CRCCARE™

no. 11

technical report

Characterisation of sites impacted by petroleum hydrocarbons
National guideline document

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Abbreviations

General

AIP	Australian Institute of Petroleum
ANZECC	Australian and New Zealand Environment Conservation Council
API	American Petroleum Institute
ARMCANZ	Agricultural and Resource Management Council of Australia and New Zealand
AS	Australian Standard
ASC	Accelerated site characterisation
AST	Aboveground storage tank
ATSDR	Agency for Toxic Substances and Disease Registry
BTEX	Benzene, toluene, ethylbenzene and xylene
C_{12}	Refers to a hydrocarbon with 12 carbon atoms in the chain
CPT	Cone penetrometer testing
CRC CARE	Cooperative Research Centre for Contamination Assessment & Remediation of the Environment
CSM	Conceptual site model
DEC	New South Wales Department of Environment and Conservation (now DECC)
DECC	New South Wales Department of Environment and Climate Change
DEWHA	Commonwealth Department of Environment, Water, Heritage and the Arts
DIPE	Diisopropyl ether
DNAPL	Dense non-aqueous phase liquid
DO	Data objective
DPT	Direct-push technology
DQO	Data quality objective
EPA	Environment Protection Authority (or Agency)
FRTR	Federal Remediation Technologies Roundtable
IARC	International Agency for Research on Cancer
ITRC	Interstate Technology and Regulatory Council
LIF	Laser-induced fluorescence
LLNL	Lawrence Livermore National Laboratory
LNAPL	Light non-aqueous phase liquid
LPG	Liquefied petroleum gas
MfE	New Zealand Ministry for the Environment
MIP	Membrane interface probe
MTBE	Methyl-tertiary-butyl ether
NAPL	Non-aqueous phase liquid
NATA	National Association of Testing Authorities
NEPC	National Environment Protection Council
NEPM	National Environment Protection Measure
PAG	Project Advisory Group
PAH	Polycyclic aromatic hydrocarbon
PDB	Passive diffusion bag
PULP	Premium unleaded petrol
QA/QC	Quality assurance/quality control

SOP	Standard operating procedure
TBA	Tertiary-butyl alcohol
TPH	Total petroleum hydrocarbon
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
UCL	Upper confidence level
ULP	Unleaded petrol
UPSS	Underground petroleum storage system
US	United States of America
UST	Underground storage tank

Units

%	percent
°C	degrees Centigrade
cm	centimetres
cP	centi-Poise
cS	centi-Stokes
g/cm^3	grams per cubic centimetre
g/L	grams per litre
J	contaminant mass flux
kg	kilograms
MQ	contaminant mass discharge
m	metres
m^2	square metres
mg/kg	milligrams per kilogram
mg/L	milligrams per litre
ppm	parts per million
µg/kg	micrograms per kilogram
µg/L	micrograms per litre
v/v	by volume

Key terms

Accelerated site characterisation	The process of collecting site characterisation information in a single mobilisation, making use of rapid and 'real-time' sampling and field analytical methods, and on-site interpretation and iteration of field data.
Conceptual site model	'…*The interpretation and assimilation of all site-related information into assumptions and hypotheses regarding contamination sources, subsurface contaminant distribution, and dominant transport/fate processes*' (US EPA 1995), which can be presented in graphical and/or written form.
Data quality objectives	'*Statements that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors…*' (US EPA 2000).
End-point strategy	The desired end-point of a site management process, and the approach required to meet it.
LNAPL	An organic liquid that is less dense than water, and generally insoluble in water. The majority of petroleum hydrocarbons (and all of those that are covered by these guidelines) are types of LNAPL.
Mobile LNAPL	Connected portions of petroleum product that are able to coalesce and migrate.
Natural attenuation	Natural attenuation, or 'weathering', includes physical, chemical and biological processes that act to reduce 'the mass, toxicity, mobility, volume or concentration of contaminants in soil or groundwater' (US EPA 1999).
Petroleum hydrocarbons	The complex liquid mixture of substances found in the Earth, formed over millions of years from compression and heating of deposited marine organic materials. These are extracted and then refined and blended into fuel mixtures and petrochemical products.
Residual LNAPL	'Trapped' petroleum product, represented by disconnected films and droplets left behind by migrating LNAPL in the unsaturated zone, and disconnected 'blobs' of LNAPL that have been cut off by water in the saturated zone.
Site characterisation	The assessment or investigation of a site to determine the extent and type(s) of contamination and potential risk(s) associated with the contamination.
Tiered approach to characterisation	Assessing the risk and complexity of a site using the preliminary CSM and assigning a Tier (Tier 1, 2 or 3, from lowest to highest complexity) to the site based on the results of the assessment. The characterisation then immediately proceeds to collect information at a level of detail appropriate to the site's Tier, rather than having to move through traditional stages or phases of investigation.

