including specific sampling sites being inaccessible at the time of sample collection,

breakage or spilling of sample during handling or shipping and sample holding time being exceeded before analysis.

Circumstances, such as where statistical parameter tests are used to assess data, may dictate a certain level of completeness, so contingency plans for resampling or re-assessment of the sampling site should be made.

Comparability - expresses the confidence with which one data set can be compared to another.

Comparability between different monitoring exercises can be assessed by considering such variables as sample site selection, how experimental results are reported (corrected to the same standard conditions e.g. dry weight, standard temperature and pressure etc.) and similarity of data quality measurement steps.

Quality Control - Samples of use in assessing the quality of environmental data are presented in Appendix 2D.

The QA programme plan

The QA programme plan is a document that commits the study overseers to a specific QA policy and sets out the requirements for data needed to support programme objectives. The QA programme plan describes the policies, organisation, objectives and functional responsibilities for achieving data quality goals.

The five major parts of a QA programme plan are as follows:

- a statement of the purpose and importance of a QA plan
- a description of the procedures that will be used to carry out the programme
- a description of the resources committed to perform the QA work
- an identification of the individual projects or packages of work in a study that require QA plans
- a description of how QA implementation will be evaluated.

The QA project plan

The QA project plan is a technical document that provides unified information on the project for all parties and provides details of specific QA and QC requirements. The QA project plan also specifies any QA/QC activities required to achieve the data quality goals of a project and describes how all data is to be assessed.

The QA project plan is readily divided into sections addressing different aspects of the assessment (e.g. sampling, analysis etc.). Alternatively a number of generic stand-alone documents may be prepared, each addressing an aspect of the work, with a simple site-specific work plan to be developed as part of each project.

A list of essential QA/QC activities and the area under which they would apply are presented here.

Overall project management

- project description
- project organisation and designated responsibilities
- quality assurance objectives for the experimental data including precision, accuracy, completeness and comparability
- experimental design and analytical procedures
- ensuring on-going quality assurance reports to management
- corrective actions
- defining statistical techniques for assessing the experimental data

Field sampling

- sampling network design
- selection of specific sampling sites

- sampling methodology - detailing procedures to be used in the field
- sampling devices, storage containers and preservatives
- sample custody, transportation, preservation, and storage
- replicate sampling
- documentation needed
- special operating conditions (e.g. heat, light, reactivity etc.)
- information on health and safety practices in sampling and field testing operations
- accepted procedures designed to control and define errors associated with field measurements.

Laboratory analysis

- sample custody
- sample storage
- instrument selection and use
- analytical methodology and standard operating procedures.
- calibration procedures and frequency
- reference standards and quality control standards
- internal quality control checks and frequency
- replicate analyses
- blank and spiked samples
- intra and inter-laboratory QC procedures
- specific routine measures to be used to assess data quality
- data reduction, validation, verification and reporting.

Practical implementation of the QA/QC framework

Assessment stages at which QA/QC elements should be reviewed

- on identifying the need for site assessment
- on seeking proposals from consultants
- on engaging a qualified consultant
- on receiving a report from the consultant
- on deciding further action.

In the above context the timing and responsibility for each of the QA/QC tasks may be as follows:

Defining the goal or purpose of the study and how it will be achieved

This should be carried out by the site owner or operator before engaging the consultant to undertake the investigation. It is one of the principal items in the brief provided to consultants. Although the owner or operator should define the goal of the study, inputs should be sought from regulatory authorities and consultants on the legislative or regulatory requirements.

Data Quality Objectives

The consultant needs to define the DQOs as an integral part of the quote for the study (refer to examples presented in Appendix 2B). The DQOs define the scope of work to scope the cost of the study (e.g. how many samples to take, what analytical methods to use etc.).

QA programme plan

The QA programme plan is a statement of the commitment to QA for the study and the outline of how this will be implemented. It would often be included in the consultant's proposal or documentation accompanying the quotation.

QA project plan

Much of the information included in the QA project plan will be normally addressed as part of the following generic documentation:

- internal company (consultant) Quality Assurance procedures, such as those complying with ISO 9000. (e.g. project organisation and responsibilities project planning, management, reporting of corrective action).
- generic field sampling manuals or procedures developed by consultants as the documented procedures employed in site assessment field investigations. An example of such procedures are presented in Appendix 2C.
- documented laboratory procedures (specific to each laboratory, and in accordance with relevant registration (e.g. sample custody and storage, instrumentation).

A site-specific work plan should also be prepared. If an item that is normally included in the generic documentation needs to be altered (e.g. number of duplicate samples to be analysed by an independent laboratory), this should be explicitly noted in the work plan. Other items that would normally be in the work plan include: the chemicals of concern; QA objectives for experimental data (e.g. precision); experimental design and analytical procedures; use of statistical techniques for data evaluation; sampling network design and definition of sampling locations; and analytical detection limits.

Appendix 2B

Example of the process of developing Data Quality Objectives (DQO)

- **State the problem to be resolved**

For example, to determine whether there is the potential for a significant adverse effect on human health or the environment from soil groundwater contamination at a gasworks site.

- **Identify the decisions that need to be made**

For example, does the site pose an immediate risk to human health or the environment? Is there a requirement for immediate remedial action? Is there potential for an adverse effect on human health or the environment in the longer term? Is there need for further, more detailed, investigation to define the extent of contamination, the current impact on human health and the environment and the specific requirements for any remedial action in the longer term?

- **Identify the inputs to the decisions**

For example, the contaminants that may be present at the site may be at concentrations near or above the guideline levels; the concentration of contaminants in soil, groundwater surface water, dust that may have accumulated on surfaces of structures, and in the air; the effects the contaminants may have on human health and the environment, and the concentration in each of the media at which those contaminants have the potential to have a significant impact on human health and the environment.; the level of protection required for human health and the environment, i.e. is it a pristine ecosystem or an urban environment.

- **Narrow the boundaries of the study**

For example, to undertake a sampling programme targeted toward identifying contaminant concentrations in the areas most likely to be contaminated, in order to provide a cost effective assessment of whether there is the potential for a significant adverse effect on human health or the environment.

- **Develop a decision rule**

For example, if the identified concentrations of contaminants in the environment exceed the guideline values nominated in the Health and Environmental Guidelines for Selected Timber Treatment Chemicals, more detailed investigation to determine the extent of contamination is required.

- **Develop uncertainty constraints**

For example, that the Relative Percent Differences[5] (RPD) shall be less than 30% for the results of QA/QC check analyses undertaken by an independent laboratory on duplicate samples; that the sampling programme will give a high level of confidence (notionally 95%); that a significant area of potential contamination, (say greater than 10 sq.m) would be sampled (such confidence would be measured, in effect, by the independent review of the plan based on professional judgement of an experienced, senior professional in the site contamination area.)

- **Optimise design for obtaining data**

[5] RPD(%) = (Co-Cs)/[(Co-Cs)/2]
where Co = concentrations in original sample
Cs = concentrations in duplicate or split sample

For example, review sampling plan to ensure all areas of significant potential contamination have been targeted, and that within an area of potential contamination the sampling is such that the level of uncertainty about whether an area of significant contamination may be missed is consistent with the constraint about uncertainty.

- **Example Data Quality Objectives**

Example DQOs for a gasworks site assessment are presented as follows:

- that the investigation shall be sufficient to determine whether there is the potential for a significant adverse effect on human health or the environment
- that the data shall at least be representative of the higher contaminant concentration that is likely to be encountered at the site, in order to determine whether a further detailed evaluation of the extent of contamination is required. (On this basis a targeted cost-effective sampling programme may be used to achieve this objective)
- that the level of confidence that a significant area of contamination shall be sampled shall be notionally greater than 90%
- if a contaminant concentration in a sample is reported as not detectable, the confidence that the actual concentration is less than one fifth the relevant acceptance criteria shall be greater than 90%
- that the reported concentration in a sample shall be representative (e.g. within +/- 50%) of the actual concentration in the media in situ at the point of sampling (this can be notional only as it cannot be measured)
- the RPD of duplicate samples analysed by independent laboratories shall be less than 30%.

Appendix 2C
Sampling plan and protocol checklists

Sampling plan checklist

What are your data quality objectives (DQOs)?

- What will you do if your DQOs are not met (i.e. resample or revise DQOs)?

Do programme objectives need exploratory or monitoring sampling, or both?

Have arrangements been made to obtain samples from the sites?

- Have alternative plans been prepared in case not all sites can be sampled?

Is specialised sampling equipment needed and/or available?

Are samplers experienced in the type of sampling required available?

Have all analytes been listed?

- Has the level of detection (LOD) for each been specified?
- Have methods been specified for each analyte?
- What sample sizes are needed based on method and desired LOD?

List specific good laboratory practice.

- Are there percentages or required numbers and types of QC samples?
- Are there specific instrument tunings or other special requirements?

What type of sampling approach will be used?

- Random, systematic, judgemental, or combinations of these?
- Will the type of sampling meet your DQOs?

What type of data analysis methods will be used?

- Geostatistical, control charts, hypothesis testing, etc.?
- Will the data analysis methods meet your DQOs?
- Is the sampling approach compatible with data analysis methods?

How many samples are needed?

- How many sample sites are there?
- How many methods were specified?
- How many test samples are needed for each method?
- How many control site samples are needed?
- What types of QC samples are needed?
    - Will the QC sample types meet your DQOs?
- How many of each type of QC samples are needed?
    - Are these QC samples sufficient to meet your DQOs?
- How many exploratory samples are needed?
- How many supplementary samples will be taken?

Number of samples = Test + control + QC + Exploratory + Supplementary

- Test samples = Methods x Sample sites x Samples per site

- Control samples = Methods x Sample sites x Samples per site
- QC samples = Methods x Type of QC sample x % Needed to meet DQOs
- Exploratory samples = (Test samples + Control samples) x 5 to 15%
- Supplementary samples = (Test samples + Control samples) x 5 to 15%

Appendix 2D
Field quality control samples

Field quality control (QC) samples include field duplicate samples, equipment rinsate blank samples, and field blank samples. Field QC samples assess sample collection techniques and monitor possible cross contamination between samples and equipment. The various types of field QC samples are as follows:

- **Field duplicate samples.**
  Field duplicate samples are collected from a single sample location in conjunction with field samples and submitted to the laboratory without indication of the association between the two samples (i.e. a "blind" sample). The field duplicate sample analyses assess the consistency of the sampling technique and the precision of the analytical laboratory. One field duplicate sample is typically collected per every 10 field samples.
- **Equipment rinsate blank samples.**
  Equipment rinsate blank samples are collected after a sampling device has been decontaminated to assess potential cross contamination between samples as a result of poor decontamination procedures.
- **Field blank samples.**
  Field blank samples are bottles of deionised water prepared in the field and included in each sample cooler containing volatile organic compounds (VOC) samples. Field blank samples are used to evaluated sample representativeness by identifying any volatile compounds that may have been introduced into the field samples during sample collection, transportation or storage at the laboratory.

Appendix 2E

Site specific health and safety plan for investigation of subsurface contamination at gasworks sites

Table of contents

Appendix 2F
Field logs

Borehole Log Report

Client:	**Page 1 of**
Job Name:	**Job Number**

Borehole location	Borehole depth	Contractor
Date hole commenced	RL casing	Driller
Date hole completed	RL surface	Drill rig
Logged by	Datum	Drilling fluid
Checked by		

Drilling method	Piezometer construction details	(1) DTW	Depth (m)	Graphic log	Material description	Field sample (analysed)	Field rank	PID reading (ppm) Other notes
			1.0					
			2.0					
			3.0					
			4.0					
			5.0					
			6.0					
			7.0					
			8.0					

Testpit Log Report

Client			**Page 1 of**			
Job Name			**Job Number**			
Test pit location			Test pit depth		Contractor	
Date pit commenced			RL surface		Excavator	
Date pit completed			Datum		Bucket size	
Logged by					Surface conditions	
Checked by						
Depth (m)	(1) SWL	Graphic Log	Material description	Field sample	Field rank	PID readings (ppm), water inflow, stability/Other notes
0.25						
0.5						
0.75						
1.0						
1.25						
1.5						
1.75						
2.0						

Chain of Custody

Client			Analytes										Sample by							Primary lab
Project													Signature							Secondary lab
Job no													Sampled by							Contact
													Signature							Method of shipment
Sample No	Date	Preservative											Containers							
													Jar	Vial	500ml	1 litre	2 litre	Winchester	Other	Comments

3

Analyses of contaminants

Analyses of contaminants

3.1 Introduction

This section provides information on the analytical methods and associated quality control requirements for the contaminants of concern at gasworks sites.

This module covers the following:

- ➔ analytical methods for organic contaminants
- ➔ analytical methods for inorganic contaminants
- ➔ sampling and sample preservation
- ➔ analytical field methods
- ➔ quality assurance requirements

Additional information on the analysis of contaminants can be found in Section 3 of the Users' Guide, including:

- ▲ reference analytical methods (Section 3.9)
- ▲ analytical field methods (Section 3.9.1)

3.2 Analytical methods for organic contaminants

The major organic contaminants found at gasworks sites include:

- polycyclic aromatic hydrocarbons (PAHs)
- benzene, toluene, ethylbenzene, xylene (BTEX)
- phenols

3.2.1 GC or GC/MS methods

Gas chromatography (GC) is the established procedure for analysing most organic contaminants in environmental samples, because of its relatively high sensitivities and its ability to separate groups of chemically similar compounds. When coupled with mass spectrometry (GC/MS), the technique becomes even more powerful in both these respects. Sample extraction and clean-up procedures are usually required with either of these analytical techniques.

The United States Environmental Protection Agency has published a series of sample clean-up and analytical procedures (SW-846, Test Methods for Evaluating Solid Waste, US EPA 1994) which are now well established, both in New Zealand and elsewhere, for these analyses. These cover:

- sample extraction procedures 3500 series
- sample clean-up 3600 series
- analysis 8000 series[1]

3.2.2 Immunoassay methods

[1] The methods for volatiles (8260) and semivolatiles (8270) have comparable methods in the EPS 600 series for wastewaters; namely 624 for volatile organics in wastewater or groundwater and 625 for semivolatiles. EPA has another equivalent series (500 series) for drinking water analysis. Thus, method 524.2 (volatile organics by capillary column GC/MS) is essentially equivalent to method 8260, while method 525.1 (determination of organic compounds in drinking water using liquid/solid extraction and capillary GCMS) is similar to method 8270.

Enzyme linked immunoassay methods are proving their worth in many applications in the environmental field. The methods are based on combining selective antibodies with sensitive enzyme reactions to produce analytical systems capable of detecting very low levels of specific chemicals. The systems were initially introduced as rapid screening techniques for use in the field, but have now been developed to the stage where some of them are approved by the US EPA as screening methods (EPA 4000 series).

The main advantage of immunoassay systems is the speed of analysis, typically 30 minutes for a complete test, from sample extraction through to the result. In addition, the systems are easily set up for field use, and this makes them well suited to investigations of contaminated sites. They should be particularly useful during site clean-ups, where decisions on the extent of any work may be dependent on analytical results.

Immunoassay test kits are commercially available for PAHs and total petroleum hydrocarbons (Millipore, Ohmicron and Ensys).

The relevant standard test methods are:

- EPA 4030 Petroleum Hydrocarbons Soil Screening by Immunoassay
- EPA 4035 PAHs Soil Screening by Immunoassay

Immunoassay field methods should be pre-calibrated against GC laboratory analyses with typical samples taken from the site under investigation.

3.2.3 Phenols by colorimetry

Several methods are available for the analysis of phenols in waters and wastewaters using colorimetric procedures (APHA 5530, ASTM D 1783-91, ISO 6439: 1990 and EPA 9065, 9066 and 9067). These generally indicate the concentration of total phenols in the sample (i.e. phenol + cresols + xylenols, etc.). The total phenol level determined, therefore, represents the minimum concentration of phenolic compounds present.

These methods can suffer interference from the presence of sulphur compounds such as sulphides, and from oils and tars, in which some phenolics could be dissolved. These interfering compounds are commonly found in gasworks samples.

These methods are not suitable as reference methods or for confirming compliance with any clean-up criteria. They may be useful, however, as screening methods during the initial stages of any site investigation and clean-up. They are generally cheaper than any of the EPA GC methods, and can be carried out using less sophisticated laboratory equipment. Simple field test kits for phenols (in waters) are also commonly available.

3.2.4 Total petroleum hydrocarbons methods

The advantage of GC analysis as a total petroleum hydrocarbon (TPH) screening technique is that it can give an indication of the type of hydrocarbon fraction(s) or product types present in the samples. For example, the hydrocarbon “fingerprint” pattern obtained could indicate the presence of compounds typical of coal tar fractions, including PAHs. Such samples could then be further examined by GC/MS for confirmation and measurement of the specific PAH content.

A GC method is being developed by RJ Hill Laboratories as a New Zealand standard TPH method for inclusion in oil industry guidelines. This method would also probably be suitable for the analysis of gasworks samples.

Other techniques for the estimation of TPH content of soil samples include EPA 3560 (Total Recoverable Petroleum Hydrocarbons by Supercritical Fluid Extraction) and EPA 4030 (Petroleum Hydrocarbons Soil Screen by Immunoassay).

3.2.5 Other methods for organics

Method	Description

Solid phase extraction	Most solid phase extraction systems are based on plastic cartridges similar in appearance to the barrel of medical syringes, but packed with a section of a selective absorbent. Samples are flushed through the tube, usually with a number of different solvents, to separate and extract the analyte fractions of interest. Solid phase extraction is now included in EPA SW-846 as a standard extraction method (EPA 3535).
Head space analysis	Headspace methods can be very useful in avoiding the matrix effects sometimes encountered with solvent extraction of complex wastes. Headspace techniques can also be used as a field screening method in conjunction with an organic vapour detector such as a photo ionisation detector (PID) or flame ionisation detector (FID). This can be a very useful technique for screening samples during the remediation phase of a site project. In gasworks samples, headspace analysis would be used mainly for BTEX analyses. A headspace screening method is included in EPA SW-846 (EPA 3810).

3.2.6 Recommendations

Contaminant	Method
BTEX and other volatile organics	• EPA 8260B (soil/solid waste or all sample matrices) • EPA 624 or EPA 602 (wastewaters or groundwaters) • EPA 524.2 (drinking water) • EPA 8020 (Volatile aromatics in solid samples)
PAHs and other semivolatile organics[2]	• EPA 8270C (soil/solid waste) • EPA 625 (wastewaters or groundwaters) • EPA 525.1 (drinking water)
Phenols[3]	• EPA 8270C or EPA 8041 (all sample matrices)
Total petroleum hydrocarbons (TPH)	• GC Method being developed by RJ Hill Laboratories for the Oil Industry Guidelines (this is provisional on this method being found suitable once developed) Alternative methods could be those (non-standard) GC/FID-GC/MS techniques discussed in Douglas et al 1992, and Roques et al 1994.

3.3 Analytical methods for inorganic contaminants

The major inorganic contaminants expected at gasworks sites are cyanides, heavy metals, inorganic sulphur compounds, and ammonia. Unlike the organic contaminants, the analytical requirements for each of these groups of chemicals are quite different.

3.3.1 Cyanides

Cyanide may be present at gasworks sites in a number of different forms:

- free cyanide
- metal-cyanide complexes
- thiocyanate.

It is important that analyses can differentiate between these forms as the toxicities or potential toxicities are quite different.

Note: Because of the toxicity of cyanide, great care must be exercised in its handling Acidification of cyanide solutions produces toxic hydrogen cyanide. All manipulations and distillations must be done in a fume hood so that any HCN gas that might escape is safely vented. This equally applies to other tests on gasworks samples that may release the cyanide

[2] These methods should, however, be modified to include, in addition to the 16 EPA priority pollutant PAH compounds, dibenzofuran and selected PAH alkyl homologues (C1-C4), such as 2-methylnaphthalene (Douglas et al 1992). The US Gas Research Institute has also compiled its own list of PAHs specific to gasworks (GRI 1987, Thomas and Lester 1994). A number of compounds, not likely to be present on gasworks sites could be deleted from the standard EPA 8270 list. These could include chlorinated compounds and pesticides.

[3] These methods should cover phenol, cresols (methylphenols) and xylenols (dimethylphenols).

content, for example, acid extraction for metal analysis. Many of the reagents used in these test methods are highly toxic. Reagents and test solutions must be disposed of properly.

APHA Standard Methods (19th Edition 1995) (APHA, AWWA, WEF 1995) specifies a number of different methods for cyanide analysis in water and wastewaters in section 4500-CN, Cyanide. The section contains the following parts:

A	Introduction
B	Preliminary treatment of samples
C	Total cyanide after distillation
D	Titrimetric method (of determination)
E	Colorimetric Method (of determination)
F	Cyanide-Selective Electrode Method (of determination)
G	Cyanides Amenable to Chlorination after Distillation
H	Cyanides Amenable to Chlorination without Distillation
I	Weak Acid Dissociable Cyanide
J	Cyanogen Chloride
K	Spot Test for Sample Screening
L	Cyanates
M	Thiocyanate

Most of these have as their starting point a distillation step which separates the cyanide from the sample matrix. Various pre-treatments are also used at this stage to distinguish between the different cyanide forms. Subsequent analysis can be by a variety of procedures including (titration, colorimetry, ion selective electrode). The choice of method is dictated by the desired detection limits, and availability of instrumentation.

APHA methods 4500-CN (C) and (I) should be acceptable for the analysis of total cyanide and free cyanide, respectively, in gasworks samples. Section 4500-CN (A) contains procedures for the extraction of cyanides from solid waste samples (A.2). The colorimetric determination procedure (4500-CN (E) should have adequate sensitivity for the required detection levels.

An analysis for total cyanide can be used as a ‘screen’ to decide if further analysis for free or complex cyanides is necessary. It would only be necessary to analyse for free cyanide if the total cyanide level exceeds the ‘trigger’ level for free cyanide.

Many ions and compounds may interfere with these cyanide determinations. The most significant in the case of gasworks materials are sulphides, sulphites, thiocyanate and other sulphur compounds. Sulphide will distill over with cyanide and adversely affect the colorimetric procedure. It must, therefore, be removed prior to the distillation step. Sulphide can convert cyanide to thiocyanate, especially at the pH of the base stabilised sample. Oxidising agents such as chlorine decompose most cyanides during storage and manipulation and their presence should, therefore, be tested for. The presence of either oxidising agents or sulphides should be determined, and they should be removed, if present, before the addition of sodium hydroxide normally used to preserve cyanide samples. Methods for preserving samples and eliminating interfering compounds are given in APHA 4500-CN, section B.

Samples should be protected from exposure to ultraviolet (UV) light, as photodecomposition of some metal-cyanide complexes may significantly increase the concentration of “free” cyanide in the samples. Samples should be stored in closed, dark bottles in a cool place and analysed as soon as possible.

Comparable methods for the analysis of cyanides are found in the ISO, ASTM and EPA collections of methods (e.g. EPA 9012).

Soils and solid wastes can also be analysed by the above procedures using an extraction pre-treatment such as is described in APHA 4500-CN (A-2) or EPA 9013 Cyanide Extraction Procedure for Solids and Oils.

Thiocyanates can be determined by the following methods:

- APHA 4500-CN (M) Thiocyanate

- ASTM D4193-89 Thiocyanate in Water

A more recent published standard method is ASTM D4374-93 Cyanides in Water - Automated Methods for Total Cyanide, Dissociable Cyanide, and Thiocyanate.

The US Gas Research Institute has carried out research on methods for the analysis of cyanides in gasworks wastes (Gas Research Institute 1989).

3.3.2 Heavy metals

The analysis of samples for heavy metals usually involves a digestion step followed by instrumental analysis of the resulting solution, using techniques such as atomic absorption (AA) or inductively coupled plasma (ICP). These techniques are well established and in common use, and so it is unnecessary to provide any detailed coverage of the various options or requirements for the range of different methods.

Standard procedures for the analysis of metals in water and wastewaters are given in the APHA Methods (3030-Preliminary Treatment of Samples, 3111-Metals by Flame Atomic Absorption Spectroscopy, 3113-Metals by Electrothermal Atomic Absorption Spectroscopy, 3120-Metals by Plasma Emission Spectroscopy) and methods in the EPA 200 series (200.2-Sample Preparation, 206-Arsenic, 213-Cadmium, 239-Lead, 245-Mercury, 249-Nickel, 289-Zinc). Methods for the determination of metals in solid waste and soil are given in EPA SW-846, 3050A-Acid Digestion of Sediments, Sludges and Soils, 3051-Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils, 6010B-Inductively Coupled Plasma-Atomic Emission Spectroscopy, 6020-Inductively Coupled Plasma-Mass Spectrometry and the 7000 series of Atomic Absorption Methods.

Given the wide range of metals that may be present at gasworks sites, multi-element techniques such as ICP and ICP/MS are the preferred analytical methods and these will be taken as the reference methods.

Multi-element X-Ray Fluorescence (XRF) may also be suitable, especially as a cost-effective screening technique. A semi-quantitative XRF scan can determine the concentrations of 57 (mostly metallic) elements from levels of 100% to a minimum detectable level of 0.001% (10mg/kg) in about 20 minutes. This can provide useful information on the overall composition of the material analysed and also indicate if higher than background levels of common elements are present.

3.3.3 Inorganic sulphur compounds

Sulphur may be present at gasworks sites as elemental sulphur, sulphates, sulphides, or thiocyanates, and each of these require a different analytical method. Alternatively, all forms may be determined as total sulphur in solid samples by, for example, the XRF technique described above.

Other methods for total sulphur are much less convenient and involve some type of total digestion step such as oxygen bomb combustion (EPA 5050), perchloric acid oxidation or fusion.

Elemental sulphur is only likely to be of interest in solid samples, and this is most easily determined using XRF (gasworks samples may contain over 50% sulphur). An alternative method for the determination of elemental sulphur is given in Method 31, Draft ANZECC Guidelines for the Analysis of Contaminated Soils (ANZECC 1994).

There are numerous methods available for sulphate analysis in water and wastewater samples. For soils, the extraction method in the ANZECC Guidelines (ANZECC 1994) will be suitable; for aqueous samples the APHA Standard Methods should be used. In both, the determinative step should be by either the APHA standard Ion Chromatographic method (4110) or the Turbidimetric method (4500-SO_4^{2-}) and these should be taken as the reference method.

Sulphides in aqueous samples can be determined by APHA methods 4500-S^{2-}, by the methylene blue procedure (method D), or by ion-selective electrode (method G). Suitable methods for soil samples are EPA 9030A-Sulphides and EPA 9031-Extractable Sulphides.

3.3.4 Ammonia

There are several methods that are suitable for the analysis of ammonia in aqueous samples. These include APHA 4500-NH_3, ASTM D 1426-93 and ISO 5664:1984. A suitable method for the extraction of ammonium in soils is given in Method 10 in the ANZECC Guidelines (ANZECC 1994). The extract solution is then analysed by the ion-selective electrode method given in APHA 4500-NH_3 (sections D or E).

3.3.5 Acidity

A method for analysing acidity of water is given in APHA 2310. A method for determination of the pH of soil or waste is given by EPA 9045B. An alternative method for determining soil pH is given in Method 6 in the ANZECC Guideline (ANZECC 1994).

3.3.6 Moisture content

For many chemical analyses, the moisture content is determined so that chemical concentrations can be expressed on a dry weight basis. A suitable method is given in Method 5 in the ANZECC Guidelines (ANZECC 1994).

3.3.7 Toxicity characteristic leaching procedure

This procedure, EPA 1311, is an agitated extraction test designed to simulate leaching in a sanitary landfill. The filtered extract from the toxicity characteristic leaching procedure (TCLP) is analysed to determine if any of the thresholds for the 40 toxicity characteristic constituents have been exceeded. This procedure is discussed more fully in the Draft Health and Environmental Guidelines for Selected Timber Treatment Chemicals (MfE/MoH 1993), and in the ANZECC Guidelines (ANZECC 1994).

This will be an important test to carry out on gasworks wastes if they are intended to be disposed of to a landfill or if a risk assessment of the leachability of the material in situ is to be determined. TCLP volatiles and TCLP semi-volatiles and metals must be determined on separate samples.

3.4 Sampling and sample preservation

Extensive discussions on correct sampling procedures and sample preparation and storage requirements are given in several other publications (ANZECC 1994, Ministry for the Environment/Ministry of Health 1993, CCME 1993) and are not, therefore, repeated in detail here. Some requirements more specific to gasworks samples are discussed briefly below (Department of the Environment 1987, ANZECC 1994).

To obtain reproducible results laboratories must use standardised procedures for the preparation of samples. It is important to ensure that no bias is introduced in the analytical results. For example, certain gasworks contaminants can be driven off or modified during drying or handling procedures. Volatile organics may evaporate, PAHs are photosensitive, aerobic biodegradation of phenols may be accelerated, sulphide and cyanide may volatilise as the acid gases, metal complex cyanides can photodissociate to release free cyanide and oxidation may occur, for example, of sulphur to sulphate or to decompose cyanides.

Table 3.1 Sample preparation

Sample	Preparation
Soils Non-volatile or "stable" contaminants	• examine visually and record observations • obtain a representative sub-sample of the laboratory sample, of at least 50% of the sample or 200g, whichever is the smaller, taking into consideration amounts required for repeat analyses,

	other analyses to be carried out on this same sample and the moisture content of the sample • remove large stones (> 5mm) and vegetation and record the proportion by weight, together with the description, of each fraction of material removed • air-dry or in draught oven (<30^{o}C, <65% relative humidity) • grind sample (mortar and pestle) and sieve to <2mm (weigh and retain the larger particles for later analysis if required) • mix and quarter (if necessary) the fraction <2 mm diameter • transfer to sealed glass container • store at 4^{o}C in the dark, pending extraction and analysis
Soils Semi-volatile analytes[4]	• follow 1st three steps above • grind sample in a mortar and pestle to produce a homogeneous test sample • transfer to sealed, air tight glass container and store at 4^{o}C in the dark, pending extraction and analysis • dry a separate, weighed portion of the original sample to determine moisture content. Report the moisture content with the analytical result so that the analyte concentrations may be estimated on a dry weight basis
Soils Volatile	• using a clean spatula, rapidly homogenise the cold laboratory sample by stirring in its original container • if large stones (> 5 mm) and vegetation can be removed rapidly without risk of significant analyte losses, do so quickly and return the sample promptly for cold storage. If not, no material is to be removed and the analysis portions are to be taken from the homogenised, "as received" sample. Record the proportion by weight, with the description, of each fraction of material removed
Liquid[5]	• filter out solids, except from samples for sulphide analysis • stabilise as necessary by cooling to 4^{o}C • separate distinct liquid phases, if present, for separate analysis

Table 3.2 Sample preservation

Sample	Preservation
Soil	• sampling containers should be filled to the brim, in order to exclude air • glass containers are preferred, although polyethylene and polypropylene are probably satisfactory (other than for organic analytes), if analysis follows promptly • where volatile contaminants are of interest, gas tight bottles should be used • samples should be placed in the dark and in cool storage (4^{o}C) as soon as possible • extracts should be prepared as soon as possible stored under optimum conditions • sensitive determinands should be analysed as soon as possible, preferably on site or within hours, and certainly within 2 days
Water	Stabilisation can normally be achieved by addition of a chemical agent on site, or in the laboratory. Preservatives for one determinand may disturb the stability of other contaminants and thus cause a bias in their analysis. A common practice for water samples from gasworks sites is to split the sample four ways and treat each as follows (Department of the Environment 1987): • for ammonia determination, stabilise with sulphuric acid • for sulphide determination, stabilise with zinc acetate and sodium hydroxide • for metal determination, stabilise with nitric acid • for phenols, semivolatile organics and cyanide, store at 4^{o}C and in dark • for volatile organics a separate sample should be taken
Cyanides	• sample containers should be filled to the top if possible so as to exclude air, and should be protected from strong sunlight to minimise cyanide oxidation and photodecomposition. Analyse as soon as possible after collection • samples likely to contain oxidising agents should be pre-treated with sodium hydroxide solution to give a pH of at least 12. Sulphide content must be removed prior to this preservation treatment
Heavy metals	• sample containers should be pre-washed with detergent and acid, and AR nitric acid added as a preservative. Water samples should be pre-filtered in the field if significant quantities of solids/sludges are present in the samples (sludges may be collected separately for independent analysis).

[4] Drying may lead to losses - this could include AHs

[5] Samples heavily contaminated with coal tar present particular difficulties in that they can be extremely cohesive. Analysis of these should not be necessary and visual assessment will indicate the need for remedial measures

Sulphur compounds	• there are no special requirements for total sulphur, elemental sulphur or sulphate. For sulphide, stabilise with zinc acetate and sodium hydroxide.
Ammonia	• use tightly sealed containers and analyse samples as soon as possible after collection. Most reliable results are obtained on fresh samples. If samples are to be analysed within 24 hours of collection, refrigerate unacidified at 4^{o}C. For preservation for up to 28 days, freeze at -20^{o}C unacidified, or preserve samples by acidifying with sulphuric acid to pH <2 and storing at 4^{o}C. If acid preservation is used, neutralise samples with NaOH or KOH before the determination (APHA, AWWA, WEF 1995).

Table 3.3 EPA Method 6010 Sample Holding Times, Required Digestion Volumes and Recommended Collection Volumes for Metal Determinations (CCME 1993)

Measurement	Digestion* Volume (mL)	Collection volume (mL)	Preservative	Holding Times
Metals (except Cr VI and Hg)				
Total recoverable	100	600	HNO_3 to pH <2	6 months
Dissolved	100	600	Filter on site, HNO_3 to pH<2	6 months
Suspended	100	600	Filter on site	6 months
Total	100	600	HNO_3 to pH <2	6 months
Chromium VI	100	400	Cool to 4^{0}C	24 hours
Mercury				
Total	100	400	HNO_3 to pH <2	28 days
Dissolved	100	400	Filter, HNO_3 to pH <2	28 days

* Solid samples should be at least 200g and usually require no preservation other than storing at 4^{o}C.

Table 3.4 Sample collection, preservation and storage (CCME 1993 and EPA SW-846)

Method Number	Sampling and Preservation	Storage
EPA-8260A Cap GC/MS Volatile organics	**Liquid samples**: Use a 40-ml glass screw-cap VOA vial with Teflon -faced silicone septum (prewashed with detergent, rinsed with distilled deionized water, and oven dried at 105^0 C for 1 h). If residual chlorine is present, collect sample in a 125 ml soil VOA container that has been pre-preserved with 4 drops of 10% sodium thiosulphate. Mix gently and transfer to a 40-mL VOA vial. Add 4 drops of concentrated HCL and cool to 4^0C. Collect bubble-free samples in duplicate.	The two vials/glasses from each sampling should be sealed in separate plastic bags and stored at 4^oC for a maximum of 14 days from date of collection.
	Soil/sediments and sludges*:* Use an 125 ml widemouthed glass with Teflon -faced silicone septum (prewashed with detergent, rinsed with distilled deionized water, and oven-dried at 105^0C for 1 h). Do not heat septum for more than 1h. Tap slightly to eliminate free air space. Collect in duplicate and cool to 4^0C.	
EPA-8270B Cap GC/MS (B/N/A) Semi-volatile organics	*Liquid samples:* Use a 1 gal. or 2 x 0.5 gal amber glass bottle with a screw-top Teflon -lined cover. Prewash with detergent and rinse with distilled water and methanol (or isopropanol). Flush glassware immediately before use with some of the same solvent that will be used in the analysis. Cool samples to 4^oC. If residual chlorine is present, add 3 ml of 10% sodium thiosulphate per gallon and cool to 4^oC.	Liquid samples must be extracted within 7 days and extracts analyzed within 40 days. Soil/sediments and sludges may be stored for a maximum of 14 days. Do not store in the presence of exhaust fumes.
	Soil/sediments and sludges: Use a 250 ml widemouthed glass with a screw-top Teflon -lined cover. Prewash with detergent and rinse with distilled water and methanol (or isopropanol). Flush glassware immediately before use with some of the same solvent that will be used in the analysis. Cool samples to 4^0C.	
EPA-524.2 Rev 3 Cap GC/MS Volatile organics	Use a 60- to 120 mL screw cap vial (prewashed with detergent, rinsed with distilled water, and oven-dried at 105^oC) with a Teflon-faced silicone septum. If residual chlorine is in the water, add about 25 mg of ascorbic acid to each vial before sample collection. Collect bubble-free samples. Add hydrochloric acid until a pH of <2 is achieved and immediately cool samples to about 4^oC.	The maximum holding time is 14 days from the date of collection. Do not store samples in a refrigerator where other volatile chemicals are stored as their vapours may contaminate these samples.
SM-6420B Phenols by GC/FID or ECD (equivalent to US EPA Method 604)	Collect grab samples in 1-L amber glass bottles fitted with a screw cap lined with Teflon. Wash and rinse bottle and cap liner with acetone or methylene chloride and dry before use. Collect composite samples in refrigerated glass containers. Optionally, use automatic sampling equipment as free as possible of plastic tubing and other potential sources of contamination, incorporate glass sample containers for	Keep samples at 4^oC from time of collection until extraction. Extract samples within 7 days of collection and analyse completely within 40 d of extraction.

Method Number	Sampling and Preservation	Storage
	collecting a minimum of 250 mL. Refrigerate sample containers at 4^0C and protect from light during compositing. Fill sample bottles and, if residual chlorine is present, add 80 mg sodium thiosulphate per litre of sample and mix well. Cool samples immediately to 4^0C	
SM-3111B (metals-flame AA) SM-3112B (Hg - AA) SM-3113B (methods - electrothermal AA) SM-3114B (As, Se - hydride AA) SM-3120B (metals by ICP)	Use sample containers made of polypropylene or linear polyethylene with a polyethylene cap. Store samples for determination of silver in light-absorbing containers. Use only containers and filters that have been acid rinsed. Preserve samples immediately after collection by acidifying with concentrated HNO_3 to pH <2. Filter samples for dissolved metals before preserving.	After acidifying sample, store at approximately 4^oC to prevent loss in volume due to evaporation. Samples with metal concentrations of several milligrams per litre are stable for up to 6 months. For microgram-per-litre metal levels, analyse samples as soon as possible after collection.
EPA-6010 - Metals by ICP	Samples should be collected in borosilicate glass, linear polyethylene, polypropylene, or Teflon bottles that have been prewashed with detergent and tap water and rinsed with 1:1 nitric acid and tap water or 1:1 hydrochloric acid and tap water.	The maximum holding times from time of collection to time of extraction is shown in Table X3 for each type of analyte.
APHA SM 4500-CN EPA-9012 Colorimetric Automated UV Total and amenable cyanide	Collect samples in 1-L or larger plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed to remove soluble materials. Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with acidified potassium iodide (KI) - starch test paper at the time of collection; a blue colour indicates the need for treatment. Add ascorbic acid a few crystals, at a time until a drop of sample produces no colour on the indicator. Then, add an additional 0.6 g of ascorbic acid for each litre of water. Samples must be preserved by adding 10N sodium hydroxide (or NaOH pellets) until sample pH is >12 at time of collection. Oxidised products of sulphide convert cyanide to thiocyanate rapidly, especially at high pH. Sulphide will also distill over with cyanide and adversely affect the determination step. Samples therefore require testing for the presence of sulphide prior to stabilisation with NaOH. Test for sulphide by placing a drop of sample on lead acetate paper previously moistened with acetic acid buffer solution, pH 4. Darkening of the paper indicates presence of sulphide. Add lead acetate or lead carbonate to precipitate the sulphide. Filter sample before raising pH for stabilisation.	Samples should be stored at 4^0C in a dark place and analyzed as soon as possible.

3.5 Analytical field methods

3.5.1 Portable gas analysers

There are a several portable gas analysers on the market which have potential application in gasworks site investigations. These analysers give "real-time" measurements on levels of gases and vapours being emitted from a site and can store information, gained over a period of time, in a data logger. They would therefore be useful in testing for unsafe vapour concentrations in air, in cases of extreme contamination.

For organic vapours, the most universal systems are those based on the photoionisation detector (PID) or the flame ionisation detector (FID). These are used as total organic vapour monitors, or can be made more selective through coupling with a portable GC. Either configuration could be used as a screening device for detecting the presence of volatile organic compounds such as the BTEX compounds on a gasworks site.

Portable gas detectors, based on electronic sensors, could also be used in testing for ammonia or hydrogen sulphide concentrations, although the odours of these gases would usually make their presence quite apparent to workers on site. More important could be gas detectors for hydrogen cyanide which could form from the photodissociation of complex cyanides and reach elevated concentrations in confined spaces such as test pits, trenches or tanks.

3.5.2 Gas detector tubes, passive badges, sorbent tubes and filters

These are available for a wide range of gases and vapours, although the most likely applications at gasworks sites would be much the same as for the portable analysers noted above; i.e. volatile hydrocarbons, ammonia, hydrogen cyanide and hydrogen sulphide. These sampling devices give "average" readings of air contaminants, over either short or long time periods, unlike the gas analysers discussed above which give "real-time" readings. They do, however, have the advantage of being much less expensive.

Gas detector tubes, such as the Gastec or Drager products operate on the colorimetric principle. A detecting reagent is adsorbed on a support medium in the tubes and, upon exposure to the test substance in the air sample, a distinct colour change occurs, giving a quantitative indication of the concentration of the test substance via the calibrated scale on the tube. Gas detector tubes are available for ammonia, carbon dioxide, carbon monoxide, hydrogen sulphide, hydrogen cyanide, mercury, mercaptan, phenol, sulphur dioxide, total hydrocarbon vapours and the BTEX compounds.

Passive badges and diffusion tubes are either of the self-indicating type or the sorbent type which require subsequent laboratory analysis. Colour indicating badges are available for ammonia, carbon dioxide, carbon monoxide, hydrogen sulphide and sulphur dioxide. A direct indicating diffusion tube is available for hydrogen cyanide. Sorbent tubes and filters are available for a wide range of organic and inorganic gases, vapours and aerosols.

3.5.3 Portable analytical equipment

A range of portable analytical equipment is now available but this has not been widely applied in New Zealand. This includes X-ray fluorescence equipment useful for the preliminary assessment of the spatial extent of elemental contamination, as well as portable GCs, GC/Mass Spectrometers, Thermal Desorption GC/MS, Infrared detectors (for organics) and Anodic Stripping Voltammeters (for trace metals).

3.6 Quality assurance requirements

Quality assurance procedures during analytical work are essential for the provision of meaningful results. This includes procedures for sample storage and preservation, sub-sampling, calibration and the analysis of quality control samples. Each of these is discussed briefly below, but laboratories should also examine the more comprehensive coverage given in some of the major references, such as EPA SWP-846 (US EPA 1994, MfE/MoH 1993, ANZECC 1994 and CCME 1993).

3.6.1 Sample containers and sample storage

Sample containers should be carefully chosen and pre-treated to ensure minimal or no interactions between the samples and the container materials. Specific recommendations for gasworks containers are given in the field sampling notes, elsewhere in these Guidelines.

Storage requirements for gasworks samples are also covered in the field sampling notes. It is essential that these be followed, to minimise the possibility of sample degradation or other changes in composition, before analysis.

3.6.2 Sample preparation and sub-sampling

Many of the samples collected from gasworks sites will be heterogeneous in nature and it is important that these be properly processed and sub-sampled prior to analysis, to ensure representative results.

Sample type	Requirements
Liquids	Samples containing visible amounts of sediment should be filtered before analysis, unless the method is intended to cover the total amounts of contaminant present in the sample. Even in this case it may be preferable to analyse the sediment separately from the liquid, because a "total" result will be affected by the relative amounts of sediment and liquids in sub-samples taken.
Soils[6] and sediments	Where the amount of material required for an analysis is greater than 10g, samples may be analysed on an "as received" (i.e. wet) basis after removal of any stones and other large objects, and thorough mixing of the samples. Any superficial water should be decanted from sediment samples prior to mixing. Any analyses for volatile contaminants such as petroleum hydrocarbons, must be carried out on as received wet samples to avoid losses during drying, or samples which are highly heterogeneous, or when test portions less than 10g are required, samples should be dried, ground and sieved before collection of the analytical portion. Samples should be air dried (30-35 C, <65% relative humidity, 16 hours or longer if required) and ground so that less than 5% is retained on a 2mm sieve. If composite samples are to be analysed, these should be prepared from equal quantities of subsamples taken through the full drying and sieving process. No more than five subsamples should be used to form a composite, to avoid excessive dilutions of individual samples. Extreme care should be taken to avoid cross contamination during the sample preparation process and to minimise spread of dust in the laboratory. Equipment and containers used must be thoroughly cleaned before each sample to prevent cross-contamination. Cleaning procedures will vary according to the analytes being determined. Generally detergent washing, followed by deionised distilled water rinsing and oven drying will suffice. For trace metal analysis it may be necessary to incorporate soaking in dilute acid before distilled water rinsing. Solvent rinsing followed by air drying will normally be required before homogenising samples for organics analysis. Frequent laboratory reagent blank analyses will be required to check for contamination.

3.6.3 Calibration and standards

All of the methods in these notes require some form of calibration to ensure the accuracy of the results. This will normally be achieved through the use of working standards, prepared as part of the analytical procedure. However, it is important that these standards be cross-referenced to primary standards, and preferably to an externally sourced reference materials as well.

It is essential that detailed procedures are in place to manage and document the traceability and validity of reference materials and derived solution standards used in analytical methods. Documentation should include at least the following:

- a suitable coding system for uniquely identifying all primary and derived standards
- records of receipt of all primary reference compounds or certified standards including source, purity and expiry date

[6] **WARNING**: **Grinding of soils to fine dimensions may produce airborne particles which present a health hazard. Preparation should be performed in a fume hood, and appropriate respiratory protection should be worn.**

- records of preparation of all stock standard solutions including dates of preparation and expiry, weight of reference material, final volume and solvent of dilution, signature of check by laboratory manager or person responsible for quality assurance policy in the laboratory
- records of preparation of all primary dilution and calibration (working) standard solutions including aliquot volume(s) or weight(s) of stock standard(s), final volume and solvent of dilution, expiry date, signature of check by laboratory manager
- records of confirmation of identity and concentrations of analytes in standard solutions including GCMS, comparisons of concentrations with those of previous standards and comparisons of concentrations with those of standard solutions exchanged with other laboratories.

3.6.4 Quality control procedures

3.6.4.1 Recommended QC procedures

It is recommended that the QC steps described in Chapter 1, "Quality Control" of "Test Methods for Evaluating Solid Waste", US EPA Publication SW-846 (US EPA 1994), be adopted for all soils analyses. They are also applicable to most water analyses.

In particular, it is expected that analysts would implement the following QC steps with each analytical batch, or with each twenty samples, whichever is the smaller.

	QC Control Procedure
Laboratory reagent blank	At least one determination of a blank to establish the contribution to the analytical signal by reagents, glassware etc. The blank should be subtracted from the gross analytical signal for each analysis before calculation of sample analyte concentration.
Replicate analysis	Duplicate analysis of at least one sample from the batch. The variation between replicate analyses should be recorded for each batch to provide an estimate of the precision of the method.
Quality control sample	Analysis of at least one control sample, either a standard reference material, a laboratory reference material or a control matrix fortified with analytes representative of the analyte class. Recovery check portions should be fortified at concentrations which are easily quantified but within the range of concentrations expected for real samples.
Surrogate analytes	Surrogates should be added to all analyses for determinations where it is appropriate (e.g. chromatographic analysis of organics). Surrogate spikes are known additions **to each sample and matrix spike or reference sample analysis**, of compounds which are similar to the analytes of interest in terms of: • extraction • recovery through clean-up procedures, and • response to chromatographic or other determinations, but which • are not expected to be found in real samples, • will not interfere with quantification of any analyte or interest, and • may be separately and independently quantified by virtue of, for example, chromatographic separation or production of different mass ions in a GC/MS system. Surrogates are added to the analysis portion **before extraction** to provide a means of checking, for every analysis, that no gross errors have occurred at any stage of the procedure leading to significant analyte losses.
Internal standards[7]	use of internal standards is highly recommended for chromatographic analysis of organics. Internal standards are added, **after all extraction, clean-up and concentration steps,** to each final extract solution. The addition is a constant amount of one or more compounds with similar qualities to 4(d), 4(e) and 4(f) above.

Internal and surrogate standards are most use for trace analytes where analyte losses during extraction or chromatography and small final volumes can give rise to considerable errors.

[7] Internal standards are used to check the consistency of the analytical step (e.g. injection volumes, instrument sensitivity and retention times for chromatographic systems) and provide a reference against which results may be adjusted in case of variation. The instrument is usually calibrated using the ratio of peak height or area for analytes compared with that for the internal standard(s). Surrogates are treated as analytes for quantification.

They are of lesser utility for samples with very high concentrations of analytes as the responses of small quantities of added standards are likely to be swamped or to be lost in dilution of final extracts.

In addition to the above within-batch QC samples, it is also strongly recommended that the laboratory participate in inter-laboratory sample exchange and collaborative study programmes, and periodically analyse certified reference materials. These QC activities provide invaluable experience and external reference to validate analytical methodology and give confidence in data produced.

It is also recommended that a field control sample, spiked with analytes in the mid-range of anticipated sample concentrations, be analysed for every matrix type from a site assessment study. Such samples provide information on the potential of the matrix to cause positive or negative bias. For soil and sediment samples the spike should be applied to fresh material which has already been dried, ground and sieved. An unspiked duplicate sample must also be analysed to establish the naturally occurring analyte concentrations.

3.6.5 Data management

Effective data management is an essential final stage of any analytical procedure, to ensure the overall validity of the results. This can involve the following steps:

- data recording and documentation, including data custody records and checks on any data transfer operations
- data validation, including checking that all calculations are correct, identification of outliers and instrument drift
- data verification, which includes checking that all the data is present and correct
- data handling, which includes data rounding and treatment of significant figures, in accordance with recognised methodologies.

This subject is more fully discussed in MfE/MoH 1993 and CCME 1993.

3.6.6 Laboratory accreditation

Where possible laboratories engaged in analytical work should be accredited by an appropriate agency such as Telarc.

3.7 References

1 Australian and New Zealand Environment and Conservation Council (ANZECC) 1994. Draft guidelines for the analysis of contaminated soil, December.

2 APHA, AWWA, WEF 1995. Standard methods for the examination of water and wastewater, 19th edition.

3 API 1987. Manual of Sampling and Analytical Methods for Petroleum Hydrocarbons in Groundwater and Soil, API Publication No. 4449, Appendix B-3.

4 CCME 1993. Guidance Manual on Sampling, Analysis, and Data Management for Contaminated Sites; Volume I, Main Report, Report CCME EPC-NCS62E, December.

5 Department of the Environment 1987. Problems arising from the redevelopment of gasworks and similar sites. Second Edition. Environmental Resources Ltd, April.

6 Douglas G S et al 1992. The use of hydrocarbon analyses for environmental assessment and remediation, Journal of Soil Contamination, 1(3), 197-216.

7 Gas Research Institute 1987. Management of manufactured gas plants sites. Report GRI-87/02601, Vols. 1-4

8 Gas Research Institute (GRI) 1989. Cyanide in MGP Wastes, Investigation of Analytical Methods, Report GRI-89/0165

9 Ministry for the Environment and Ministry of Health (MfE/MoH) 1993. Draft Health and Environment Guidelines for Selected Timber Treatment Chemicals. December.

10 Roques D E, Overton E B, and Henry C B 1994. Using GC/MS Fingerprint Analysis to Document Process and Progress of Oil Degradation, Journal or Environmental Quality, 23, July-August.

11 Thomas A O and Lester J N 1994. The Reclamation of Disused Gasworks Sites: New Solutions to an Old Problem, The Science of the Total Environment 152 , 239-260.

12 US EPA 1994. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, 3rd Edition, November 1986, plus subsequent updates, to Proposed Update III, January.

13 US EPA 1995. Methods considered within the scope of existing wastewater methods under the EMMC performance-based methods system. Office of Science and Technology, June.

Appendix 3A
Definitions[8]

Internal standard	A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component. In practice internal standards are added prior to the final instrumental determining stage.
Surrogate analyte	A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. Where mass spectrometric detection is used, internal standards or surrogate standards may be isotopically labelled analogues of one or more of the analytes.
Laboratory duplicates	Two sample aliquots taken in the analytical laboratory and analysed separately with identical procedures. Analyses of duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
Field duplicates	Two separate samples collected at the same time and placed under identical conditions and treated exactly the same throughout field and laboratory procedures. These give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.
Laboratory reagent blank (LRB)	An aliquot of reagent water or quartz sand that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
Field control sample (FCS)	A sample of field matrix which contains levels of analytes of interest which are low compared to those expected in test samples. The FCS should otherwise be as similar as possible to the test samples. Aliquots of FCS, alone and fortified with analytes, carried through the complete method provide essential data on interferences, analyte recoveries and detection levels for a method as being applied in a given laboratory at a given time.
Laboratory performance check solution (LPC)	A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.
Laboratory fortified blank (LFB)	An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analysed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.
Laboratory fortified sample matrix (LFM)	A portion of an environmental sample, usually a field control sample, to which known quantities of the method analytes are added in the laboratory and then analysed exactly like a sample. Its purpose is to determine whether the sample matrix contributes bias to the analytical results, i.e. whether the matrix causes interferences or reduced recoveries of the analytes. The background concentrations of the analytes in the sample matrix alone must be determined in a separate aliquot and used to correct the measured values in the LFM.
Stock standard solution	A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a simple analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.
Primary dilution standard solution	A solution of one or more analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.
Calibration	A solution prepared from the primary dilution standard solution of the analytes and stock

[8] Ministry for the Environment and Ministry of Health (1993). Draft Health and Environmental Guidelines for Selected Timber Treatment Chemicals, December.

standard (CAL)	standard solutions of the internal standard(s) and surrogate analyte(s). The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
Quality control sample (QCS)	A sample matrix containing method analytes, portions of which are regularly analysed to check that a method is in control. A QCS can be a fortified sample matrix (either laboratory or external). A thoroughly homogenised field sample with analytes present as weathered residues can also be used as a QCS. The QCS may be locally prepared from a bulk sample containing analytes in relevant concentration ranges (laboratory reference material) or from external sources where the QCS may have been carefully validated by a inter-laboratory collaborative study.
Accuracy	Closeness of a result or the mean of a set of results to the true value. Accuracy is assessed by means of laboratory fortified matrix samples or external QC samples.
Precision	A measurement of the agreement of a set of replicate results amongst themselves without assumption of any prior information as to the true result. Laboratory precision is assessed by means of analysis of duplicate/replicate sub-samples.
Repeatability	The precision, usually expressed as a standard deviation, that measures the variability among results of measurements at different times on the same sample at the same laboratory.
Reproducibility	The precision, usually expressed as a standard deviation, that measures the variability among results of measurements of the same sample at different laboratories.
Replicates	Repeated but independent determination on the same sample by the same analyst at essentially the same time and under the same conditions.
Method detection level or limit (MDL)	The lowest concentration at which individual measurements for a specific analyte are statistically different from a laboratory blank with a specified confidence level for a given method and representative matrix. For a 95% confidence interval MDL = 3 S_B/M. where M = slope of calibration line for analyte S_B = standard deviation of the noise level or the background signal (usually from a field control sample).
Reliable detection level (RDL)	Lowest recommended concentration of analyte for making qualitative decisions based on individual measurements for a given method and representative matrix. Recommended to be 2 x MDL (CCME 1993)
Reliable quantitation level (RQL)	Lowest recommended concentration of analyte for making quantitative decisions based on individual measurements for a given method and representative matrix. Recommended to be 4 x MDL (CCME 1993).
Estimated quantitation limit (EQL)	Lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL.

Appendix 3B
Summaries of test methods

Method	Comment
SW-846 Method 8270B (Capillary GC-MS for Semi-volatile Organics in Solid or Liquid Waste)	This is a screen based on solvent extracts prepared using the 3500 series protocols. However the low resolution mass spectrometric detection (full scan mode) covers a wider range of contaminants with higher selectivity than ECD or FID. The high resolution capillary column separation also improves selectivity and inertness in the analytical system.
EPA-600 Method 525.1, rev 2.2, 1991 (Determination of Organic Compounds in Drinking Water using Liquid/Solid Extraction and Capillary GCMS)	This screen is similar to SW 846 8270B in the determination of a wide range of contaminants using capillary GCMS except that revised phase adsorbents (column or disk) are used to concentrate contaminants from water samples.
SW-846 Method 8040A, rev. 1, 1990 (Phenols by gas chromatography)	This concentrates on the determination steps but indicates that phenols can be recovered from waters by liquid-liquid partition (Method 3510 Separating funnel or Method 3520 Continuous liquid-liquid) or from solid waste by solvent extraction (Method 3540B Soxhlet or Method 3550B Sonication). Clean-up is by acid base partitioning (Method 3650A) and, for low levels in soil, gel permeation chromatography (Method 3640A). The specificity of packed column GC-FID is low and interferences from other acidic compounds may be expected. Also acidic phenols are liable to tailing and other adsorption effects in the GC, effects which can be variable and influenced by co-extractives and therefore lead to poor quantitation. The method also provides for a derivation step to form pentafluorobenzyl-ethers of the phenols which have more reliable GC performance and give high responses to the electron capture detector (ECD) However, a time-consuming silica gel chromatographic clean-up is required to remove interferences including derived co-extractives. The method has been validated for a range of phenolics including cresols.
SW-846 Method 8260 (Volatile Organics by Gas Chromatography/Mass Spectrometry: Capillary Column Technique)	This is a screen based on a purge-and-trap extraction technique. The method is applicable to nearly all types of samples, regardless of water content, including groundwater, soils, and sediments. It covers 58 volatile organic compounds including all of the monocyclic aromatic hydrocarbons and naphthalene. The low resolution mass spectrometric detection (full scan mode) covers a wider range of contaminants with higher selectivity than ECD or FID. The high resolution capillary column separation also improves selectivity and inertness in the analytical system.
EPA 524	GC/MS method used for detection of extremely low levels of halocarbons and aromatic hydrocarbons in drinking water.
EPA 624	GC/MS method used for detection of ppb levels of halocarbons and aromatic hydrocarbons in wastewater or groundwater.
EPA 3510B	GC/MS method used for detection of ppb levels of halocarbons and aromatic hydrocarbons in wastewater or groundwater.
EPA 3540B	Soxhlet extraction procedure for the extraction of non-volatile and semi-volatile organic compounds from solids such as soil, sludges and wastes. The procedure is undertaken in such a way that will ensure intimate contact of the sample matrix with the extraction solvent.
EPA 3550A	Ultrasonic extraction procedure for the extraction of non-volatile and semi-volatile organics compounds from solids such as soils, sludges and wastes.

	The procedure involves the use of a horn-type probe sonicator or equivalent device that will ensure intimate contact of the sample matrix with the extraction solvent.
EPA 3560	Supercritical fluid extraction procedure for the extraction with supercritical fluids of total petroleum hydrocarbons (TPH) from soils, sediments and other solid matrices which are amenable to extraction with conventional solvents. The method is suitable for use with any supercritical fluid extraction system that allows the temperature, pressure and flowrate to be adjusted to achieve separation of the TPHs from the matrices of concern. This method is not suitable for the extraction of low boiling TPHs such as gasoline.
EPA 3040	Prepares oily waste samples for soluble metals determination by AA and ICP methods. The samples are dissolved and diluted in organic solvent prior to analysis. The method is applicable to the organic extract in the oily waste EP procedure and other samples high in oil, grease or wax (and tar) content.
EPA 3050	Prepares waste samples for total metals determination by AA and ICP. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. The method is applicable to soils, sludges and solid waste samples.
EPA 3051	Prepares sludges, sediments, soils, and oils for total metals determination by AA and ICP. Nitric acid is added to the representative sample in a Teflon digestion vessel and heated in a microwave unit prior to metals determination.

4

Generic soil acceptance criteria

Appendices

Generic soil acceptance criteria

4.1 Introduction

This module covers the following:

- ➔ development of generic health-based soil acceptance criteria
- ➔ ecological considerations
- ➔ aesthetic considerations
- ➔ health effect summaries for selected gasworks contaminants

Additional information on the generic soil acceptance can be found in Section 4 of the Users' Guide, including:

- ▲ land uses (Section 4.2.1)
- ▲ hazard identification (Section 4.2.2)
- ▲ exposure assessment (Section 4.2.3)
- ▲ toxicity assessment (Section 4.2.4)
- ▲ risk characterisation (Section 4.2.5)
- ▲ derivation of generic soil acceptance criteria (Section 4.2.6)
- ▲ summary of the generic soil acceptance criteria (Section 4.2.7)
- ▲ ecological considerations (Section 4.2.8)
- ▲ aesthetic considerations (Section 4.2.9)
- ▲ application of generic soil acceptance criteria (Section 4.2.10)
- ▲ development of site-specific acceptance criteria (Section 4.4)

4.2 Development of generic health-based soil acceptance criteria

In developing soil acceptance criteria reference has been made to the information and methodologies from a range of sources, including:

- exposure assessment equations developed by the USEPA, particularly USEPA (1991) "Risk Assessment Guidance for Superfund, Human Health Evaluation Manual, Part B, Development of Preliminary Remediation Goals"
- exposure factor information agreed in the developing of previous industry-based guidelines in New Zealand and information presented in other sources such as Langley (1993, 1996) and by the USEPA and WHO
- toxicological information and dose response factors established in New Zealand in the New Zealand Drinking Water Standards, and information presented by the WHO and USEPA
- precedents established in New Zealand regarding the level of acceptable risk.

Information on the toxicity and dose response factors for contaminants of concern at gasworks sites are presented in Appendix 5A.

4.2.1 Land uses

Health-based generic soil acceptance criteria are derived for the following land uses:

- Agricultural/Horticultural
- Standard Residential (50% of produce home grown)
- Standard Residential (10% of produce home grown)
- High Density Residential
- Commercial/Industrial
- Parkland/Recreational

4.2.2 Hazard identification

4.2.2.1 Contaminants of concern

See Section 4.2.2.1 of the Users' Guide for information on the contaminants of concern.

4.2.2.2 Receptors

See Section 4.2.2.2 of the Users' Guide for information on receptors.

4.2.3 Exposure assessment

The exposure assessment in risk assessment is a measure of the likely exposure of the receptors (site users). Exposure assessment involves:

- identification of complete exposure pathways
- estimation of contaminant concentrations in media in which receptors may be exposed
- estimation of dose likely to be experienced by each receptor

The overall approach adopted for exposure assessment when deriving the generic acceptance criteria is based on the USEPA protocol for the development of preliminary remediation goals (USEPA, 1991). This is consistent with the approach used for the development of soil acceptance criteria for the timber industry (MfE/MoH, 1993). The exposure factors adopted for the derivation of the acceptance criteria have been modified to reflect New Zealand conditions and policy. In addition, some of the fate and transport modelling components of this section differ from the approach adopted by the USEPA for the development of preliminary remediation goals.

Because of the importance of the inhalation of volatiles in deriving criteria for BTEX and other volatile contaminants found at gasworks sites, particular attention has been given to modelling the emission of volatiles from contaminated soil. As volatilisation depends on soil properties, assumptions have been made regarding soil properties and depth to the contamination. The generic acceptance criteria have been based on a sandy loam soil, with criteria developed for surface soil (<1 m) and subsurface soil (>1m).

Exposure assessment depends on assumptions about a range of exposure factors. In practice, there is uncertainty regarding the value of many exposure factors (e.g. the quantity of soil ingested by children), whereas other exposure factors vary through the population (e.g. body weight). Conservative assumptions are mainly used to account for this uncertainty and variability, thus ensuring protection of public health.

The use of conservative point estimates in calculations involving many such parameters, however, can result in a compounding conservatism. Further, information on the level of conservatism inherent in the acceptance criteria is lost. Probabilistic techniques such as Monte Carlo analysis may be used to improve the assessment of uncertainty. These techniques have not been used routinely in the development of generic criteria to date although the potential exists for this in the future.

The impact of soil contamination on groundwater quality is best assessed by direct measurement of groundwater quality and assessment in accordance with the principles set out in Module 3. Therefore soil acceptance criteria based on the protection of groundwater quality have not been developed.

4.2.3.1 Exposure pathway analysis

Soil contamination only poses a risk to a receptor, if there is a complete pathway between the source of contamination and the receptor. Where the exposure pathway is incomplete there is no risk.

An exposure pathway consists of the following elements:

- a source and mechanism for release
- storage and/or transport media
- an exposure point, where the receptor comes in contact with the contamination, and
- an exposure route (e.g. inhalation).

For example, where a former gasworks site is redeveloped for residential use, some relevant exposure pathways are likely to include:

- ingestion of contaminated soil that may be exposed in the vicinity of the house
- consumption of home grown produce, and
- inhalation of volatiles, particularly benzene, in indoor air as a result of soil contamination beneath the building.

Inhalation of particulates is a complete exposure pathway, but in most circumstances the contribution of this pathway to the overall exposure is negligible. The exception is exposure scenarios involving high concentrations of suspended particulates, limited exposure via other routes, and contaminants exhibiting low volatility and significantly higher toxicity via the inhalation route, (e.g. arsenic, hexavalent chromium). None of the contaminants considered in deriving acceptance criteria satisfy these conditions. On this basis, exposure via inhalation of particulates has not been considered further.

See Section 4.2.3.1 of the Users' Guide for the table of exposure pathways.

4.2.3.2 Exposure concentration estimation

Many of the contaminants found at gasworks sites are relatively mobile in the soil and exposure may occur by contact with media other than that originally contaminated. To derive acceptance criteria to protect human health, it is necessary to find the relationship between contaminant concentrations in soil and those in other media to which site users may be exposed. Estimating contaminant concentrations at the point of exposure is one of the most critical elements of the risk assessment, and a source of uncertainty.

To determine contaminant concentrations at the point of exposure it is necessary to either directly measure contaminant concentrations at the relevant point, or predict the fate and transport of contaminants. Clearly, direct measurement is preferred in most cases, but, often this is not possible or practical (e.g. houses have not yet been built on the former gasworks site). For most initial site assessments, it is assumed that contaminant concentrations will be measured in soil and groundwater, but not in other media such as ambient air or produce.

As part of the development of acceptance criteria, an estimate of the relationship between contaminant concentrations in different media is required for the following exposure pathways:

- **Inhalation of volatiles**

  An estimate of the contaminant concentration in indoor air and outdoor air, based on the concentration in soil is required.

- **Consumption of home grown produce**

  An estimate of the uptake of contaminants by produce, based on the contaminant concentrations in soil, is required.

Volatilisation

The relationship between contaminant concentrations in air within the breathing zone indoors and outdoors, and the concentration in soil is described using the Volatilisation Factor (VF), which is defined as follows:

VF = Concentration in air (mg/m^3) / Concentration in soil (mg/kg)

The Volatilisation Factor is a function of soil and contaminant properties, the depth and thickness of contamination and the building or outdoor air characteristics. Modelling the transport of volatile contaminants from soil to indoor and outdoor air is one of the most important factors in deriving the acceptance criteria for volatile contaminants, such as benzene. A range of models have been developed for assessing the transport of volatile contaminants, however considerable uncertainty remains and development work in this area continues. The fate and transport of volatile contaminants in the subsurface is complex, involving a wide range of processes, few of which are well understood. Most of the available models consider only a small subset of the fate and transport processes which actually occur, and are based on simplified conceptual models of contamination (e.g. uniform contaminant concentrations through the contaminated zone).

Limited validation of the volatilisation models suggest they significantly over predict the transport of contaminants to indoor or outdoor air, although further work is required to determine the reasons for this.

Plant uptake

The primary concern with the uptake of contaminants by plants is the presence of contaminants in produce consumed by humans. The relationship between contaminant concentrations in soils and edible plant materials is highly specific to the specific plant species. The relationship between contaminant concentrations in edible produce and the concentration in soil is described using the Plant Uptake Factor (PUF), which is defined as follows:

$$\text{PUF} = \frac{\text{Concentration in edible portion of plant (mg/kg)}}{\text{Concentration in soil (mg/kg)}}$$

A range of published correlations between plant and soil concentrations are available. Most correlations are empirical, assuming a linear relationship between the plant and soil concentrations, and defining the ratio between the plant and soil concentrations in terms of K_{ow} or K_{oc} and the organic carbon content of the soil.

The available plant uptake models usually overestimate the concentration of many gasworks related contaminants for the following reasons:

- most hydrocarbons are readily degraded in the soil, particularly under conditions favouring biological activity such as those found in vegetable gardens (e.g. regular watering, fertiliser)
- significant losses by volatilisation are expected to occur within a period of, for example, a year
- enhanced degradation of contaminants may be expected in the plant root zone, and

- the depth range of most interest in a vegetable garden context is the upper 200 to 300 mm, where losses by volatilisation and other mechanisms are likely to be most pronounced.

As acceptance criteria have been based on long term exposure to contamination (e.g. 30 years for carcinogenic contaminants), less weight has been attached to criteria based on plant uptake and consumption of home grown produce, given that the derivation assumes constant soil concentrations.

Information on the uptake of inorganic chemicals is limited and the standard correlations used for organic chemicals do not apply. At gasworks sites cyanide is generally present as complex cyanide which has relatively low bioavailability and therefore uptake by plants is expected to be limited. Because of this, plant uptake has not been considered in deriving criteria for cyanide.

4.2.3.3 Exposure estimation

Generic acceptance criteria for the protection of human health, have been based on an estimate of the reasonable maximum exposure (RME) for a particular scenario (USEPA, 1989a). The RME combines upper bound and average exposure factors so that the result represents an exposure scenario that is both protective and reasonable. It is not the absolute worst case but represents a reasonable maximum exposure. (USEPA, 1991b).

The approach to exposure assessment and the development of health-based acceptance criteria is based on the procedures developed by the USEPA (1989, 1992). Assumptions employed in the risk assessment are based on recommendations by the USEPA (1989a, 1990b, 1991b, 1991d), information presented in Langley (1993, 1996) and precedents established in similar guidance for the timber industry (MfE/MoH, 1993).

The estimated exposure (or intake) is normalised for time and body weight and is generally calculated as:

$$\text{Intake} = \frac{\text{Concentration} \times \text{Contact Rate} \times \text{Exposure Frequency} \times \text{Exposure Duration}}{\text{Body Weight} \times \text{Averaging Time}}$$

The above equation may be rearranged to give health-based acceptance criteria on a route-specific basis as follows:

$$\text{Acceptance criteria} = \frac{\text{Acceptable Intake} \times \text{Body Weight} \times \text{Averaging Time}}{\text{Contact Rate} \times \text{Exposure Frequency} \times \text{Exposure Duration}}$$

Where Acceptable Intake = (Proportion of RfD assigned to contaminated soil) x (Reference Dose (RfD))

The above equation may be further rearranged to account for multiple exposure routes.

4.2.3.4 Exposure factors

The exposure factors adopted for developing screening criteria are consistent with those adopted in the revised "Health and Environmental Guidelines for Selected Timber Treatment Chemicals" and are in accordance with Ministry of Health policy.

For developing soil screening criteria for agricultural and residential land use, two age groups have been considered:

- Adults
- Children (1 to 6 years)

In a residential use, children and adults may live at a given site. and children may often spend the majority of their childhood at one residence. Consequently it is assumed that the exposure period begins when the child is a toddler and continues through childhood to adult life. Therefore, adult exposure may notionally be considered to correspond to 6 to 30 years of age.

The establishment of criteria based on exposure from 6 months to 30 years will also protect adults exposed for 30 yrs. For those contaminants for which a non-threshold dose response model has been adopted, the lifetime average daily dose relevant for risk assessment reflects a weighted mean of childhood and adult exposures. Where a threshold dose response model

has been adopted, a year-averaged exposure is used to determine acceptance criteria, with children the limiting receptor group. The exposure parameters for children reflect those of a 2-year-old child as soil ingestion is generally greatest at this time, whereas the exposure parameters for residents greater than 7 years old reflect those for adults.

Exposure via most of the pathways considered in deriving acceptance criteria is assumed to be constant with time i.e. contaminant concentrations do not decrease with time. This approach results in a significant over-estimate of exposure in the case of inhalation of volatiles, as depletion of the contaminated soil results in decreasing indoor and outdoor air concentrations with time. It is therefore necessary to determine average indoor and outdoor air concentrations, based on an assumed averaging time.

See Section 4.2.3.4 of the Users' Guide for the summary table of exposure factors.

4.2.3.5 Agricultural

Protection of human health

The major exposure assumptions are summarised below based on published typical average and upper bound values:

- exposure duration = 30 yrs, assuming exposure from 0 to 30 yrs of age, 6 years as child, 24 years as an adult.

The exposure duration is based on the reasonable maximum time spent on the one site in a rural context based on USEPA (1989).

- exposure frequency = 350 d/y (USEPA, 1989b)

Studies have shown that a child is likely to spend less than 200 days/year playing outside. However, Hawley (1985) estimated that 80% of indoors dirt is derived from local soil, meaning a child may be exposed whenever they are on-site, not just outdoors.

- body weight: child (1-6 yrs) = 15kg (USEPA, 1992)
  adult (7-30 yrs) = 70kg (ANZECC, 1992)
- soil ingestion rate: child (1-6 yrs) = 100mg/d (ANZECC, 1992)
  adult (7-30 yrs) = 25mg/d
- inhalation rate: child (1-6 yrs) = 3.8m^3/d (Langley, 1993)
  adult (7-30 yrs) = 22m^3/d
- exposed skin surface area: child (1-6 yrs) = 2625 cm^2 (Langley, 1993)
  adult (7-30 yrs) = 4700 cm^2
- soil adherence: 1 mg/cm^2 allowing for soil contact typical of farming activities (USEPA, 1988)
- ingestion of produce: child (1-6 yrs) = 0.13kg/d (Langley, 1989b)
  adult (7-30 yrs) = 0.45kg/d
- proportion of produce grown on site = 100% (MoH, 1995)

The assumed garden produce ingestion rates are based on the average daily consumption of fruit and vegetables derived from national dietary surveys, as presented in Langley (1993).

Dermal exposure is defined by the duration and frequency of exposure, body weight, the adherence of soil to exposed skin, the area of skin exposed, and the skin absorption factor. Soil adherence values consistent with those adopted in previous New Zealand guidelines were adopted as a default, although uncertainty remains.

The absorption of contaminants through skin is uncertain, particularly where contaminants are applied in the form of a soil mixture. Published information was reviewed in order to

develop estimates for the skin absorption factors as follows (ASTM, 1994, USEPA, 1992, GRI, 1988):

- **Standard Residential/Agricultural/Horticultural**

PAHs	1 %
BTEX, Phenolics	5%

- **Parkland/Recreational**

PAHs	0.5%
BTEX, Phenolics	2.5%

- **Commercial/Industrial**

PAHs	0.6 %
BTEX, Phenolics	3 %

The assumed values take into account the matrix effects associated with application of contaminants in soil. Higher values have been reported for BTEX compounds, but most reported information does not account for losses by volatilisation from a thin film of soil in skin, and therefore lower values may be justified.

Protection of plant and livestock

The impact of ground contamination on plant life and livestock may involve the following factors:

- protection of human health of residents who may consume produce
- protection of plant life — phytotoxicity
- maintenance of acceptable levels of contaminants in produce and livestock for sale.

The suitability of fruit and vegetable produce for human consumption may be assessed by comparing predicted produce concentrations with published Maximum Residue Limits (MRL). In the absence of MRLs for most of the contaminants of concern, the suitability of produce for human consumption may be assessed using health risk assessment techniques assuming 100% of produce consumed is from a contaminated source.

Livestock (e.g. cattle, sheep, poultry) may be exposed to contaminants in soil and contaminants may accumulate in edible portions of livestock, increasing exposure of consumers. In practice the organic contaminants of concern at gasworks sites, although lipophilic, are readily metabolised and therefore are unlikely to accumulate at significant levels in livestock. In contrast, many chlorinated organics are not readily metabolised and may accumulate within livestock. Cyanide and complex cyanide are not lipophilic and are less likely to accumulate. On this basis, exposure via the consumption of livestock products where livestock have been reared on contaminated land is unlikely to be a significant route of exposure and therefore criteria have not been derived for this pathway.

Criteria developed for the protection of human health in an agricultural context are expected to broadly protect livestock health, based on consideration of:

- the higher soil consumption/body weight ratio for cattle and other livestock compared to humans
- the shorter lifespan of livestock reducing concern associated with cancer and points, and
- a lower level of protection (i.e. not all sensitive individuals protected) required in the case of livestock.

Information on the protection of plant life is limited for most of the contaminants of concern at gasworks sites.

4.2.3.6 Residential

Soil guidelines have been developed on the basis of reasonable maximum exposure assumptions. The major exposure assumptions are summarised below:

- exposure duration = 30 years, assuming exposure from 0 to 30 years of age; 6 years as a 'child', 24 years as an 'adult'.

  The exposure duration is based on the reasonable maximum time spent on the one site in a rural residential context based on USEPA (1989).

- exposure frequency = 350 days/year (USEPA, 1989 b)

  Studies have shown that a child is likely to spend less than 200 days/year playing outside, however, Hawley (1985) estimated that 80% of indoors' diet is derived from local soil meaning a child may be exposed wherever on site, not just outdoors.

• body weight:	child (1-6 yrs)	=15 kg	(USEPA, 1992)
	adult (7-30 yrs)	=70 kg	(ANZECC, 1992)
• soil ingestion rate:	child (1-6 yrs)	=100 mg/d	(ANZECC, 1992)
	adult (7-30 yrs)	=25 mg/d	
• inhalation rate:	child (1-6 yrs)	=3.8 m^3/d	(Langley, 1993)
	adult (7-30 yrs)	=20 m^3/d outdoors	(ASTM, 1994)
		15 m^3/d indoors	
exposed skin surface area:	child (1-6 yrs)	=2625 cm^2	(Langley 1993)
	adult (7-30 yrs)	=4700 cm^2	
• soil adherence:	0.5 mg/cm^2		(USEPA, 1988)
produce ingestion rate:	child (1-6 yrs)	=0.13 kg/d	(Langley, 1993)
	adult (7-30 yrs)	=0.45 kg/d	
proportion of produce grown on site:	rural residential	= 50%	(Langley, 1993)
	urban	= 10%	

4.2.3.7 Commercial/industrial

Human health is the primary on-site concern with regard to ground contamination where an ongoing industrial use is proposed. Where off-site transport of contaminants via soil movement, groundwater or surface water is likely, off-site environmental or health impacts may be most important. Acceptance criteria based on human health have been developed on the basis of reasonable maximum exposure assumptions. The major exposure assumptions are summarised below:

- exposure duration = 20 yrs (USEPA, 1989 b) (reasonable maximum time in one job, corresponds to 90th percentile time since last job in the US) (Finley, 1994)
- soil ingestion rate = 25 mg/day (for workers not directly involved in excavation) (ANZECC, 1992)
- inhalation rate = 9.6 m^3/d (based on 8 hour working day) (Langley, 1993)
- skin surface area = 4700 cm^2, based on exposure of 24% of total adult body surface area (Langley, 1993)
- soil adherence = 1.0 mg/cm^2 (USEPA, 1989)

The protection of human health is the primary on-site concern with regard to soil contamination where commercial/industrial site use is proposed. Where contaminated areas are fully paved and the integrity of the paving is maintained, the exposure to non-volatile soil

contaminants should be eliminated. However, the effectiveness of pavement as a barrier to the exposure of workers to ground contamination is highly dependent on the integrity and design of the pavement and on the nature of the underlying soils. Spreading and other transport of contaminated soil from areas where contaminated soil is unpaved or from areas of failed pavement may mean that protection against worker exposure to contaminated soil is reduced. The migration of volatiles through pavement, and the subsequent exposure, must also be assessed.

The acceptable contaminant concentration in soil on a paved industrial site may be controlled by exposures associated with ongoing maintenance of subsurface services or other subsurface works. For example, exposure associated with subsurface maintenance works may be effectively mitigated by the use of an appropriate site management plan requiring the use of protective clothing and equipment whenever the pavement is broken by subsurface works, and the diligent clean-up of soil and repair of the damaged areas.

4.2.3.8 Parkland/recreational

There is potential for human exposure to soil contamination in recreational areas with children the key exposure concern. Off-site migration of contaminated soil or dust may also occur. For exposure by the inhalation route, where there are buildings on site, e.g. kiosk or storeroom, this is the key exposure concern, and the criteria for commercial/industrial land use have been used for this route (to be protective of any works spending the majority of their time indoors at the site). The major exposure assumptions are summarised below:

- exposure duration = 30 years, assuming exposure from 0 to 30 years of age; 6 years as a 'child', 24 years as an 'adult'.
- exposure frequency = 350 days/year (USEPA, 1989 b)
- body weight: child (1-6 yrs) =15 kg (USEPA, 1992)
  adult (7-30 yrs) =70 kg (ANZECC, 1992)
- soil ingestion rate: child (1-6 yrs) =50 mg/d (ANZECC, 1992)
  adult (7-30 yrs) =10 mg/d
- inhalation rate: child (1-6 yrs) =1.1 m^3/d (Langley, 1993)
  adult (7-30 yrs) =2.4 m^3/d
  exposed skin surface area: child (1-6 yrs) =2625 cm^2 (Langley 1993)
  adult (7-30 yrs) =4700 cm^2
- soil adherence: 1.0 mg/cm^2 (USEPA, 1988)

4.2.3.9 Maintenance

For each of the above site uses, with the possible exception of agricultural use, there is potential for significant human exposure to ground contamination associated with subsurface maintenance works e.g. repair and replacement of services. Whilst the duration of such works is generally much shorter than the other exposure scenarios considered, the rate of intake of various contaminants is likely to be much higher and such exposure may be significant where undertaken routinely by the same person.

In order to develop reasonable but protective soil guideline values goals for adult workers involved in subsurface maintenance, the following exposure factors have been assumed:

- exposure duration = 20 yrs, 90% upper bound for time spent in one job (USEPA, 1989b)
- soil ingestion rate = 100 mg/d (for workers directly involved in excavation) (GRI, 1988).
- exposure frequency = 50 d/yr
- inhalation rate = 10 m^3/d (Langley, 1993)
- skin soil adherence = 1.5 mg/cm^2 (USEPA, 1988)

The above assessment assumes that maintenance workers wear normal work clothes. The use of appropriate personal protective equipment may reduce worker exposure allowing work within areas with contaminant concentrations above the proposed criteria.

4.2.4 Risk characterisation

4.2.4.1 Carcinogens (non-threshold)

See Section 4.2.5.1 of the Users' Guide for information on carcinogens.

4.2.4.2 Non-carcinogens

Where more than one species has the same health effect or where exposure to a species may occur by more than one route, the HQ for each combination is summed to give a hazard index, HI. In the absence of further information, it is common practice to consider exposure to each substance separately. Where it is likely that substances have an additive or synergistic effect, this can be taken into account and the toxicological assessment should not be undertaken independently of such effects.

There is some evidence that toluene, ethylbenzene and xylene may act in a similar manner, particularly in relation to neurological effects. It may be argued, therefore, that additive or synergistic effects should be considered. Similarly some of the PAHs may be expected to show similar effects. However for the purposes of deriving generic acceptance criteria, each of the contaminants has been considered separately, with the exception of the carcinogenic PAHs.

The toxicological model underlying the USEPA assessment approach for non-carcinogenic health effects assumes the effects and dose are not necessarily cumulative over a lifetime. The USEPA RfDs for chronic health effects have developed for exposure durations of months to years. On this basis, a year average Chronic Daily Intake is used to estimate the HQ in equation 7.7.

As chronic health effects may be experienced by children exposed to a substance over a period of months to years, if exposures to children and adults are combined for the assessment of non-carcinogenic health effects over, say, the 30 year exposure duration for a residential scenario, the year-averaged CDI for children would be underestimated, as would the likelihood of adverse health effects.

In particular, the year-averaged CDI for children would be underestimated when the higher exposure rates experienced by children for, for example, 6 years, are combined with lower rates of exposure experienced by adults for a longer period of time, and expressed as a year-average over a period of, for example, 30 years. Consequently, the assessment of non-carcinogenic health effects for residential and agricultural land uses are based on a year-average CDI for the most sensitive group (or the group with the highest weight-standardised exposure rate), i.e. children, rather than averaging over the entire 30 year exposure.

See Section 4.2.5.2 of the Users' Guide for information on non-carcinogens.

4.2.3 Derivation of generic soil acceptance criteria

Contaminant concentrations corresponding to the target risk level have been estimated for each exposure route e.g. inhalation of indoor air, inhalation of outdoor air, ingestion of soil, consumption of home grown produce and dermal absorption.

It may be argued that the exposure associated with each exposure route may be considered to be additive, and therefore that the acceptance criteria should be based on the soil concentration corresponding to the target risk level based on the cumulative exposure from all exposure routes (this is readily undertaken based on acceptance criteria for each individual exposure route). The above position is based on the assumption that a contaminant acts by a similar mechanism, despite exposure occurring by different exposure routes. While this is true for some contaminants, many exceptions are noted.

In practice, one exposure route is frequently dominant (resulting in a route specific acceptance criterion that is much lower than for other exposure routes). Therefore the acceptance criteria may be determined by selecting the lowest of the route specific acceptance criteria. Where more than one exposure route is significant, the impact of the combined exposure has been considered, and a note is included to this effect.

See Section 4.2.7 of the Users' Guide for a summary of the generic soil acceptance criteria.

4.3 Ecological considerations

Ecological considerations are an essential part of any assessment of the impact of former gasworks sites. Where sensitive ecological receptors are located near the site, ecological impact can be the limiting consideration.

Most gasworks sites are not located within pristine environments for which a very high level of protection of the surrounding ecosystems is required. Rather, most sites are located within a modified environment and the primary requirements for ecological protection relate to the protection of off-site environment quality and the associated ecosystems, and protection of on-site environmental quality is required to protect functions relevant to the site use e.g. protection of native and imported plants in the context of a residential use.

Policy objectives regarding the level of protection to be given to on-site ecosystems in the context of other land uses must be decided before the development of ecological investigation level guidelines for sensitive land uses.

The following precedents have been established regarding the development of guideline values based on environmental protection:

- **Agricultural**

  Protection of plant and livestock health, protection of human health via the consumption of produce from contaminated areas.

- **Residential**

  Protection of plant life and the protection of human health via the consumption of produce from contaminated areas.

- **Commercial/industrial**

  No specific requirement for protection of the on-site ecosystems.

The underlying premise in these precedents is that protection of on-site ecosystems is only required to the extent necessary to facilitate use of the land (e.g. protection of plant life to allow normal gardening activities in a residential context).

For each land use there is a residual requirement for the protection of the off-site environment, including groundwater quality, although these considerations are not explicitly incorporated in the derivation of soil guideline values. Rather, such considerations must be addressed on a site-specific basis. Where on-site ecosystems need protection in excess of that outlined above, published information such as the Environmental Quality Objectives for the Netherlands (including the Intervention Values) may be useful. Some published ecologically-based environmental quality objectives are presented in Appendix 4B.

In considering the possible impact of soil contamination on the off-site environment, the first step involves identification of:

- possible sensitive ecological receptors associated with the site (e.g. adjoining wetland ecosystems)
- possible exposure pathways for migration of the contaminant from the source to the ecological receptor (e.g. leaching from soil to groundwater, migration in

groundwater and discharge to the wetland). Possible exposure pathways should also be reviewed to ensure completeness.

Where a sensitive ecological receptor and a complete or potentially complete exposure pathway is identified, a further, more detailed evaluation of ecological risk should be undertaken.

Not enough work has been carried out in establishing the ecological considerations associated with gasworks contaminants. This is a field of work which is developed in the area of contaminated sites, and it is hoped that more attention can be focused on this area in the future.

More information of ecological considerations can be found in Section 4.2.8 of the Users' Guide.

4.4 Aesthetic considerations

Aesthetic impacts or impairment of the aesthetic qualities of a site are an important consideration in the management of contaminated land. There are several examples of sites that have been considered to be 'safe' in terms of their possible impacts on human health and the environment, yet have been deemed to be unsuitable for a sensitive use because of aesthetic impacts.

On gasworks sites, specific aesthetic concerns include free tars or 'tar balls'. Phenolic compounds have also been responsible for tainting of potable water flowing through plastic pipes in contaminated soil. The complex cyanides present in gasworks wastes can stain the soil a distinctive blue.

Of the effects noted above, odour is possibly the most sensitive aesthetic effect and can be associated with contamination by relatively light hydrocarbon compounds or the heavier tar materials.

While it is not possible to completely define the constituents responsible for odour impacts at gasworks, possible sources include;

- light PAHs such as naphthalene
- phenolic compounds e.g. cresol, and
- sulphurous odours associated with spent oxides.

Some odour may also be noted where manufactured gas is trapped within the soil matrix.

Weathering can have an important effect on both the odour associated with contaminated soil and the specific contaminants associated with such odour. As contamination weathers, the lighter organic compounds (e.g. benzene, naphthalene) are lost due to volatilisation and biodegradation, leaving the less volatile and more recalcitrant compounds.

In the assessment of aesthetic impact a tension exists between:

- the need to assess sites individually due to the site-specific nature of odour and the aesthetic effects, and
- the convenience and objectivity of establishing threshold soil concentrations for the protection of aesthetic quality. Assessment of aesthetic impact on a site by site basis relies on the notoriously subjective assessment of odour.

In practice, aesthetic impact is readily assessed on a site-specific basis and therefore generic criteria based on aesthetic impact have not been developed.

In assessing possible aesthetic impacts of contaminated soil, the following criteria may be considered:

- no perceptible odour associated with the soil (in close proximity to the soil)
- no perceptible discolouration of the soil

- no impact on soil structure, and
- no sheen development if a soil sample is submerged in water.

Aesthetic considerations are important when assessing the significance of soil contamination in the context of a sensitive land use, however, these considerations are of much lesser importance for less sensitive land uses, e.g. industrial. Although residents at a site may reasonably expect that the aesthetic quality of the soil is protected, on industrial land other aesthetic impacts associated with activities at the site would make it unreasonable to seek a protection of a high level of aesthetic soil quality. In an industrial context, concern would be associated with possible off-site aesthetic impacts. However an off-site impact is unlikely to be associated with contaminated soil within the site unless there is bulk soil movement or excavation.

Although contaminated soil at depth may be of concern with regard to human health, depending on the concentration of benzene and other volatiles, there is less concern about aesthetic impacts due to soil contamination at depth. Aesthetic effects are most likely to be noticed in close proximity to the soil, such as during gardening activities, and therefore concern is focused on the surface soils rather than the sub surface soils, i.e. those soils with which residents are most likely to come in direct contact.

More information on aesthetic considerations can be found in Section 4.2.9 of the Users' Guide.

4.5 References

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15 USEPA (1991b) “Risk Assessment Guidance for Superfund, Volume 1, Human Health Evaluation Manual, Part B, Development of Preliminary Remediation Goals”.

16 USEPA (1992) “Dermal Exposure Assessment: Principles and Applications”, EPA/600/8-91/011B.

17 USEPA (1993) “Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons”.

Appendix 4A
Health effects summaries for selected gasworks contaminants

Introduction

The health effects associated with a range of contaminants encountered at former gasworks sites have been reviewed in order to:

- provide background information for assessing the significance of contamination
- review basis for establishing response factors for use in the assessment of risk and the derivation of acceptance criteria
- nominate dose response factors for use in the derivation of acceptance criteria.

Procedures for the development of dose response factors for carcinogenic chemicals in soil are currently under review by the National Health and Medical Research Council (NHMRC). The adopted dose response factors for carcinogenic chemicals are therefore subject to review following the release of guidance from the NHMRC.

General principles

Background

The assessment of the human toxicity of selected gasworks constituents has been based on published information relating to the observed effects of exposure of humans and animals to each of these compounds. The information available is limited in that:

- the observed effects are associated with exposure to the chemical of interest at a higher level than that of interest in nominating acceptance criteria for contaminated land. In setting acceptance criteria, attention is focused on a level of exposure that results in no appreciable risk or no effect. In contrast, most suitable studies focus on levels of exposure that result in an effect which is necessarily higher
- the duration of exposure may be less than is of interest when assessing the risk associated with contaminated land
- effects are observed in animals rather than humans, and there is some uncertainty as to the relevance of animal data in predicting likely effects in humans.

Human data are used preferentially in the assessment of chemical toxicity. However, when human data are not available, animal data has been used to extrapolate an exposure limit that is without an appreciable risk of an adverse effect in humans. When animal data are used, considerations are given to the suitability of the animal models for extrapolation to humans. The appropriate animal models would consider their relevance to humans such as xenobiotic metabolism and exposure routes. The approach is conservative and safety factors are used in deriving the exposure limits. Acceptable concentrations of the chemical in soil and groundwater may be estimated on the basis of the “acceptable” level of exposure.

The reported adverse effects in humans and animals associated with exposure to each of the selected gasworks constituents have been reviewed in order to develop an understanding of the range of health effects in humans that may be associated with exposure to these chemicals.

In developing health-based acceptance criteria, it is necessary to make a quantitative estimate of the relationship between exposure or dose and response. The relationship between exposure and response (i.e. dose response relationship) is frequently assessed separately for carcinogenic health effects and other health effects. Whereas one approach has been generally used for the assessment of non-carcinogenic health effects, a range of approaches have commonly been used to assess carcinogenic health effects.

The assessment of the toxicity of the gasworks constituents and, in particular, development of the quantitative dose response relationships, has been undertaken in accordance with the ANZECC/NHMRC (1992) "Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites" (ANZECC Guidelines). The ANZECC Guidelines nominate that, where available, the WHO/FAO PTWIs or ADIs should be used as the basis for the development of Investigation Thresholds. In regard to the site-specific assessment of risk, the ANZECC Guidelines note that “where effects other than cancer are concerned, an acceptable daily intake has often been established by dividing the NOEL by a safety factor of 100”.

Whilst no specific guidance is provided regarding the assessment of carcinogenic health effects, the ANZECC Guidelines provide some guidance in which two broad approaches are suggested for deriving the Investigation Thresholds. Firstly, a ‘threshold’ model is used to Investigation Thresholds where the WHO/FAO PTWIs or ADIs are available. Secondly, where the WHO/FAO PTWIs or ADIs are not available, a ’non-threshold’ model using mathematical linear extrapolation (slope factors) from high to low doses is used.

The ANZECC Guidelines indicate that as part of toxicity assessment, reference should be made to:

- Toxicological Profiles prepared by the ATSDR, in collaboration with the USEPA
- Environmental Health Criteria, prepared by the World Health Organization
- IARC Monographs on the Evaluation of Carcinogenic Risks to Humans.

Although there is no clear consensus on the appropriate methodology for the assessment of genotoxic carcinogens and germ cell mutagens, a non-threshold model for the assessment of carcinogen has generally been adopted. This approach is consistent with the WHO approach in setting "Guidelines for Drinking Water Quality"(1993) and with the NZDWG which make a distinction between genotoxic and non-genotoxic carcinogens.

The NHMRC Working Party on Cancer Risk Assessment are developing guidance for cancer risk assessment. In the interim, an approach generally consistent with the NZDWG has been adopted in the selection of dose response factions for deriving soil and water acceptance criteria of specific chemicals will follow release of the guidelines. It is understood that the NHMRC Working Party are considering adoption of a benchmark dose approach, based on that outlined by WHO (1994) in EHC 170, for the assessment of carcinogenic contaminants in soil.

Reference has been made to the approaches adopted by a range of organisations (e.g. NHMRC, WHO, USEPA, ATSDR etc.) in developing dose response factors, given the lack of definitive guidance in the ANZECC Guidelines regarding the assessment of carcinogenic health effects in the context of site specific risk assessment.

Classification of carcinogens

The International Agency for Research on Cancer (IARC) first developed a system for qualitatively categorising carcinogens in 1977. This system was based on weight-of-evidence data which involves assessment of all toxicity data originating from human, animal and in-vitro studies to ascertain if a chemical can be classified as carcinogenic. Assessment of all the data often indicates lack of adequate data for humans, hence if sufficient evidence of carcinogenicity in animals exists, then the chemicals are regarded as carcinogenic to humans as well. A classification system was also produced by the USEPA in the late 70s and was

modeled on the IARC system. Table 4A.1 shows the different carcinogenic classifications developed by the two agencies.

Dose response factors

In order to quantify the health risks or likelihood of an adverse health effect associated with human exposure to various contaminants, a number of dose response factors, such as Reference Doses (RfD) Acceptable Daily Intakes (ADI), Benchmark Doses, and Cancer Potency Factor (CPF) or Cancer Slope Factors (CSF), have been defined by organisations such as the United States Environmental Protection Agency (USEPA) and the World Health Organisation (WHO).

In risk assessment, dose response factors are used to relate estimates of exposure or intake of contaminants to the likelihood of adverse health effects.

Dose response factors have been developed on the basis of human and animal studies, in order to relate an estimated intake of a contaminant to health risk. The available human data relating dose to response is limited for most chemicals, as discussed above, and therefore it is necessary to extrapolate from the available animal data to determine exposure levels that are consistent with no appreciable risk in humans. Such extrapolation may represent the single largest source of uncertainty and conservatism in the risk assessment process. Published dose response factors (e.g. WHO, USEPA) are generally conservative, incorporating a number of safety factors or uncertainty to account for the inherent uncertainties in the available data and the extrapolation process. The acceptable levels of exposure may have been used to determine health-based acceptance criteria for various environmental media (e.g. soil).

In assessing the dose response relationship in accordance with the approach adopted in the NZDWG, chemical contaminants and their associated health effects may be divided into two broad classes, as follows:

- Contaminants that exhibit a threshold:

  For such contaminants it is proposed that a threshold dose exists below which there is no appreciable risk of critical adverse health effects.

  A RfD or Acceptable Daily Intake (ADI) is an estimate (with uncertainty spanning perhaps an order of magnitude or greater) of a daily exposure level for the human population, including sensitive sub-populations, that is likely to be without an appreciable risk of deleterious effects during a lifetime. Chronic RfDs are specifically developed to be protective for long-term exposure to a compound. In developing a RfD or ADI, safety or uncertainty factors are used to modify the available experimental data (e.g. a No Observable Effect Level from an animal study) to account for (if applicable):

  - extrapolation from animals to humans
  - sensitive sub-populations
  - extrapolation from a Lowest Observable Effect Level (LOEL) to a No Observable Effect Level (NOEL).

- Contaminants that exhibit no threshold:

  For some contaminants and some health effects, it is assumed that there is no threshold dose below which there is no appreciable risk; rather the likelihood of a response increases as the dose increases (i.e. no dose is completely risk free). This approach is most commonly applied to carcinogens, particularly genotoxic carcinogens.

  To quantify the risk associated with a given exposure, the Cancer Slope Factor (CSF) is used. The Cancer Slope Factor is a plausible upper-bound estimate (95th percentile) of the probability of a response per unit intake of a chemical over a lifetime. The CSF is used to estimate an upper-bound probability of an individual developing cancer as a result of a lifetime of exposure to a particular level of a

potential carcinogen. The Cancer Slope Factor should be regarded as an upper bound estimate, rather than as an estimate of the actual risk.

The existence of a threshold (or lack of it) for some health effects, particularly cancer endpoints, is subject to considerable debate. If the NHMRC Working Party adopt an approach to the assessment of carcinogens based on the concept of a benchmark dose, then the distinction between threshold and non-threshold contaminants may be lessened.

The dose response relationship for various contaminants may depend on the route of exposure. Most of the available dose response data relates to the oral route, although some information is available regarding the inhalation route particularly from occupational studies or specific animal studies. The oral exposure route is the route of most concern for the contaminants. The available information has been combined to determine an acceptable daily intake or similar dose response factor for the combined exposure from all routes. This approach requires specific consideration of the bioavailability absorption, and metabolism of contaminants by each route.

Some important considerations extrapolating dose response data from route to route, include:

- lipid solubility. If a compound is highly lipid soluble it is more readily absorbed via the dermal route. Further lipid solubility affects the hepatic metabolism of contaminants
- does first pass metabolism of contaminants occur following oral exposure and, if so, are the metabolites active or inactive in terms of the outcome of interest (e.g. cancer)? If contaminants are immediately metabolised to an active intermediate following oral exposure, then extrapolation of dose response data from the oral route to other routes may be compromised.

A single dose response factor for the combined exposure via all routes will not be adopted where:

- the site of the effect is very close to the point of exposure
- there is marked difference in the sensitivity of animals and humans by exposure route (e.g. due to differing metabolic processes for each route).

Table 4A.1 IARC and EPA classification of carcinogenic risk to humans[1]

IARC				Evaluation of Agent Mixture or Occupation	EPA		
Classification Grouping	**Evidence from[(2)]**				**Classification Grouping**	**Evidence from[(2)]**	
	Humans	Animals	Other Relevant Data[(3)]			Humans	Animals
1	S			**IS** carcinogenic	A	S	
2A or or	L L I/ND	S S	 Supp Supp	is **PROBABLY** carcinogenic	B1 B2 or	L I ND	 S S
2B or or	L I/ND I	 S L	 Supp	is **POSSIBLY** carcinogenic	C	ND	L
3	I/ND	L		is **NOT CLASSIFIABLE** as to its carcinogenicity	D	Inadequate evidence or no data available	
4	No evidence for carcinogenicity			is **PROBABLY NOT** carcinogenic	E	No evidence for carcinogenicity	

Notes 1 Based on Table from Langley (1993)

2 S - sufficient Supp - supportive
L - limited ND - no data
I - inadequate

3 Other relevant data include structure - activity considerations, pharmakokinetics and metabolism, toxicity, genetic and related effects.

Assessment of chemical mixtures

A significant limitation with regard to most toxicity assessments is that the available information generally relates only to exposure to a single chemical, whereas in practice exposure to a range of chemicals occurs simultaneously. The effect of simultaneous exposure to multiple chemicals is generally not well understood. The effects of such combined exposures may be synergistic, additive or antagonistic. An example of synergistic interaction between chemicals is found in one of the proposed mechanisms of cancer formation, where initiation and promotion of the tumour may require exposure to different agents, such that a tumour does not occur unless exposure to both chemicals occurs.

Some information may be obtained regarding the possible effects of simultaneous exposure to more than one chemical by considering the route of absorption, distribution, metabolism and target organ. Where chemicals affect different target organs and there is little or no interaction between the metabolism and distribution of the chemicals in the body, then there may be some justification for assuming the effects are independent.

Examples of groups of contaminants likely to be found together at former gasworks sites and which may act in a similar manner include (although differences may be apparent in some effects):

- carcinogenic PAHs
- non-carcinogenic endpoints associated with PAHs (both carcinogenic and non-carcinogenic)
- toluene and ethylbenzene

Health effects summaries for individual chemicals

Overview

The health effects associated with selected chemicals of concern at former gasworks sites have been discussed in terms of the following issues:

- Kinetics and metabolism
- Animal toxicity
- Genotoxicity and carcinogenicity
- Human toxicity
- Dose response.

The discussion of dose response includes nomination of dose response factors used in the derivation of soil and water acceptance criteria. The discussion of dose response factors may require revision following the release of the report on the assessment of carcinogenic chemicals from the NHMRC Working Party.

Benzene

Primary reference

WHO (1993) “Environmental Health Criteria 150, Benzene” IPCS

Kinetics and metabolism

Benzene is well absorbed in humans and experimental animals following exposure via the oral and inhalation route, however dermal absorption is generally poor in humans. Benzene tends to accumulate in tissues with a high lipid content, and it crosses the placenta.

Benzene metabolism occurs mainly in the liver, is mediated primarily through the cytochrome P-450 IIE1 enzyme system, involving the formation of a series of unstable reactive metabolites. Experimental evidence suggests the formation of two putative toxic metabolites, benzoquinone and muconaldehyde, in rodents can be saturated. This may have important implications in establishing a dose-response relationship for benzene, as a higher

proportion of the benzene will be converted to toxic metabolites at low doses than at high doses.

Metabolism of benzene in the liver is responsible for the detoxification of benzene via the formation of etheral sulfate, glucuronides and glutathione conjugates. However metabolism of benzene in the liver also leads to the production of metabolites, such as hydroquinone, p-benzoquinone and muconaldehyde which appear to be associated with benzene toxicity in bone marrow. The metabolic products of benzene are primarily excreted in the urine.

Animal toxicity

The available evidence suggests benzene is of low acute toxicity in a range of animal species, with LD_{50} values for rats following oral exposure ranging between 3000 and 8100 mg/kg body weight. Reported LC_{50} values based on inhalation exposure range from 15 000 mg/m3 (8 h) in mice to 44 000 mg/m^3 (4 h) in rats.

There is no evidence that benzene is associated with teratogenic effects at doses lower than those required to produce maternal toxicity, however foetal toxicity has been demonstrated.

Genotoxicity and carcinogenicity

In vitro tests indicate that benzene is not mutagenic, however, benzene, or its metabolites, have been shown to cause chromosomal aberrations in experimental animals and sister chromatid exchange (SCE) and micronuclei in polychromatic red blood cells.

Benzene has been associated with several types of neoplasms in rats and mice following oral or inhalation exposure, including various types of epithelial neoplasms, e.g., Zymbal gland, liver, mammary tissue and nasal cavity neoplasms, and some lymphomas and leukaemias.

The evidence of carcinogenic health effects associated with benzene resulting from observation of occupationally exposed populations is presented in the following section.

Benzene has been classified as a Group 1 chemical (confirmed human carcinogen) by IARC.

Human toxicity

The most significant adverse effects from short- or long-term exposure to benzene are haematotoxicity, i.e. bone marrow suppression, immunotoxicity, genotoxicity and carcinogenicity.

Benzene is a well-established human carcinogen. Epidemiological studies of benzene-exposed workers have demonstrated a causal relationship between benzene exposure and the production of myelogenous leukaemia. A relationship between benzene exposure and the production of lymphoma and multiple myeloma remains to be clarified.

There is at present no adequate animal model for benzene-induced leukaemia in humans which limits the ability of researchers to conduct experiments that may assist in understanding the metabolism and mechanisms of action. The limited metabolic data suggests that several reactive metabolites of benzene are formed and these can form adducts both with DNA and protein. The failure to produce leukaemia in animals may be due to inadequate formation of leukaemogenic metabolites or the need to produce bone marrow damage prior to the induction of leukaemia.

Continuos exposure to benzene over a period of 10 years or more is expected to result in some toxicity, for both high and low doses. A high level of both bone marrow depression and aplastic anaemia may be seen at the higher doses although some damage would also be observed at lower doses.

The neurotoxicity and immunotoxicity of benzene has not been well studied in experimental animals or humans.

The risk of adverse health effects, particularly leukemia, associated with low-level benzene exposure has not been clearly established. Studies of workers exposed to relatively low concentrations of benzene (TWA: < 3.2-32 mg/m^3, < 1-10 ppm) revealed no alteration in cell-cycle kinetics and in sister chromatid exchange rate, which are possible markers of

carcinogenic process. Only a marginal increase in chromosomal aberrations (chromatid deletions and gaps) was noted at the low levels of exposure outlined above.

Dose response

A guideline value of 0.01 mg/litre was recommended by WHO (WHO, 1984) for benzene in drinking-water based on data for the production of leukaemia after inhalation exposures in humans and using a linear multistage extrapolation model and a life-time risk level of 1 in 100,000. This risk specific dose would correspond to a slope factor of 0.035 $(mg/kg/day)^{-1}$.

Benzene is considered a non-threshold toxicant by the USEPA due to its carcinogenicity. An oral slope factor value of 0.029 $(mg/kg/day)^{-1}$ has been derived based on the observance of leukemia from occupational exposure by inhalation.

In derivation of the NZDWS, the Ministry of Health adopted an acceptable daily intake of 0.29 μg/kg/day, based on the WHO guideline, which corresponds to slope factor of 0.035 $(mg/kg/day)^{-1}$.

For the purposes of deriving soil and water acceptance criteria, a slope factor of 0.029 $(mg/kg/day)^{-1}$ has been adopted.

Toluene

Primary reference

WHO (1986) "Environmental Health Criteria 52, Toluene" IPCS

Kinetics and metabolism

Studies on humans and animals have shown that toluene is readily absorbed from the respiratory tract with 40 to 60% uptake reported in humans. Liquid toluene is also rapidly absorbed through the skin (14 to 23 mg/cm2/h), although absorption from the gastrointestinal tract appears to be slower.

Following absorption, toluene is rapidly distributed, with highest levels observed in adipose tissue followed by bone marrow, adrenal glands, kidneys, liver, brain, and blood. The relationship between arterial blood and alveolar air concentration has been found to exhibit a close linear correlation. Therefore, measuring the toluene concentration in alveolar air during exposure, allows the estimation of the arterial blood concentration.

Some 60 to 75% of absorbed toluene is metabolised to benzoic acid by the microsomal mixed-function oxidase system, with subsequent conjugation with glycine to form hippuric acid. It is eliminated in this form through the kidneys. Approximately 10 to 20% of the absorbed toluene is excreted as benzoyl glucuronide. Small amounts of toluene undergo ring hydroxylation to form o-, m-, and p-cresol, which are excreted in the urine as sulfate or glucuronide conjugates. A proportion of the absorbed toluene (20 to 40%) is eliminated unchanged in expired air. After a single exposure, the elimination of toluene and its metabolites is almost complete in 24 hours. The half-life of toluene in subcutaneous adipose tissue has been estimated to be between 0.5 and 2.7 days.

Toluene has been shown to affect biotransformation of several solvents, altering the likelihood and severity of associated adverse health effects. Toluene decreased n-hexane metabolism and neurotoxicity, and benzene metabolism and effects on the haematopoietic system. However, toluene has been associated with increased hepatotoxicity resulting from exposure to carbon tetrachloride.

Animal toxicity

Acute inhalation data suggests that the sensitivity of various species to toluene decreases as follows: rabbit, guinea-pig, mouse, and rat. Inhalation LC_{50} values have been reported in the range of approximately 20 0000 to 26 000 mg/m^3 for mice and 45 000 mg/m^3 for rats.

The reported oral LD_{50} for toluene in rats is between 2.6 and 7.5 g/kg body weight, depending on the strain, age, and differences in sex. Toluene is a slight dermal irritant and a moderate

eye irritant in animals and humans. The acute dermal toxicity of toluene appears to be quite low (rabbit: LD_{50} 14.1 ml/kg body weight).

No effect was observed in short-term and long-term inhalation studies on experimental animals using toluene, at concentrations up to 375 mg /m^3 for a period of 24 months. In oral exposure studies, administration toluene at a rate of 590 mg/kg body weight/day, for 6 months did not produce any observable adverse effects. At low doses the target organs in rats appear to include the kidneys and testes, while at higher doses liver changes and effects on the central nervous system are observed.

Numerous studies using pure toluene have failed to demonstrate adverse effects on the blood.

Toluene can affect the central nervous system (CNS), but not the peripheral nervous system (PNS), although this is usually observed at high doses.

Toluene does not appear to be teratogenic in mice, rats, or rabbits, however fetotoxic effects were observed in rats at doses that were non-toxic to the dams (e.g. toluene concentrations up to 1000 mg/m^3), and spontaneous abortion occurred in rabbits exposed to 1000 mg/m^3 during the period of organogenesis (which includes the period or organ development).

Oral exposure to toluene has been associated with teratogenic effects in CD-1 mice. Exposure of CD-1 mice to toluene at 870 mg/kg body weight for days 6 to 15 significantly increased the incidence of cleft palate. No observable teratogenic effect was associated with exposure to toluene at a rate of 430 mg/kg body weight.

Genotoxicity and carcinogenicity

In general, very little evidence has been reported suggesting genotoxic or carcinogenic effects associated with exposure to toluene, and thereroe toluene is normally regarded as non-carcinogenic.

Skin-painting studies on mice, where toluene was used as a vehicle control, and one inhalation study on rats exposed to toluene (112.5 to 1125 mg/m^3, 6 h/day, 5 days/week, for 24 months) did not report evidence of carcinogenic effects.

The results of studies on the mutagenic effects of toluene in microbial, mammalian-cell, or whole-organism test systems have, in most cases, been negative. Positive findings were reported in 5 studies using in vivo mammalian assays. However, in these studies the purity of the toluene used was not stated and the possibility of impurities contributing to the observed effect cannot be discounted.

Toluene has not been classified as a possible, probable or confirmed human carcinogen by either the USEPA or IARC.

Human toxicity

Information on the toxicity of toluene in humans has been primarily derived from individuals exposed to toluene via inhalation either in occupational settings or during episodes of intentional abuse of solvent mixtures containing toluene.

The primary effect of acute exposure to toluene is on the central nervous system (CNS). The effect may be depressant or stimulatory, with euphoria in the induction phase, and may lead to convulsion or coma.

Single, short-term exposures to toluene (750 mg/m^3 for 8 h) have been associated with transient eye and respiratory tract irritation at 1500 mg/m^3.

Repeated occupational exposures to toluene over a period of years at concentrations in the range 750 to 1500 mg/m^3 have resulted in some evidence of neurological effects. Inhalation of toluene was reported to be an important cause of brain diseases in children (aged 8 - 14 years), possibly leading to permanent neurological damage.

Transient abnormalities of hepatic enzyme activities have been found in abusers of toluene mixtures, but significant permanent hepatic damage has not been observed. Renal damage in

glue-sniffers have been reported but there is no evidence that toluene results in adverse effects on the blood or the heart.

Epidemiological information regarding the effects of exposure to toluene is limited (frequently information is confounded by concurrent exposure to a range of chemicals).

Dose response

The USEPA has nominated the following RfDs for toluene;

- 0.2 mg/kg/day by oral route, with a safety factor of 1000, based on NOAEL for effects on liver and kidneys in rats; and
- 0.4 mg/m^3 by inhalation with a safety factor of 300, based on LOAEL for neurological effects observed in a small population of workers.

In derivation of the NZDWS, the Ministry of Health adopted an acceptable daily intake of 0.22 mg/kg/day based on hepatotoxicity in mice from a 15-week gavage study and an uncertainty factor of 1000. This approach is consistent with that adopted by the WHO in the derivation of a drinking water guideline value.

For the purposes of deriving soil and water acceptance criteria, a Reference Dose of 0.2 mg/kg/day has been adopted for the oral route, and a Reference Concentration of 0.4 mg/m^3 has been adopted for the inhalation route.

Ethylbenzene

Primary reference

WHO (1996) " Guidelines for Drinking-Water Quality-Health criteria and other supporting information".

Kinetics and metabolism

Ethylbenzene is readily absorbed by oral, inhalation or dermal routes. Once absorbed, the distribution and excretion are rapid. In humans, storage of ethylbenzene in fat has been reported, and the compound has been observed to cross the placental barrier. Biotransformation in humans to mandelic acid and phenylglyoxalic acid is almost complete, both the metabolites being excreted in the urine. In animals, the metabolism of ethylbenzene differs from that in humans in that benzoic acid is the major metabolite together with mandelic acid. Urinary excretion of metabolites is rapid and is complete within 24 hours.

Animal toxicity

In a 6-month oral study in rats, doses of 400 mg/kg and above produced effects on liver and kidneys, with a NOAEL of 136 mg/kg. Liver effects were also observed in a number of inhalation studies with the LOAEL at 1305 mg/m3 and NOAEL at 218 or 430 mg/m3.

Although teratogenicity studies have been carried out in rats and rabbits, via the inhalation route, no definite conclusion could have been drawn.

Genotoxicity and carcinogenicity

Studies on the mutagenic activity of ethylbenzene to bacteria, insects, mammalian cells(in vitro) and intact mammals have shown ethylbenzene to be devoid of mutagenic activity.

No carcinogenicity data on ethylbenzene are available.

Human toxicity

Ethylbenzene is mildly toxic to humans following skin contact or inhalation, and has been associated with systemic effects in humans. Ethylbenzene has been associated with irritation of the eyes, skin, nose, throat and respiratory tract at concentrations in the order of 0.2% (v/v)**)** . The lowest reported acutely toxic concentration (TC_{l0}) of ethylbenzene by inhalation for human is 100 ppm.

Ethylbenzene has been classified by the USEPA as a Class D chemical i.e. not classifiable as to human carcinogenicity due to inadequate humans and animal evidence.

Dose response

The USEPA has nominated the following dose response factors for ethylbenzene:

- an oral RfD of 0.1 mg/kg day with a safety factor of 1000, based on NOAEL by oral route for liver and kidney toxicity observed in rats
- an inhalation RfC of 1 mg/m^3, with a safety factor of 300, based on NOAEL for developmental toxicity in rats and rabbits.

In derivation of the NZDWS, the Ministry of Health adopted an acceptable daily intake of 0.1 mg/kg/day based on hepatotoxicity and nephrotoxicity in rats reported as part of a limited 6 month study. A safety/uncertainty factor of 1000 was adopted reflecting limitations in the animal data used.

For the purposes of deriving soil and water acceptance criteria, the Reference Dose of 0.1 mg/kg/day has been adopted for oral route, and a Reference Concentrations of 1 mg/m^3 has been adopted for inhalation route.

Xylenes

Primary reference

WHO (1996) " Guidelines for Drinking-Water Quality- Health criteria and other supporting information".

Kinetics and metabolism

Xylene is readily absorbed following inhalation and is also absorbed to some extent via the skin. However, there are no data available on human absorption after ingestion. Xylene is rapidly distributed following uptake. Once absorbed, xylenes is rapidly metabolised almost completely to methyl benzoic acid which is excreted in the urine as hippuric acid. Xylenes have been found to cross the placental barrier and are stored in adipose tissue in both animals and humans. The elimination half-life of xylenes from subcutaneous fat in humans ranges from 25 to 128 hours.

Animal toxicity

A 2-year feeding study has been carried out in rats and mice. In rats, decreased growth at high dose of 500 mg/kg/day with no observable compound related histological lesions. The NOAEL for rats was 250 mg/kg/day. Although embryotoxicity and developmental toxicity has been observed in mice, the observations were not conclusive due to the concurrent maternal toxicity.

Exposure to xylene by inhalation caused liver enzyme induction at high concentration ($\geq$ 217 mg/m3). No developmental toxicity has been observed in rodents due to inhalational exposure of xylene.

Genotoxicity and carcinogenicity

The mutagenicity studies of xylene in bacteria and mammalian cells, both in vitro and in vivo, have shown negative results. Xylene did not cause carcinogenicity at oral doses up to 500 mg/kg/day in rats and up to 1000 mg/kg/ in mice.

Xylene has been classified as a Class D chemical by the USEPA, i.e. it is not classifiable as to its human carcinogenicity due to inadequate human and animal evidence.

Human toxicity

In humans, exposure to xylene vapour has been associated with irritation of the eyes, nose and throat and some light-headedness at concentrations in excess of 200 ppm. Neurobehavioural effects were also reported after a 5-6 hours of exposure to xylenes at a concentration in the order of 100 ppm.

Dose response

The USEPA has nominated an oral RfD for xylenes of 2.0 mg/kg/day, incorporating a safety factor of 100 and based on the NOAEL of 179 mg/kg/day for decreased body weight and increased mortality in rats from a 103 week gavage study.

In derivation of the NZDWS, the Ministry of Health adopted an acceptable daily intake of 0.18 mg/kg/day based on the same study in rats but an uncertainty factor of 1000.

For comparison, a tolerable daily intake of 0.01 mg/kg/day was used in the derivation of soil acceptance criteria by the Dutch agencies.

For the purpose of deriving soil and water criteria, the oral Acceptable Daily Intake of 0.18 mg/kg/day has been adopted.

Polycyclic aromatic hydrocarbons

Primary reference

WHO (1996) " Guidelines for Drinking-Water Quality-Health criteria and other supporting information".

Introduction

Polycyclic aromatic hydrocarbons (PAHs) is a large class of chemicals with two or more fused aromatic rings structure. PAHs occur in the environment as complex mixtures of which only a few components have been adequately characterised. Most of the available literature on PAHs is concerned with benzo[a]pyrene B[a]P the most abundant naturally occurring and anthropogenic PAH, and only limited information is available on the relative toxicity of the PAHs.

The concern over PAH contamination in the environment relates mainly to the carcinogenic and mutagenic activity of some of these compounds. B[a]P benzo[a]pyrene is an indicator compound due to its carcinogenicity. For the purposes of this assessment, PAHs classified by the USEPA as Class D chemicals have been regarded as non-carcinogenic PAHs. Other PAHs may be grouped with B[a]P because of uncertainties in their carcinogenicity and because they accumulate or bioconcentrate in living tissue.

Kinetics and metabolism

Absorption of PAHs mainly occurs following oral and inhalation exposure and rapidly distributed to the various organs and tissues. PAHs can also be absorbed following dermal exposure. The rate of absorption of the different PAHs is influenced by their lipid solubility. PAHs is highly lipophilic and may be stored in the breast and fat tissues. B[a]P has been shown to cross the placenta and is distributed in the developing foetus.

The metabolism of B[a]P occurred primarily in the liver involving oxidation and hydroxylation by the mixed-function oxygenases (MFOs) and detoxication by glucuronosyl-, sulfo- or glutathione transferases.

Animal toxicity

The reported oral LD50s for PAHs range from 40 to 18 000 mg/kg of bodyweight. No treatment-related effects were observed in mice given anthracene by gavage at doses up to 1000 mg/kg/day for at least 90 days. Subchronic oral administration of naphthalene (50 mg/kg/day) has been associated with decreased body weight in rats. Mice subchronically exposed to fluoranthene at doses developed adverse effects in the kidney, liver and haematological system. Haematological and kidney effects have also been observed in mice following exposure to fluorene (125-500 mg/kg/day) and pyrene (127-917 mg/kg/day), respectively. Slight morphological changes in the liver and kidney of rats following oral exposure to acenaphthene for 40 days have been reported.

Reproductive effects were observed in offspring of mice given oral doses of B[a]P with reduction of fertility at doses as low as 10 mg/kg/day.

Genotoxicity and carcinogenicity

B[a]P has been shown to be mutagenic in bacteria and in cultured human lymphoblastoid cells, after metabolic activation. It is considered that the diol-epoxides metabolites of B[a]P is considered to be more potent than the parent compound. B[a]P has also caused sister chromatid exchanges in *in vivo* and *in vitro* test systems.

PAHs have been shown in animals to affect proliferating tissues such as bone marrow, lymphoid organs, gonads and intestinal epithelium.

Many PAHs mixtures have been associated with increased incidences of cancer. Of the 16 PAHs identified by the USEPA in their primary pollutants list, seven are classified as probable human carcinogens (B2) ie. benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene. The basis for the carcinogenic classification of these compounds is varied. For example, no human data is available for chrysene, however it has been found to produce skin carcinomas and malignant lymphoma in mice. Benzo(a)pyrene has been shown to be carcinogenic to rodent and non rodent species following exposure by all three major pathways.

In humans, the evidence of carcinogenicity mainly comes from studies of workers who are exposed to mixtures containing PAHs in their occupations which involved processes such as coke production, oil refining or coal gasification. As inhalation and dermal exposures are the common exposure routes, cancers associated with exposure to the PAH-containing mixtures in humans are also commonly found in the lungs and skin.

Human toxicity

Studies on human health effects of PAHs are limited. Skin lesions have been observed in human subjects skin-painted with benzo(a)pyrene.

Death caused by acute haemolytic anaemia due to accidental poisoning by naphthalene has also been reported. Although no human healths have been reported following exposure to other PAHs, it can be assumed that acute exposure to sufficiently high doses of PAHs can be lethal based on the observation of death in animals following oral exposure.

As indicated earlier, occupational studies indicate an increased incidence of cancers associated with exposure to PAH-containing mixtures in workers. Epidemiological studies have also indicated increased incidence of lung cancer in humans exposed to PAH-containing mixtures, ie. coke-oven emissions and cigarette smoke. However, it is not possible to evaluate the contribution of any individual PAH to the total carcinogenicity of these mixtures in humans due to the complexity of the mixtures and the presence of other carcinogens.

Dose response

Non-carcinogenic PAHs/Size

The USEPA derived chronic oral RfDs for the non-carcinogenic PAHs as follows:

- 0.06 mg/kg/day for acenaphthene based upon NOAEL of 175 mg/kg/day with critical effect of hepatotoxicity in mice exposed by gavage for 90 days
- 0.3 mg/kg/day for anthracene based upon NOEL of 1000 mg/kg/day in mice exposed by gavage for 90 days
- 0.04 mg/kg/day for fluoranthene based upon NOAEL of 125 mg/kg/day with critical effects of nephropathy, liver weight changes and haematological alterations in mice exposed by gavage for 90 days
- 0.04 mg/kg/day for fluorene based upon NOAEL of 125 mg/kg/day with critical effects of decreased red blood cell count, packed cell volume and haemoglobin concentration in mice exposed by gavage for 13 weeks
- 0.03 mg/kg/day for pyrene based upon NOAEL of 75 mg/kg/day with critical effect of renal toxicity in mice exposed by gavage for 13 weeks.

The chronic RfDs for acenaphthene, fluoranthene, fluorene and pyrene were all derived using an uncertainty factor of 3,000. These values are adopted in this assessment for the derivation of the soil acceptance criteria.

For naphthalene, the chronic reference dose of 4×10^{-3} mg/kg/day used for risk calculation in the Health Risk Assessment for Soils Contaminated with Fuel hydrocarbons: Petrol in Australia (Lindon P, 1991), which based on decrease body weight gain in rats (HEAST, 1991), was adopted in this assessment for the derivation of the soil acceptance criteria.

There is currently no RfD value established for phenanthrene which is still under review by the USEPA. However, a oral RFD of 3×10^{-2} was available from the 1993 IRIS database and is adopted for this assessment.

The NZDWS and NZDWG in considering PAHs only present a health based guideline value for benzo(a)pyrene, based on a cancer endpoint. The non-carcinogenic PAHs are generally not a limiting consideration.

Carcinogenic PAHs

The carcinogenic potency of these compounds is most commonly determined using data from animal studies, largely due to the lack of human studies from which the observed effects may be directly attributed to a specific PAH compound or group of compounds. The dose associated with a particular increased lifetime cancer risk, or the slope of the risk-dose relationship (slope factor) is estimated using the available human and animal data.

In general, the risk estimates for benzo(a)pyrene have been calculated from two studies in different species of rodents, orally exposed to benzo(a)pyrene, where forestomach cancer was observed (Neal and Rigdon, 1967; Brune *et al*., 1981). The data set were separately fitted to the Linearised Multistage (LMS) model to provide a low-dose extrapolation. A 95% upper confidence limit is applied to determine an upper bound for the slope of the line (Slope Factor) derived by the LMS model. The cancer slope factor of 7.3 $(mg/kg/day)^{-1}$ for benzo(a)pyrene was based on the geometric mean of risk estimates calculated from these studies.

To streamline the assessment of the carcinogenic PAHs, a relative potency approach has been developed to estimate cancer potency of the other carcinogenic PAHs based on their relative potency to benzo(a)pyrene. The toxicity equivalency factor (TEF), based on carcinogenicity, nominated by various organisations are shown in Table 4A.2. The TEFs nominated by the USEPA in provisional guidance (USEPA, 1993) are suggested for use in the assessment of gasworks sites. TEFs may be used to express the relative potency of a mixture of carcinogenic PAHs in terms of equivalent benzo(a)pyrene concentration.

Using the TEFs, calculated oral slope factors for the carcinogenic PAHs range from 7.3 $(mg/kg/d)^{-1}$ for benzo(a)pyrene to 0.073 $(mg/kg/d)^{-1}$ for chrysene.

In derivation of the NZDWS, the Ministry of Health adopted a tolerable daily intake for benzo(a)pyrene of 0.00002 mg/kg/day, corresponding to an excess life-time cancer risk of 1 in 100 000 (or a Slope Factor of 0.5) based on a quantitative risk assessment conducted using the two-stage birth-death mutation model.

The USEPA derived slope factor for benzo(a)pyrene of 7.3 $(mg/kg/d)^{-1}$ has been adopted for the derivation of acceptance criteria. The TEFs nominated by the USEPA should be used in assessing the risk associated with carcinogenic PAH mixtures.

Table 4A.2 Toxic fequivalence factors (TEFS) for carcinogenic PAHs

Chemical	US	Californian	Dutch (RIVM) [3]	Health	Adopted

	EPA [1]	EPA [2]		Canada [4]	
Benzo(a)pyrene	1.0	1.0	1.0	1.0	1.0
Benzo(a)anthracene	0.1	0.1	0.1		0.1
Benzo(b)fluoranthene	0.1	0.1		0.06	0.1
Benzo(k)fluoranthene	0.01	0.1	0.1	0.04	0.1
Chrysene	0.01		1.0		0.01
Dibenz(a,h)anthracene	1.0	0.4			1.0
Indeno(1,2,3-cd)pyrene	0.1	0.1	0.1	0.12	0.1

[1] USEPA (1993) "Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons".

[2] California Environmental Protection Act (1994).

[3] RIVM Netherlands (1991) "Voorstel voor de humaan-toxicologische onderbouwing van C-(toetsings)waarden". Report no. 725201005.

[4] Canadian Environmental Protection Act (1994) "Polycyclic aromatic hydrocarbons".

[5] USEPA Carcinogen Classification System. Class B2 denotes probable human carcinogen based on limited (or no) human data and sufficient animal data.

Phenol

Primary reference

WHO (1994) "Environmental Health Criteria 161, Phenol" IPCS

Kinetics and metabolism

Phenol is readily absorbed by all routes of exposure and is rapidly distributed to all tissues. The liver, the lung, and the gastrointestinal mucosa are the most important sites for phenol metabolism. The relative importance of each of these sites depends on route of administration and dose.

Absorbed phenol forms conjugates with glucuronic acid and sulfuric acid and, to a lesser extent, hydroxylates into catechol and hydroquinone. Phosphate conjugation also occurs. The formation of reactive metabolites (4,4-biphenol and diphenoquinone) has been demonstrated in vitro studies with human white blood cells (ie. activated neutrophils and leucocytes). The relative amounts of glucuronide and sulfate conjugates vary with dose and animal species. A shift from formation of sulfate conjugated to formation of glucuronide conjugates was observed in rats after increasing dosage.

Urinary excretion is the major route of phenol elimination in animals and humans. The rate of urinary excretion varies with dose, route of administration, and species. Excretion in faeces and elimination in expired air are relatively minor routes..

Benzene and phenol derivatives may, in vivo conversion, represent a source of phenol exposure from within the body.

Animal toxicity

Phenol exhibits moderate acute toxicity in mammals. Oral LD_{50} values in rodents range from 300 to 600 mg/kg body weight. Dermal LD_{50} values for rats and rabbits range from 670 to 1400 mg/kg body weight, respectively, while the 8-h LC_{50} for rats by inhalation is more than 900 mg/m^3.

There is evidence that phenol is not associated with skin sensitisation.

The most important effects reported in short-term animal studies were neurotoxicity, liver and kidney damage, respiratory effects and growth retardation. In a limited 14-day study involving rats, an oral no-observed-adverse-effect level (NOAEL) of 12 mg/kg per day was reported, based on kidney effects.

No adequate studies examining the reproductive toxicity of phenol were identified. Phenol has been identified as a developmental toxicant in studies with rats and mice. In two multiple dose rat studies, NOAEL values of 40 mg/kg per day (the lowest-observed-adverse-effect level (LOAEL) was 53 mg/kg per day) and 60 mg/kg per day (the LOAEL was 120 mg/kg per

day) have been reported. In the mouse study, a NOAEL of 140 mg/kg per day (the LOAEL was 280 mg/kg per day) was identified.

Phenol and some of its metabolites can be cytotoxic as they have been demonstrated to covalently bind to tissue and plasma proteins.

Genotoxicity and carcinogenicity

The majority of bacterial mutagenicity tests have reported negative results for phenol, however mutations, chromosomal damage and DNA effects have been observed in mammalian cells in vitro. Induction of micronuclei in bone marrow cells of mice has been observed in some studies at high doses.

In carcinogenicity studies conducted with male and female rats and mice receiving phenol in their drinking-water, malignancies (e.g., C-cell thyroid carcinoma, leukaemia) were only seen in low-dose male rats. Two-stage carcinogenicity studies have shown that phenol, applied repeatedly to mouse skin, has promoting activity.

No evidence of carcinogenicity has been reported for phenol in human studies, although animal studies have indicated it may be a promoter and/or weak skin carcinogen in some species of mice. Phenol has not been classified as a human carcinogen (confirmed, probable or possible) by the USEPA (Class D)..

Human toxicity

Most of the information regarding adverse effects in humans associated with phenol exposure relates to acute rather than chronic exposure.

Clinical symptoms observed in humans following acute exposure include neuromuscular hyperexcitability and severe convulsions, necrosis of skin and mucous membranes of the throat, and effects on lungs, nerve fibres, kidneys, liver, and the pupil response to light.

Gastrointestinal irritation has been reported following ingestion of phenol. Local effects following dermal exposure range from painless blanching or erythema to corrosion and cell death.

Systemic effects associated with exposure to phenol include cardiac dysrhythmias, metabolic acidosis, hyperventilation, respiratory distress, acute renal failure, renal damage, dark urine, methaemoglobinaemia, neurological effects (including convulsions), cardiovascular shock, coma and death. The lowest reported dose resulting in a human death was 4.8 g by ingestion; death occurred within 10 min.

The potential for poisoning through inhalation of phenol vapours has long been recognised, however no cases of death following this route of exposure have been reported. Symptoms associated with inhalation of phenol included anorexia, weight loss, headache, vertigo, salivation and dark urine.

There is no evidence that Phenol is a sensitising agent.

Dose response

The lowest NOAEL values identified in animal experiments are for kidney and developmental effects, and in rats lie within the range of 12-40 mg/kg body weight per day. Using an uncertainty factor of 200, exposure in the range 60 to 200 µg/kg body weight per day is recommended as the upper limit for the total daily intake (TDI). Based on the upper-limit estimate for human daily intake of 100 µg/kg body weight per day, it is concluded that on average the general population exposure to phenol from all sources is below this range.

The USEPA have nominated a Reference Dose for phenol of 0.6 mg/kg/day, based on the NOAEL of 60 mg/kg/day in a developmental study in rats and an uncertainty factor of 100.

The Ministry of Health has not set a guideline value for the NZDWS.

The reference dose of 0.6 mg/kg/day has been adopted for deriving the acceptance criteria.

Cresols

Primary reference

WHO (1995) "IPCS Environmental Health Criteria 168, Cresols"

Cresols are also known as methylphenols and have 3 possible isomers (ortho, meta, and para).

Kinetics and metabolism

Cresols are rapidly absorbed following oral or dermal exposure, and are distributed to all major organs. Following absorption cresols are largely metabolised through the glucuronidation and sulfation processes and eliminated as conjugates in the urine. Significant quantities of cresols are also excreted in the bile, however, most of the cresols excreted in the bile are hydrolysed by the gut bacteria and reabsorbed.

In humans, endogeneous p-cresol production occurs by anaerobic gut bacteria from tyrosine, and amino acids. Thus, it has been reported that an average of 50 mg of p-cresol is excreted in urine daily by healthy adults.

Animal toxicity

The available information indicates that all three isomers of cresols are toxic to rodents in dose-related manners with mice being more sensitive than rats. Systemic toxicity and death can result from all routes of exposure, although acute toxicity following exposure to cresol vapours is less likely due to the low vapour pressure of these compounds.

Cresols are strong skin and eye irritants. Oral and inhalational exposure to cresols has been associated with reproductive toxicity in female mice and rats, however no major compound-related reproductive toxicity has been reported in studies involving male rodents. O- and p-cresols cause mild fetotoxicity in the rats and rabbits, however only minor developmental effects have been reported.

Genotoxicity and carcinogenicity

The three cresol isomers have produced positive results in genetic toxicity studies both individually and in cresol mixtures. Cresols have been classified as possible human carcinogens (Class C) by the USEPA based on an increased incidence of skin papillomas in mice as part of a tumour initiation-promotion study.

Human toxicity

Oral exposure to cresols in humans mainly affects the blood and kidneys, although effects on the lungs, liver, heart and central nervous system have also been reported. Acute dermal exposure has been associated with skin burns, scarring and systemic toxicity. High level, acute exposure to cresols may result in coma and death.

Dose response

The USEPA have nominated an RfD for cresol (the ortho and meta isomers) of 5.0×10^{-2} mg/kg/day, based on neutrotoxicity in rat studies and an uncertainty factor of 1000. An RfD for p-cresol has not been nominated by the USEPA in the Integrated Risk Information System (IRIS) database. A similar RfD (5.0×10^{-3} mg/kg/day) had previously been nominated for p-cresol in the USEPA Health Effects Assessment Summary Tables (HEAST), however this was not ratified following review by the USEPA.

No Slope Factor has been nominated for cresols despite them being classified as a Class C chemical (possible human carcinogen).

The WHO has determined an NOAEL of 50 mg/kg/day for all three isomers based on the results of subchronic studies. WHO applied an uncertainty factor of 300, an ADI of 0.17mg/kg/day.

For the purpose of deriving soil and groundwater criteria, the USEPA Reference Dose for o-, m-m p-Cresol of 0.05 mg/kg/day for cresols has been adopted.

Cyanide

Primary reference

Turczynowicz L. (1993) "The Assessment and Management of Gasworks Sites" Proc. 2nd National Workshop on the Health Risk Assessment and Management of Contaminated Land, SA Health Commission.

WHO (1996) " Guidelines for Drinking-Water Quality-Health criteria and other supporting information".

Kinetics and metabolism

Cyanide is absorbed following inhalation and ingestion and via the eye and skin, although the rate of adsorption depends very heavily on the form of cyanide (eg. free cyanide compared to complex cyanide). Cyanide is rapidly distributed via the blood to all organs and tissues. Cyanide ions exhibit a high affinity for haemoglobins in the red blood cells and plasma proteins.

Metabolism of cyanide in the liver occurs via the enzyme rhodanase, converting cyanide to thiocyanate. In humans, the metabolism occurs within 20 min to 1 hour following exposure. Cyanide is excreted primarily in the urine in the form of thiocyanate.

Animal toxicity

The mechanism of cyanide toxicity is associated with the ability of cyanide to bind to heme moiety and proteins. Dissociation of hydrogen cyanide and cyanide salts in vivo releases cyanide ions that disrupt enzymes systems by complexing with heavy metal ions contained in the enzyme systems. For example, cyanide (CN^-) forms a stable complex with ferric ion (Fe3+) in the cytochrome oxidase enzymes consequently inhibiting oxidase, the terminal oxidase in the mitochondrial respiratory chain and causing cytotoxic anoxia (oxygen depletion with the cell).

The target organs of cyanide include the central nervous system, cardiovascular and respiratory systems and the thyroid.

Developmental toxicity has been observed in rats orally exposed to cyanide, with a LOAEL of approximately 51.2 mg/kg CN^- per day reported.

Effects on behavioural patterns and serum biochemistry were observed in pigs exposed for 6 months at 1.2 mg/kg.bw/day (nominated as a LOAEL), pigs may be more sensitive to cyanide than many of the other species tested.

Genotoxicity and carcinogenicity

Cyanide has not been shown to be genotoxic and has not been associated with carcinogenic effects in animals or humans.

Human toxicity

A human oral LD_{50} of cyanide was estimated to be 1.52 mg/kg based on reported incidences of abuse. A dermal LD_{50} of 100 mg/kg bw has also been estimated for HCN.

Chronic exposure to low levels of cyanide salts has been associated with enlargement of the thyroid gland in humans. Persistent neuropsychiatric effects resulting from one or more acute exposure episodes have also been observed.

Exacerbation of vitamin B12 deficiency and increased incidence of goitre in humans have been associated with exposure to cyanide.

Complex cyanides

There is limited information on the health effects associated with exposure to complex cyanides. In general, the toxicity of these complexes is expected to be low compared to the toxicity of free cyanides and related to the degree of dissociation forming free cyanide.

In a 90-day subchronic feeding study of rats using sodium ferrocyanide in the diet, a NOEL of 0.05 % (in the diet) was established, which equated to an intake of 25 mg/kg bw/day.

Dose response

The USEPA has nominated an RfD of 0.02 mg/kg/day for cyanide based on a chronic oral rat study, which reported a NOAEL of 10.8 mg/kg/day for decreased body weight, thyroid effects and nerve degeneration, with an uncertainty factor of 100 and modifying factor of 5 applied.

In derivation of the NZDWS, the Ministry of Health adopted a tolerable daily intake for cyanide (free) of 0.012 mg/kg/day, based on the LOAEL of 1.2 mg/kg/day for behavioural patterns and serum bichemistry from the subchronic study in pigs and application of an uncertainty factor of 100.

Turczynowicz (1993) indicated an ADI for complex cyanide of 0.025 mg/kg/day which was based on the 90-day subchronic study by the Gas Research Institute, using rats exposed to sodium ferrocyanide in diet. The ADI was derived from the NOAEL of 25 mg/kg/day for kidney effects, with a safety factor of 1000 applied.

For the purposes of deriving soil and water acceptance criteria, an Acceptable Daily Intake of 0.01mg/kg/day has been adopted for free cyanide and 0.025 mg/kg/day for complex cyanide.

Table A4.3 Summary of dose response factors

Contaminant	Carcinogenic Category [1]	Parameter[2]	Source			Adopted
			USEPA [3]	Australian [4]	NZ [5]	
Non-carcinogenic PAHs						
naphthalene		oral RfD	NA	4×10^{-3}		4×10^{-3}
acenaphthene	D	oral RfD	6×10^{-2}			6×10^{-2}
acenaphthylene	D	oral RfD	3×10^{-2}			3×10^{-2}
anthracene	D	oral RfD	3×10^{-1}			3×10^{-1} 3×10^{-1}
phenanthrene	D	oral RfD	3×10^{-2}			3×10^{-2}
fluoranthene	D	oral RfD	4×10^{-2}			4×10^{-2}
fluorene	D	oral RfD	4×10^{-2}			4×10^{-2}
pyrene	D	oral RfD	3×10^{-2}			3×10^{-2}
Carcinogenic PAHs						
benzo (a) pyrene	B2	oral SF	7.3		0.5	7.3
Phenolics						
phenol	D	oral RfD [8]	6×10^{-1}	6×10^{-1}	NA	6×10^{-1}
cresol (o, m)	C	oral RfD	5×10^{-2}		NA	5×10^{-2}
2,4-dimethylphenol		Oral RfD	0.02		NA	0.02
BTEX						
Benzene	A	oral SF inhal UR	0.029 0.000008		0.03	0.029
Toluene	D	oral RfD inhal UR	0.2 0.4		0.22	0.2
Ethylbenzene	D	oral RfD inhal RfC	0.1 1		0.1	0.1
Xylene	D	oral RfD	2		0.18	0.18
Inorganics						
Cyanide-Free Complex	D	oral RfD oral RfD	0.02	0.01 0.025	0.012	0.01 0.025

1 USEPA Carcinogen Classification System.
2 Units: oral SF, $(mg/kg/day)^{-1}$; inhalation UR, $(\mu g/m^3)^{-1}$; oral RfD, mg/kg/day.
3 From USEPA Integrated Risk Information System (1993, 1995 and 1996), .
4 Monograph Series "National Workshop on the Health Risk Assessment and Management of Contaminated Sites" (1991 and 1993).
5 Guidelines for Drinking Water Quality and Management in New Zealand (1995).
6 Refer to discuss of PAH Toxic Equivalent Factors in 4.1.2(c).

Appendix 4B
Ecologically-based investigation thresholds

Guidelines for ecological risk assessment in Australia which will incorporate ecological investigation levels, are currently being developed under ANZECC. The current ANZECC Guidelines present environmental investigation thresholds for a range of chemicals, some of which may be of concern at former gasworks sites. The ANZECC environmental investigation level guidelines have been developed based on consideration of phytotoxicity (protection of plant life), background concentrations (particularly for heavy metals) and other considerations depending on the contaminant. While environmental investigation guideline values have been developed for a range of metals, values have been nominated for few organic contaminants. The environmental investigation level guidelines nominated in the ANZECC Guidelines are presented in Table 4A.3.

The ANZECC Guidelines note that where an environmental investigation level guideline has not been nominated for a specific chemical, reference may be made to the Dutch B guidelines. The Dutch guidelines have since been revised and the ABC level guidelines have been replaced with Target and Intervention Values based on human health and ecological considerations. In the interim the average of the Target and Intervention Values (as used by the Dutch as an investigation threshold) has been proposed as an environmental investigation level guideline where the ANZECC Guidelines do not nominate a value. The Dutch Target and Intervention Values for gasworks related contaminants are presented in Table 4B.1 for information.

Table 4B.1 Environmental soil quality guidelines (mg/kg)

Substance	ANZECC Environmental Investigation Level	Dutch Target Values	Dutch Intervention Value
Heavy Metals			
Antimony Sb	20	-	-
Arsenic As	20	29	55
Cadmium Cd	3	0.8	12
Chromium Cr	50	100	380
Copper Cu	70	36	190
Lead Pb	300	85	530
Manganese Mn	500	-	-
Mercury Hg	1	0.3	10
Nickel Ni	60	35	210
Tin Sn	50	20	-
Phenolic Compounds			
Phenols	-	0.05	40
Cresols		DL[1]	5
BTEX			
Benzene	1	0.05	1
Toulene		0.05	130
Ethylbenzene		0.05	50
Xylene		0.05	25

Substance	ANZECC Environmental Investigation Level	Dutch Target Values	Dutch Intervention Value
Polycyclic Aromatic Hydrocarbons (PAH)			
PAH (total)		1	40
Benzene (a) pyrene		0.025	-
Inorganics			
Cyanide		1	20 free
		5	650 complex pH <5
		5	50 complex pH >5

1 DL denotes Direction Limit.

As part of the development of guidelines for ecological risk assessment, the ANZECC/NHMRC Technical Working Group on Contaminated Sites are developing ecological investigation levels, developed in accordance with the guidelines for ecological risk assessment. The ecological investigation levels will supersede the existing environmental investigation level guidelines. The guidelines for ecological risk assessment and the ecological investigation level guidelines are expected to be released in draft form in May, 1997.

The focus for ecological risk assessment and the derivation of ecological investigation thresholds has been sensitive land uses, such as residential, agricultural and various forms of open space. While there is a requirement for the protection of the off-site environment irrespective of land use, very limited protection of on-site ecosystems is usually required in the context of commercial and industrial land uses. In most cases, protection of the off-site environment (for example, via leaching of contaminants from soil into groundwater, followed by off-site transport) and human health on-site are the limiting considerations in the assessment of contaminated land where industrial or commercial use is proposed.

The resolution of policy objectives regarding the level of protection to be afforded to on-site ecosystems in the context of other land uses is a prerequisite for the development of ecological investigation level guidelines for sensitive land uses.

In the New Zealand context the following precedents have been established regarding the development of guideline values based on environmental protection.

Appendix 4C
Exposure equations

Specific forms of the general equations are presented in this attachment for the following exposure routes:

- ingestion of soil
- inhalation of volatiles
- dermal absorption
- consumption of home grown produce

Ingestion of contaminated soil

The Chronic Daily Intake (CDI) may be determined by the following expression:

$$\mathbf{CDI} = \frac{\mathbf{C \times CF \times IR_{adj} \times EF \times MF}}{\mathbf{AT}}$$

where C = concentration of species in the soil
CF = conversion factor = 10^{-6} kg/mg
EF = exposure frequency
AT = averaging time = (ED x 365) days for non-carcinogens by convention or (70 years x 365) days for carcinogens, representing lifetime exposure, by convention (USEPA, 1989a)
MF = matrix factor, accounts for reduced bioavailability of contaminant due to binding to the soil matrix. In the absence of necessary information, MF usually taken as 1.0. (USEPA, 1989a)
IR_{adj} = age adjusted ingestion rate

$$= \frac{ED_i \times IR_i}{BWi}$$

where ED_i = exposure duration (yr) for age group 'i'
IR_i = ingestion rate (mg/d) for age group 'i'
BW_i = body weight (kg) for age group 'i'

The CDI determined is a weighted average, taking account of variation in body weight and ingestion rate with age.

Inhalation of volatile contaminants

The Chronic Daily Intake (CDI) by inhalation of volatile may be determined by the following expression:

$$\mathbf{CDI} = \frac{\mathbf{IR \times C \times VF \times EF \times ED}}{\mathbf{AT \times BW}}$$

where C = concentration of species in soil
VF = volatilisation factor
EF = exposure frequency
AT = averaging time = (ED x 365) days for non-carcinogens by convention or (70years x 365) days for carcinogens, a lifetime by convention
ED = exposure duration (yr)
IR = ingestion rate (mg/d)
BW = body weight (kg)

The significance of soil contamination by volatile components such as BTEX depends on the depth to the contaminated layer. Acceptance criteria based on the inhalation of volatiles have been derived for two assumed depths to the contaminated layer, as follows:

- **Surface soils, <1 m**

  Surface contamination is of primary concern in health risk assessment due to the range of exposure routes that are likely to be complete. Normal digging activities, say, in a residential context are unlikely to extend beyond a depth of 1 m.

- **Sub-surface soils, >1 m**

  The depth to contamination has an important impact on the rate of volatilisation of contaminants and on the relevant exposure pathways. Where contaminated soil is located at depths greater than 1 m it is assumed that normal users of the site are less likely to come in direct contact with contaminated soils. Hence Tier 1 Acceptance Criteria for this depth range do not consider ingestion of soil, dermal adsorption and home produce consumption.

In order to properly account for source depletion in volatilisation modelling it is necessary to make an assumption regarding the thickness of the contaminated zone. For the purposes of deriving acceptance criteria a thickness of 2 m has been assumed throughout.

Soil type has a significant impact on the rate at which contaminants may volatilise from soil, and particularly the rate at which vapours may diffuse through the soil column. Criteria for volatile contaminants may be developed for a range of soil types, reflecting the varying soil conditions likely to be encountered at gasworks sites. This approach was adopted in the development of guidelines for the oil industry. In order to streamline the presentation of acceptance criteria for gasworks sites, criteria have been developed for sand/sandy loam only. The assumed soil properties are relatively conservative, ie. they are likely to overestimate the emission of volatiles at most sites.

Table 4C.1 presents the assumed soil properties for use in volatilisation modelling.

Table 4C.1 Soil Properties for Volatilisation Modelling

Soil Type	Air Filled Porosity (unitless)	Water Filled Porosity (unitless)	Total Porosity (unitless)	Organic Carbon Content (%)	Bulk Density (tonne/m^3)	Capillary Fringe Thickness (m)
Sand, sandy loam, silty sand	0.26	0.12	0.38	0.3	1.9	0.05

Dermal absorption from contaminated soil

The Chronic Daily Intake (CDI) for dermal absorption from contaminated soil may be determined using the following expression:

$$\mathbf{CDI} = \frac{\mathbf{C \times AH_{adj} \times AR \times AF \times EF \times PC}}{\mathbf{AT}}$$

where: C= concentration of species in the soil
AR= area of exposed skin (face, neck, forearms, hands)
AF= absorption factor
EF= exposure frequency
AT= averaging time = (ED x 365) days for non-carcinogens by convention or (70 years x 365) days for carcinogens, a lifetime by convention

AH_{adj} = age adjusted soil adherence

$$= \frac{AH_i \times ED_i}{BW}$$

where Ah_i = soil adherence (mg/cm^2) for age group 'i'
Ed_i = exposure duration (yr) for age group 'i'
Bw_i = body weight (kg) for age group 'i'

The CDI determined is a weighted average, taking into account variation in body weight, skin area and exposure patterns with age.

Ingestion of produce

The Chronic Daily Intake (CDI) for ingestion of produce may be estimated using the following expression:

$$\mathbf{CDI = \frac{C \times PUF \times IP_{adj} \times EF \times Pg}{AT}}$$

where: CP = concentration of species in soil (mg/kg)
PUF = product uptake factor (unitless)
EF = exposure frequency (d/yr)
AT = averaging time = (ED x 365) days for non-carcinogens by convention or (70 yrs x 365) days for carcinogens by convention
Pg = proportion of produce grown on-site
IP_{adj} = age adjusted ingestion rate for produce

$$= \frac{IP_i \times EDi}{BW_i}$$

where: IP_i = ingestion rate for produce (kg/d) for age group 'i'
ED_i = exposure duration (yrs) for age group 'i'
BW_i = body weight (kg) for age group 'i'

The CDI estimated is a weighted average taking into account variation in body weight and produce consumption with age.

The development of acceptance criteria based on exposure via the consumption of produce depends on estimation of the plant uptake factor, PUF.

An empirical formula has been derived by Travis and Arms (1988) to simulate contaminant uptake by plants. The octanol-water partition coefficient (K_{ow}) is the key parameter for making these predictions.

The bioconcentration factor is the measure of a chemical's potential to accumulate in an organism. For vegetation, this is defined as is the ratio of the concentration in aboveground parts (mg of compound / kg of dry plant) to the concentration in soil (mg of compound / kg of dry soil). The geometric mean functional regression method is used to determine the proper correlation between bioconcentration factors and K_{ow} .

This yields the equation

$$\log B_v = 1.588 - 0.578 \log K_{ow}$$

where: B_v = Bioconcentration Factor for Vegetation

K_{ow} = Octanol Water Partition Coefficient.

The bioconcentration factor (B_v) for an organic in vegetation is inversely proportional to the square root of the octanol-water partition coefficient (K_{ow}).

B_v is based on the dry weight of vegetation and the PUF is based on the fresh weight of vegetation which is 80% moisture.

$$\mathbf{PUF = } \frac{10^{(1.588 - 0.578 \times \log Kow)}}{5}$$

where 5 = conversion of B_v from dry weight to fresh weight.

Table 4C.2 Health Risk Based Acceptance Criteria - Agricultural Site Use

Site Use	Residential	Exposure Frequency	350 d/yr	Exposure Dur (1-6 yrs)	6 yrs
Receptor	Children resident	Averaging Time (carc)	70 yrs	Exposure Dur (7-30 yrs)	24 yrs
	on site for up to 30 yrs	(non-carc)	30 yrs	Ingestion Rate (1-6 yrs)	100 mg/d
		Age Adjusted Ingestion factor	48.57 mg.yr/kg.d	Ingestion Rate (7-30 yrs)	25 mg/d
Target Risk	0.00001	Age adjusted dermal exposure factor	2.7E+03	Skin Area (1-6 yrs) (sq.cm)	2625
Target HI	1	Body weight	15 kg	Skin Area (7-30 yrs)(sq.cm.)	4700
		Body weight	70 kg	Soil Adherennce (mg/sq.cm.)	1
				Produce Ingestion (1-6 yrs, kg)	0.13
				Produce Ingestion (7-30 yrs, kg)	0.45
				Proportion of produce from contaminated source	1
				Proportion root produce	0.5

				Acceptable CDI				**Health Based Acceptance Criteria (mg/kg)[1]**					
Contaminant	Skin Absorption	SF (1/(mg/kg/d)	RfD (mg/kg/d)	Carcinogenic		Non-carcinogenic		Carcninogenic			Non-carcinogenic		
	Factor	Oral	Oral	Oral	Dermal	Oral	Dermal	Oral	Dermal	Produce	Oral	Dermal	Produce
Phenolics													
phenol	0.05		3.00E-01			3.0E-01	3.0E-01				4.7E+04	3.6E+04	3.25E+01
cresol (o)	0.05		2.50E-02			2.5E-02	2.5E-02				3.9E+03	3.0E+03	5.20E+00
cresol (m)	0.05		2.50E-02			2.5E-02	2.5E-02				3.9E+03	3.0E+03	5.27E+00
cresol (p)													
BTEX													
benzene	0.05	2.90E-02		3.4E-04	3.4E-04			5.2E+02	1.9E+02	2.65E-01			
toluene	0.05		1.00E-01			1.0E-01	1.0E-01				1.6E+04	1.2E+04	5.88E+01
ethylbenzene	0.05		5.00E-02			5.0E-02	5.0E-02				7.8E+03	6.0E+03	5.14E+01
xylene	0.05		9.00E-02			9.0E-02	9.0E-02				1.4E+04	1.1E+04	1.07E+02
Non-carcinogenic PAHs													
napthalene	0.01		2.00E-03			2.0E-03	2.0E-03				3.4E+02	1.2E+03	1.71E+00
acenaphthene	0.01		3.00E-02			3.0E-02	3.0E-02				4.7E+03	1.8E+04	8.59E+01
anthracene	0.01		1.50E-01			1.5E-01	1.5E-01				2.3E+04	8.9E+04	8.70E+02
fluorene	0.01		2.00E-02			2.0E-02	2.0E-02				3.1E+03	1.2E+04	8.10E+01
phenanthrene	0.01		1.50E-02			1.5E-02	1.5E-02				2.3E+03	8.9E+03	8.82E+01
pyrene	0.01		1.50E-02			1.5E-02	1.5E-02				2.3E+03	8.9E+03	1.54E+02
fluoranthene	0.01		2.00E-02			2.0E-02	2.0E-02				3.1E+03	1.2E+04	3.23E+02
acenaphthylene	0.01		1.50E-02			1.5E-02	1.5E-02				2.3E+03	8.9E+03	5.25E+01
Carcinogenic PAHs													
benzo(a)pyrene	0.01	7.30E+00		1.4E-06	1.4E-06			2.1E+00	3.8E-00	1.79E-01			
Inorganics													
cyanide (free)			2.50E-03			2.5E-03	2.5E-03				3.9E+02		
cyanide (complex)			6.25E-03			6.3E-03	6.3E-03				9.8E+02		

Table 4C.3 Health risk based acceptance criteria - Agricultural Site use

[1] These criteria are based on 30 years, criteria for non-carcinogens are based on the most critical 6 years.

Estimation of target soil concentraion - produce based

	Target produce concentration (mg/kg)		Koc	Kow	Uptake Factor	1/(Plant Uptake Factor)	Target Soil Concentration (mg/kg)	
Contaminant	Carcinogenic	Non-carcinogenic					Carcinogenic	Non-carcinogenic
Phenolics								
phenol		3.61E+01	1.60E+01	2.88E+01	1.11E+00	9.01E-01		3.25E+01
cresol (o)		3.01E+00	1.03E+02	8.91E+01	5.78E-01	1.73E+00		5.20E+00
cresol (m)		3.01E+00	3.46E+01	9.12E+01	5.70E-01	1.75E+00		5.27E+00
cresol (p)								
BTEX								
benzene	1.22E-01		8.30E+01	1.32E+02	4.61E-01	2.17E+00	2.65E-01	
toluene		1.20E+01	3.02E+02	5.37E+02	2.05E-01	4.89E+00		5.88E+01
ethylbenzene		6.02E+00	1.10E+03	1.41E+03	1.17E-01	8.55E+00		5.14E+01
xylene		1.08E+01	2.40E+02	1.82E+03	1.01E-01	9.89E+00		1.07E+02
Non-carcinogenic PAHs								
napthalene		2.41E-01	1.29E+03	1.02E+03	1.41E-01	7.09E+00		1.71E+00
acenaphthene		3.61E+00	4.60E+03	8.32E+03	4.20E-02	2.38E+01		8.59E+01
anthracene		1.80E+01	1.60E+04	2.82E+04	2.07E-02	4.82E+01		8.70E+02
fluorene		2.41E+00	5.01E+03	1.51E+04	2.97E-02	3.37E+01		8.10E+01
phenanthrene		1.80E+00	2.29E+04	2.88E+04	2.05E-02	4.88E+01		8.82E+01
pyrene		1.80E+00	3.80E+04	7.59E+04	1.17E-02	8.54E+01		1.54E+02
fluoranthene		2.41E+00	4.17E+04	1.66E+05	7.44E-03	1.34E+02		3.23E+02
acenaphthylene		1.80E+00	4.79E+03	1.18E+04	3.44E-02	2.91E+01		5.25E+01
Carcinogenic PAHs								
benzo(a)pyrene	4.85E-04		3.89E+05	9.55E+05	2.71E-03	3.69E+02	1.79E-01	
Inorganics								
cyanide (free)		3.01E-01						0.00E+00
cyanide (complex)		7.52E-01						0.00E+00

Table 4C.4 Health risk based acceptance criteria - Standard residential site use (10% produce consumed)

Site Use	Residential	Exposure Frequency	350 d/yr	Exposure Dur (1-6 yrs)	6 yrs
Receptor	Children resident	Averaging Time (carc)	70 yrs	Exposure Dur (7-30 yrs)	24 yrs
	on site for up to 30 yrs	(non-carc)	30 yrs	Ingestion Rate (1-6 yrs)	100 mg/d
		Age Adjusted Ingestion factor	48.57 mg.yr/kg.d	Ingestion Rate (7-30 yrs)	25 mg/d
Target Risk	0.00001	Age adjusted dermal exposure factor	2.7E+03	Skin Area (1-6 yrs) (sq.cm)	2625
Target HI	1	Body weight	15 kg	Skin Area (7-30 yrs)(sq.cm.)	4700
		Body weight	70 kg	Soil Adherennce (mg/sq.cm.)	0.5
				Produce Ingestion (1-6 yrs, kg)	0.13
				Produce Ingestion (7-30 yrs, kg)	0.45
				Proportion of produce from contaminated source	0.1
				Proportion root produce	0.5

				Acceptable CDI				Health Based Acceptance Criteria (mg/kg)[2]					
Contaminant	Skin Absorption Factor	SF (1/(mg/kg/d) Oral	RfD (mg/kg/d) Oral	Carcinogenic		Non-carcinogenic		Carcninogenic			Non-carcinogenic		
				Oral	Dermal	Oral	Dermal	Oral	Dermal	Produce	Oral	Dermal	Produce
Phenolics													
phenol	0.05		3.00E-01			3.0E-01	3.0E-01				4.7E+04	7.2E+04	3.25E+02
cresol (o)	0.05		2.50E-02			2.5E-02	2.5E-02				3.9E+03	3.0E+03	5.20E+01
cresol (m)	0.05		2.50E-02			2.5E-02	2.5E-02				3.9E+03	3.0E+03	5.27E+01
cresol (p)													
BTEX													
benzene	0.05	2.90E-02		3.4E-04	3.4E-04			5.2E+02	1.9E+02	2.65E-01			
toluene	0.05		1.00E-01			1.0E-01	1.0E-01				1.6E+04	2.4E+04	5.88E+02
ethylbenzene	0.05		5.00E-02			5.0E-02	5.0E-02				7.8E+03	1.2E+04	5.14E+02
xylene	0.05		9.00E-02			9.0E-02	9.0E-02				1.4E+04	2.1E+04	1.07E+03
Non-carcinogenic PAHs													
napthalene	0.01		2.00E-03			2.0E-03	2.0E-03				3.4E+02	2.4E+03	1.71E+01
acenaphthene	0.01		3.00E-02			3.0E-02	3.0E-02				4.7E+03	3.6E+04	8.59E+02
anthracene	0.01		1.50E-01			1.5E-01	1.5E-01				2.3E+04	1.8E+05	8.70E+03
fluorene	0.01		2.00E-02			2.0E-02	2.0E-02				3.1E+03	2.4E+04	8.10E+02
phenanthrene	0.01		1.50E-02			1.5E-02	1.5E-02				2.3E+03	1.8E+04	8.82E+02
pyrene	0.01		1.50E-02			1.5E-02	1.5E-02				2.3E+03	1.8E+04	1.54E+03
fluoranthene	0.01		2.00E-02			2.0E-02	2.0E-02				3.1E+03	2.4E+04	3.23E+03
acenaphthylene	0.01		1.50E-02			1.5E-02	1.5E-02				2.3E+03	1.8E+04	5.25E+02
Carcinogenic PAHs													
benzo(a)pyrene	0.01	7.30E+00		1.4E-06	1.4E-06			2.1E+00	7.5E+00	1.79E-01			
Inorganics													
cyanide (free)			2.50E-03			2.5E-03	2.5E-03				3.9E+02		
cyanide (complex)			6.25E-03			6.3E-03	6.3E-03				9.8E+02		

Table 4C.5 Health risk based acceptance criteria - Standard residential site use (10% produce consumed)

[2] These criteria are based on 30 years, criteria for non-carcinogens are based on the most critical 6 years.

Estimation of target soil concentrations - produce based

	Target produce concentration (mg/kg)		Koc	Kow	Uptake Factor	1/(Plant Uptake Factor)	Target Soil Concentration (mg/kg)	
Contaminant	Carcinogenic	Non-carcinogenic					Carcinogenic	Non-carcinogenic
Phenolics								
phenol		3.61E+02	1.60E+01	2.88E+01	1.11E+00	9.01E-01		3.25E+02
cresol (o)		3.01E+01	1.03E+02	8.91E+01	5.78E-01	1.73E+00		5.20E+01
cresol (m)		3.01E+01	3.46E+01	9.12E+01	5.70E-01	1.75E+00		5.27E+01
cresol (p)								
BTEX								
benzene	1.22E+00		8.30E+01	1.32E+02	4.61E-01	2.17E+00	2.65E+00	
toluene		1.20E+02	3.02E+02	5.37E+02	2.05E-01	4.89E+00		5.88E+02
ethylbenzene		6.02E+01	1.10E+03	1.41E+03	1.17E+01	8.55E+00		5.14E+02
xylene		1.08E+02	2.40E+02	1.82E+03	1.01E-01	9.89E+00		1.07E+03
Non-carcinogenic PAHs								
napthalene		2.41E+00	1.29E+03	1.02E+03	1.41E-01	7.09E+00		1.71E+01
acenaphthene		3.61E+01	4.60E+03	8.32E+03	4.20E-02	2.38E+01		8.59E+02
anthracene		1.80E+02	1.60E+04	2.82E+04	2.07E-02	4.82E+01		8.70E+03
fluorene		2.41E+01	5.01E+03	1.51E+04	2.97E-02	3.37E+01		8.10E+02
phenanthrene		1.80E+01	2.29E+04	2.88E+04	2.05E-02	4.88E+01		8.82E+02
pyrene		1.80E+01	3.80E+04	7.59E+04	1.17E-02	8.54E+01		1.54E+03
fluoranthene		2.41E+01	4.17E+04	1.66E+05	7.44E-03	1.34E+02		3.23E+03
acenaphthylene		1.80E+01	4.79E+03	1.18E+04	3.44E-02	2.91E+01		5.25E+02
Carcinogenic PAHs								
benzo(a)pyrene	4.85E-03		3.89E+05	9.55E+05	2.71E-03	3.69E+02		
Inorganics								
cyanide (free)		3.01E+00					1.79E+00	0.00E+00
cyanide (complex)		7.52E+00						0.00E+00

Table 4C.6 Health risk based acceptance criteria - Standard residential site use (50% produce consumed)

Site Use	Residential	Exposure Frequency	350 d/yr	Exposure Dur (1-6 yrs)	6 yrs
Receptor	Children resident	Averaging Time (carc)	70 yrs	Exposure Dur (7-30 yrs)	24 yrs
	on site for up to 30 yrs	(non-carc)	30 yrs	Ingestion Rate (1-6 yrs)	100 mg/d
		Age Adjusted Ingestion factor	48.57 mg.yr/kg.d	Ingestion Rate (7-30 yrs)	25 mg/d
Target Risk	0.00001	Age adjusted dermal exposure factor	2.7E+03	Skin Area (1-6 yrs) (sq.cm)	2625
Target HI	1	Body weight	15 kg	Skin Area (7-30 yrs)(sq.cm.)	4700
		Body weight	70 kg	Soil Adherennce (mg/sq.cm.)	0.5
				Produce Ingestion (1-6 yrs, kg)	0.13
				Produce Ingestion (7-30 yrs, kg)	0.45
				Proportion of produce from contaminated source	0.5
				Proportion root produce	0.5

				Acceptable CDI				Health Based Acceptance Criteria (mg/kg)[3]					
Contaminant	Skin Absorption Factor	SF (1/(mg/kg/d) Oral	RfD (mg/kg/d) Oral	Carcinogenic		Non-carcinogenic		Carcninogenic			Non-carcinogenic		
				Oral	Dermal	Oral	Dermal	Oral	Dermal	Produce	Oral	Dermal	Produce
Phenolics													
phenol	0.05		3.00E-01			3.0E-01	3.0E-01				4.7E+04	7.2E+02	6.51E+01
cresol (o)	0.05		2.50E-02			2.5E-02	2.5E-02				3.9E+03	6.0E+03	1.04E+01
cresol (m)	0.05		2.50E-02			2.5E-02	2.5E-02				3.9E+03	6.0E+03	1.05E+01
cresol (p)													
BTEX													
benzene	0.05	2.90E-02		3.4E-04	3.4E-04			5.2E+02	3.8E+02	2.65E-01			
toluene	0.05		1.00E-01			1.0E-01	1.0E-01				1.6E+04	2.4E+04	1.18E+02
ethylbenzene	0.05		5.00E-02			5.0E-02	5.0E-02				7.8E+03	1.2E+04	1.03E+02
xylene	0.05		9.00E-02			9.0E-02	9.0E-02				1.4E+04	2.1E+04	2.14E+02
Non-carcinogenic PAHs													
napthalene	0.01		2.00E-03			2.0E-03	2.0E-03				3.1E+02	2.4E+03	3.41E+00
acenaphthene	0.01		3.00E-02			3.0E-02	3.0E-02				4.7E+03	3.6E+04	1.72E+02
anthracene	0.01		1.50E-01			1.5E-01	1.5E-01				2.3E+04	1.8E+05	1.74E+03
fluorene	0.01		2.00E-02			2.0E-02	2.0E-02				3.1E+03	2.4E+04	1.62E+02
phenanthrene	0.01		1.50E-02			1.5E-02	1.5E-02				2.3E+03	1.8E+04	1.76E+02
pyrene	0.01		1.50E-02			1.5E-02	1.5E-02				2.3E+03	1.8E+04	3.08E+05
fluoranthene	0.01		2.00E-02			2.0E-02	2.0E-02				3.1E+03	2.4E+04	6.47E+02
acenaphthylene	0.01		1.50E-02			1.5E-02	1.5E-02				2.3E+03	1.8E+04	1.05E+02
Carcinogenic PAHs													
benzo(a)pyrene	0.01	7.30E+00		1.4E-06	1.4E-06			2.1E+00	7.5E+00	3.58E-01			
Inorganics													
cyanide (free)			2.50E-03			2.5E-03	2.5E-03				3.9E+02		
cyanide (complex)			6.25E-03			6.3E-03	6.3E-03				9.8E+02		

[3] These criteria are based on 30 years, criteria for non-carcinogens are based on the most critical 6 years.

Table 4C.7 Health risk based acceptance criteria -Standard residential site use (50% produce consumed)
Estimation of target soil concentrations - produce based

	Target produce concentration (mg/kg)		Koc	Kow	Uptake Factor	1/(Plant Uptake Factor)	Target Soil Concentration (mg/kg)	
Contaminant	Carcinogenic	Non-carcinogenic					Carcinogenic	Non-carcinogenic
Phenolics								
phenol		7.22E+01	1.60E+01	2.88E+01	1.11E+00	9.01E-01		6.51E+01
cresol (o)		6.02E+00	1.03E+02	8.91E+01	5.78E-01	1.73E+00		1.04E+01
cresol (m)		6.02E+00	3.46E+01	9.12E+01	5.70E-01	1.75E+00		1.05E+01
cresol (p)								
BTEX								
benzene	2.44E-01		8.30E+01	1.32E+02	4.61E-01	2.17E+00	5.30E-01	
toluene		2.41E+01	3.02E+02	5.37E+02	2.05E-01	4.89E+00		1.18E+02
ethylbenzene		1.20E+01	1.10E+03	1.41E+03	1.17E-01	8.55E+00		1.03E+02
xylene		2.17E+01	2.40E+02	1.82E+03	1.01E-01	9.89E+00		2.14E+02
Non-carcinogenic PAHs								
napthalene		4.81E-01	1.29E+03	1.02E+03	1.41E-01	7.09E+00		3.41E+00
acenaphthene		7.22E+00	4.60E+03	8.32E+03	4.20E-02	2.38E+01		1.72E+02
anthracene		3.61E+01	1.60E+04	2.82E+04	2.07E-02	4.82E+01		1.74E+03
fluorene		4.81E+00	5.01E+03	1.51E+04	2.97E-02	3.37E+01		1.62E+02
phenanthrene		3.61E+00	2.29E+04	2.88E+04	2.05E-02	4.88E+01		1.76E+02
pyrene		3.61E+00	3.80E+04	7.59E+04	1.17E-02	8.54E+01		3.08E+02
fluoranthene		4.81E+00	4.17E+04	1.66E+05	7.44E-03	1.34E+02		6.47E+02
acenaphthylene		3.61E+00	4.79E+03	1.18E+04	3.44E-02	2.91E+01		1.05E+02
Carcinogenic PAHs								
benzo(a)pyrene	9.70E-04		3.89E+05	9.55E+05	2.71E-03	3.69E+02	3.58E-01	
Inorganics								
cyanide (free)		6.02E-01						0.00E+00
cyanide (complex)		1.50E+00						0.00E+00

Table 4C.8 Health risk based acceptance criteria - High density residential site use

Site Use	Residential high density	Exposure Frequency	350 d/yr	Exposure Duration (1-6 yrs)	6 yrs
Receptor	Children resident on site for up to 30 yrs	Averaging time (carc)	70 yrs	Exposure duration (7-30 yrs)	24 yrs
		(non-carc)	30 yrs	Ingestion rate (1-6 yrs)	25 mg/d
		Age adjusted ingestion factor	11.71 mg.yr/kg.d	Ingestion rate (7-30 yrs)	5 mg/d
Target risk	0.00001	Skin area (1.6 yrs) (sq.cm.)	2625	Soil adherence (mg/sq.cm.)	0.1
Targat HI	1	Skin area (7-30 yrs) (sq.cm.)	4700	Age adjusted dermal exposure factor	2.7E+03
		Body weight (1-6 yrs)	15 kg		
		Body weight (7-30 yrs)	70 kg		

				Acceptable CDI				Health Based Acceptance Criteria (mg/kg)[4]					
Contaminant	Skin Absorption Factor	SF (1/(mg/kg/d) Oral	RfD (mg/kg/d) Oral	Carcinogenic Oral	Carcinogenic Dermal	Non-carcinogenic Oral	Non-carcinogenic Dermal	Carcninogenic Oral	Carcninogenic Dermal	Carcninogenic Produce	Non-carcinogenic Oral	Non-carcinogenic Dermal	Non-carcinogenic Produce
Phenolics													
phenol	0.05		3.00E-01			3.0E-01	3.0E-01				1.9E+05	3.6E+05	
cresol (o)	0.05		2.50E-02			2.5E-02	2.5E-02				1.6E+04	3.0E+04	
cresol (m)	0.05		2.50E-02			2.5E-02	2.5E-02				1.6E+04	3.0E+04	
cresol (p)													
BTEX													
benzene	0.05	2.90E-02		3.4E-04	3.4E-04			2.1E+03	1.9E+03				
toluene	0.05		1.00E-01			1.0E-01	1.0E-01				6.3E+04	1.2E+05	
ethylbenzene	0.05		5.00E-02			5.0E-02	5.0E-02				3.1E+04	6.0E+04	
xylene	0.05		9.00E-02			9.0E-02	9.0E-02				5.6E+04	1.1E+05	
Non-carcinogenic PAHs													
napthalene	0.01		2.00E-03			2.0E-03	2.0E-03				1.3E+03	1.2E+04	
acenaphthene	0.01		3.00E-02			3.0E-02	3.0E-02				1.9E+04	1.8E+05	
anthracene	0.01		1.50E-01			1.5E-01	1.5E-01				9.4E+04	8.9E+05	
fluorene	0.01		2.00E-02			2.0E-02	2.0E-02				1.3E+04	1.2E+05	
phenanthrene	0.01		1.50E-02			1.5E-02	1.5E-02				9.4E+03	8.9E+04	
pyrene	0.01		1.50E-02			1.5E-02	1.5E-02				9.4E+03	8.9E+04	
fluoranthene	0.01		2.00E-02			2.0E-02	2.0E-02				1.3E+04	1.2E+05	
acenaphthylene	0.01		1.50E-02			1.5E-02	1.5E-02				9.4E+03	8.9E+04	
Carcinogenic PAHs													
benzo(a)pyrene	0.01	7.30E+00		1.4E-06	1.4E-06			8.5E+00	3.8E+01				
Inorganics													
cyanide (free)			2.50E-03			2.5E-03	2.5E-03				1.6E+03		
cyanide (complex)			6.25E-03			6.3E-03	6.3E-03				3.9E+03		

[4] These criteria are based on 30 years, criteria for non-carcinogens are based on the most critical 6 years.

Table 4C.9 Health risk based acceptance criteria - Commercial site use

Site Use	Commercial	Exposure Frequency	240 d/yr	Exposure Dur	20 yrs
Receptor	Industrial Adult	Averaging time (carc)	70 yrs		
	Worker for 20 yrs	(non-carc)	20 yrs	Ingestion rate	25 mg/d
Target risk	0.00001	Skin area (sq.cm.)	4700	Soil adherence (mg/sq.cm.)	1
Target HI	1	Body weight	70 kg		

				Acceptable CDI				Health Based Acceptance Criteria (mg/kg)[5]					
Contaminant	Skin Absorption Factor	SF (1/(mg/kg/d)	RfD (mg/kg/d)	Carcinogenic		Non-carcinogenic		Carcninogenic			Non-carcinogenic		
		Oral	Oral	Oral	Dermal	Oral	Dermal	Oral	Dermal	Produce	Oral	Dermal	Produce
Phenolics													
phenol	0.03		3.00E-01			3.0E-01	3.0E-01				1.3E+06	2.3E+05	
cresol (o)	0.03		2.50E-02			2.5E-02	205E-02				1.1E+05	1.9E+04	
cresol (m)	0.03		2.50E-02			2.5E-02	2.5E-02				1.1E+05	1.9E+04	
cresol (p)													
BTEX													
benzene	0.03	2.90E-02		3.4E-04	3.4E-04			5.1E+03	9.1E+02				
toluene	0.03		1.00E-01			1.0E-01	1.0E-01				4.3E+05	7.6E+04	
ethylbenzene	0.03		5.00E-02			5.0E-02	5.0E-02				2.1E+05	3.8E+04	
xylene	0.03		9.00E-02			9.0E-02	9.0E-02				3.8E+05	6.8E+04	
Non-carcinogenic PAHs													
napthalene	0.006		2.00E-03			2.0E-03	2.0E-03				8.5E+03	7.6E+03	
acenaphthene	0.006		3.00E-02			3.0E-02	3.0E-02				1.3E+05	1.1E+05	
anthracene	0.006		1.50E-01			1.5E-01	1.5E-01				6.4E+05	5.7E+05	
fluorene	0.006		2.00E-02			2.0E-02	2.0E-02				8.5E+04	7.6E+04	
phenanthrene	0.006		1.50E-02			1.5E-02	1.5E-02				6.4E+04	5.7E+04	
pyrene	0.006		3.00E-02			1.5E-02	1.5E-02				1.3E+05	1.1E+05	
fluoranthene	0.006		2.00E-02			2.0E-02	2.0E-02				8.5E+04	7.6E+04	
acenaphthylene	0.006		1.50E-02			1.5E-02	1.5E-02				6.4E+04	5.7E+04	
Carcinogenic PAHs													
benzo(a)pyrene	0.006	7.30E+00		1.4E-06	1.4E-06			2.0E+01	1.8E+01				
Inorganics													
cyanide (free)			2.50E-03			2.5E-03	2.5E-03				1.1E+04		
cyanide (complex)			6.25E-03			6.3E-03	6.3E-03				2.7E+04		

[5] These criteria are based on 30 years, criteria for non-carcinogens are based on the most critical 6 years.

Table 4C.10 Health risk based acceptance criteria - Commercial site use (maintenance worker)

Site Use	Commercial	Exposure frequency	50 d/yr	Exposure duration	20 yrs
Receptor	Worker for 20 yrs	Averaging time (carc)	70 yrs		
		(non-carc)	20 yrs	Ingestion rate	100 mg/d
Target risk	0.00001	Skin Area (sq.cm.)	4700	Soil adherence (mg/sq.cm.)	1.5
Target HI	1	Body weight	70 kg		

				Acceptable CDI				Health Based Acceptance Criteria (mg/kg)[6]					
Contaminant	Skin Absorption Factor	SF (1/(mg/kg/d)	RfD (mg/kg/d)	Carcinogenic		Non-carcinogenic		Carcninogenic			Non-carcinogenic		
		Oral	Oral	Oral	Dermal	Oral	Dermal	Oral	Dermal	Produce	Oral	Dermal	Produce
Phenolics													
phenol	0.03		3.00E-01			3.0E-01	3.0E-01				1.5E+06	7.2E+05	
cresol (o)	0.03		2.50E-02			2.5E-02	2.5E-02				1.3E+05	6.0E+04	
cresol (m)	0.03		2.50E-02			2.5E-02	2.5E-02				1.3E+05	6.0E+04	
cresol (p)													
BTEX													
benzene	0.03	2.90E-02		3.4E-04	3.4E-04			6.2E+03	2.9E+03		5.1E+05	2.4E+05	
toluene	0.03		1.00E-01			1.0E-01	1.0E-01				2.6E+05	1.2E+05	
ethylbenzene	0.03		5.00E-02			5.0E-02	5.0E-02				4.6E+05	2.2E+05	
xylene	0.03		9.00E-02			9.0E-02	9.0E-02						
Non-carcinogenic PAHs													
napthalene	0.06		2.00E-03			2.0E-03	2.0E-03				1.0E+04	2.4E+04	
acenaphthene	0.06		3.00E-02			3.0E-02	3.0E-02				1.5E+05	3.6E+05	
anthracene	0.06		1.50E-01			1.5E-01	1.5E-01				7.7E+05	1.8E+06	
fluorene	0.06		2.00E-02			2.0E-02	2.0E-02				1.0E+05	2.4E+05	
phenanthrene	0.06		1.50E-02			1.5E-02	1.5E-02				7.7E+04	1.8E+05	
pyrene	0.06		3.0E-02			3.0E-02	3.0E-02				1.5E+05	3.6E+05	
fluoranthene	0.06		2.00E-02			2.0E-02	2.0E-02				1.0E+05	2.4E+05	
acenaphthylene	0.06		1.50E-02			1.5E-02	1.5E-02				7.7E+04	1.8E+05	
Carcinogenic PAHs													
benzo(a)pyrene	0.006	7.30E+00		1.4E-06	1.4E-06			2.5E+01	5.8E+01				
Inorganics													
cyanide (free)			2.50E-03			2.5E-03	2.5E-03				1.3E+04		
cyanide (complex)			6.25E-03			6.3E-03	6.3E-03				3.2E+04		

[6] These criteria are based on 30 years, criteria for non-carcinogens are based on the most critical 6 years.

Table 4C.11 Health risk based acceptance criteria - Parkland/recreational site use

Site Use	Parkland/recreational	Exposure Frequency	350 d/yr	Exposure Duration (1-6 yrs)	6 yrs
Receptor	Children resident on site for up to 30 yrs	Averaging time (carc)	70 yrs	Exposure duration (7-30 yrs)	24 yrs
		(non-carc)	30 yrs	Ingestion rate (1-6 yrs)	50 mg/d
		Age adjusted ingestion factor	23.43 mg.yr/kg.d	Ingestion rate (7-30 yrs)	10 mg/d
Target risk	0.00001	Skin area (1-6 yrs) (sq.cm.)	2625	Soil adherence (mg/sq.cm.)	1
Target HI	1	Skin area (7-30 yrs) (sq.cm.)	4700	Age adjusted dermal expsure factor	2.7E+03
		Body weight (1-6 yrs)	15 kg	Body weight (7-30 yrs)	70kg

				Acceptable CDI				Health Based Acceptance Criteria (mg/kg)[7]					
Contaminant	Skin Absorption Factor	SF (1/(mg/kg/d)	RfD (mg/kg/d)	Carcinogenic		Non-carcinogenic		Carcninogenic			Non-carcinogenic		
		Oral	Oral	Oral	Dermal	Oral	Dermal	Oral	Dermal	Produce	Oral	Dermal	Produce
Phenolics													
phenol	0.025		3.00E-01			3.0E-01	3.0E-01				9.4E+04	7.2E+04	
cresol (o)	0.025		2.50E-02			2.5E-02	2.5E-02				7.8E+03	6.0E+03	
cresol (m)	0.025		2.50E-02			2.5E-02	2.5E-02				7.8E+03	6.0E+03	
cresol (p)													
BTEX													
benzene	0.025	2.90E-02		3.4E-04	3.4E-04			1.1E+03	3.8E+02				
toluene	0.025		1.00E-01			1.0E-01	1.0E-01				3.1E+04	2.4E+04	
ethylbenzene	0.025		5.00E-02			5.0E-02	5.0E-02				1.6E+04	1.2E+04	
xylene	0.025		9.00E-02			9.0E-02	9.0E-02				2.8E+04	2.1E+04	
Non-carcinogenic PAHs													
napthalene	0.005		2.00E-03			2.0E-03	2.0E-03				6.3E+02	2.4E+03	
acenaphthene	0.005		3.00E-02			3.0E-02	3.0E-02				9.4E+03	3.6E+04	
anthracene	0.005		1.50E-01			1.5E-01	1.5E-01				4.7E+04	1.8E+05	
fluorene	0.005		2.00E-02			2.0E-02	2.0E-02				6.3E+03	2.4E+04	
phenanthrene	0.005		1.50E-02			1.5E-02	1.5E-02				4.7E+03	1.8E+04	
pyrene	0.005		1.50E-02			1.5E-02	1.5E-02				4.7E+03	1.8E+04	
fluoranthene	0.005		2.00E-02			2.0E-02	2.0E-02				6.3E+03	2.4E+04	
acenaphthylene	0.005		1.50E-02			1.5E-02	1.5E-02				4.7E+03	1.8E+04	
Carcinogenic PAHs													
benzo(a)pyrene	0.005	7.30E+00		1.4E-06	1.4E-06			4.3E+00	7.5E+00				
Inorganics													
cyanide (free)			2.50E-03			2.5E-03	2.5E-03				7.8E+02		
cyanide (complex)			6.25E-03			6.3E-03	6.3E-03				2.0E+03		

[7] These criteria are based on 30 years, criteria for non-carcinogens are based on the most critical 6 years.

5

Generic acceptance criteria for groundwater and surface water

Appendices

Generic acceptance criteria for surface water and groundwater

5.1 Introduction

The derivation of generic surface water and groundwater acceptance criteria is presented in a summary only in this section. Information on the toxicity and dose response factors for contaminants of concern at gasworks sites is presented in Appendix 4A of Module 4 on disk.

This module covers the following:

- ➔ groundwater uses
- ➔ potable use
- ➔ stock watering use
- ➔ irrigation use
- ➔ aquatic ecosystem protection
- ➔ primary contact recreation

Additional information can be found in Section 4 of the Users' Guide, including:

- ▲ potable use (Section 4.3.1.1)
- ▲ stock watering use (Section 4.3.1.2)
- ▲ irrigation use (Section 4.3.1.3)
- ▲ aquatic ecosystem protection (Section 4.3.1.4)
- ▲ primary contact recreation (Section 4.3.1.5)
- ▲ the summary of the generic water acceptance criteria (Section 4.3.2)
- ▲ application of the generic acceptance criteria (Section 4.3.3)
- ▲ developing site specific acceptance criteria (Section 4.4)

5.2 Groundwater uses

The significance of groundwater contamination depends on the uses of the groundwater which require protection. The quality and yield of groundwater can define the range of uses for which it may be suitable. Some uses are dependent on extraction of the groundwater (e.g. potable use, stock watering), and therefore there is no need to protect these uses if groundwater cannot be extracted at a useful rate.

Salinity is used as a primary indicator of groundwater quality and its suitability for various uses. For example, the New Zealand Drinking Water Standards (NZDWS) indicate that a total dissolved solids concentration of 1000 mg/L is an upper limit for drinking water of an acceptable quality.

As the significance of groundwater contamination depends on the uses of the groundwater which are to be protected, defining the potential groundwater uses is an integral step in the assessment of groundwater contamination. These uses will depend on the quality and yield of the aquifer. A range of groundwater uses has been considered in the development of the groundwater acceptance criteria:

- potable use
- stock watering
- irrigation
- aquatic ecosystem support

- primary contact recreation.

5.3 Potable use

Guidelines for the concentration of contaminants in potable water generally consider:

- the protection of public health
- aesthetic considerations including taste and odour, and
- the protection of the water supply assets (e.g. corrosion of pipework).

When assessing the impact of contamination on potable use of the groundwater, reference should be made to the NZDWS 1995, and the New Zealand Drinking Water Guidelines (NZDWG) (Ministry of Health 1995). These guidelines are summarised in Table 5.1.

In the absence of health-based guideline values for gasworks contaminants, health-based acceptance criteria have been derived for the contaminants of concern using the procedures outlined in Module 4.

Health-based acceptance criteria may be summarised as follows:

$$\textbf{Acceptance criterion} = \frac{\textbf{Allowable intake (mg/kg/day) x Body Weight (kg)}}{\textbf{Water Consumption Rate (L/day)}}$$

Where:

Allowable Intake = (Reference Dose (RfD)) x (Proportion of RfD assigned to drinking water)

In accordance with the policies for the derivation of MAVs (Maximum Acceptable Values) in the NZDWS (MoH, 1995), the derivation of health-based acceptance criteria for gasworks contaminants has been based on the following assumptions:

- water consumption rate = 2 L/day
- body weight = 70 kg
- proportion of RfD assigned to drinking water = 0.1 (default assumption)

For details of the reference doses for gasworks contaminants, refer to Appendix 4A of Module 4. The health-based criteria for gasworks contaminants are summarised in Table 5.1 below.

Table 5.1 Summary of potable water quality guidelines (mg/L)

Contaminant	NZDWS MAV[1] (1995)		NZDWG MAV[1] (1995)	NHMRC/ARMCANZ[5] (1996)		Health-Based Acceptance Criteria[5]
	Health-based	Aesthetic	Aesthetic	Health-based	Aesthetic	
PAH	NAD[2]					
Non-carcinogenic PAHs						
Naphthalene						0.01
Acenaphthene						0.2
Anthracene						1.1
Fluorene						0.1
Phenanthrene						0.1
Pyrene						0.1
Fluoranthene						0.1
Acenaphthylene						0.1
Carcinogenic PAHs						
Benzo[a]pyrene	0.0007			0.00001		

BTEX						
Benzene	0.01			0.001		
Toluene	0.8	0.024	0.024-0.17	0.8	0.025	
Ethylbenzene	0.3	0.002	0.002-0.2	0.3		
Xylene	0.6	0.02	0.02-1.8	0.6	0.02	
Phenolics						
Phenol						2.0
Cresol (o,m)						0.2
Cresol (p)						0.02
Inorganic						
Ammonia		1.5	1.5	—[3]	0.5	
Cyanide as CN^-	0.08			0.08		
free[4]						0.1
complexed[4]						0.2
Nitrate	50			50		
Nitrite	3			3		
Sulphate		250	250	500	250	
Sulphide as H_2S		0.05	0.05	-(3)	0.05	

1. MAV - Maximum Acceptable Value
2. NAD - No adequate data to permit recommendation of health-based MAV human health at concentrations normally found in drinking water.
3. Insufficient data to set a guideline value based on health considerations.
4. Proportion of RfD assigned to drinking water = 0.2 consistent with derivation of guideline value for CN^- in the NZDWS.
5. National Health and Medical Research Council/Agricultural and Resource Management Council of New Zealand and Australia "Australian Drinking Water Guidelines", 1996.
6. Nominated where no relevant published guideline is available.

Additional information on potable use can be found in Section 4.3.1.1 of the Users' Guide.

5.4 Stock watering

The derivation of groundwater acceptance criteria for stock water use may include consideration of:

- protection of stock health via the consumption of livestock products
- protection of human health
- palatability of the water for stock.

As there are no stock water quality guidelines in New Zealand for the contaminants of concern, reference is made to guidelines released in other countries, particularly the ANZECC (1992) "Australian Water Quality Guidelines for Fresh and Marine Waters". For most of the organic contaminants of concern at gasworks contaminated sites, these guidelines indicate that the potable use guideline values should be used as a conservative default. In practice the potable use values are expected to be conservative, and less stringent criteria may be justifiable for the protection of stock health and the protection of human health where exposure may occur via the consumption of contaminated livestock products.

5.4.1 Protection of stock health

Acceptance criteria for the protection of stock health may be derived using an approach similar to that used for the derivation of potable use acceptance criteria (refer Module 4). Cattle have been selected as representative of livestock as they exhibit a relatively high water consumption per unit body weight. Acceptance criteria are calculated as follows:

$$\text{Acceptance Criterion} = \frac{\text{Acceptable Intake x Body Weight}}{\text{Water consumption rate}}$$

Assumptions used in the derivation of criteria are as follows:

body weight	=	550 kg for cattle (Shell, 1994)
water consumption rate	=	55 L/day (for lactating cows) (Shell, 1994)

In selecting dose-response factors for determining stock water acceptance criteria, based on those used in the derivation of the potable use acceptance criteria, the following are assumed:

- cancer is not a relevant endpoint for cattle given the relatively short lifespan compared to humans
- full protection of sensitive sub-populations is not required, and therefore the safety factor (of 10) for intraspecies variability, incorporated in Acceptable Daily Intake (ADI) and RfD estimates, need not be applied in determining the Acceptable Intake for stock.

Criteria for the protection of livestock health are presented in Table 5.2. Where the potable use criterion for a contaminant is based on a cancer endpoint assuming a non-threshold dose response relationship, an alternative endpoint has been selected. In particular, the criterion for benzene is based on the most stringent acceptable intake for BTEX and other carcinogenic PAHs.

Table 5.2 Stockwater quality guidelines and groundwater acceptance criteria for stock watering based on livestock health (mg/L)

Contaminant	ANZECC Guideline Stock watering	Acceptable Intake (mg/kg/day)	Acceptance Criteria (mg/L)
PAH (total)		0.3[1]	3
Naphthalene		0.04	0.4
Benzene		1	10
Toluene		2	20
Ethylbenzene		1	10
Xylene		1.8	18
Phenol		6.0	60
Cresol (o,m)		0.5	5
Cresol (p)		0.05	0.5
Ammonia			
Cyanide - free		0.1	1
- complexed		0.25	2.5
Nitrate	30[2]		
Nitrite	10[2]		
Sulphate	1000		

1. Based on pyrene
2. Nitrate, nitrite - as N

5.4.2 Protection of human health

Humans may be exposed to contaminants in groundwater used for stock watering if the contaminants accumulate in edible portions of the animal, particularly in fat. Surface water and groundwater acceptance criteria for stock watering, based on the protection of human health, may be derived based on;

- correlations between the intake and the residue concentrations in cattle, and
- Maximum Residue Levels (MRLs) for specific contaminants in livestock (or in the absence of an MRL, risk-based criteria assuming 100% of animal products are from a contaminated source).

For contaminants to accumulate in livestock to a significant extent, the contaminants must be lipophilic. Contaminants that are lipophilic, however, are generally not present in

groundwater at high concentrations. BTEX, such as benzene, are only moderately lipophilic and are therefore unlikely to accumulate significantly in livestock.

Initial estimates suggest most contaminants of concern at gasworks are unlikely to accumulate in stock to levels that affect the health of consumers of livestock products. Based on available correlations between contaminant intake and concentrations in livestock products (Travis and Arms, 1988), a relatively low stock water criterion may be predicted for benzo(a)pyrene. The published correlations have generally been developed for pesticides or chlorinated or other persistent compounds which are likely to resist metabolism in mammals. In practice benzo(a)pyrene is readily metabolised in mammals, greatly reducing bioaccumulation. The benzo(a)pyrene concentrations expected in groundwater at gasworks sites are unlikely to result in significant bioaccumulation in livestock.

On this basis, criteria based on the protection of human health and bioaccumulation of contaminants in livestock have not been nominated.

5.4.3 Palatability for stock

No information on the palatability of contaminated groundwater from a gasworks site for stock water use has been identified. Anecdotal information suggests livestock may consume significantly contaminated waters if required.

Additional information on stock watering use can be found in Section 4.3.1.2 of the Users' Guide.

5.5 Irrigation use

The proposed groundwater quality acceptance criteria for irrigation are based principally on the protocol developed by BP (Walden 1996). The protocol has been developed for spray irrigation in a domestic setting, however it is of more general applicability. The following processes have been considered in the development of irrigation water criteria:

- contaminant loss by volatilisation due to spray irrigation
- inhalation of vapours and aerosols by site users
- dermal absorption and ingestion of water by children playing under sprinklers, and
- plant uptake of contaminants applied in irrigation water and consumption of home grown produce (assumption of 100% of produce being home grown would be protective of the general public in the absence of MRLs).

The domestic irrigation scenario was used as the basis of the irrigation water criteria. In this context dermal absorption by children playing with water is estimated to be limiting. In the context of agricultural irrigation higher values may be acceptable.

5.5.1 Derivation of acceptance criteria

A procedure has been developed for the development of irrigation water guidelines based on the work of Walden (1996). The procedure incorporates a number of simplifying assumptions that suggest the derived criteria are likely to be conservative. In particular, the protocol assumes;

- no leaching or volatile losses of contaminants once they have entered the soil. First order biodegradation kinetics are assumed in estimating the steady-state soil concentration resulting from irrigation with contaminated groundwater, and
- no metabolism or degradation of contaminants within the plant.

Surface water and groundwater acceptance criteria for irrigation use have been derived considering both the uptake of contaminants from soil, following accumulation associated with irrigation, and on the uptake of contaminants through direct contact of foliage with irrigation water. The procedures available for estimating the health risk from contaminated

groundwater and surface water for irrigation are subject to uncertainty and therefore the criteria developed should be regarded as preliminary only.

Groundwater criteria based on irrigation use are presented in Table 5.3 (details of the derivation of criteria are presented in Appendix 5B).

Table 5.3 Groundwater criteria based on irrigation use

Contaminant	Generic Acceptance Criteria
Non carcinogenic PAHs	
Naphthalene	0.2
Acenaphthene	2.3
Anthracene	7.9
Fluorene	1.3
Phenanthrene	0.8
Pyrene	0.4
Fluoranthene	0.7
Acenaphthylene	1.0
Carcinogenic PAHs	
Benzo[a]pyrene	0.0002
BTEX	
Benzene	0.3
Toluene	13
Ethylbenzene	5.2
Xylene	8.8
Phenolics	
Phenol	44
Cresol (o,m)	4
(p)	3.3
Cyanide - free	0.5
- complexed	1.2

1. Based on domestic irrigation scenario. Higher values may be acceptable in an agricultural context.

Additional information on irrigation use can be found in Section 4.3.1.3 of the Users' Guide.

5.6 Aquatic ecosystem protection

The Ministry for the Environment is currently developing guidelines for the protection of aquatic ecosystems based on the requirements of the Resource Management Act 1991 (RM Act). These will provide information on both the procedures for deriving acceptable contaminant concentrations in surface water, and guidelines values for a range of common surface water contaminants in New Zealand. The first step in this process is the development of a framework, as outlined in the discussion paper Ministry for the Environment (1995) "A Process for the Development of Guidelines for the Protection of Aquatic Ecosystems".

The provisions of the RM Act require that surface waters be protected so that there is no significant adverse impact on the ecosystem associated with the surface water body. In the absence of definitive New Zealand guidance regarding the protection of ecosystems, guideline values nominated by a number of overseas agencies have been summarised in Table 5.4. Guideline values nominated by the following agencies have been included:

- Australian and New Zealand Environment and Conservation Council (ANZECC)
- United States Environment Protection Agency (USEPA)
- Council of Canadian Ministers for the Environment (CCME).

The guidelines for the protection of aquatic ecosystems are designed to provide effectively full protection to a relatively pristine environment, based on an understanding of "no significant adverse effect". Each of the agencies, however, can define this concept slightly differently. In addition, the data sets underlying each set of guidelines are expected to differ.

Table 5.4 Summary of overseas guidelines for the protection of aquatic ecosystems (mg/L)

	Guideline Values						
	ANZECC (1992)		USEPA[3] (1995)				CCME (1991)
Contaminant	Aquatic Ecosystems (Fresh waters)	Human Consumption of Fish[1]	Freshwater		Marine		Freshwater Aquatic Ecosystems
			Acute	Chronic	Acute	Chronic	
PAHs	0.003	0.00003					ID[2]
Non carcinogenic PAHs							
Naphthalene		0.001					
Acenaphthene		0.00002					
Anthracene					0.3		
Fluorene							
Phenanthrene			0.03	0.0063	0.0077	0.0046	
Pyrene							
Fluoranthene							
Acenaphthylene					0.3		
Carcinogenic PAHs							
Benzo[a]pyrene					0.3		
BTEX							
Benzene	0.3	0.04	5.3[4]		5.1[4]	0.7[4]	0.3
Toluene	0.3	0.00025	17.5		6.3	5.0	0.0003
Ethylbenzene		0.00025	32		0.43		0.7
Xylene			ND	ND	ND	ND	
Phenolics							
Phenol	0.05	0.001-00.01	10.2	2.56	5.8		0.001(total)
Cresol (m)		0.0002					
(o)		0.0004					
(p)		0.0001					
Ammonia							2.2
Cyanide - free	0.005		0.022	0.0052	0.001		0.005
- complexed							
Nitrate							
Nitrite							0.06
Sulphate							
Sulphide as H_2S							

1. Includes consideration of human health and tainting.
2. ID = insufficient data to recommend a guideline.
3. Ambient Water Quality Criteria for Aquatic Organisms (USEPA, 1995)
4. Ambient Water Quality Criteria for Aquatic Organisms (USEPA, 1991)

Additional information on aquatic ecosystem protection can be found in Section 4.3.1.4 of the Users' Guide.

5.7 Primary contact recreation

Limited published information is available on acceptable concentrations of contaminants in water to be used for primary contact recreation, such as swimming. The ANZECC (1992) guidelines indicate that water containing chemicals which are either toxic or irritating to the skin or mucous membrane is unsuitable for primary contact recreation and that the concentration of toxic substances should not exceed levels given for untreated drinking water.

In order to better quantify the potential adverse effects of bodily immersion in water containing contaminants, health risk assessment procedures have been used. The resulting health risk-based acceptance criteria for recreational water are presented in Table 5.5. Details of the procedure used for derivation of criteria for primary contact recreational use are presented in Appendix 5C.

5.7.1 Derivation of acceptance criteria

Primary contact recreational activities, such as bathing, necessarily involve intimate contact between those involved and the potentially contaminated water. Both children and adults are considered in this assessment. The acceptance criteria presented in Table 5.5 are based on a commercial swimming pool scenario assuming regular training, which represents a reasonable worst case scenario. Higher values may be acceptable in the context of recreational bathing in a domestic swimming pool or bathing in surface waters. Criteria based on a typical surface water bathing scenario are presented in Appendix 5C. Both incidental ingestion of water during bathing and dermal absorption have been included in this assessment.

To quantify the health risks associated with exposure to various contaminants, several dose-response factors, such as Reference Dose (RfD) and Slope Factors (SF) by the USEPA and the Acceptable Daily Intake (ADI) or Provisional Tolerable Weekly Intake (PTWI) by the WHO, have been used (refer Appendix 4A of Module 4). These dose-response factors, developed from available human and animal studies, relate the estimated intake of a contaminant to the likelihood of health effects.

For exposure through primary contact recreation, the proposed acceptance criteria have been based on the dose-response factors with a correction for background exposure (default allowance of 50% of the RfD or ADI, refer Appendix 5C).

The assumptions to define the exposure scenario for derivation of the primary contact recreational use criteria are based on a reasonable estimate of the exposure frequency and duration.

Table 5.5 Health-based surface water and groundwater acceptance criteria for primary contact recreational use[1]

Contaminant	Generic Acceptance Criteria
PAHs	
Non carcinogenic PAHs	
Naphthalene	0.3
Acenaphthene	1.8
Anthracene	5.6
Fluorene	1.0
Phenanthrene	0.5
Pyrene	0.4
Fluoranthene	0.3
Acenaphthylene	0.7
Carcinogenic PAHs	
Benzo[a]pyrene	0.00003
BTEX	

Benzene	0.3
Toluene	15
Ethylbenzene	5
Xylene	8
Phenolics	
Phenol	150
Cresol (o,m)	10
(p)	1.0
Inorganic	
Ammonia	
Cyanide - free	1.8
-complexed	5

1. Based on commercial swimming pool scenario assuming regular training. Higher values may be acceptable in the context of domestic swimming pools and bathing in surface waters.

Additional information on primary contact recreation can be found in Section 4.3.1.5 of the Users' Guide.

5.8 References

1. ANZECC 1992 “Australian Water Quality Guidelines for Fresh and Marine Waters”, Australian & New Zealand Environment & Conservation Council , November.
2. CCME (1991) “Canadian Water Quality Guidelines”, Environment Canada, Ottawa.
3. Langley A (1993) “Refining Exposure Assessment” Proc. 2nd Nat. Workshop on the Health Risk Assessment of Contaminated Sites, South Australian Health Commission, Canberra, August.
4. Ministry for the Environment (1995) “A Process for the Development of Guidelines for the Protection of Aquatic Ecosystems”.
5. Ministry of Health (1995). “New Zealand Drinking-Water Standards for New Zealand”, January 1995.
6. Ministry of Health (1995). Drinking-Water Standards for New Zealand.
7. Ministry of Health, “Guidelines for Drinking Water Quality Management in New Zealand”, July.
8. NHMRC/ARMCANZ 1995 “Australian Drinking Water Guidelines” National Health and Medical Research Council/Agricultural and Resource Management Council of Australia and New Zealand.
9. Shell (1994) “The Concepts of HESP, Reference Manual, Human Exposure to Soil Pollutants, Version 2.10a”.
10. Travis C and Arms A (1988) “Bioconcentration of Organics in Beef, Milk, and Vegetation” Environ. Sci. Technol., Vol. 22, No.3, 271-274, American Chemical Society.
11. USEPA 1992 “Dermal Exposure Assessment: Principles and Applications”, EPA/600/8-91/011B.
12. USEPA (1988) “Exposure Assessment Manual”.
13. USEPA (1989) “Risk Assessment Guidance for Superfund, Human Health Evaluation Manual”.
14. USEPA (1990) “Exposure Factors Handbook”.
15. USEPA (1991) “Risk Assessment Guidance for Superfund, Volume 1, Human Health Evaluation Manual Supplement Guidance, Standard Default Exposure Factors, Interim Final”.
16. USEPA (1992) “Dermal Exposure Assessment : Principles and Applications, Interim Report”.
17. USEPA (1996) “Integrated Risk Information System Database”
18. Walden T and Spence L (1996) “Risk-Based BTEX Clean-up Goals in Groundwater for an Irrigation Scenario” BP Oil internal report.

Appendix 5A
Calculation of criteria for stock water use

Overview

The uptake of contaminants by stock is unlikely to be a limiting consideration where the groundwater is suitable for potable use. It is an important consideration, however, when high salinity limits potable use.

Groundwater acceptance criteria for the protection of stock water use have been set to:

- protect stock health, and
- protect human health where livestock products (e.g. milk and meat) are consumed.

The derivation of stock water criteria is highly uncertain due to inadequate information regarding the accumulation of contaminants in stock and relevant thresholds for the palatability of water for stock. Aesthetic limits for stock water have generally been set a factor of ten higher than the respective limits for potable use.

Uptake model

Summary

The uptake and accumulation of contaminants by stock depends on a range of complex biological processes affecting absorption, distribution, metabolism and elimination of contaminants. Simplified empirical formulae are available which indicate the level of uptake of contaminants by stock. These formulae are presented in numerous research papers. The equations used for the derivation of the groundwater acceptance criteria can be found in the following reference:

- Travis C and Arms A, "Bioconcentration of Organics in Beef, Milk, and Vegetation", Environmental Science and Technology, Vol 22, No 3, 1988.

Pathways

Contaminants are taken up by stock through ingestion of stock water. Contaminants may accumulate within animal tissue or fat reservoirs (e.g. milk) and through the consumption of animal products humans may be exposed to these contaminants. For the purposes of deriving criteria two main pathways, by which humans may ingest contaminants, have been assumed:

- ingestion of meat
- ingestion of milk and dairy products.

Travis and Arms present equations for the uptake of contaminants in beef, which for the purposes of deriving Tier 1 criteria have been assumed to apply to a range of livestock. Equations for the uptake of contaminants in milk are also presented.

Equations

The biotransfer factors for beef (Bb) and milk (Bm) are defined as:

$$Bb = \frac{\text{concentration in beef (mg / kg)}}{\text{daily intake of organic (mg / d)}} \quad \textbf{(A1)}$$

$$Bm = \frac{\text{concentration in milk (mg / kg)}}{\text{daily intake of organic (mg / d)}} \quad \textbf{(A2)}$$

The calculation of the biotransfer factors are calculated as follows:

$$\log Bb = -7.6 + \log K_{ow} \quad \textbf{(A3)}$$

$$\log Bm = -8.1 + \log K_{ow} \quad \textbf{(A4)}$$

where: K_{ow} = Octanol Water Partition Coefficient.

Groundwater criteria calculation

Exposure parameters

Acceptance criteria calculations are made for both meat and milk pathways. The exposure parameters are presented in Table 5A.1.

Table 5A.1 Exposure parameters

Parameter	Value	Reference
Stock		
Stock water ingestion rate	55 L/d	Shell, 1994
Human Reception		
Exposure frequency	365 d/y	
Exposure duration	70 yrs	
Averaging time	70 yrs	
Body weight	70 kg	ANZECC, 1992
Meat ingestion rate	152 g/d	Langley, 1993
Milk ingestion rate	269 g/d	Langley, 1993

Meat and milk concentrations

The contaminant concentrations in the meat and milk corresponding to the acceptable daily intake (e.g. RfD) are calculated using the following equations:

$$Ci = \frac{ADI \times AT \times 365 \times BW}{EF \times IR \times ED} \quad \textbf{(A5)}$$

where:
- Ci = Concentration of contaminant in beef or milk (mg/kg)
- ADI = Average daily intake (mg/kg/d)
- IR = Ingestion rate of beef or milk (kg/d)
- ED = Exposure duration (years)
- AT = Averaging time (70 years for carc., ED for non-carc)
- BW = Body weight (kg)

For carcinogenic contaminants:

$$ADI = \text{Target Risk} / SF \quad \textbf{(A6)}$$

For non-carcinogenic contaminants:

$$ADI = \text{Target Hazard Index} \times RfD \quad \textbf{(A7)}$$

where:
- SF = Slope factor $(mg/kg/d)^{-1}$
- RfD = Reference dose factor (mg/kg/d)

Groundwater concentration

The contaminant concentrations in beef and milk corresponding to the acceptable intake are used to calculate the groundwater acceptance criteria. The beef and milk concentrations are substituted into equations A1 and A2 to calculate the allowable daily intake of contaminants by stock. From this the groundwater concentration is calculated from the equation:

$$\text{Groundwater Concentration (mg / L)} = \frac{\text{Daily intake of contaminants by stock (mg / d)}}{\text{Ingestion rate of stock water (L / d)}} \quad \textbf{(A8)}$$

Groundwater concentrations are calculated for both exposure pathways (i.e. beef and milk consumption), however, risk calculations should combine both sources to determine the groundwater concentration. The combined pathway groundwater acceptance criterion is calculated by:

$$\text{Groundwater Acceptance Criterion (mg / L)} = \frac{1}{\frac{1}{Cb} + \frac{1}{Cm}} \quad \textbf{(A9)}$$

Appendix 5B
Calculation of criteria for irrigation use

Overview

The derivation of groundwater acceptance criteria for the protection of irrigation use has been based on:

- protection of the health of adults and children who may come in contact with contaminated groundwater during irrigation
- protection of the health of residents associated with the inhalation of vapours during use of contaminated groundwater
- protection of the health of residents consuming home grown produce that may have been affected by the use of contaminated groundwater for irrigation
- consideration of aesthetic impacts, including odour.

Walden and Spence (1996) developed a protocol for the development of groundwater acceptance criteria for irrigation use and this has been used as the main basis for the derivation of groundwater acceptance criteria for irrigation. Some modifications have been made to the exposure factors assumed by Walden and Spence in order to retain consistency with exposure factors used in other parts of these guidelines. The protocol developed by Walden and Spence has been modified to account for the adsorption and accumulation of heavier PAHs in the soil.

A general overview of the approach used in derivation of criteria for the protection of irrigation use is presented.

The derivation of irrigation water criteria is discussed in terms of the following:

- shower model (used to estimate volatilisation of contaminants from irrigation water)
- accumulation and loss in soil
- plant uptake
- derivation of Water Criteria based on vegetable consumption
- inhalation of aerosols
- dermal exposure
- odour impact.

Shower model

The shower model is used to estimate the vapour emissions from the sprayed water and the concentration in water hitting the ground. The concentrations in the air are estimated using the following assumptions:

- shower is fully mixed for the entire duration.
- dilution uses a simple box model.
- two film gas-liquid mass transfer.

Volatilisation is limited by mass transfer rates. The overall mass transfer coefficient is calculated as:

$$K_L = \left[\frac{1}{k_l} + \frac{RT}{Hk_g} \right]^{-1} \qquad \textbf{(B1)}$$

where: K_L = overall mass transfer coefficient (cm/hr)
H = Henry's Law constant for contaminant (atm.m^3 / mol)
R = gas constant (assumed to be 8.2E-5) (atm.m^3 / mol.K)
T = absolute temperature (assumed to be 293) (K)
k_g = gas phase mass transfer coefficient (cm/hr)

k_l = liquid phase mass transfer coefficient (cm/hr)

The gas and liquid phase mass transfer coefficients for contaminants may be estimated from measure values for CO_2 and H_2O and the following correlations:

$$k_{g(VOC)} = k_{g(H_20)}\left[\frac{18}{MW_{VOC}}\right]^{0.5} \quad \textbf{(B2)}$$

$$k_{l(VOC)} = k_{l(CO_2)}\left[\frac{44}{MW_{VOC}}\right]^{0.5} \quad \textbf{(B3)}$$

where: $k_{g(H20)}$ = gas phase mass transfer coefficient for water (cm/hr)
= 3000 cm/hr
$k_{l(CO2)}$ = liquid phase mass transfer coefficient for carbon dioxide (cm/hr)
= 20 cm/hr
18 = molecular weight of water
44 = molecular weight of carbon dioxide
MW_{VOC} = molecular weight of contaminant

The overall mass transfer coefficient must be adjusted for shower temperature and the viscosity of water at the slower temperature.

$$K'_{L(Ts)} = K_L\left[\frac{T_l \mu_S}{T_S \mu_l}\right]^{-0.5} \quad \textbf{(B4)}$$

where: $K'_{L(Ts)}$ = adjusted overall mass transfer coefficient (cm/hr)
T_l = calibration water temperature of K_L (K)
T_S = shower water temperature (K)
μ_l = water viscosity at T_l (g/m.s)
μ_S = water viscosity at T_S (g/m.s)

Water viscosity may be estimated from the following relationships (T in ^oC):

If $T \leq 20\ ^oC$: $\mu = 100 \,.\, 10^y$

where: $$y = \frac{1301}{998.33 + 8.1855(T-20) + 0.00585(T-20)^2} - 3.30233 \quad \textbf{(B5)}$$

If $T > 20\ ^oC$: $\mu = 1.002 \,.\, 10^y$

where: $$y = \frac{-1.37272(T-20) - 0.001053(T-20)^2}{T + 105} \quad \textbf{(B6)}$$

Volatilisation is assumed to be a first order process:

$$C_{sh} = C_o e^{-K'_L t/600d} \quad \textbf{(B7)}$$

where: C_{sh} = concentration of contaminant in shower droplet after time t (mg/L)
C_o = concentration of contaminant in shower water (mg/L)
d = shower droplet diameter (cm)
= 0.2 cm
t = shower droplet drop time (s)
= 10 s

C_{sh} is the concentration of the shower drop which enters the soil.

The total amount of contaminant that volatilises is given by:

$M_{sh} = f_v \,.\, Q \,.\, time_{sh} \,.\, C_o$ **(B8)**

where: M_{sh} = mass of contaminant volatilised (mg)
f_v = the fraction of contaminant volatilised $(1 - e^{-K_L' t/600d})$ (mg/mg)
Q = the volumetric flow rate of water (L/min)
$time_{sh}$ = the duration for which the shower water is flowing (min)
C_o = the concentration of contaminant in the shower water (mg/L)

The concentration of the shower air can be estimated from:

$$C_{sh} = \frac{M_{sh}}{V_{sh}} \quad \textbf{(B9)}$$

where: C_{sh} = air concentration in the shower (mg/m^3)
V_{sh} = volume of air in the shower (m^3)

Accumulation and loss in soil

In order to calculate a produce contaminant concentration it is required to know at what concentration the contaminant exists in the soil, which depends on the following parameters:

- garden area of concern
- volume and mass of soil affected by watering
- rate of water flow
- frequency of watering
- concentration of contaminant in droplets (after volatilisation) and
- half-life of contaminants in soil.

The first step is to calculate the total amount of contaminants sprayed onto the soil for any one event. To determine this the following assumptions are used:

- the concentration of the irrigation water is after volatilisation has occurred, calculated by the shower model
- 100 L of water is used for every 10 m^2 of garden to be watered
- 1 % of the water is lost as aerosol during watering, leaving 99 L of water to enter the soil.

Since events do not occur every day the 100 L per event is changed to L/day by averaging the watering frequency over a year. This is to account for the degradation of the contaminants in the soil.

The next step is to calculate the total addition of contaminant per watering (based on the yearly day average) per unit mass of soil. The assumptions used here are:

- total volume of soil is 3 m^3 (2m x 5m x 0.3m);
- using a bulk density of 2.0 t/m^3 the soil weight is 6000 kg; and
- contaminant disperses uniformly throughout entire soil mass.

The final consideration is contaminant degradation. It is assumed that the concentration of a contaminant in the soil is at steady state. i.e. sufficient time has elapsed such that the rate of degradation and accumulation are equal. This soil concentration is given by the following:

$$Cs = D \ / \ k \quad \textbf{(B10)}$$

where: Cs = Steady state soil concentration (mg/kg)
D = Daily (averaged) addition of contaminant (mg/kg/day)
k = Degradation constant (day^{-1})

and: $k = (Ln\ 2) / t_{1/2}$ **(B11)**

where: Ln 2 = Natural log of 2
$t_{1/2}$ = Half life of contaminant (day)

Plant uptake

The uptake of contaminants by plants is a complex biological process. There is no accurate, theoretically robust model for predicting the concentration of a contaminant in plant material, however, empirical formula have been derived by numerous sources to simulate contaminant uptake by plants.

The following reference is used for modeling the uptake of contaminants by plants:

- C.C. Travis and A.D. Arms, *Bioconcentration of Organics in Beef, Milk and Vegetation*, Environ. Sci. Technol., Vol. 22, No. 3, 1988, pp271-274.

Travis and Arms have developed correlations for the uptake of contaminants in beef, milk and vegetation. The primary contaminants of concern are pesticides, although information is included for benzo(a)pyrene uptake by plants and the same methodology may be used for other contaminants.

Travis and Arms make use of a concept known as the Biotransfer Factor. In the case of plants this may also be known as the uptake factor. This is defined as:

$$B_v = \frac{\text{concentration in vegetation (mg / kg)}}{\text{soil contaminant concentration (mg / kg)}} \qquad \textbf{(B12)}$$

The biotransfer factor of an organic compound is directly proportional to its octanol-water partition coefficient. Based on review studies involving various chemicals the following correlation was derived:

$$\log B_v = 1.588 - 0.578 \log K_{ow} \qquad \textbf{(B13)}$$

The above is the biotransfer for plants. This may be considered to be the uptake factor.

Deposited water

As part of the ingestion pathway, residual water on plants is a consideration given in SAHC. The amount of water deposited on the plant surface is considered to be 1 % of the weight of the vegetable and 50% is removed by peeling/washing processes leaving a residual of 0.5% of the weight of the vegetable.

The concentration of this water is that calculated in the shower model left in the water droplet after spraying. Knowing the consumption rate, the total intake of contaminants may be calculated. A factor of 5 is allowed for accumulation following deposition and removal processes such as precipitation, photolysis and photooxidation.

Inhalation of aerosols

As well as inhalation of volatilised contaminants through the shower model, the receptors inhale water mist. It has been assumed that 1 percent of water sprayed on the garden forms an aerosol. Of this 0.1 % is inhaled by the receptors. This inhalation pathway is added to the volatilised contaminants inhaled by the receptors during gardening.

Dermal exposure

Children are subjected to dermal contact when playing under the sprinkler. It is assumed that the child's entire body is exposed to the contaminated water and the concentration of the water is that of the groundwater C_o.

The average daily dose (mg/kg.d) is calculated by the equation:

$$ADD = \frac{10^{-3} C_w \times SA \times ET \times PC \times EF \times ED}{365\ AT \times BW} \qquad \textbf{(B14)}$$

where: C_w = concentration of contaminant in groundwater (mg/L)
SA = total skin surface area (cm^2)
ET = activity duration (hr/day)
PC = chemical specific skin permeability coefficient (cm/hr)
EF = exposure frequency for playing/gardening (d/yr)

ED = exposure duration (yrs)
AT = averaging time (yrs)
= 70 yrs for carcinogenic contaminants
= ED for non-carcinogenic contaminants
BW = body weight

The USEPA (Dermal Exposure Assessment: Principles and Applications, 1992) have estimates of permeability coefficients. These are estimated by the following equation:

$$\text{Log } K_p = -2.72 + 0.71 \text{ Log } K_{ow} - 0.0061 \text{ MW} \quad \textbf{(B15)}$$

where: K_p = permeability coefficient (cm/hr)
K_{ow} = Octanol Water Partition Coefficient
MW = Molecular weight (g/mol)

Table 5B.1 shows the permeability coefficients used in the model.

Table 5B.1 Permeability coefficients for dermal exposure

Contaminant	Permeability Coefficient, Kp (cm/hr)
Naphthalene	0.07
Acenaphthalene	0.13
Anthracene	0.23
Fluorine	0.17
Phenanthrene	0.23
Pyrene	0.46
Fluoranthene	0.36
Acenaphthylene	0.17
Benzo(a)pyrene	1.2
Phenols	0.0055
Cresol(o,m)	0.01
2,4-Dimethylphenol	0.015
Benzene	0.021
Toluene	0.045
Ethylbenzene	0.074
Xylene	0.080
Cyanide (free & complex)	0.001

Table 5B.2 Exposure parameters for irrigation model

Parameter	Child	Adult
Water ingestion rate (L/day)	0.25	-
Vapour inhalation rate (m^3/hr)	0.83	0.83
Gardening/play activity duration (hr/d)	0.5	2
Gardening/play exposure frequency (d/yr)	100	100
Gardening exposure duration (yrs)	6	30
Vegetable ingestion exposure frequency (d/y)	350	350
Vegetable ingestion. exposure duration (yrs)	6	30
Vegetable ingestion rate (g/day)	130	450
Fraction of vegetables home grown	0.10	0.10
Vegetable water retention (%)	80	80
Skin surface area (cm^2)	6800	-
Wind speed (m/s)	2	2
Inhalation “box” volume (m^3)	21,600	86,400
Sprinkler flow rate (L/min)	30	30
Water temperature (^oC)	25	25
Lifetime (yrs)	70	70
Body weight (kg)	15	70

Odour based criteria

Odour based criteria were determined using threshold values obtained from literature and air concentration values calculated from the shower model. Shower air concentrations were

calculate for a water concentration of 1 mg/L. A proportional relationship allows the calculation of the water concentration, which would produce a shower concentration equal to the odour threshold.

Odour threshold air concentrations were obtained from in the following references:

- T. Walden and L. Spence, *Risk-Based BTEX Cleanup Goals in Groundwater for Irrigation Scenarios,* 1996.
- *Odor Thresholds for Chemicals with Established Occupational Health Standard,* American Industrial Hygiene Association, 1989.

Table 5B.3 Groundwater acceptance criteria Irrigation use

Site Use	Residential	Exposure duration (child)	6 yrs	Garden duration (child)	0.5 hr/d	Produce ingestion (child)	0.13kg/d
Receptor	Children resident on site for up to 30 yrs	Exposure duration (adult)	30 yrs	Garden duration (adult)	2 hr/d	Produce ingestion (adult)	0.45 kg/d
		Exposure duration (ad,com)	24 yrs	Garden exp frequency	100 d/yr	Proportion home grown	0.1
Target Risk	0.00001	Ave time (carc)	70 yrs	Inhale rate (child)	20 m3/d	Produce exposure frequnecy	350 d/yr
Target HI	1	(non-carc, child)	6 yrs	Inhale rate (adult)	20 m3/d	Skin area (child)	6800cm2
		(non-carc, adult)	30 yrs	Water ingestion (child)	0.25 L/d		
		Body weight (child)	15 kg	Water ingestion (adult)	0 L/d		
		Body weight (adult)	70 kg				

Contaminant	Skin Absorption Factor	SF (1/(mg/kg/d)) Oral	RfD (mg/kg/d) Oral	SF (1/(mg/kg/d)) Inhalation	RfD (mg/kg/d) Inhalation	Acceptable CDI (mg/kg/d)						Acceptable Criteria (mg/L-H2O)		
						Carcinogenic			Non-carcinogenic			Child	Adult	Child-> Adult
						Oral	Dermal	Inhalation	Oral	Dermal	Inhalation			
PAHs									2.00E-03	2.00E-03	2.00E-03	2.12E-01	4.93E+00	
napthalene	7.00E-02		2.00E-03		2.00E-03				3.00E-02	3.00E-02	3.00E-02	2.29E+00	9.10E+01	
acenaphthene	1.30E-01		3.00E-02		3.00E-02				1.50E-01	1.50E-01	1.50E-01	7.85E+00	7.59E+02	
anthracene	2.30E-01		1.50E-01		1.50E-01				2.00E-02	2.00E-02	2.00E-02	1.29E+00	7.66E+01	
fluorene	1.70E-01		2.00E-02		2.00E-02				1.50E-02	1.50E-02	1.50E-02	7.85E+00	7.83E+01	
phenanthrene	2.30E-01		1.50E-02		1.50E-02				1.50E-02	1.50E-02	1.50E-02	4.50E-01	1.31E+02	
pyrene	4.60E-01		1.50E-02		1.50E-02				2.00E-02	2.00E-02	2.00E-02	7.36E-01	1.07E+02	
fluoroanthene	3.60E-01		2.00E-02		2.00E-02				1.50E-02	1.50E-02	1.50E-02	9.68E-01	5.25E+01	
acenaphthylene	1.70E-01		1.50E-02		1.50E-02							2.02E-04	6.78E-02	2.02E-04
benzo(a)pyrene	1.20E+00	7.30E+00		7.30E+00		1.37E-06	1.37E-06	1.37E-06						

Contaminant	Pathway contribution to risk											
	Child				Adult				Child->Adult			
	Inhalation	Produce ingestion	Water ingestion	Skin absorption	Inhalation	Produce ingestion	Water ingestion	Skin absorption	Inhalation	Produce ingestion	Water ingestion	Skin absorption
PAHs	%	%	%	%	%	%	%	%	%	%	%	%
napthalene	1.62	4.01	48.34	46.02	30.80	69.20	0.00	0.00	-	-	-	-
acenaphthene	0.83	2.52	34.92	61.73	25.70	74.30	0.00	0.00	-	-	-	-
anthracene	0.33	1.09	23.88	74.70	21.97	78.03	0.00	0.00	-	-	-	-
fluorene	0.71	1.53	29.52	68.25	32.91	67.09	0.00	0.00	-	-	-	-
phenanthrene	0.25	1.14	23.89	74.72	15.90	84.10	0.00	0.00	-	-	-	-
pyrene	0.08	0.41	13.71	85.79	10.48	89.52	0.00	0.00	-	-	-	-
fluoroanthene	0.63	0.23	16.81	82.33	75.27	24.73	0.00	0.00	-	-	-	-
acenaphthylene	0.81	1.62	29.46	68.11	34.84	65.18	0.00	0.00	-	-	-	-
benzo(a)pyrene	0.03	0.07	5.77	94.14	11.23	88.77	0.00	0.00	0.05	0.22	5.76	93.97

Table 5B.4 Irrigation criteria calculation
Shower model

Water conc		1 mg/L							
Viscosity	T	25C	Drop diameter	0.2cm	Gardening exposure time			Area of soil	10m2
	if T<20		Drop time	10s		adult	2hr	Weight of soil	6000kg
		y -2.050650852				child	0.5hr	Total flow for A	27.4L (ave over year)
		u 0.889916272	Wind speed	2 m/s				Total flow	100
	if T>20		Sprinkler dis.	4 m	Box volume	adult	86400m3	fr aerosol inh	0.01
		y -0.051248654	Receptor height	1.5 m		child	21600m3	fr aerosol on pla	0.005
		u 0.890469539	Flowrate	30 L/min				fr aerosol inhal	0.001
	u	0.890469539 g/m.s							

Chemical	MW g/mol	H @ 20C L-H2O/L-air	H atm.m3/mol	kg cm/hr	kl cm/hr	KI cm/hr	KF cm/hr	Cspray mg/L
Naphthalene	128		4.83E-04	1125	11.7260394	7.722214783	7.248437956	0.547969037
Acenaphthene	154.2		1.90E-04	1024.979833	10.68351458	4.608868287	4.308197935	0.696362832
Anthracene	178		6.50E-05	953.998092	9.943661524	2.049092199	1.915414855	0.852469451
Fluorene	166.2		2.10E-04	987.2837697	10.29060301	4.693532169	4.387338569	0.693772246
Phenanthrene	178.2		3.90E-05	953.4625892	9.9380799	1.3390483641	1.251786132	0.900940996
Pyrene	202.3		1.10E-05	894.8692109	9.327352555	0.392465471	0.366862084	0.969890754
Fluoranthene	202.3		1.69E-02	894.8692109	9.327352555	9.191156739	8.591550032	0.48872149
Acenaphthylene	152.2		2.80E-04	1030.692281	10.75347941	5676515375	5.306194556	0.6426321
Benxo(a)pyrene	252.3		2.00E-06	801.3068992	8.352138908	0.66174816	0.061857746	0.994858451

Chemical	Cshower mg/L	Mass vol (mg) adult	Csh (mg/m3) adult	Half life days	Soil Conc mg/kg	Kow	Uptake Factor	Cplant g/g	Odour threshold mg/m3	Odour based criteria (mg/L)
Naphthalene	0.452030963	1627.311469	0.018834623	258	0.922114329	1995	0.479328226	4.41995E-07	0.2	10.6
Acenaphthene	0.301637168	1085.893805	0.012588215	397	1.808342421	8317	0.210019319	3.797897E-07	-	-
Anthracene	0.147530549	531.1099749	0.006147106	397	2.207386477	28180	0.103737101	2.28988E-07	-	-
Fluorene	0.306227754	1102.419913	0.01275949	397	1.796455547	15140	0.14855499	2.66872E-07	4.5	352.7
Phenanthrene	0.099059004	356.6124153	0.004127459	397	2.332898812	28840	0.102358224	2.38791E-07	8	1938.2
Pyrene	0.030109246	108.393286	0.001254552	506	3.200975735	123000	0.044262388	1.41683E-07	8.7	6934.7
Fluoranthene	0.51127851	1840.602637	0.021303271	530	1.689453922	166000	0.037220099	6.28816E-08	0.35	16.43
Acenaphthylene	0.3573679	1286.524439	0.014890329	397	1.664033128	11750	0.171995907	2.86207E-07	0.20	13.43
Benxo(a)pyrene	0.005141549	18.50957627	0.000214231	530	3.439111126	1096000	0.012502288	4.29968E-08	-	-

Adult	Risk/HI inhalation	Risk/HI produce	Risk/HI total	Child	Risk/HI inhalation	Risk/HI vegetation	Risk/HI water ing	Risk/HI dermal	Risk/HI total
Naphthalene	6.25E-02	1.40E-01	2.03E-01	Naphthalene	7.67E-02	1.89E-01	2.28E+00	2.17E+00	4.72E+00
Acenaphthene	2.82E-03	8.16E-03	1.10E-02	Acenaphthene	3.61E-03	1.10E-02	1.52E-01	2.69E-01	4.36E-01
Anthracene	2.90E-04	1.03E-03	1.32E-03	Anthracene	4.16E-04	1.39E-03	3.04E-02	9.52E-02	1.27E-01
Fluorene	4.30E-03	8.76E-03	1.31E-02	Fluorene	5.49E-03	1.18E-02	2.28E-01	5.28E-02	7.73E-01
Phenanthrene	2.03E-03	1.07E-02	1.28E-02	Phenanthrene	3.19E-03	1.45E-02	3.04E-01	9.52E-01	1.27E+00
Pyrene	7.99E-04	6.82E-03	7.62E-03	Pyrene	1.82E-03	9.19E-03	3.04E-01	1.90E+00	2.22E+00
Fluoranthene	7.04E-03	2.31E-03	9.36E-03	Fluoranthene	8.55E-03	3.12E-03	2.28E-01	1.12E+00	1.36E+00
Acenaphthylene	6.64E-03	1.24E-02	1.91E-02	Acenaphthylene	8.34E-03	1.67E-02	3.04E-01	7.04E-01	1.03E+00
Benxo(a)pyrene	1.68E-05	1.31E-04	1.47E-04	Benxo(a)pyrene	1.24E-05	3.53E-05	2.86E-03	4.66E-02	4.95E-02

Adult (com)	Risk/HI inhalation	Risk/HI produce	Child->Adult	Risk/HI inhalation	Risk/HI vegetation	Risk/HI water ing	Risk/HI dermal	Risk/HI total
Naphthalene			Naphthalene					
Acenaphthene			Acenaphthene					
Anthracene			Anthracene					
Fluorene			Fluorene					
Phenanthrene			Phenanthrene					
Pyrene			Pyrene					
Fluoranthene			Fluoranthene					
Acenaphthylene			Acenaphthylene					
Benxo(a)pyrene	1.32E-05	7.40E-05	Benxo(a)pyrene	2.56E-05	1.09E-04	2.86E-03	4.66E-02	4.96E-02

Table 5B.5 Groundwater acceptance criteria
Irrigation use

Site Use	Residential	Exposure duration (child)	6 yrs	Garden duration (child)	0.5 hr/d	Produce ingestion (child)	0.13kg/d
Receptor	Children resident on site	Exposure duration (adult)	30 yrs	Garden duration (adult)	2 hr/d	Produce ingestion (adult)	0.45 kg/d
	for up to 30 yrs	Exposure duration (ad,com)	24 yrs	Garden exp frequency	100 d/yr	Proportion home grown	0.1
Target Risk	0.00001	Ave time (carc)	70 yrs	Inhale rate (child)	20 m3/d	Produce exposure frequnecy	350 d/yr
Target HI	1	(non-carc, child)	6 yrs	Inhale rate (adult)	20 m3/d	Skin area (child)	6800cm2
		(non-carc, adult)	30 yrs	Water ingestion (child)	0.25 L/d		
		Body weight (child)	15 kg	Water ingestion (adult)	0 L/d		
		Body weight (adult)	70 kg				

Contaminant	Skin Absorption Factor	SF (1/(mg/kg/d)) Oral	RfD (mg/kg/d) Oral	SF (1/(mg/kg/d)) Inhalation	RfD (mg/kg/d) Inhalation	Acceptable CDI (mg/kg/d)						Acceptable Criteria (mg/L-H2O)		
						Carcinogenic			Non-carcinogenic			Child	Adult	Child-> Adult
						Oral	Dermal	Inhalation	Oral	Dermal	Inhalation			
Phenolics														
Phenol	5.50E-02		3.00E-01		3.00E-01				3.00E-01	3.00E-01	3.00E-01	4.39E+01	2.11E+02	
Cresol (o,m)	1.00E-02		2.50E-02		2.50E-02				2.50E-02	2.50E-02	2.50E-02	4.04E+00	3.42E+01	
Dimethylphenol	1.50E-02		2.00E-02		2.00E-02				2.00E-02	2.00E-02	2.00E-02	3.25E+00	4.19E+01	
BTEX														
Benzene	2.10E-02	2.90E-02		2.90E-02		3.45E-04	3.45E-04	3.45E-04				5.32E-01	6.29E-01	3.18E-01
Toluene	4.50E-02		1.00E-01		1.00E-01				1.00E-01	1.00E-01	1.00E-01	1.30E+01	3.65E+02	
Ethylbenzene	7.40E-02		5.00E-02		5.00E-02				5.00E-02	5.00E-02	5.00E-02	5.19E+00	1.33E+02	
Xylene	8.00E-02		9.00E-02		9.00E-02				9.00E-02	9.00E-02	9.00E-02	8.84E+00	1.80E+02	
Inorganics														
Cyanide -free	1.00E-03		2.50E-03		2.50E-03				2.50E-03	2.50E-03	2.50E-03	4.69E+01	4.88E+00	
Complexed	1.00E-03		6.25E-03		6.25E-03				6.25E-03	6.25E-03	6.25E-03	1.17E+00	1.22E+01	

Contaminant	Pathway contribution to risk											
	Child				Adult				Child->Adult			
%	Inhalation	Produce ingestion	Water ingestion	Skin absorption	Inhalation	Produce ingestion	Water ingestion	Skin absorption	Inhalation	Produce ingestion	Water ingestion	Skin absorption
Phenolics												
Phenol	0.27	27.97	66.77	4.99	0.30	99.70	0.00	0.00	-	-	-	-
Cresol (o,m)	0.31	15.81	73.83	10.04	0.68	99.32	0.00	0.00	-	-	-	-
Dimethylphenol	0.33	10.33	74.20	15.14	1.23	98.77	0.00	0.00	-	-	-	-
BTEX												
Benzene	2.90	19.52	60.34	17.23	14.39	85.61	0.00	0.00	7.51	46.14	36.05	10.30
Toluene	2.74	1.70	59.28	36.28	64.53	35.47	0.00	0.00	-	-	-	-
Ethylbenzene	2.15	2.83	47.36	47.66	48.19	53.81	0.00	0.00	-	-	-	-
Xylene	2.00	4.38	44.84	48.78	34.00	66.00	0.00	0.00	-	-	-	-
Inorganics												
Cyanide -free	0.34	12.86	85.63	1.16	0.76	99.24	0.00	0.00	-	-	-	-
Complexed	0.34	12.86	85.63	1.16	0.76	99.24	0.00	0.00	-	-	-	-

Table 5B.6 Irrigation criteria calculation
Shower model

Water conc		1 mg/L							
Viscosity	T	25C	Drop diameter	0.2cm	Gardening exposure time			Area of soil	10m2
	if T<20		Drop time	10s		adult	2hr	Weight of soil	6000kg
		y -2.050850852				child	0.5hr	Total flow for A	27.4L (ave over year)
		u 0.889916272	Wind speed	2 m/s				Total flow	100
	if T>20		Sprinkler dis.	4 m	Box time	adult	86400m3	fr aerosol inh	0.01
		y -0.051248654	Receptor height	1.5 m		child	21600m3	fr aerosol on pla	0.005
		u 0.890469539	Flowrate	30 L/min					
	u	0.890469539 g/m.s							

Chemical	MW g/mol	H @ 20C L-H2O/L-air	H atm.m3/mol	kg cm/hr	kl cm/hr	KI cm/hr	KF cm/hr	Cspray mg/L
Phenol	94	-	3.30E-07	1312.784923	13.6833491	0.018007529	0.016832766	0.998598253
Cresol (o,m)	108	-	1.00E-06	1224.744871	12.76569477	0.050773066	0.047460766	0.996052747
Dimethylphenol	122	-	2.00E-06	1152.331919	12.01092399	0.095163729	0.0889555	0.99261445
Benzene	78.11	-	5.50E-03	1440.13826	15.01077153	14.35706435	13.42044752	0.326811859
Toluene	92	-	6.64E-03	1326.977605	13.8312815	13.3285957	14.45907344	0.354071602
Ethylbenzene	106	-	8.43E+00	1236.245076	12.88556308	12.8851803	12.04458529	0.366515143
Xylene	106	-	7.60E-03	1236.245076	12.88556308	12.47451706	11.66071263	0.378429285
Cyanide - free	-	-	-	-	-	-	-	1
Complexed	-	-	-	-	-	-	-	1

Chemical	Cshower mg/L	Mass vol (mg) adult	Csh (mg/m3) adult	Half life days	Soil Conc mg/kg	Kow	Uptake Factor	Cplant g/g	Odour threshold mg/m3	Odour based criteria (mg/L)
Phenol	0.001401747	5.046289648	5.84061E-05	63	0.410336734	28.84	5.547824856	2.27648E-06	0.23	3937.9
Cresol (o,m)	0.003947523	14.21011029	0.000164489	63	0.409290753	93.3	2.814546382	1.15197E-06	0.0027	16.4
Dimethylphenol	0.00738555	26.4879804	0.000307731	63	0.407877913	199.5	1.813982127	7.39883E-07	-	-
Benzene	0.673188141	2423.477306	0.028049506	365	0.778036407	134.9	2.274327974	1.76951E-06	4.5	160.4
Toluene	0.645928398	2325.342232	0.026913683	63	0.145492529	537	1.023469401	1.48907E-07	8	297.2
Ethylbenzene	0.633484857	2280.545485	0.026395202	228	0.545049337	1413	0.585083473	3.18899E-07	8.7	329.6
Xylene	0.621570715	2237.654573	0.02589878	365	0.900920871	1413	0.585083473	5.27114E-07	0.35	13.51
Cyanide - free	0	0	0	-	-	-		0.0000008	-	-
Complexed	0	0	0	-	-	-		0.0000008	-	-

Adult	Risk/HI inhalation	Risk/HI produce	Risk/HI total	Child	Risk/HI inhalation	Risk/HI vegetation	Risk/HI water ing	Risk/HI dermal	Risk/HI total
Phenol	1.43E-05	4.73E-03	4.74E-03	Phenol	6.23E-05	6.38E-03	1.52E-02	1.14E-03	2.28E-02
Cresol (o,m)	1.99E-04	2.90E-02	2.92E-02	Cresol (o,m)	7.78E-04	3.91E-02	1.83E-01	2.48E-02	2.47E-01
Dimethylphenol	2.95E-04	2.36E-02	2.39E-02	Dimethylphenol	1.02E-03	3.18E-02	2.28E-01	4.66E-02	3.08E-01
Benzene	2.29E-06	1.36E-05	1.59E-05	Benzene	5.45E-07	3.67E-06	1.14E-05	3.24E-06	1.88E-05
Toluene	1.77E-03	9.72E-04	2.74E-03	Toluene	2.11E-03	1.31E-03	4.57E-02	2.79E-02	7.70E-02
Ethylbenzene	3.47E-03	4.04E-03	7.52E-03	Ethylbenzene	4.15E-03	5.45E-03	9.13E-02	9.19E-02	1.93E-01
Xylene	1.89E-03	3.68E-03	5.57E-03	Xylene	2.27E-03	4.95E-03	5.07E-02	5.52E-02	1.13E-01
Cyanide - free	1.57E-03	2.03E-01	2.05E-01	Cyanide - free	7.31E-03	2.74E-01	1.83E+00	2.48E-02	2.13E+00
Complexed	6.26E-04	8.14E-02	8.20E-02	Complexed	2.92E-03	1.10E-01	7.31E-01	9.94E-03	8.53E-01

Adult (com)	Risk/HI	Risk/HI	Child->Adult	Risk/HI	Risk/HI	Risk/HI	Risk/HI	risk/HI

	inhalation	produce		inhalation	vegetation	water ing	dermal	total
Phenol			Phenol					
Cresol (o,m)			Cresol (o,m)					
Dimethylphenol			Dimethylphenol					
Benzene	1.82E-06	1.09E-05	Benzene	2.36E-06	1.45E-05	1.14E-05	3.24E-06	3.15E-05
Toluene			Toluene					
Ethylbenzene			Ethylbenzene					
Xylene			Xylene					
Cyanide - free			Cyanide - free					
Complexed			Complexed					

Appendix 5C

Calculation of criteria for primary contact recreation

Ingestion of contaminated water

The Chronic Daily Intake (CDI) may be determined by the following expression:

$$\mathbf{CDI} = \frac{\mathbf{C_i \times IR_{adj} \times EF \times MF}}{\mathbf{AT}}$$

where: C_i = concentration of species "i" in the water (mg/L)
EF = exposure frequency(events/yr)
AT = averaging time
= (ED x 365) days for non-carcinogens by convention or (70 years x 365) days for carcinogens, a lifetime, by convention
IR_{adj} = age adjusted ingestion rate (L/d)
MF = matrix factor, accounts for reduced bioavailability of contaminant due to binding to the soil matrix. In the absence of necessary information, MF usually taken as 1.0.

$$\mathbf{IR_{adj}} = \sum \frac{\mathbf{ED \times IR \times CF}}{\mathbf{BW}}$$

where: ED = exposure duration (yr)
IR = ingestion rate (mL/d)
CF = conversion factor
= 0.001 L/mL
BW = body weight (kg)

Dermal absorption from contaminated water

The Chronic Daily Intake (CDI) for dermal absorption from contaminated water may be determined by the following expression (USEPA, 1989)[1]:

$$\mathbf{CDI} = \frac{\mathbf{t \times AV_{adj} \times C \times PC \times EF \times CF}}{\mathbf{AT}}$$

where: t = duration of exposure (hours/event)
AV_{adj} = age adjusted skin surface area (cm^2)
C = contaminant concentration in water (mg/L)
PC = dermal permeability constant (cm/hr)
EF = exposure frequency (event/yr)
AT = averaging time (days)
CF = conversion factor
= 10^{-3} L/cm^3

$$\mathbf{AV_{adj}} = \sum \frac{\mathbf{AV} \times \mathbf{ED}}{\mathbf{BW}}$$

where: AV = skin surface area (cm^2)
ED = exposure duration (yr)
BW = body weight (kg)

Note, for the purposes of developing human health-based acceptance criteria for non-carcinogenic health effects only, the most sensitive receptor, i.e. children, is considered in the

[1] Based on steady state model dermal absorption, subject to review.

assessment of primary contact recreational exposure. In the case of carcinogenic health effects it is necessary to consider an age weighted exposure.

Primary contact recreation

Health based acceptance criteria have been developed for both the ingestion and dermal absorption exposure routes, employing plausible or reasonable worst case assumptions. The major exposure assumptions are summarised as follows:

• exposure duration	=	Child (4-10 yrs): 6 yrs Adult: 24 yrs	
• water ingestion rate	=	100 mL/event	(ANZECC, 1992)
• skin surface area	=	Child (4-10 yrs): 8290 cm^2 Adult: 18000 cm^2	(USEPA, 1989)
• body weight	=	Child (4-10 yrs): 30 kg Adult: 70 kg	(USEPA, 1989)
• exposure frequency	=	150 event/yr	(USEPA, 1992)
• event duration	=	1 hr/ event	(USEPA, 1992)

For recreational bathing in surface water bodies, an exposure frequency of 7 events/yr and an event duration of 2.6 hrs/event may be used.

Table 5C.1 Health-based acceptance criteria
Primary recreational use of surface water
Typical

Receptor	Children and adults resident on site up to 30 yrs	Target risk	0.00001
		Target HI	1
Exposure frequency	7 d/yr	Body weight (4-10 yrs)	30 kg
Averaging time (carc)	70 yrs	Body weight (adult)	70 kg
(non-carc)	6 yrs	Exposure duration (4-10 yrs)	6 yrs
Ingestion rate	100 mL/event	Exposure duration (adult)	24 yrs
Event duration (t)	2.6 hr/d (av.)	Surface area (4-10 yrs)	8290 sq.cm 50% CI
		Surface area (adult)	18000sq.cm 50% DI

Contaminant	ADI		Permeability[2]	Water Quality Criteria (mg/L)[3]		
	Oral	Dermal	Constant (cm/h)	Oral	Dermal	Combined
Phenolics						
phenol	3.00E-01	3.00E-01	5.54E-03	4.69E+03	3.93E+03	2.14E+03
cresol (o)	2.50E-02	2.50E-02	1.01E-02	3.91E+02	1.79E+02	1.23E+02
cresol (m)	2.50E-02	2.50E-02	1.03E-02	3.91E+02	1.76E+02	1.21E+02
cresol (p)	2.50E-03	2.50E-03	9.97E-03	3.91E+01	1.82E+01	1.24E+01
BTEX						
benzene	3.45E-04	3.45E-04	2.04E-02	2.32E+01	3.03E+00	2.68E+00
toluene	1.00E-01	1.00E-01	4.45E-02	1.56E+03	1.60E+02	1.45E+02
ethylbenzene	5.00E-02	5.00E-02	7.41E-02	7.82E+02	4.90E+01	4.61E+01
xylene	9.00E-02	9.00E-02	8.87E-02	1.41E+03	7.36E+01	7.00E+01
Non-carcinogenic PAHs						
napthalene	2.00E-03	2.00E-03	4.33E-02	3.13E+01	3.35E+00	3.03E+00
acenaphthene	3.00E-02	3.00E-02	1.33E-01	4.69E+02	1.64E+01	1.59E+01
anthracene	1.50E-01	1.50E-01	2.26E-01	2.35E+03	4.82E+01	4.72E+01
fluorene	2.00E-02	2.00E-02	1.71E-01	3.13E+02	8.47E+00	8.24E+00
phenanthrene	1.50E-02	1.50E-02	2.29E-01	2.35E+02	4.76E+00	4.66E+00
pyrene	1.50E-02	1.50E-02	3.24E-01	2.35E+02	3.36E+00	3.31E+00
fluoroanthene	2.00E-02	2.00E-02	5.65E-01	3.13E+02	2.57E+00	2.55E+00
acenaphthylene	1.50E-02	1.50E-02	1.74E-01	2.35E+02	6.25E+00	6.08E+00
Carcinogenic PAHs						
benzo(a)pyrene	1.37E-06	1.37E-06	9.70E-01	9.20E-02	2.53E-04	2.52E-04
Inorganics						
cyanide (free)	2.50E-03	2.50E-03	NA	3.91E+01	NA	3.91E+01
cyanide (complex)	6.25E-03	6.25E-03	NA	9.78E+01	NA	9.78E+01

$$\log K_p = -2.72 + 0.71 \log K_{ow} - 0.00610\ MW$$

Contaminant	MW	K_{ow}	$\log K_{ow}$	$\log K_p$	K_p
Phenolics					
phenol	94	28.84	1.459995256	-2.25680337	0.00553601
cresol (o)	108	89.13	1.950023907	-1.99428303	0.01013251
cresol (m)	108	91.20	1.959994838	-1.98720366	0.01029903
cresol (p)	108	87.10	1.940018155	-2.00138711	0.00996811
BTEX					
benzene	78.11	132.00	2.120573931	-1.69086351	0.02037682
toluene	92	537.00	2.729974286	-1.32491826	0.04540271
ethylbenzene	106	1413.00	3.150142162	-1.12999907	0.07413118
xylene	106	1820.00	3.260071388	-1.05194931	0.08872596
Non-carcinogenic PAHs					
napthalene	128	1203.00	3.009875634	-1.3637883	0.04327427
acenaphthene	154.2	8317.00	3.919966701	-0.87744364	0.13260392
anthracene	178	28180.00	4.449940989	-0.6463419	0.22576577
fluorene	166.2	15140.00	4.180125875	-0.76593063	0.17142311
phenanthrene	178.2	28840.00	4.459995256	-0.64042337	0.22886355
pyrene	202.3	75858.00	4.880001388	-0.48922901	0.32416863
fluoroanthene	202.3	166000.00	5.220108088	-0.24775326	0.56525803
acenaphthylene	152.2	11750.00	4.070037867	-0.75869311	0.17430381
Carcinogenic PAHs					
benzo(a)pyrene	252.3	954993.00	5.980000188	-0.01322987	0.96999643
Inorganics					
cyanide (free)	26.02				
cyanide (complex)	26.02				

[2] Permeability constant data (Kp) from Dermal Exposure Assessment Interim Report USEPA/600/8-91/011B
[3] Water quality criteria for carcinogens are based on entire 30 yrs. For non-carcinogens based on most critical 6 yrs.

Table 5C.2 Health-based acceptance criteria Primary recreational use of surface water Reasonable maximum

Receptor	Children and adults resident on site up to 30 yrs	Target risk	0.00001
		Target HI	1
Exposure frequency	7 d/yr	Body weight (4-10 yrs)	30 kg
Averaging time (carc)	70 yrs	Body weight (adult)	70 kg
(non-carc)	6 yrs	Exposure duration (4-10 yrs)	6 yrs
Ingestion rate	100 mL/event	Exposure duration (adult)	24 yrs
Event duration (t)	2.6 hr/d (av.)	Surface area (4-10 yrs)	8290 sq.cm 50% CI
		Surface area (adult)	18000sq.cm 50% DI

Contaminant	ADI		Permeability[4]	Water Quality Criteria (mg/L)[5]		
	Oral	Dermal	Constant (cm/h)	Oral	Dermal	Combined
Phenolics						
phenol	3.00E-01	3.00E-01	5.54E-03	2.19E+02	4.77E+02	1.50E+02
cresol (o)	2.50E-02	2.50E-02	1.01E-02	1.83E+01	2.17E+01	9.92E+00
cresol (m)	2.50E-02	2.50E-02	1.03E-02	1.83E+01	2.14E+01	9.84E+00
cresol (p)	2.50E-03	2.50E-03	9.97E-03	1.83E+00	2.21E+00	9.99E-01
BTEX						
benzene	3.45E-04	3.45E-04	2.04E-02	1.08E+00	3.68E-01	2.75E-01
toluene	1.00E-01	1.00E-01	4.45E-02	7.30E+01	1.94E+01	1.53E+01
ethylbenzene	5.00E-02	5.00E-02	7.41E-02	3.65E+01	5.94E+00	5.11E+00
xylene	9.00E-02	9.00E-02	8.87E-02	6.75E+01	8.93E+00	7.86E+00
Non-carcinogenic PAHs						
napthalene	2.00E-03	2.00E-03	4.33E-02	1.46E+00	4.07E-01	3.18E-01
acenaphthene	3.00E-02	3.00E-02	1.33E-01	2.19E+01	1.99E+00	1.83E+00
anthracene	1.50E-01	1.50E-01	2.26E-01	1.10E+02	5.85E+00	5.55E+00
fluorene	2.00E-02	2.00E-02	1.71E-01	1.46E+01	1.03E+00	9.60E-01
phenanthrene	1.50E-02	1.50E-02	2.29E-01	1.10E+01	5.77E-01	5.48E-01
pyrene	1.50E-02	1.50E-02	3.24E-01	1.10E+01	4.07E-01	3.93E+01
fluoroanthene	2.00E-02	2.00E-02	5.65E-01	1.46E+01	3.12E-01	3.05E-01
acenaphthylene	1.50E-02	1.50E-02	1.74E-01	1.10E+01	7.58E-01	7.09E-01
Carcinogenic PAHs						
benzo(a)pyrene	1.37E-06	1.37E-06	9.70E-01	4.30E-03	3.07E-05	3.05E-05
Inorganics						
cyanide (free)	2.50E-03	2.50E-03	NA	1.83E+00	NA	1.83E+00
cyanide (complex)	6.25E-03	6.25E-03	NA	4.56E+00	NA	4.56E+00

$$\log K_p = -2.72 + 0.71 \log K_{ow} - 0.00610\ MW$$

Contaminant	MW	K_{ow}	$\log K_{ow}$	$\log K_p$	K_p
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BTEX					
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toluene	92	537.00	2.729974286	-1.32491826	0.04540271
ethylbenzene	106	1413.00	3.150142162	-1.12999907	0.07413118
xylene	106	1820.00	3.260071388	-1.05194931	0.08872596
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anthracene	178	28180.00	4.449940989	-0.6463419	0.22576577
fluorene	166.2	15140.00	4.180125875	-0.76593063	0.17142311
phenanthrene	178.2	28840.00	4.459995256	-0.64042337	0.22886355
pyrene	202.3	75858.00	4.880001388	-0.48922901	0.32416863
fluoroanthene	202.3	166000.00	5.220108088	-0.24775326	0.56525803
acenaphthylene	152.2	11750.00	4.070037867	-0.75869311	0.17430381
Carcinogenic PAHs					
benzo(a)pyrene	252.3	954993.00	5.980000188	-0.01322987	0.96999643
Inorganics					
cyanide (free)	26.02				
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[4] Permeability constant data (Kp) from Dermal Exposure Assessment Interim Report USEPA/600/8-91/011B

[5] Water quality criteria for carcinogens are based on entire 30 yrs. For non-carcinogens based on most critical 6 yrs.

6

Site management

Site management

6.1 Introduction

Management of risk associated with contaminated soil and groundwater at former gasworks is the primary objective of any site assessment and management programme. Risk assessment provides the framework for making decisions about the assessment and management of contamination.

Some questions fundamental to the risk management process include:

- does the site pose an unacceptable risk to human health or the environment?
- is action required to reduce the risk to within acceptable boundaries?
- does the uncertainty associated with the assessment of risk warrant either further investigation or management to minimise the risk?
- what action is the most appropriate, giving consideration to environmental and human health risk reduction, cost, possible future use of the site, practicality, and social and political concerns?
- is ongoing site management or monitoring required?

This module covers the following:

- ➔ intrinsic remediation
- ➔ containment systems
- ➔ remedial treatment systems
- ➔ disposal of gaswork contaminants to landfill
- ➔ monitoring

Additional information on site management can be found in Section 5 of the Users' Guide, including:

- ▲ the evaluation, selection and implementation of site management options (Section 5.3)
- ▲ legislation (Section 5.4)
- ▲ land use controls (Section 5.5.1)
- ▲ management controls (Section 5.5.2)
- ▲ intrinsic remediation (Section 5.5.3)
- ▲ containment options (Section 5.5.4)
- ▲ remedial treatment systems (Section 5.5.5)
- ▲ disposal of contaminants to landfill (Section 5.5.6)
- ▲ site management plans (Section 5.6)

6.2 Intrinsic remediation

This form of treatment may be used alone or in combination with other forms of clean-up or site control. Intrinsic remediation is most commonly used in combination with methods such as capping and installation of a cut-off wall.

If intrinsic remediation is used, detailed fate and transport modelling will probably be needed in support of land use and discharge consents, together with detailed site monitoring and the development of a site management plan.

A summary of the key issues associated with the use of intrinsic remedial options is given in Table 6.1.

Table 6.1. Intrinsic remediation

Remedial Status	• Currently in use in New Zealand for a wide range of contaminated sites • Widely used overseas for the management of contaminated sites, and commonly used on gasworks sites in conjunction with other remedial techniques
Contaminant Type	• Organic contaminants primarily • Mobile tar waste should be removed from site
Advantages	• No site disturbance • Low cost
Disadvantages	• Only suitable for sites where adverse human health and environmental effects are limited • Long-term management and monitoring programme required
Achieve Clean-up Levels	• Will result in reduced contaminant concentrations • No active clean-up
Downstream Effects	• Changes in site use may require more active remediation of the site
Timeframe	• Long timeframe, depending on the level and type of contamination and the site conditions (5 to 20+ years)
Cost	• Not given/available
Resource Consent Requirements	• Air discharge consent for vapours and odours may be required • Consent for discharges to stormwater and groundwater may be required
Long-term Site Management Plan Issues	• Management plan should address potential change in site end use or subsequent below ground works on site • Long-term groundwater/surface water monitoring requirements

Additional information on intrinsic remediation can be found in Section 5.5.3 of the Users' Guide.

6.3 Containment methods

The use of containment systems prevents or reduces the migration of contamination, while the contamination remains on-site. As a consequence, the liability associated with the contamination will remain. In addition, it will be necessary for a site management plan to be developed and land use control measures to be applied to the site. These measures will ensure the continued integrity of the containment system and that adverse human health and environmental effects do not arise in the future.

Containment methods include:

- capping systems
- cut-off walls
- groundwater interception
- on-site repository

6.3.1 Capping systems

Infiltration, resulting in leaching of contaminants, and direct contact with the contaminated soil can be minimised by installation of a low permeability cap at the site. The cap may be constructed from soil, clay, synthetic membranes, asphalt or concrete. Compacted clay caps are most commonly used where a clear site is available; the design of such systems drawing heavily on landfill design principles. Capped sites are most often redeveloped for commercial/industrial and recreational purposes, although they have been used for medium and high density residential purposes.

The key elements of cap containment system are shown schematically in Figure 6.1 and a summary of capping technology issues is given in Table 6.2.

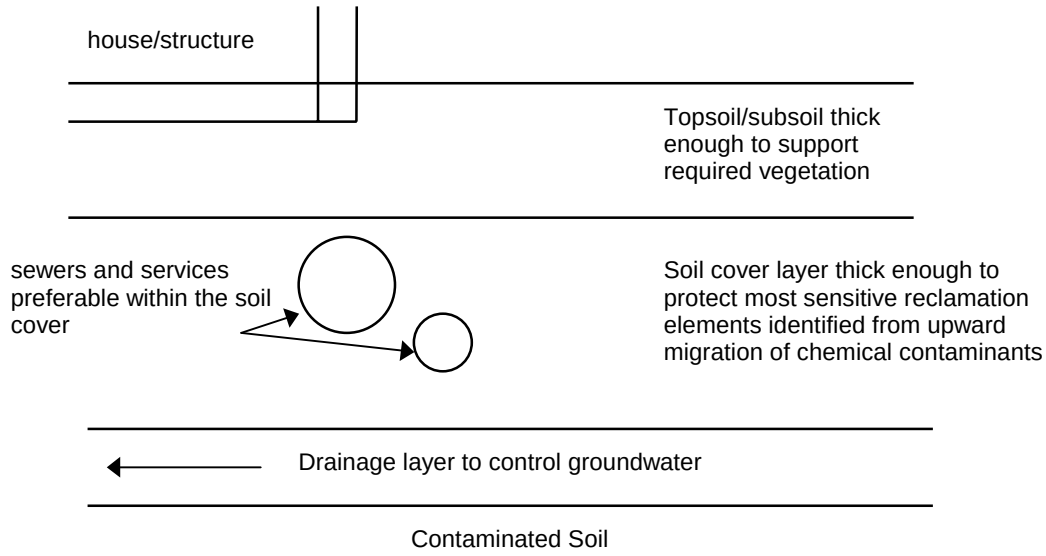


Figure 6.1 Capping technology

In conjunction with cut-off drains up-gradient of the site to divert clean groundwater around the site, the cap prevents permeation of surface water and limits migration (leaching) of soil contaminants.

Table 6.2 Capping systems

Remedial Status	• Currently in use in NZ • Widely utilised overseas, and is commonly used in conjunction with other remedial and management approaches. Approach commonly used on gasworks sites
Contaminant Type	• All contaminant types • Not appropriate for containment of mobile tar waste on site - this should be removed from site
Advantages	• Ideal where landfill access is limited • Reduces recharge to groundwater • Reduces human exposure to surface contaminants
Disadvantages	• Long-term liability issues associated with leaving contamination in-situ • Long-term management plan required
Achieve Clean-up Levels	• Direct contact to contaminants prevented by placement of cover
Downstream Effects	• No direct effects. Changes in land use may require more active remediation of the site
Timeframe	• Relatively short (weeks to months)
Cost	• Refer Table 6.23
Resource Consent Requirements	• Consent to discharge contaminants to groundwater may be required

6.3.2 Cut-off walls

Off-site migration of groundwater and free phase hydrocarbon can be minimised by construction of cut-walls surrounding the contaminated zone. A cut-off wall may be constructed using clay, a bentonite/clay or soil mixture, cement grout, HDPE or steel sheet piling. Ideally such cut-off walls should be keyed into a low permeability strata underlying the site to minimise underflow. The cut-off wall can be installed either in a trench if the wall is relatively shallow, or by injection of grout through closely spaced boreholes to create a low permeability barrier, if the total depth of the wall is significant.

The key elements of a cut-off wall are shown schematically in Figure 6.2 and summarised in Table 6.3.

Table 6.3. Cut-off walls technology

Remedial Status	• Currently in use in NZ • Widely used overseas for containing contaminated groundwater on variety of sites, including gasworks sites
Contaminant Type	• All contaminant types • Principally aimed at preventing off-site migration of groundwater contamination
Advantages	• Avoids excavation and treatment, removal or disposal of contaminated soil and groundwater
Disadvantages	• Possible disposal of excavated contaminated soil following wall construction • Aggressive soil or groundwater may attack cut-off wall materials • Excavated cut-off walls generally only applicable in unconsolidated materials - cannot be installed into bedrock • High level of quality assurance required to ensure integrity of cut-off wall
Achieve Clean-up Levels	• Clean-up levels not achieved - migration of groundwater contamination off-site is prevented or limited
Downstream Effects	• Changes in site use may require more active remedial works
Timeframe	• Medium term (weeks to months)
Cost	• Refer Table 6.23
Resource Consent Requirements	• An earthworks consent likely to be required • A consent to discharge contaminants to groundwater may be required
Long-term Management Plan Issues	• Plan should ensure the integrity of the cut-off wall is maintained • Long-term groundwater monitoring will be required • Plan should address future excavations given that contamination will remain on site

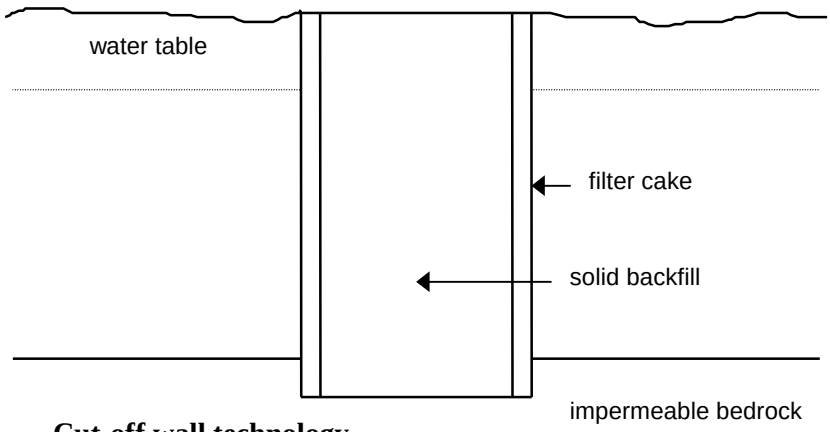


Figure 6.2 Cut-off wall technology

6.3.3 Groundwater interception

An interception trench or a series of groundwater extraction wells installed downgradient of a contaminated area may allow the interception of contaminated groundwater moving off-site. Groundwater may then be extracted and treated before disposal or re-injection. In this way a hydraulic barrier to contaminant migration can be established. The trench or extraction wells must be designed to take into account the presence of free phase hydrocarbons (both dense non-aqueous phase liquids (DNAPLs) and light non-aqueous phase liquids (LNAPLs), and the specific hydrogeological conditions encountered at the site e.g. the trench must be installed to a depth that minimises the underflow of contaminated water. Although the object of such systems is to contain the groundwater contamination plume, they can also be used as part of a groundwater remediation system.

The key elements of a hydraulic control system are shown schematically in Figure 6.3 and summarised in Table 6.4.

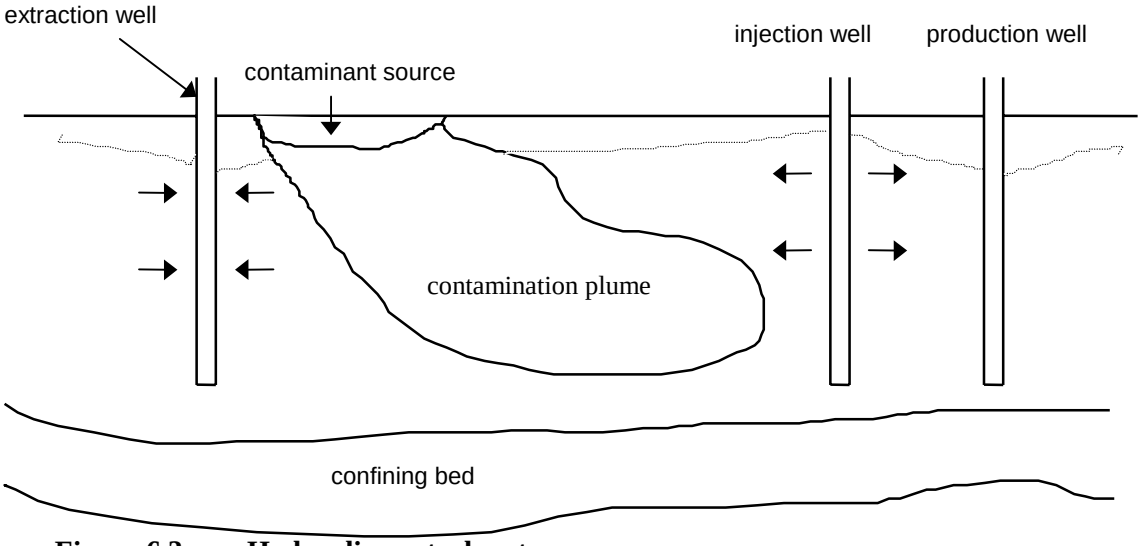


Figure 6.3 Hydraulic control system

Table 6.4 Groundwater interception

Remedial Status	• Currently in use in NZ • Widely used overseas for management of contaminated groundwater (US and Europe) in conjunction with pump and treat technologies. Approach has been used extensively on gasworks sites
Contaminant Type	• All contaminant types • Principally aimed at preventing off-site migration of groundwater contamination
Advantages	• Excavation, removal and disposal of contaminated soil is not necessary • Clean-up of groundwater achieved as part of remediation
Disadvantages	• High level of equipment maintenance required • Contaminated groundwater must be treated and disposed • System prone to mechanical failure
Achieve Clean-up Levels	• Clean-up of contaminated groundwater migrating from the site achieved • Generally only a short-term option. Expensive to run for a long time
Downstream Effects	• Changes in site use may require more active remedial works
Timeframe	• Long term (as long as contamination source(s) are present on-site)
Cost	• Not given/available
Resource Consent Requirements	• A consent may be required to extract groundwater • A consent may be required to discharge groundwater to stormwater or sewer or reinject to groundwater
Long-term Management Plan Issues	• Long-term groundwater monitoring will be required • Plan should address future below surface maintenance works given that contamination will remain on-site • Plan should ensure a regular maintenance schedule for pumps

6.3.4 On-site repositories

To obtain sufficient integrity of containment or to allow aggregation of wastes in one area of the site (thus freeing other area of the site for redevelopment), wastes may be excavated and placed in a secure repository constructed at the site. A secure repository may be considered as a purpose-designed landfill, and may include a low permeability liner and cap and leachate collection and treatment. Repository construction and design draws very heavily on landfill design and construction principles. Mechanisms for the ongoing management and maintenance of the repository are essential.

A summary of the key issues associated with construction and operation of an on-site repository system is given in Table 6.5.

Table 6.5 On-site repository

Remedial Status	• Currently in use in NZ • Widely used overseas for remediation of gasworks sites (US and Europe)

Contaminant Type	• All contaminant types • Not appropriate for disposal of mobile tar waste
Advantages	• Highly effective. Restrict area requiring management
Disadvantages	• Long-term liability issues • Need to ensure long-term performance of repository • Long-term management plan required • Leachate management required
Achieve Clean-up Levels	• Achieve clean-up levels
Downstream Effects	• Treatment/disposal of leachate • May sterilise part of the site i.e. cannot be used for other activities
Timeframe	• Short to medium timeframe (months) • Construction of repository could be incorporated into site redevelopment works
Costs	• Refer Table 6.23
Resource Consent Requirements	• Consents to discharge contaminants to ground may be required • Land use consent may be required • Earthworks consent may be required
Long-term Site Management Plan Issues	• Ensure integrity of repository is maintained • Long-term groundwater monitoring likely • Restrictions on future land use likely

Additional information on containment systems can be found in Section 5.5.4 of the Users' Guide.

6.4 Remedial treatment systems

6.4.1 Stabilisation and solidification

The use of solidification/stabilisation reduces both the mobility of the contaminants and the exposure pathways through which adverse effects can occur.

6.4.1.1 In-situ

Cementing agents may be added to the contaminated soil to bind the contaminants and prevent the movement in leachate or groundwater. Binding agents include lime, cement, pozzolanic fly ashes and organic polymers. The binder can be applied via large diameter augers, or other treatment processes. Overlapping zones are needed to ensure all the soil is treated.

This method is suitable for low permeability soils and where there is heavy metal contamination, which is not amenable to thermal treatment or bioremediation. It does not result in any reduction in contaminant concentrations, but rather in the formation of a solid mass in which contaminants are strongly bound (both physically and chemically). Following treatment the site may be suitable for a restricted range of future land uses. Other compounds, such as high levels of sulphates, some metal salts, phenols, coals, and oil and grease, present in the soil can interfere with the setting of the binder. Such techniques have been used in the United States and Europe for the treatment of contaminated soil, but application to gasworks sites is unknown. There has been no significant application of this technology in Australia or New Zealand.

The in-situ stabilisation process is shown schematically in Figure 6.4 and the key issues associated with this technology are given in Table 6.6.

Table 6.6 Stabilisation and solidification

IN-SITU

Remedial Status	• Not currently in use in NZ • Has been used commercially overseas (US and Europe), but generally not used for full-scale remediation of gasworks sites
Contaminant Type	• Ideal for metals - interference by other gasworks contaminants, particularly organics and sulphates
Advantages	• Highly effective for metals
Disadvantages	• Contamination not destroyed - mobility is reduced or minimised • Possible restrictions on future land use • Limited in highly heterogeneous soils • Effectiveness of stabilisation and solidification may decrease over time
Achieve Clean-up Levels	• Clean-up levels not achieved - contaminants immobilised
Downstream Effects	• None, provided integrity of stabilisation works remains intact
Timeframe	• Short to medium term, works can be incorporated into site redevelopments (weeks to months)
Cost	• Refer Table 6.23
Resource Consent Requirements	• Consent to discharge contaminants to ground/groundwater may be required
Long-term Management Plan Issues	• Integrity of stabilised material needs to be maintained • Long-term groundwater monitoring required. • Restrictions on future land use likely
EX-SITU	
NZ/Remedial Status	• Currently in use in NZ (has been utilised primarily for timber treatment wastes and dredged material, although some gasworks wastes have been stabilised) • Has been used commercially overseas (US and Europe), but generally not utilised for full-scale remediation of gasworks sites
Contaminant Type	• Ideal for metals - interference by other gasworks contaminants
Advantages	• Highly effective for metals • Effective at treating a wide variety of soil types
Disadvantages	• PAHs, cyanides and sulphur compounds will affect waste binding and retard the setting and therefore physical strength of the cement matrix • Careful control of stabilisation process required
Achieve Clean-up Levels	• Achieve clean-up levels through removal of contamination from site
Downstream Effects	• None provided integrity and stabilisation works remain intact
Timeframe	• Short term, excavation works can be incorporated into site redevelopment (weeks)
Cost	• High cost, except for hotspot mix asphalt (Refer Table 6.23)
Resource Consent Requirements	• Earthworks consent may be required
Long-term Management Plan Issues	• No long-term management plan, unless residual contamination remains on-site

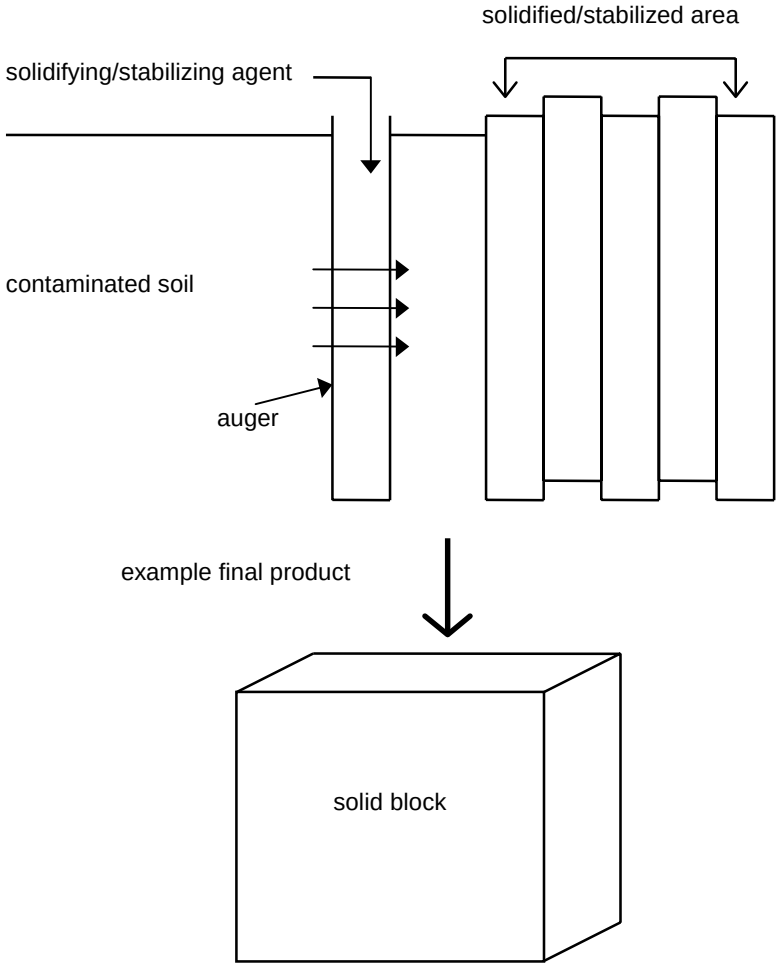


Figure 6.4 In-situ solidification/stabilisation

6.4.1.2 Ex-situ

Frequently waste materials must be stabilised before to disposal to landfill, or placement in another form of secure waste repository, to comply with the relevant leachate test criteria. In waste from gasworks sites, free tar from tar wells or gas holders is the primary waste stream which may require stabilisation. Other waste streams possibly requiring stabilisation include heavy metal contaminated soil and spent oxide.

Such wastes may be stabilised using cementing reagents to form a solid mass for disposal. Stabilisation of tars requires careful control to ensure adequate setting of the stabilised material. An alternative form of stabilisation for tar and heavily tar contaminated soil is the use of such materials in hot or cold mix asphalt.

As discussed above (Section 6.4.1.1) some contaminants may interfere with the setting of the binder and this must be considered when evaluating the technology.

The key issues associated with this remedial technology are given in Table 6.6.

6.4.2 Bioremediation

A range of bioremediation techniques been developed in recent years and these may be classified in terms of the microorganisms used and the physical arrangement of the system. Although increasing attention has been focused on in-situ techniques such as bioventing, in practice gasworks wastes are generally difficult to degrade and therefore the more intensive ex-situ bioremediation methods are probably more applicable.

Bioremediation has been widely applied to the degradation of a range of organic contaminants, particularly petroleum contaminants. However, the application of bioremediation to the treatment of soils from gasworks sites has been more difficult. A number of bioremediation trials have been conducted internationally and in New Zealand with limited success. Some of the key factors which have arisen in this work include:

- robustness of processes under field conditions
- removal efficiencies obtainable may not be sufficient to comply with the nominated landfill acceptance criteria
- plateau in contaminant removal, possibly associated with limited bioavailability.

The soil acceptance criteria nominated for benzo(a)pyrene and other heavier PAHs are generally relatively low, however these components are also some of the most difficult to degrade. Successful bioremediation of gasworks wastes has generally relied upon:

- relatively low initial concentrations of the heavier PAHs (such that 30% to 70% removal is sufficient)
- the nominated criteria are based on total PAH concentrations such that the higher removal achieved for the lighter PAHs can offset the lower removal of the heavier PAHs
- comparatively high acceptance criteria are nominated for a non-sensitive end use e.g. commercial or disposal to landfill (i.e. remediate highly contaminated soils to a level acceptable within a landfill).

Gasworks wastes may contain heavy metals in addition to the primary organic contaminants, and some of the organic contaminants, particularly 4, 5 and 6 ring PAHs and their breakdown products, are toxic to many bacteria strains. Biological processes may therefore be inhibited by specific contaminants. Where particular wastes contain both organic and heavy metal contaminants at significant concentrations, bioremediation may not feasible.

6.4.2.1 In-situ

In-situ bioremediation techniques are generally based on stimulation of contaminant degradation by the naturally occurring microorganisms in the soil and groundwater by the addition of oxygen and nutrients. Oxygen is supplied by injecting air or oxygen-saturated water through wells or sub-surface vents (bioventing) to areas of contamination above the water table. Below the water table the oxygen can be supplied as hydrogen peroxide dissolved in water or as slow release solids, or by air injection or sparging. Some of the emerging areas in the application of in-situ bioremediation include the use of bioaugmentation - the use of alternative electron acceptors and the addition of carbon sources to act as co-substrates for the organisms. Bioventing, involving the injection of air only, has been the most widely implemented in-situ bioremediation technique.

In-situ methods have had some success in permeable soils where the contaminant is a light hydrocarbon product, including lighter PAHs (such as those predominant in creosote). Heavier products and 4, 5 and 6 ring PAHs are less suited due to lower bioavailability, and metals cannot be treated.

Further, based on the organic contaminants present (i.e. 4, 5 and 6 ring PAHs) anaerobes or methanothrophs may provide more effective degradation, especially where co-metabolism of these contaminants can occur.

Resource consents are likely to be required for the implementation of the bioremediation works and on completion of the works, given that some form of residual contamination may remain in-situ. If residual contamination remains, following completion of the bioremediation works, liability issues may also remain.

A summary of the key issues associated with in-situ bioremediation works is given in Table 6.7.

Table 6.7 In-situ bioremediation (soil and groundwater)

Remedial Status	• Currently used in New Zealand but limited mainly to petrochemical/oil industry sites • Has been used commercially overseas (US and Europe) for full-scale remediation of gasworks sites.
Contaminant Type	• Organic only (less suited to heavy end PAHs)
Advantages	• Minimal site disturbance • High level of public acceptance • Effective on soluble light end PAHs and BTEX
Disadvantages	• Ineffective on inorganic contaminants • may be inhibited by the presence of heavy metals, oxides, cyanides or low pH conditions which are common on gasworks sites • Not suitable for low permeability heterogeneous soils
Achieve Clean-up Levels	• Effective at cleaning up monocyclic aromatics and light molecular weight PAHs. Limited success with 4, 5 and 6 ring PAHs
Downstream Effects	• Degradation of some PAHs may form toxic recalcitrant compounds
Timeframe	• Medium to long-term timeframe, with remediation timeframes generally longer than ex-situ bioremediation techniques • Remediation timeframe dependent on organic compounds present, site geology and other environmental factors (i.e. climate)
Cost	• Refer Table 6.23
Resource Consent Requirements	• Land use consent may be required • Consent to discharge inoculant (i.e. nutrients) to soil and or groundwater may be required
Long-term Site Management Plan Issues	• None (should acceptable clean-up levels be achieved)

6.4.2.2 Ex-situ

More recalcitrant compounds usually require a more intensive process such as land farming, soil biopiles, composting or soil slurry reactors. Breakdown is stimulated by providing oxygen and, if necessary, nutrients such as nitrogen and phosphorus. Some work has focused on the addition of microorganisms (bioaugmentation) although generally biostimulation is proposed for the remediation of gasworks materials and other similar hydrocarbons.

Oxygen is supplied either by turning the soil regularly to expose it to the atmosphere ***(landfarming)*** or by creating aerated piles ***(biopiles)***. In biopiles, air is supplied to covered piles of soil via a perforated pipe network. The moisture, oxygen and nutrient contents can be closely monitored and controlled to ensure optimum conditions and hence rapid hydrocarbon degradation.

Soil amendments, such as organic matter, may be added to improve the soil structure and moisture retention.

Composting is the degradation of contaminants using naturally present communities of microorganisms supplemented with organic material. The interaction between various microorganisms allows degradation by a range of mechanisms, with different microorganisms contributing at different stages of the degradation process. Composting is often more effective than simpler bacterial processes. The addition of large volumes of organic matter results in increased areas required for treatment and can increase costs in disposal of treated material.

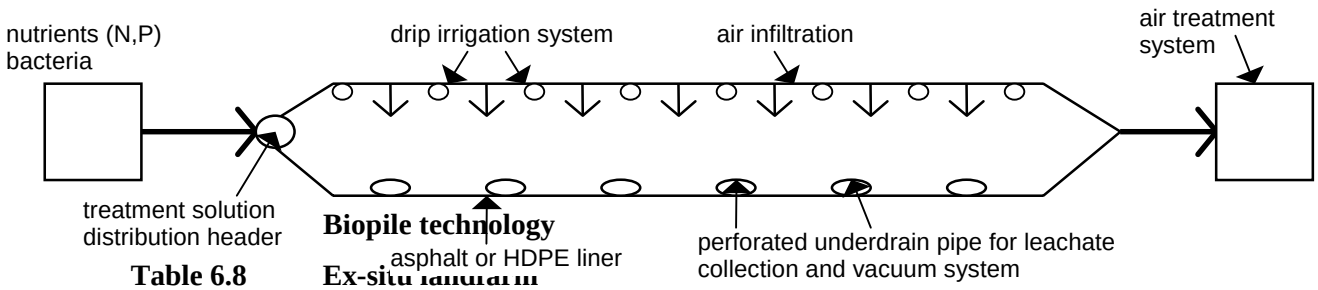
Soil slurry reactors can be used as a starting point for bacterial systems, allowing optimal delivery of nutrients, surfactants and organisms (if required), improved system control and a higher rate of degradation. Slurry bioreactors are used for pilot trial work but rarely for full scale remediation due to the cost associated with such systems. Soil slurry reactors do not generally increase the overall removal efficiency, but rather they increase the rate of degradation.

Fungal systems and the use of white rot fungi have the potential to degrade many compounds resistant to bacterial degradation or which inhibit other microorganisms. The processes are largely based on extra-cellular enzyme activity and the generation of free radicals, which are powerful oxidants, by the fungi. The free radical chemistry of white rot fungi degradative processes is relatively non-specific, degrading a wide variety of compounds. This contrasts with many bacteria whose degradative enzymes are highly substrate specific, and therefore chemical specific. Fungal systems have been applied to PCP contaminated soils and hence conceivably could be applied to gasworks contaminated soils.

Remediation of contaminated soil requires the addition of an inoculum, separately prepared, and provision of a growth medium (e.g. wood chips) as the fungi are not generally capable of using the compounds of concern as a sole carbon or energy source (i.e. co-metabolism). This is a sensitive process, with moisture content and temperature important variables. Contamination by wild fungi has also been reported as a problem. The biodegradation processes of white rot fungi can be used in a slurry bioreactor system, although a variation on a soil biopile or landfarming technique is more common.

Operation of an ex-situ bioremediation system is likely to require a number of resources consents, including a land use consent and an air discharge consent.

A schematic of a biopile system is shown in Figure 6.5 and a summary of the key issues associated with the operation of an ex-situ bioremediation system is given in Tables 6.8 through to 6.12.



Biopile technology

Table 6.8 Ex-situ landfarm

Remedial Status	• Currently used in New Zealand and has been used with limited success on gasworks contaminated soils • Commercially used overseas (US and Europe) for remediation of selected gasworks contaminated soils
Contaminant Type	• Organic only (less suited to heavy molecular weight PAHs)
Advantages	• High level of public acceptance • Allows photodegradation of UV sensitive heavy end PAHs • Allows volatilisation of light end PAHs and monocyclic aromatics • Allows easy aeration of contaminated soils
Disadvantages	• Metals and cyanides may be toxic and inhibit degradation rates • Sensitive to feed stock and to soil grain size - sandy soils preferred • May create odours and vapours • Requires effective stormwater control and leachate management
Achieve Clean-up Levels	• Generally more effective than in-situ bioremediation especially due to the photodegradation of PAHs • Degradation rates for 4, 5 and 6 ring PAHs may still be slow
Downstream Effects	• Degradation of some PAHs may form toxic, recalcitrant compounds • Disposal of treated soil
Timeframe	• Medium to long term timeframe (depends on organic compounds). Remediation times typically in the order of 12 months
Cost	• Refer Table 6.23

Resource Consent Requirements	• Land use consent may be required • Consent to discharge contaminants to ground may be required • Earthworks consent for excavation works may be required • Air discharge consent for vapours and odours may be required
Long-term Site Management Plan Issues	• None (should acceptable clean-up levels be achieved)

Table 6.9 Biopile remediation

Remedial Status	• Currently in use in NZ, but limited to petrochemical and oil industry sites • Used commercially overseas (US and Europe) for remediation of gasworks contaminated soils
Contaminant Type	• Organic only (less suited to heavy end PAHs)
Advantages	• Allows control of environmental factors limiting biodegradation • High level of public acceptance • Can be used to increase volatilisation of light end PAHs and BTEX through heating or forced venting
Disadvantages	• Limited success on low permeability soils • Sensitive to feed stock/soil grain size - sandy soils preferred • Ineffective on inorganic contaminants and may be inhibited by presence of heavy metals or low pH conditions
Achieve Clean-up Levels	• Effective at cleaning up monocyclic aromatic and light molecular weight PAHs • Limited success with 4, 5 and 6 ring PAHs
Downstream Effects	• Degradation of some PAHs may result in the formation of toxic recalcitrant compounds • Disposal of treated soil
Timeframe	• Medium to long-term timeframe (depending on the organic compounds present). Generally remediation times between 12 and 18 months for typical gasworks contaminants
Cost	• Refer Table 6.23
Resource Consent Requirements	• Land use consent may be required • Consent may be required for discharges to land • Earthworks consent for excavation works may be required • Air discharge consent for vapours and odours may be required
Long-term Site Management Plan Issues	• None (should acceptable clean-up levels be achieved)

Table 6.10 Compositing bioremediation

Remedial Status	• Currently, limited use in New Zealand • Has been used commercially overseas for treatment of gasworks contaminated soils, but primarily limited to pilot scale projects
Contaminant Type	• Organic only, used especially for contaminants that must be co-metabolised
Advantages	• High level of public acceptance • Allows cometabolism of recalcitrant 4, 5 and 6 ring PAHs • Suitable for the bioremediation of low permeability soils
Disadvantages	• May create odour and air discharge issues • Sensitive to feed stock/soil grain size - sandy soils preferred • Involves a significant increase in the volume of material which must be disposed
Achieve Clean-up Levels	• Effective at cleaning up monocyclic aromatic and light molecular weight PAHs • Allows cometabolism of 4, 5 and 6 ring PAHs, however may still be limited success with degrading these compounds due to bioavailability
Downstream Effects	• Degradation of some PAHs may form toxic, recalcitrant compounds • Disposal of treated soil
Timeframe	• Medium to long timeframe (depends on organic compounds present. Generally remediation times between 12 and 18 months for typical gasworks contaminants

Cost	• Not given/available
Resource Consent Requirements	• Land use consent may be required • Consent may be required for discharges to ground • Earthworks consent for excavation works may be required • Air discharge consent for vapours and odours may be required
Long-term Site Management Plan Issues	• None (should acceptable clean-up levels be achieved).

Table 6.11 Soil slurry bioremediation

Remedial Status	• Used for agricultural wastes and to remediate PAH contaminated soil at a former coal carbonisation site[1] in New Zealand • Has been used commercially overseas (US and Europe), but limited primarily to treatment of wastes containing high concentrations of recalcitrant compounds i.e. 4, 5 and 6 ring PAH's
Contaminant Type	• Organic only, used especially for contaminants that must be cometabolised
Advantages	• Allows optimal delivery of oxygen and nutrients • Can be utilised with surfactants to enhance bioavailability of contaminants i.e. 4, 5 and 6 ring PAHs • Increased degradation rates
Disadvantages	• High energy inputs and generally treats small quantities of soil at one time • Sensitive to feed stock/soil grain size - sandy soils preferred • Mixture has to be transferred in and out of slurry phase • Generally the most costly bioremediation system
Achieve Clean-up Levels	• Effective remediation system as maximises the contaminant water interface and therefore may result in faster degradation of low solubility contaminants i.e. 4, 5 and 6 ring PAHs
Downstream Effects	• Requires management and treatment of surplus liquids from the slurry bioreactor • Disposal of treated soil
Timeframe	• Short to medium remediation timeframes but treat small quantities of soil. Generally remediation times between 1 and 3 months for typical gasworks contaminants
Cost	• Refer Table 6.23
Resource Consent Requirements	• Land use consent may be required • Earthworks consent for excavation works may be required • Air discharge consent for vapours and odours may be required
Long-term Site Management Plan Issues	• None (should acceptable clean-up levels be achieved)

Table 6.12 Fungal bioremediation

Remedial Status	• Currently not in use within New Zealand • Limited commercial application overseas, primarily pilot scale and trial remediation, but not necessarily on gasworks sites
Contaminant Type	• Has been shown to treat a wide range of monocyclic aromatic and PAHs in trials and limited remediation projects overseas
Advantages	• Able to degrade many compounds resistant to bacterial degradation • Potential high level of public acceptance
Disadvantages	• Limited background information on limitations of the technology • Sensitive to feed stock/soil grain size - sandy soils preferred • Requires intensive management of environmental factors and therefore is costly
Achieve Clean-up Levels	• Based on current literature technology appears able to clean-up both monocyclic aromatics and light and heavy PAHs

[1] The operating parameters of the sluury-phase bioreactor are important, particularly the solids concentrations which should not exceed 30%. By adhering to this value, the range of soils suitable for treatment by this method can be extended. Further information is available from the US EPA.

Downstream Effects	• Unknown, degradation may result in the formation of more toxic compounds
Time Fame	• Medium to long term timeframe (depending on the organic compounds present) • Typical remediation times between 12 and 18 months
Cost	• Not given/available
Resource Consent Requirements	• Land use consent may be required • Earthworks consent for excavation works may be required • Air discharge consent for vapours and odours may be required
Long-term Site Management Plan Issues	• None (should acceptable clean-up levels be achieved)

6.4.3 Thermal desorption

Thermal desorption is a proven technology for the treatment of PAH contaminated soil from gasworks sites although careful control is required to achieve destruction or removal of contaminants. Thermal desorption generally involves heating of the soil to approximately 450°C in a rotary kiln or retort. Both direct and indirect fired thermal desorbers have been used for the treatment of gasworks wastes. Following desorption of the volatile contaminants, the hot gases may pass to an afterburner for destruction. More recently some configurations have allowed for recovery of the volatilised material by condensation, giving a concentrated oil or tar for disposal or recycling.

There is some evidence that direct fired thermal desorbers allow more effective heat penetration, however directly heated units generate relatively large gas volumes. Therefore, recovery of the desorbed material is only practical where indirectly heated thermal desorption has been used. Thermal desorption has not yet been applied to the treatment of gasworks wastes in New Zealand, although it has been used for the treatment of soil contaminated by other materials in Australia and has been tested for the treatment of wastes from several Australian gasworks sites. Although Australian trials of thermal desorption applied to gasworks sites have been successful, the low cost of landfill disposal has precluded its use on a commercial scale.

Operation of a thermal desorption system is likely to require several consents, namely a land use consent and an air discharge consent.

A summary of the key issues associated with the operation of a thermal desorption system is given in Table 6.13.

Table 6.13 Thermal desorption

Remedial Status	• Not currently available in NZ (may be available within next 2 to 5 years) • Has been used commercially overseas (Australia, US and Europe) for treating a wide range of wastes including gasworks contaminants
Contaminant Type	• Generally limited to organics
Advantages	• Minimises damage to soil - does not create an ash • System has good public acceptance (USA) • System more mobile and energy efficient than incinerators
Disadvantages	• Sensitive to feed stock and soil grain size - sandy soils preferred • Low pH conditions may corrode system components • Air pollution control methods must be capable of dealing with dioxins and furans if secondary combustion used • Soil is sterilised after heating which limits the end uses to situations not requiring biological activity.
Achieve Clean-up Levels	• Achieve clean-up levels, but dependent on organic contaminants present and soil type • Limited application to inorganic contaminants

Downstream Effects	• Emissions require treatment • Materials may require further treatment for inorganic contamination • Waste water may have to be treated if wet scrubbers are used to treat air emissions • Disposal of treated material
Timeframe	• Short treatment timeframe, but treatment limited to approximately 50 tonnes per day with a mobile unit
Cost	• Refer Table 6.23
Resource Consent Requirements	• Earthworks consent may be required to excavate materials on site • Land use consent may be required to establish mobile unit on site • Air discharge consent required for atmospheric discharge
Long-term Management Plan Issues	• No long-term management plan required, unless residual contamination remains on site

6.4.4 Incineration

The use of centralised incineration processes for waste disposal is well established. However due to the cost and transport requirements, such an approach is usually reserved for highly contaminated waste streams. Therefore, centralised incineration is not generally applicable to the treatment of contaminated soils from gasworks sites. However, it may be applied to concentrated waste streams. In particular, incineration has been applied to free tars recovered from abandoned tar wells and gas holders. Incinerators are generally available for the destruction of waste solvents and may be used for the incineration of free tars (although some blending with other wastes may be required to reduce the viscosity of the tars).

6.4.4.1 Mobile on-site incineration

The use of mobile high temperature incinerators for the treatment of hazardous wastes is well established in the United States. Approximately ten former gasworks sites have been remediated using high temperature incineration in the United States and it is one of the few technologies deemed reliable and effective for the treatment of gasworks wastes.

A range of process configurations have been proposed for mobile incinerators however the most common design includes a rotary kiln operating at approximately 1,000°C, together with an afterburner usually sized to ensure effective dioxin destruction (i.e. 1,500°C for 1.5s). To comply with relevant emission standards comprehensive emission control systems are usually required, often incorporating wet scrubbers and bag-house filters.

Operation of a mobile on-site incinerator is likely to require a number of consents namely a land use consent and an air discharge consent.

A summary of the key issues associated with the operation of an incinerator is given in Table 6.14.

Table 6.14 Incineration

Remedial Status	• Not currently available in NZ • Has been used commercially (US and Europe) for treatment of gasworks wastes and is generally the preferred approach especially for recalcitrant wastes
Contaminant Type	• Can be used for treatment of a wide range of organic and inorganic contaminants i.e. directly or indirectly through volume reduction
Advantages	• Reduces the volume of material requiring disposal • Complete destruction of organic contaminants possible • Material handling can be minimised if mobile incineration units are used

Disadvantages	• Poor public perception of incineration • Involves large inputs of energy • Non-combustible contaminants concentrate in ash and therefore ash requires appropriate disposal • Requires treatment of air discharges and requires air discharge consents • Low pH conditions may corrode system components • Air pollution control measures must be capable of dealing with dioxins/furans if secondary combustion
Achieve Clean-up Levels	• Can achieve a high level of clean-up especially for combustible organic compounds
Downstream Effects	• Emission treatment required • Disposal of ash (likely to have elevated heavy metal concentrations) • Waste water may have to be treated if wet scrubbers are used to treat air emissions
Cost	• Refer Table 6.23
Resource Consent Requirements	• Earthworks consent may be required to excavate materials on site • Land use consent may be required to establish mobile unit on-site • Air discharge consent required for atmospheric discharge
Long-term Management Plan Issues	• No long-term management plan required, unless residual contamination remains on site

6.4.4.2 Cement kilns

The burning of a range of hazardous wastes in cement kilns has been proposed for many years. However, to date most cement kiln operators have only burnt less hazardous wastes such as tires and oils. Burning solid wastes in a cement kiln requires some modification to the normal arrangement, however such approaches have been used successfully in Europe. Cement kilns operate at conditions similar to those found in incinerators, with the advantage of a much larger thermal mass and the ability to bind metals contained in the wastes within the cement matrix. Trial burns of gasworks wastes in a cement kiln have been proposed in Australia, although these were abandoned due to possible public concern.

The key factor preventing the use of cement kilns to treat gasworks waste in New Zealand is obtaining an air discharge consent. There are significant air quality concerns associated with the running of cement kilns.

A summary of the key issues associated with the operation of a cement kiln for the treatment of gasworks waste is given in Table 6.15.

Table 6.15 Cement kiln incineration

NZ/Remedial Status	• Not currently available in NZ (although cement kilns do exist) • Has been used commercially overseas (US and Europe) for treatment of a wide range of wastes including gasworks contaminants
Contaminant Type	• Generally limited to organics, but can treat some metals
Advantages	• Reliable and robust • Recovery of calorific value of waste • Effective destruction
Disadvantages	• May need to transport contaminated waste some distance • Non-combustible contaminants concentrate in ash and therefore ash requires appropriate disposal • Requires treatment of air discharges and requires air discharge consents • Air pollution control methods must be capable of dealing with dioxins/furans if secondary combustion used
Achieve Clean-up Levels	• Can achieve a high level of clean-up, especially for combustible organic compounds
Downstream Effects	• Emission treatment required • Waste water may have to be treated if wet scrubbers are used to treat air emissions

Timeframe	• Short treatment timeframe but volume treatable is limited.

Cost	• Not given/available
Resource Consent Requirements	• Earthworks consent may be required • Air discharge consent may be required
Long-term Management Plan Issues	• No long-term management plan required, unless residual contamination remains on-site

6.4.5 Soil washing

6.4.5.1 In-situ soil flushing

In soil flushing a wash solution is injected into the soil in-situ to mobilise contaminants. The wash liquor is then collected at drains or recovery wells downgradient of the contaminated zone. It is then treated and often recycled back through the contaminated zone. The washing solution may be water where the contaminant is soluble, although a surfactant is likely to be required if the contamination includes less soluble constituents. Several washings may be needed to effectively remove contaminants, and the process may be inhibited by areas of lower permeability and high organic content which causes strong sorption.

It is applicable to a wide range of contaminant types including free and dissolved product, and avoids the need for excavation and therefore disturbance. The process generates contaminated water and requires a treatment process at the surface to enable the disposal or reuse of the wash water. If surfactants are left in the soil, any residual contamination may spread as the surfactants will tend to increase their mobility. Ensuring a uniform flow of the wash solution through the soil can be difficult and therefore this technique is best suited to permeable soils.

Operation of an in-situ soil washing system is likely to require a number of discharge consents, namely a consent to discharge washing fluid (such as a solvent). On completion of the remedial works it may prove necessary to apply for a consent to discharge contaminants depending on the level of residual contamination remaining.

A schematic of the workings of an in-situ soil washing system is given in Figure 6.6 and a summary of the key issues associated with in-situ bioremediation works is given in Table 6.16.

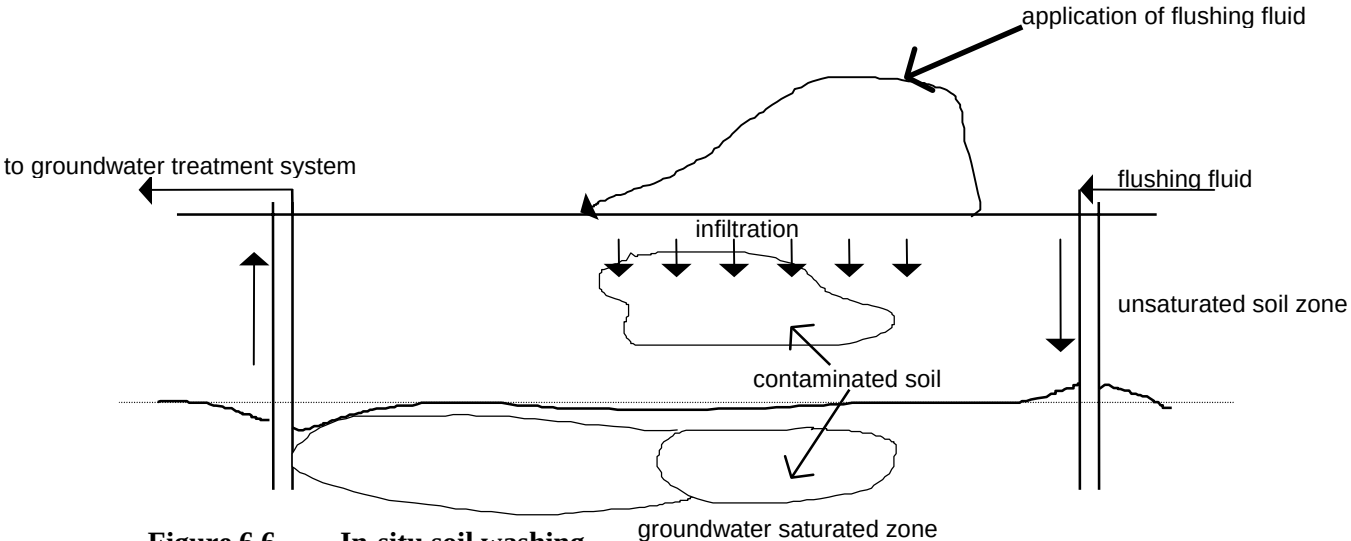


Figure 6.6 In-situ soil washing

Table 6.16 In-situ soil flushing

Remedial Status	• Not currently used in NZ • Has been tested overseas (US and Europe) on gasworks sites, but limited commercial applications
Contaminant Type	• Generally used to treat organics - can be used to treat metals
Advantages	• Works undertaken in-situ
Disadvantages	• Not applicable to low permeability soils • Incomplete treatment in heterogeneous soils • Difficult to validate effectiveness of method • Complex mix of organic and metal contaminants causes difficulties in establishing appropriate flushing fluids • Site hydrogeology must permit capture of groundwater • Treatment and discharge of contaminated groundwater • Bench scale studies have been successful, but field applications have not been that successful (Anderson 1993)
Achieve Clean-up Levels	• Achieve clean-up levels, but dependent on contaminants present and the soil flushing fluid used
Downstream Effects	• Abstraction and treatment of contaminated groundwater • Disposal of sludges from water treatment • Use of surfactants will result in difficult treatment of abstracted groundwater
Cost	• Refer Table 6.23
Timeframe	• Medium to long term timeframe(months to years)
Resource Consent Requirements	• Consent to discharge contaminants to ground or groundwater may be required • Consent to discharge treated groundwater to stormwater, sewer or to groundwater may be required
Long-term Management Plan Issues	• Long-term groundwater monitoring required

6.4.5.2 Ex-situ soil washing

Soil washing is a generic term that has been applied to both size classification processes and surfactant based particle scrubbing systems. Some soil washing systems include both of these processes. Size classification processes are based on the phenomenon that contaminants tend to bind preferentially to fine particles within the soil. Wet size classification processes, known as soil washing, can be used to separate the cleaner coarse materials from the more contaminated fine fraction. This process can be effective in reducing the volume of contaminated material for disposal. Soil scrubbing systems usually incorporate size classification, but may also include high turbulence, attrition processes to remove contaminants from coarse to medium size particles, often with the assistance with surfactants. Generally soil washing processes involve a large amount of plant and equipment, including mixers, clarifiers, cyclones and attrition scrubbers. Simpler soil washing techniques have been proposed but these are generally less effective.

Soil washing is generally limited to soils with a low fines fraction as the process relies on volume reduction. Dewatering and disposal of the fines fraction can be the most difficult element of the process. Test work for the East Perth gasworks indicated soil washing was not viable if the fines content was greater than 17%.

A summary of the key issues associated with the use of ex-situ soil washing techniques is given in Table 6.17.

Table 6.17 Ex-situ soil washing

Remedial Status	• Currently not in use in NZ, although technology available in New Zealand • Has been used commercially overseas (Australia, US and Europe) on petrochemical and gasworks sites
Contaminant Type	• All contaminant types (except for tar waste) • Solvent extraction for organic contaminants

Advantages	• Reduce volume of contaminated material requiring treatment • Can be combined with biological degradation of contaminants
Disadvantages	• Limited to soils with a low % of fines • In soils in which contaminants strongly bound (clay) the residual contamination may still be high after treatment
Achieve Clean-up Levels	• Can achieve clean-up levels, but dependent on contaminants present and soil type
Downstream Effects	• Treatment and disposal of fine grained contaminated materials • Treatment of volatiles from solvent washing • Disposal and/or treatment of washing solution
Timeframe	• Short to medium (months)
Cost	• Refer to Table 6.23
Resource Consent Requirements	• Earthworks consent may be required to excavate material • Land use consent may be required to establish washing unit • Air discharge consent may be required for use of solvents and treatment of washing solution • Discharge of contaminants to ground may be required if treated material is disposed of on-site
Long-term Management Plan Issues	• No long-term management plan requirements, unless residual contaminants remains in-situ

6.4.6 Groundwater treatment

The principal gasworks related contaminants of concern in groundwater are naphthalene and other light PAHs, phenolic compounds (cresol and phenol), BTEX and the inorganic constituents e.g. ammonia, sulphate, cyanide.

In selecting an appropriate groundwater treatment method, consideration must be given to:

- the capability of removing contaminants of concern
- reliability and maintenance requirements
- cost effectiveness
- compatibility with site conditions
- conformance with regulatory requirements.

In general, two primary groundwater treatment options exist:

- in-situ treatment
- pump and treat (ex-situ treatment).

6.4.6.1 In-situ treatment

In-situ treatment is practically limited to biological destruction of organics or the transfer of contaminants from a dissolved phase into a gaseous phase i.e. sparging for volatile organics only. However, inorganic contaminants can be treated by changes to the pH conditions in the soil and/or groundwater, especially in situations where low or high pH conditions exist. Changes in pH conditions result in a reduction in the solubility and mobility of the contaminants.

In-situ bioremediation of contaminated groundwater, like bioremediation of contaminated soils, aims to optimise conditions for bacterial growth and replication. Natural biodegradation can be assisted by the addition of nutrients and oxygen if required. Oxygen may be added by a range of techniques including air sparging and injection of hydrogen peroxide. As with other in-situ processes, delivery of nutrients and oxygen can be difficult in practice due to heterogeneous soil conditions, so these types of remediation technologies are limited in low permeability soils.

In general the consent requirements for in-situ treatment options are minimal, with a high level of public acceptance of in-situ bioremediation technologies.

6.4.6.2 Ex-situ treatment

Pump and treat is the most common approach to remediation of residual organics and inorganics within groundwater. This remediation approach involves extraction of groundwater followed by treatment and disposal or re-injection of treated groundwater. Generally, the groundwater is extracted using conventional groundwater extraction systems such as extraction wells and trenches.

A range of treatment processes may be considered depending on the contaminants present in the groundwater and the requirements for disposal (e.g. sewer disposal, trade waste bylaws, surface water discharge or re-injection to groundwater). Disposal of groundwater to sewer is frequently the preferred option due to the stringent acceptance criteria usually applicable for disposal to surface water or re-injection.

Some form of treatment may, however, be required prior to disposal to sewer or groundwater. A number of treatment options exist and these include:

- air stripping (volatile organics)
- carbon adsorption (organics and some inorganics)
- biological treatment (organics)
- UV oxidation (organics)
- chemical addition and pH adjustment (inorganics).

The most commonly used techniques involve air stripping (volatile organics only) and biological treatment of organics and these are relatively inexpensive. The latter is effective on the majority of dissolved organics detected in groundwater on gasworks sites. However these systems remove light end PAHs less efficiently, and the more costly carbon adsorption or UV oxidation technologies required to remove these contaminants. Both these systems have high removal efficiencies for heavier end PAHs given both the polarity of these molecules and their sensitivity to UV oxidation.

An advantage of using carbon adsorption is the excellent adsorption potential for specific inorganics; these include arsenic, chromium and mercury. However carbon adsorption is usually used as a final treatment (polisher) due to the high treatment cost.

Groundwater treatment of inorganics on gasworks sites is generally limited. However, inorganics are generally treated using standard lime clarification techniques, with the addition of chemical reagents e.g. arsenic removal through the addition of iron and lime.

If free phase hydrocarbons are associated with the groundwater, care must be taken to remove this material. If LNAPL is present, product recovery systems such as those used at petroleum contaminated sites may be used (e.g. skimmer pumps, passive skimmers, total fluids pumps). If DNAPLs are present, specialised extraction systems must be used. In general the viscosity of free phase hydrocarbons encountered at gasworks sites is significantly greater than that found at petroleum contaminated sites, making recovery of product more difficult.

The extraction of groundwater may require a consent from the regional council. Likewise the treatment works and the discharge of treated water may also require consent from Local and Regional Councils. A summary of the key issues associated with the treatment of abstracted groundwater is given in Tables 6.18 through to 6.22.

Table 6.18 Water treatment - air stripping

Remedial Status	• Currently used on petrochemical and oil industry sites in NZ • Has been used commercially overseas (US and Europe) for full scale remediation of aquifers contaminated with volatile organic compounds
Contaminant Type	• Limited to only volatile organic compounds
Advantages	• Low cost and low maintenance requirements • High removal efficiencies for monocyclic aromatics
Disadvantages	• Low removal efficiencies for light molecular weight PAHs • Sensitive to hydraulic loading and air temperature
Achieve Clean-up Levels	• Effective at cleaning volatile organic compounds especially monocyclic aromatics
Downstream Effects	• Treatment of volatile air emissions
Timeframe	• Short to medium timeframe, depending on the level and type of contamination and the site conditions (weeks to months)
Cost	• Refer Table
Resource Consent Requirements	• Consent for abstraction of groundwater may be required • Discharge consent for air emissions may be required • Consent for discharges of treated groundwater to stormwater, council sewers and/or reinjection to groundwater may be required
Long-term Site Management Plan Issues	• None provided full site clean-up is achieved

Table 6.19 Water treatment - activated carbon adsorption

Remedial Status	• Currently only limited use in New Zealand • Has been used commercially overseas (US and Europe) for the full scale remediation of contaminated aquifers, including gasworks sites
Contaminant Type	• A wide range of volatile and semi-volatile inorganics and selected inorganics (i.e. arsenic, cyanide)
Advantages	• High removal efficiencies for monocyclic aromatics, PAHs and phenols • Tolerant of fluctuations in hydraulic loading • No air emissions, contaminants strongly bound to activated carbon
Disadvantages	• Intolerant to high levels of suspended solids and oil and grease • High operation costs • Spent carbon requires either regeneration or disposal
Achieve Clean-up Levels	• Effective at cleaning a wide range of contaminants in a relative short time
Downstream Effects	• Contaminants not destroyed, only transferred from water to activated carbon. Spent carbon requires either regeneration or disposal
Timeframe	• Short to medium timeframe (weeks to months)
Cost	• Refer to Table 6.23
Resource Consent Requirements	• Consent for abstraction of groundwater may be required • Consent for discharges of treated groundwater to stormwater, council sewers and/or reinjection to groundwater may be required
Long-term Site Management Plan Issues	• None, provided full site clean-up is achieved

Table 6.20 Water treatment - ex-situ biological treatment

Remedial Status	• Currently used in New Zealand for a wide range of petrochemical and oil industry sites • Has been used commercially overseas (US and Europe) for full-scale remediation of petrochemical sites, some limited application to gasworks sites
Contaminant Type	• A wide range of volatile and semi-volatile organics
Advantages	• Positive public perception • Limited emissions with contaminants degraded • Excellent for removal of phenols • Proven technology
Disadvantages	• High capital operating and maintenance costs • High monitoring requirement • High potential for malfunctions
Achieve Clean-up Levels	• Effective at cleaning a wide range of organic contaminants. Ineffective at treating inorganic contaminants.
Downstream Effects	• No major effects
Timeframe	• Medium to long timeframe depending on the types of contaminants and loadings (months to years)
Cost	• Not given/available
Resource Consent Requirements	• Consent for abstraction of groundwater may be required • Air discharge consent may be required • Consent for discharges of treated groundwater to stormwater, council sewers and/or reinjection to groundwater may be required
Long-term Site Management Plan Issues	• None, provided full site clean-up is achieved

Table 6.21 Water treatment - UV oxidation

Remedial Status	• Currently limited application in NZ • Has been used commercially overseas (UK and Europe), especially for treatment of aquifers contaminated with halogenated organics and PAH's
Contaminant Type	• A wide range of volatile and semivolatile organics (very effective on monocyclic aromatics and PAHs)
Advantages	• Involves complete oxidation of organic molecules and catalyses oxidation/complexing of inorganics • Provides the highest removal efficiencies
Disadvantages	• High capital operating and maintenance costs
Achieve Clean-up Levels	• Effective at cleaning a wide range of organic contaminants • Oxidises or catalyses complexion of inorganics
Downstream Effects	• No major effects
Timeframe	• Short to medium timeframe depending on hydraulic setting
Cost	• Refer Table 6.23
Resource Consent Requirements	• Consent for abstraction of groundwater may be required • Consent for discharges of treated groundwater to stormwater, council sewers and/or reinjection to groundwater may be required
Long-term Site Management Plan Issues	• None, provided full site clean-up is achieved

Table 6.22 Water treatment - pH adjustment and chemical treatment

Remedial Status	• Widely used for industrial wastewater treatment in NZ • Has been used commercially overseas (US and Europe) in both for ex-situ and in-situ applications, but application to gasworks sites has been limited.
Contaminant Type	• A wide range of inorganic contaminants
Advantages	• Can provide very high removal efficiencies for a wide range of contaminants. • Proven technology
Disadvantages	• Can involve large inputs of raw materials
Achieve Clean-up Levels	• Effective at cleaning a wide range of inorganic contaminants. Involves complexion and precipitation of inorganics
Downstream Effects	• No major effects
Timeframe	• Short to medium timeframe depending on hydraulic setting (weeks to months)
Cost	• Refer Table 6.23
Resource Consent Requirements	• Consent for abstraction of groundwater may be required • Consent for discharges of treated groundwater to stormwater, council sewers and/or reinjection to groundwater may be required
Long-Term Site Management Plan Issues	• None, provided full site clean-up is achieved

Additional information on remedial treatment systems can be found in Section 5.5.5 of the Users' Guide.

Table 6.23 gives an indication of the costs of all the remedial options discussed above.

Table 6.23 Ball park remedial costs

Management/ Treatment Method	Cost in $NZ[1] (Stinson et al 1992)	Cost in $NZ[1] (CIRIA 1996)	$NZ Costs 1996
Groundwater monitoring (assume 10 wells, 6 monthly monitoring and analysis for BTEX, PAHs and Cyanide)			10,000/yr
Capping (Clay)			50-75/m^3
Clay wall			230/m^2(2)
Soil/bentonite slurry wall	45 - 115/m^3	110 - 180/m^2	
Cement/bentonite slurry wall	45 - 115/m^3	110 - 180/m^2	
Injection grout wall	130 - 570/m^2	630/m^3	
Steel pile wall	690+/m^2	180+/m^2	
On-site repository (clay lined)			100-150/m^3
Ex-situ stabilisation/solidification		100 - 120/long ton	120/t (soil)[3] 900/m^3 (tar waste)[4]
In-situ stabilisation/solidification	430 - 1,400/short ton	470 - 630/short ton	
In-situ bioremediation	220+/m3		
Landfarming	70 - 115/m^3	115 - 190/short ton	150/long ton (soil)[4] 500/m3 (tar waste)[3]
Biopiles	140 - 220/m^3	150 - 250/m^3	
Soil slurry bioremediation		85 - 215/m^3	
Thermal desorption	115 - 500/short ton	60 - 600/short ton	250/long ton

Incineration (fixed system)		100 - 170/short ton	
In-situ soil washing	70 - 170/m³	150 - 310/m³	
Ex-situ soil washing	70 - 300/short ton	35 - 320/m³	
Water - air stripping			0.50 - 3.00/1000 US gal
Water - activated carbon	0.22 - 2.52/1000 US gal		
Water - UV oxidation	70 - 150/1000 US gal		
Water - pH adjustment/chemical	0.07 - 0.28/1000 US gal		

1. Costs have been converted into NZ($) from US dollars (0.70) and UK pounds (0.45).
2. Costs include transportation, off-site disposal of excavated material and supervision.
3. Costs allow for off-site disposal following treatment.
4. Costs allow for off-site disposal following treatment (will depend on heavy metal concentrations).

6.5 Disposal of gasworks contaminants to landfill

Excavation and off-site disposal of contaminated soil to an appropriate landfill has been the most common means of remediating former gasworks sites in New Zealand, Australia, UK and the United States. Site remediation by excavation and off-site disposal is relatively quick and may be cost effective depending on the cost of landfilling. Off-site disposal of contaminated soil in an appropriately designed landfill is seen as a reliable and secure means addressing concerns associated with contaminated sites. However, it is unlikely that highly contaminated material could be disposed of off-site without some form of pretreatment.

Other matters associated with the disposal of contaminated soil to landfill include:

- availability of appropriate landfills
- requirements for pretreatment in order to comply with leachate requirements
- risk associated with transport of hazardous wastes
- residual liability
- public perception.

When considering the disposal of contaminants as a site management option, it is important to consult the regional council and the territorial authority to discuss any regulatory requirements.

6.5.1 Gasworks waste types, composition and nature

The general philosophy to the landfilling of gasworks wastes can be found in Section 5 of the Users' Guide.

Waste materials generated at a former gasworks and which may require landfilling will tend to fall into two broad categories:

- contaminated soils and fill materials, including oxides and tar clumps
- building rubble and demolition materials (monolithic materials) which may be heavily contaminated with tar.

At a majority of the gasworks sites in New Zealand free tar may still be contained on site in some form of below ground structure (such as a tar well). This material should not be landfilled without some form of pre-treatment, such as bioremediation or stabilisation.

When assessing the level of contamination at the gasworks it is likely that the contaminated soils will fall into two broad categories:

- low level contaminated materials which meet the landfill acceptance criteria for Class 1 and 2 landfills

- high level contaminated materials, which exceed the landfill acceptance criteria and either require pre-treatment before landfilling or disposal in a purpose-built repository.

6.5.2 Landfill type and processes

In general the landfill principles and the practice in New Zealand has resulted in the identification of three classes of landfills, as follows:

Class 1 Represents the formation of small, specially developed and lined cells within a Class 2 site

Class 2 A site that is suitable for co-disposal of limited quantities of wastes containing relatively low concentrations and quantities of hazardous constituents

Class 3 An appropriately sited, engineered and operated landfill of older design receiving municipal waste only.

Classification criteria for the landfills are summarised in Table 6.24.

A comprehensive set of New Zealand specific landfill engineering guidelines was produced by the University of Canterbury (CAE 1992). It is noted that there are many sites in New Zealand currently used for waste disposal, that do not conform even to the standard of a Class 3 landfill. Such uncontrolled waste disposal sites are not considered suitable for the disposal of gasworks contaminated wastes.

A list of some of the criteria for distinguishing various landfill classes is given in Table 6.24.

Table 6.24 Landfill classification

Class	Landfill Design and Operation Criteria
1	• Meets Class 2 criteria • Accepts hazardous wastes to be mixed with mature refuse if appropriate, and disposed of in discrete cells with low permeability capping and lining material • Has leachate capture and either recirculation, treatment, or disposal to sewage treatment facility.
2	• Meets Class 3 criteria • Has an appropriately designed and operated leachate and groundwater quality surveillance programme which indicates insignificant levels of groundwater contamination and will be regularly monitored for potentially hazardous constituents following acceptance • Applies cover on a daily basis and low permeability intermediate and final cover • Has adequate low permeability/attenuating lining materials and appropriate subsoil conditions as evaluated by a detailed hydrogeological investigation • Is further than 3 km from any significant point of water abstraction and use within the same hydrogeological catchment.
3	• Is securely fenced and has personnel in attendance during all times of operation capable of assessing whether documentation with wastes is adequate. Additionally, personnel must be available who can decide how to evaluate specific wastes and determine the required disposal option, and who are fully instructed in the requirements for safe handling of the particular waste both for themselves and other landfill users. Where wastes are proposed to be accepted, appropriate testing (concentration and leachability of constituents) should be carried out. • Has at least a 4m depth of well compacted refuse available above the site base • Has acceptable control of stormwater, and applies cover at least on a weekly basis • Is further than 1 km from any significant point of water abstraction and use • Closure includes a low permeability protective cap • Is further than 500 m from residential areas • Is located and engineered so that extreme meteorological events will not cause significant mobilisation of wastes by such processes as erosion, wave action, and stormwater run-off • Has in place appropriate operational, quality assurance, emergency response, and post closure management plans.

This should be considered to be indicative of desirable site characteristics for the various

classes rather than rigidly specific. In some cases the particular features of a landfill may make certain criteria unnecessary for that particular landfill (e.g. impermeable geological features may obviate the need for engineered lining requirements). For many disposal cases, more detailed consideration in accordance with risk assessment principles should be undertaken before wastes with potentially hazardous constituents are accepted into a particular landfill.

Conformity with the classification criteria should be considered to be indicative only and subject to confirmation. The three classes allow for a graduation in landfill quality commensurate with graduated levels of waste strength. As the waste strength increases, the controls placed on the landfill in terms of management and engineering become more rigorous. **On no account should waste materials be diluted to allow them to be placed in a lower class of landfill site.** This issue of dilution should also be borne in mind when undertaking/assessing the results of pre-treatment works of heavily contaminated gasworks materials, such as bioremediation. Such pre-treatment may result in reduced contaminant concentrations through dilution/substrate bulking and not as a result of chemical and/or other processes.

Processes within the landfill itself, which can essentially be considered to be a 'bio-reactor', will reduce the contaminant concentrations of the soils and waste materials landfilled. Attenuation is one of the principal contaminant reducing processes within the landfill, which can be broadly defined as a reduction in the aqueous phase concentration of a contaminant, and may be a result of physical, chemical and biological processes (Williams 1996).

Physical processes (dilution by dispersion, and matrix diffusion) would seem to offer the least complicated and thus the most quantifiable and predictable of the reactions. However, when consideration is given to chemical and biological processes, then these reactions are complicated by the chemical and micro-biological heterogeneity of the landfill. As a consequence, quantification of these processes is very complex and beyond the scope of these guidelines.

Biological and chemical processes in the landfill can reduce cyanide concentrations through a number of reactions (DoE 1978), including :

- conversion to volatile hydrogen cyanide
- conversion to complex cyanides, some of which may be only marginally soluble
- hydrolysis (in aqueous solution) to ammonium formate
- the formation of thiocyanate in the presence of certain sulphur compounds
- biodegradation.

In general the above reactions will result in the destruction of cyanide or conversion to relatively harmless substances, particularly where the cyanide contaminated waste has been landfilled with domestic waste.

Likewise BTEX, PAHs and phenolic contaminated gasworks wastes that may be deposited in a landfill will be subject to biodegradation. Whilst quantification of these processes is not practical or possible, both laboratory and field experiments have shown these contaminants to actively biodegrade (DoE 1978). However, it is important to note that the landfill system should not be overloaded with high levels of contamination. At high concentrations the contaminants can act as biocides which can result in sterilisation of the microbial population of the landfill and prevent further biodegradation occurring.

6.5.3 Leachability testing

All landfills generate a leachate which, depending on the nature of the wastes deposited and the way in which the landfill is operated, will contain a range of organic and inorganic contaminants at varying concentrations. The range and concentration of the contaminants forming the leachate will vary over the operational and closed life of the landfill. However, the leachate may become sufficiently contaminated that there is the potential for the leachate

to adversely affect the environment outside the landfill.

Laboratory based leaching tests have been developed in the United States and Europe to simulate/model the leaching processes within a landfill. A previous review and evaluation of leach test protocols (MoH 1993) identified and recommended the United States Environmental Protection Agency's Toxicity Characteristic Leaching Procedure (TCLP) as the standard leach test procedure for New Zealand.

In the United States the TCLP is primarily used for the assessment of whether a waste displays the characteristic of toxicity and must be rated as such under section 40 of the Code Federal Regulations (OFRNARA 1993). A waste is considered to possess the characteristic if the concentrations of any one of forty toxic pollutants in the test extract exceed specified regulatory levels. However, for gasworks waste there are only a small number of the contaminants of concern listed by the federal hazardous regulations, as summarised in Table 6.25.

The TCLP does provide a good indication of whether contaminants are likely to leach from contaminated soils that are to be landfilled. It can be used to establish possible contaminant concentrations in leachate generated from landfilled contaminated soils. One negative aspect to the leach test work is the cost involved in undertaking the TCLP on contaminated soils, particularly gasworks contaminated soils because of the large number of potentially soluble contaminants.

Table 6.25 USEPA maximum concentrations of contaminants for the TCLP test

Contaminant	TCLP Leachate Concentration (mg/l)
Arsenic	5.0
Benzene	0.5
Cadmium	1.0
o-Cresol	200.0
m-Cresol	200.0
p-Cresol	200.0
Cresol	200.0

The TCLP protocol requires that all wastes for testing pass through a 9.5 mm sieve, and makes no provision for the testing of waste that is monolithic in nature i.e. concrete and brick contaminated materials. In keeping with the draft Health and Environmental Guidelines for Selected Timber Treatment Chemicals (MoH/MfE 1993) it is recommended that monolithic waste be broken down to the size that meets the TCLP requirements.

Interpretation of TCLP extract contaminant concentrations in the New Zealand context is more sharply focused on the way in which such information can be used to indicate the likelihood of adverse effects on the environment resulting from disposal of a waste in a landfill. The significance of the TCLP extract concentration for a particular waste is dependent on three factors:

- the limitation of the TCLP technique in providing information on the **rate** at which leaching occurs, i.e. the test can be interpreted as providing information on the average leaching rate over a period, but the test cannot predict the maximum concentration of a constituent in landfill leachate arising from the deposition of a specific waste
- the levels of constituent attenuation in the landfill and leachate dilution in receiving water that can reasonably be expected before the constituent impacts on the environment
- the requirement of the Resource Management Act 1991 that discharges should not cause adverse effects at their point of impact. Depending on the point of discharge, an acceptable waste constituent concentration may vary from a water quality standard protective of sensitive aquatic life (if the leachate were to enter surface water of designated value in a regional plan), to levels based on the

drinking water standards, or a wastewater treatment plant's ability to remove or assimilate the substance.

Of the three factors, the third is the only one which is defined (or has the potential to be defined) in regulation. Only estimates can be made of the effect that the other two factors have on the concentration of a waste substance at the point of impact. Such estimates require knowledge of typical landfill attenuation and receiving water dilution factors, and also some information about the rate at which leaching will occur over the waste's lifetime in a landfill.

6.5.4 Landfilling of low level gasworks wastes

The process and management of landfilling gasworks contaminated materials will tend to be controlled by the operating practices of the landfill and the consent conditions that apply to the landfill. However, there are a number of operational issues that should be considered when co-disposing of contaminated wastes to landfill to ensure that optimum contaminant degradation occurs, wherever possible. A number of the key issues are set out below and discussed further in Lowe 1996:

- the circulation of fluids, landfill gas and leachate within the landfill should not be impeded
- contaminated materials should be brought into the closest contact possible with the co-disposal medium to ensure that degradation processes are optimised
- the contaminated waste materials should not be placed directly into leachate or areas of the landfill cell that will become completely saturated by leachate, and should be placed at least 2 m above the maximum anticipated leachate level and underlain by at least 2 m of normal solid waste
- large bodies of mainly inert materials, such as contaminated soils, will tend to create a barrier to movement of fluids through the landfill. As a consequence, creation of large horizontal barriers that cause the perching of leachate, should be avoided wherever possible
- gasworks wastes deposited in any given landfill cell should not exceed 1 percent of the total cell volume (CAE 1992).

6.5.5 Landfilling of high level gasworks wastes in repositories

A repository may be located at the former gasworks site or a specially constructed landfill repository at the landfill site. Construction and operation of an on-site repository will utilise standard landfill design techniques, comprising a fully engineered, lined and capped facility. Consents are likely to be required by the territorial authorities and regional councils for the construction and operation of a repository. The principal features of an on-site repository are described below.

Lining and Capping

The base and side walls of the repository should be lined with an engineered liner, as shown in Figures 6.7 and 6.8. The choice of lining system depends on site specific variables, such as site hydrogeology, site re-use, availability of natural clay etc. The base of the repository should be graded to allow any leachate generated to drain to a collection sump During infilling, a vertical sand blinding/drainage layer should be installed between the liner and the placed materials. The repository should be capped, with the cap overlapping the side walls of the repository. A sand blinding layer should be placed below the cap, which will also act as a filter blanket and a capillary break (see Figure 6.7).

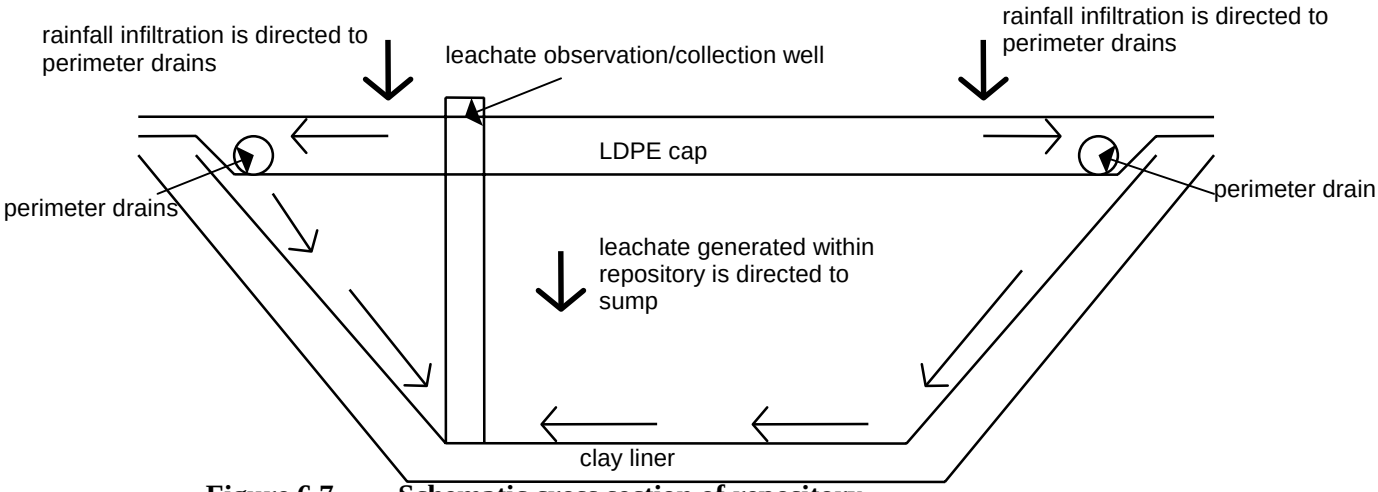


Figure 6.7 Schematic cross section of repository

Placement and Compaction of Fill Materials

Given the range of materials that will be placed within the repository and to enable adequate material compaction to be achieved, it is necessary to screen and split the materials into broad categories (such as granular and cohesive) and to place and compact the materials in discrete layers.

The soil/fill materials should be laid in relatively thin layers, in the order of 250 mm (although the layer thickness will probably be in the order of 500 mm or greater for monolithic materials), and compacted to a nominal highways compaction specification. Such a high level of compaction is required for the following reasons:

- reduce soil/fill settlement within the repository
- compaction of contaminated fill has been shown to significantly reduce the leachability of the contaminants (Cairney 1992), principally through a reduction in material permeability (as shown in Table 6.26).

Table 6.26 Leachate generated from uncompacted and compacted tar wastes

Parameters	Wastes Finely Ground but Uncompacted (mg/l)	Wastes Compacted to Highways Standards (mg/l)
Naphthalene	24 to 84	< 1
Acenaphthylene	10 to 12	< 1
Acenaphthene	2 to 7	2 to 7
Fluorene	7 to 19	<1 to 3
Anthracene	7 to 15	< 1
Phenathrene	5 to 20	<1 to 3
Fluoranthene	5 to 18	<1 to 3
Pyrene	6 to 27	<1 to 4
Benzo anthracene	7 to 43	< 1
Chrysene	7 to 16	< 1
Benzo(b)fluoranthene	7	<1 to 3
Benzo(k)fluoranthene	< 10	-
Indeno(1,2,3-cd)pyrene	< 30	< 1
Dibenzo(a,h)anthracene	< 30	< 1
Benzo(g,h,i)perylene	< 30	< 1
Toluene extract	46 to 96	1 to 6
Phenol	420 to 610	<1 to 1.9
Sulphates	80 to 312	30 to 95

Leachate Control and Drainage

It is likely that the repository should only generate a very small volume of leachate for the following reasons:

- repository infilling will be undertaken in a manner that minimises the ingress of surface water. This will be principally achieved through phased infilling and the control of stormwater ingress into the repository
- the use of a low permeability cap and collection of surface infiltration through the grass cover will result in little or no infiltration into the repository.

Internally within the repository, any generated leachate should ultimately drain to the base of the repository and collect in the leachate sump (as shown in Figure 6.8). Periodically collected leachate should be removed from the sump via leachate abstraction/monitoring wells and disposed of in an appropriate manner off site. Surface infiltration (stormwater) on to the repository cap should be collected and discharged to the local stormwater system.

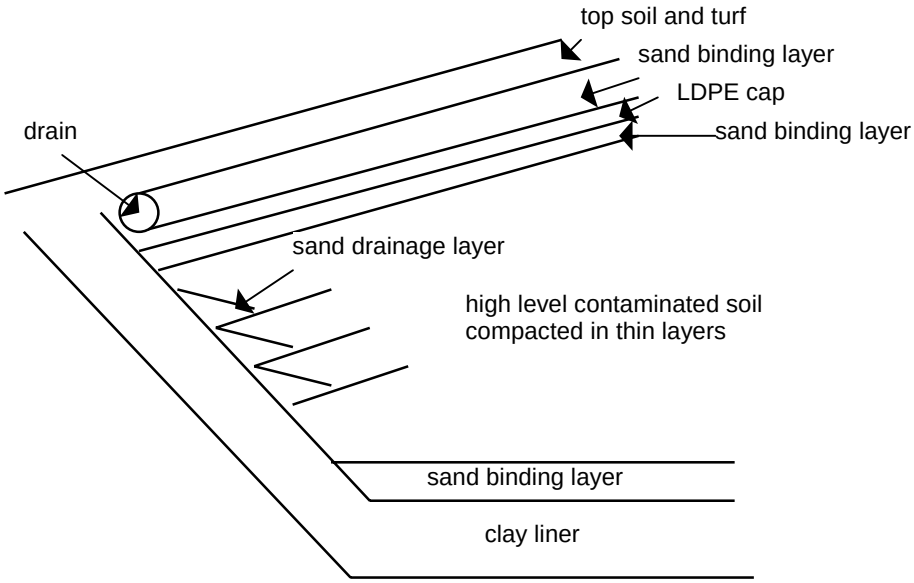


Figure 6.8 Schematic cross section of a repository lining system

Vapour Management

Excavation and placement of high level contaminated soil and fill materials that contain elevated concentrations of relatively volatile compounds (i.e. BTEX compounds, light end PAHs and phenols) could result in the short-term generation of hydrocarbon vapours.

A significant amount of this vapour should vent passively during placement of the materials. However, following capping of the repository, some vapours may still be generated and, given the completely sealed nature of a repository, it may be necessary to allow the vapours to vent. This can be achieved through the installation of vent pipes within the repository cap. Depending on the volume of vapour generated and vapour contaminant concentrations, it may be necessary to treat the vapour to prevent any adverse effects.

Additional information on the disposal of gasworks contaminants to landfill can be found in Section 5.5.6 of the Users' Guide.

6.6 Monitoring

The information in this section can be considered to be a check list for the implementation of environmental monitoring. Because each gasworks site will have its own site-specific environmental monitoring requirements, only generic issues are discussed.

The issues covered by this section comprise:

- post-investigation/pre-remediation environmental monitoring
- remediation environmental monitoring
- post remediation environmental monitoring
- monitoring determinands
- monitoring frequency.

6.6.1 Post investigation/pre-remediation monitoring

6.6.1.1 Groundwater

Prior to implementing remedial works, and following on from investigation works, it may be necessary to establish seasonal variations in the groundwater flow direction at the site or variations in groundwater levels as part of the remediation design. This monitoring would also assist in deciding between remedial options. Groundwater quality data will also have to be obtained over a period to allow for variations in quality and extent of contamination plumes, as these factors are obviously critical to a remedial design.

For example, if a passive/management remedial option is being considered, i.e. one that allows for intrinsic remediation of groundwater contamination and management of risks, then data on the migration of groundwater contamination will need to be established at least over a one-year seasonal cycle in order to ensure that potential adverse effects are unlikely to arise.

6.6.1.2 Surface water

Should the gasworks site lie close to a surface water course which receives run-off from the site (i.e. perhaps up to 20 m to 50 m depending on topography) or reticulated stormwater generated by the site be discharged to a nearby surface water course, then it may be necessary to establish quality data for the water course prior to starting remedial works. This data will assist in establishing whether the site poses any potential risk and will determine background concentrations before any high level short term discharges that may occur during remedial works. Obviously, any discharges will need a consent from the regional council.

6.6.1.3 Atmospheric monitoring

If excavation-type remedial works are planned for the site, it would be prudent to establish background air quality data (i.e. dust and hydrocarbon vapour) before starting the works. This monitoring will be particularly important if the gasworks site lies in a residential area and dust, vapour or odour could pose a potential human health or environmental risk or nuisance. Equally commercial or industrial areas could be affected by atmospheric contamination.

6.6.2 Remediation monitoring

During remedial works it will be necessary to undertake a range of monitoring to ensure that potential adverse human health and environmental effects do not arise. In addition, the monitoring will, depending on the nature of the remedial works, indicate the effectiveness of the remedial works and whether further works are required to meet the required clean-up levels. The typical range of environmental parameters monitored during remediation monitoring are discussed in the following section.

Given the likely range of environmental parameters that may be monitored during remedial works and the number of regulatory authorities that have a mandate to ensure that adverse effects do not arise from the works, it is advisable to detail the remedial works and the monitoring requirements in a Remediation Management Plan. This Plan can then be used as a working document during the remedial works by regulators, contractors, site owners, consultants etc.

Remedial works may take a few days to a number of weeks or months to complete. Obviously the monitoring frequency should reflect the duration of the remedial works.

Consents will obviously be needed for the remedial works and the consent conditions will stipulate the monitoring frequency and determinands that should be covered by the monitoring.

6.6.2.1 Groundwater levels and quality

Regular monitoring of groundwater levels may be necessary during the remedial works, particularly where pump and treat or barrier remedial options are used. This will ensure that the design principles of the remedial system are being achieved and, if necessary, allow modifications to the remedial system to be made, e.g. changes in pumping rates.

Depending on the length of remedial works (i.e. how long areas of the site are left exposed to recharge) and the nature of the remedial works (i.e. pump and treat or in-situ bioremediation), it may be necessary to consider assessing groundwater quality on a number of occasions during the course of the remedial work. However, the routine analysis of the groundwater samples during the remedial operation may be limited to contamination indicator parameters (such as total petroleum hydrocarbons, dissolved oxygen etc.), obviously the choice of parameters will be dictated by the remedial works.

6.6.2.2 Surface water monitoring

If there are surface water courses in close proximity to the site and/or site stormwater discharges to a nearby surface water course, and depending on the nature of the remedial works, it may be necessary to undertake routine surface water sampling and analysis to confirm that there have been no adverse effects.

6.6.2.3 Trade waste/sewer discharge

Contaminated surface water from the gasworks site or contaminated groundwater abstracted as part of remedial works may be discharged to sewer, if treatment and discharge to stormwater or re-injection to groundwater is inappropriate. As a consequence, and in most cases, it will be necessary to routinely monitor stormwater discharges to sewer.

6.6.2.4 Atmospheric monitoring

Remedial works at a gasworks site are likely to generate both dust and vapour emissions which could result in adverse off-site effects and nuisance. As a consequence it will usually be necessary to routinely monitor dust emissions and vapour (such as volatile hydrocarbons). It may be necessary to do this daily during commissioning and redevelopment.

6.6.2.5 Noise monitoring

Any remedial or construction works, or similar, will have to comply with local council noise requirements and, given the location of most gasworks sites within urban areas these requirements could be quite onerous. Actual standards and monitoring requirements will have to be confirmed and agreed with the local council prior to commencement of works.

6.6.3 Post-remediation monitoring

A summary of possible monitoring requirements include:

Groundwater

Verification monitoring and sampling, on completion of remedial works, will require revised groundwater contours to be derived for the site and detailed quality data to prove the effectiveness of the remedial works.

Long-term groundwater monitoring requirements will typically comprise groundwater level monitoring and quality monitoring of selected key indicator parameters. The selection of key parameters will be based on the original site investigation data. Often the determinands measured and the frequency of sampling will be gauged against trigger levels, i.e. if the contamination levels exceed set trigger levels then more detailed monitoring will be undertaken.

Surface Water

Where stormwater run-off from the former gasworks site and where contaminated groundwater enters a nearby surface water course, it may be necessary to undertake verification sampling following completion of the remedial works and to include the water course in the long-term monitoring plan.

Soil

Depending on the choice of remedial works utilised, it may be necessary to undertake verification soil sampling and analysis to prove the residual level of soil contamination. Soil samples may be collected from the base and side walls of an excavation where "excavate and landfill" remedial methods have been used, or it may be necessary to drill boreholes to recover soils where in-situ remedial methods have been utilised. Often this soil sampling work will be done in tandem with the remedial works to determine the depth and extent of contamination and hence excavation works.

Generally, it may not be necessary to analyse the soil samples for the full range of gasworks contaminants, but rather key indicator parameters.

6.6.4 Monitoring determinands and frequency

The choice of monitoring determinands and monitoring frequency will be dictated by a combination of factors, including the nature and extent of the contamination, the remedial methods used, and the nature of potential adverse effects. A summary of "typical" monitoring determinands and monitoring frequencies is given in Tables 6.27 through to 6.30.

6.6.4.1 Determinands

The determinands measured to establish surface water, groundwater quality etc. are likely to comprise a range of "indicator" parameters and, if necessary, more detailed and comprehensive "quantitative" parameters. Indicator parameters may include determinands which can be measured in the field with hand held meters, such as pH and conductivity measurements in water or total volatile organics in air, or a visual description, such as the presence of sheens on a surface water course.

Quantitative measurements will typically entail the collection of soil, water or atmospheric (air) samples and analysis in the laboratory.

The choice of determinands measured will be controlled by a number of factors, including:

- nature of the contamination and nature of remedial and management option(s)
- sensitivity of the receiving environment and nature and magnitude of the potential adverse effect(s)
- monitoring frequency, and
- reason for monitoring (i.e. part of a routine monitoring programme or verification samples collected on completion of remedial works).

6.6.4.2 Monitoring frequency

The frequency at which the monitoring should be undertaken will be controlled by a combination of factors:

- proposed remediation or management strategy
- potential for adverse effects to arise and the magnitude/significance of the adverse effect(s), and
- possible seasonal variations in the parameters of concern.

It is likely that before commissioning a remedial or management option some form of long-term monitoring will be undertaken to identify seasonal variations or trends and then factored into the remedial/management design. During the initial stages of the remedial works it may be necessary to undertake short-term daily or weekly monitoring to ensure that adverse effects are not arising and that the remedial system is performing. More medium-term

monitoring (perhaps monthly) may be undertaken once a remedial system is up and running to ensure that the system is performing in the long-term and to enable changes to the system to be made (such as pumping rates).

On completion of remedial works, long-term monitoring may be undertaken to ensure that the level of clean-up has been achieved, allowing for seasonal fluctuations in contamination levels, and that some form of contamination "rebound" has not occurred, particularly with in-situ remediation techniques.

In establishing the monitoring frequency contingency measures should be allowed for catastrophic type events, such as earthquake and flood events, should they arise.

Table 6.27 Post investigation/pre-remediation monitoring

MEDIUM	POSSIBLE DETERMINANDS		AIMS AND FREQUENCY
	INDICATOR PARAMETERS	QUANTITATIVE PARAMETERS	
GROUNDWATER	• Depth to groundwater and product thickness (if present). • Conductivity • pH • Dissolved oxygen (important if assessing bioremediation rates)	• Total petroleum hydrocarbons • Volatile organics • Semi-volatile organics • Total cyanide • Total sulphate • Heavy metals • Total colony forming units (important for assessing bioremediation rates)	To determine seasonal changes in groundwater elevations, groundwater flow direction and contamination patterns. The monitoring frequency will be determined by the proposed remediation method/strategy and the proposed programme between completion of the site investigation works and remediation.
SURFACE WATER	• Flow rates • Conductivity • pH • Dissolved oxygen • Visual signs of sheens, turbidity or discharges to surface water course	• Total petroleum hydrocarbons • Volatile organics • Semi-volatile organics • Total cyanide/free cyanide • Total sulphate • Heavy metals • Suspended solids	To determine seasonal/major storm event changes in water quality, especially where groundwater is in hydraulic continuity with surface water courses and/or when stormwater discharges from the site into surface water courses. In addition, baseflow and stormflow changes in surface water quality may be investigated. The frequency of monitoring will be determined by the potential for contamination to enter surface water courses and the magnitude of potential impacts.
AIR	• Total volatile organics • Total particulate matter	• BTEX • Naphthalene (and isomers) etc. • Hydrogen sulphide • Hydrogen cyanide	Long-term monitoring to determine seasonal changes in vapour/gas concentrations around the site (only where elevated vapour/gas concentrations have been detected on site) Short-term daily monitoring to determine background concentrations of vapour/gases and dust, prior to undertaking remedial works (generally only required where the site is to be excavated).
SEWER/TRADE WASTE	• Generally not required	• Generally not required	Generally not required
SOIL	• Generally not required	• Generally not required	Generally not required

Table 6.28 Remediation monitoring

MEDIUM	POSSIBLE DETERMINANDS		AIMS AND FREQUENCY
	INDICATOR PARAMETERS	QUANTITATIVE PARAMETERS	
GROUNDWATER	• Depth to groundwater and product thickness (if present). • Conductivity • pH • Dissolved oxygen (important if assessing bioremediation rates)	• Total petroleum hydrocarbons • Volatile organics • Semi-volatile organics • Total cyanide • Total sulphate • Heavy metals • Total colony forming units (important if assessing in-situ bioremediation rates)	The frequency of monitoring will be determined by the remediation options used on site, and the length of time over which the remedial works are being operated. Typically short-term daily monitoring of indicator parameters will be carried out during commissioning of the remedial works, to ascertain performance and allow modifications to the remedial design to optimise remediation rates Groundwater samples may be collected and tested for quantitative indicators of groundwater quality at intermittent time intervals (i.e. once every two months) to determine remediation progress.
SURFACE WATER	• Visual evidence of sheens discharges into surface water, or courses turbidity • Flow rates • Conductivity • pH • Dissolved oxygen	• Total petroleum hydrocarbons • Volatile organics • Semi-volatile organics • Total cyanide/free cyanide • Total sulphate • Heavy metals • Suspended solids	The frequency and scale of monitoring will be determined by the remediation options used on site and the length of time over which the remedial works are being operated. Typically short-term daily monitoring of several indicator parameters will be carried out during commissioning of the remedial works, to ascertain performance and allow modifications to the remedial design to optimise remediation rates and minimise discharges to surface water courses (i.e. stormwater run-off). Surface water samples may be collected and tested for detailed parameters at intermittent intervals (i.e. once every two months) to determine remediation progress and compare surface water quality pre and post remediation. After commissioning the remediation system, routine monitoring of the remediation systems and remediation progress is likely to be carried out (i.e. monthly to two monthly).
AIR	• Total volatile organics • Total particulate matter	• BTEX • Naphthalene (and isomers) • Hydrogen sulphide • Hydrogen cyanide	The frequency of monitoring will be determined by the remediation options utilised on site and the length of time over which remedial works are being undertaken. Typically short-term daily monitoring will be carried out during commissioning of the remedial works (i.e. excavate and cart off site), to allow monitoring of dust/gas concentrations and allow measures to be adopted to mitigate any adverse effects. After remediation commissioning, or completion of the remedial works a period of short-term daily monitoring is generally carried out to allow comparison of dust/vapour/gas emission pre and post remediation.

SEWER/TRADE WASTE	• Flow rates • Conductivity • pH	• Total petroleum hydrocarbons • Volatile organics • Semi-volatile organics • Total cyanide/free cyanide • Total sulphate • Heavy metals • COD/BOD	Only required if stormwater and or groundwater from the site is to be discharged to sewer/trade waste. The frequency of monitoring is likely to be determined by the regulatory authority in charge of waste water treatment. Where stormwater/groundwater is contained/stored prior to discharge the regulatory authority may require testing prior to discharge. Continuous discharges will be tested according to a frequency specified in the trade waste permit.
NOISE		• Quantitative noise monitoring	The need and frequency of monitoring will be determined by the remedial options used. Excavation type works may require almost continuous/daily monitoring to ensure compliance with territorial authority noise level requirements, whilst mechanical systems may only require commissioning monitoring to ensure compliance.

Table 6.29 Post-remediation verification monitoring

MEDIUM	POSSIBLE DETERMINANDS		AIMS AND FREQUENCY
	INDICATOR PARAMETERS	QUANTITATIVE PARAMETERS	
GROUNDWATER	• Depth to groundwater and product thickness (if present). • Conductivity • pH • Dissolved oxygen (important if assessing bioremediation rates)	• Total petroleum hydrocarbons • Volatile organics • Semi-volatile organics • Total cyanide • Total sulphate • Heavy metals • Total colony forming units (important if assessing bioremediation rates)	The frequency of monitoring will be determined by the nature of remedial works undertaken at the site. Typically verification groundwater monitoring is carried out after completion of the remedial works (i.e. when a groundwater treatment system has been in operation) and/or at 6 monthly intervals for the first year. One year after completion of the remedial works, further groundwater monitoring is covered by the long-term management plan.
SURFACE WATER	• Visual evidence of sheens, discharges into surface water courses or turbidity • Flow rates • Conductivity • pH • Dissolved oxygen	• Total petroleum hydrocarbons • Volatile organics • Semi-volatile organics • Total cyanide/free cyanide • Total sulphate • Heavy metals • Suspended solids	The frequency of monitoring will be determined by the remediation options utilised on site and whether the surface water course was being impacted prior to remediation. Typically surface water monitoring is carried out on completion of the remedial works and at frequent intervals for the first year. Based on the analytical results received for the first year the frequency of monitoring will be reviewed. Generally, one year after completion of the remedial works, further surface water monitoring is covered by the long-term management plan
AIR	• Total volatile organics • Total particulate matter	• BTEX • Naphthalene (and isomers) • Hydrogen sulphide • Hydrogen cyanide	Generally post remediation air quality monitoring is limited. Short-term daily monitoring may be carried after completion of remedial works, especially where large scale excavation works have been undertaken, to allow comparison of pre and post remediation dust/vapour and gas concentrations.
SEWER/TRADE WASTE	• Generally not required	• Generally not required.	Generally not required.
SOIL		• Total petroleum hydrocarbons • Volatile Organics • Semi-volatile organics • Total cyanide • Total sulphate • Heavy metals	Generally associated with large scale excavation works to verify that the majority of contamination has been excavated and removed from site. Sampling is carried out on completion of the excavation works and prior to backfilling. Backfilling of the excavations may not be carried out until receipt of the analytical results. Where in-situ remedial techniques have been undertaken it may be necessary to drill boreholes to obtain soil verification samples.

Table 6.30 Long-term monitoring

MEDIUM	POSSIBLE DETERMINANDS		AIMS AND FREQUENCY
	INDICATOR PARAMETERS	QUANTITATIVE PARAMETERS	
GROUNDWATER	• Depth to groundwater and product thickness (if present). • Conductivity • pH • Dissolved oxygen	• Total petroleum hydrocarbons • Volatile organics • Semi-volatile organics • Total cyanide/free cyanide • Total sulphate • Heavy metals	The frequency of monitoring will be determined by the nature of remedial works undertaken at the site, and potential downgradient impacts. Annual long-term monitoring is generally required indefinitely where remedial management options have been adopted i.e. cut-off walls, capping etc. Annual long-term monitoring may be carried out for the first couple of years after completion of any physical/chemical or biological remedial works to ensure contamination is not migrating off-site. It will be necessary to have a review process to assess the collected data after a number of years (for example 5 years) and redesign the monitoring programme.
SURFACE WATER	• Visual evidence of sheens, discharges into surface water courses or turbidity • Flow rates • Conductivity • pH • Dissolved oxygen	• Total petroleum hydrocarbons • Volatile organics • Semi-volatile organics • Total cyanide/free cyanide • Total sulphate • Heavy metals	The frequency of monitoring will be determined by the remediation options utilised on site, whether stormwater discharges from the site are still entering surface water courses and whether groundwater is in hydraulic continuity with an adjacent stream. Annual long-term monitoring is generally required indefinitely where remedial management options have been adopted i.e. cut-off walls, capping etc and the surface water courses are in close proximity. It will be necessary to have a review process to assess the collected data after a number of years (for example 5 years) and redesign the monitoring programme.
AIR	• Total volatile organics • Total particulate matter	• BTEX • Naphthalene (and isomers) • Hydrogen sulphide • Hydrogen cyanide	Generally long-term air quality monitoring is limited. Monitoring may be carried out in the rare cases where highly elevated vapour/gas concentrations were detected in the site investigation and where the risk level is high.
SEWER/TRADE WASTE	• Generally not required	• Generally not required	Generally not required.
SOIL	• Generally not required	• Generally not required	Generally not required.

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