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1. Introduction

Sites impacted by petroleum hydrocarbons represent a significant proportion of Australia's contaminated land, and proper characterisation of these sites is therefore a major concern. Poorly planned and executed site characterisation is likely to result in additional expense, both during the investigation and subsequent remediation, and inadequate or misleading data may also result in an increased risk to human health and the environment. A number of guidance documents related to contaminated site characterisation currently exist in Australia; however, these are typically regional, outdated or do not provide information specific to characterising petroleum hydrocarbon impacts.

CRC CARE, in consultation with industry, consultants and regulators, recognised the need to prepare national guidelines for the characterisation of petroleum hydrocarbon-impacted sites, to unify current guidance and provide support for innovative technologies and approaches. These guidelines have therefore been prepared under CRC CARE's National Contaminated Sites Demonstration Program. Preparation of the guidelines forms part of a larger Site Characterisation Project scope, which has also included the formation of a Petroleum Projects Project Advisory Group (PAG) to provide direction and feedback from industry, consultants, researchers and state regulators. A review of relevant existing Australian and international guidance, protocols and techniques has also been previously completed (Davis et al. 2006) and taken into consideration during the development of these guidelines.

1.1 Purpose of the guidelines

These guidelines have been designed to provide industry, consultants and regulators with a unified and improved national approach to the characterisation of petroleum hydrocarbon impacts at sites. By emphasising an early consideration of potential end-points for the site and a focus on land use considerations, it is envisaged that this will assist in facilitating the provision of accurate information to a level of detail appropriate for the goals of the site characterisation.

The guidelines are intended to be usable, practical and systematic, with scope to be updated as experience, knowledge and the availability of technology grows. It

should be noted that while significant information and guidance is provided within the document, the guidelines are targeted to users with at least a basic grounding and some experience in contaminated site assessment.

1.2 Applicability

The guidelines are focused on sites that have stored, handled or distributed oil or petroleum products, such as petrol (gasoline), diesel, kerosene, jet fuel, lubricating oil and fuel oil. These are all types of light non-aqueous phase liquids or LNAPLs. The term LNAPL generally refers to organic liquids that are less dense than, and largely insoluble in, water. The petroleum hydrocarbon contaminants referred to in this guideline are all types of LNAPL. These guidelines are not intended to be used for the characterisation of sites impacted by petroleum hydrocarbons that are dense non-aqueous phase liquids (DNAPLs), such as coal tar or creosote.

These are guidelines only, to assist those involved in the assessment of petroleum hydrocarbon-impacted sites, and do not articulate any legislative requirements.

1.3 Structure of the guidelines

These guidelines have been structured to provide the necessary information, tools and references to allow users to conduct effective characterisation works at petroleum hydrocarbon-impacted sites. Section 2 provides an overview of petroleum hydrocarbons, including their properties, use and potential impacts, in addition to their behaviour in subsurface environments. Section 3 provides guidance for developing an appropriate site characterisation strategy, emphasising the importance of the conceptual site model (CSM). A range of investigation techniques are presented in Section 4 along with a discussion of their applicability. It is noted that conducting intrusive site investigations presents a number of potential hazards and Section 4.2 should be referred to for further information on these risks. Section 5 provides guidance on presenting and reporting the information gained during the characterisation process. Finally, the process of applying the guidelines to an actual site characterisation is discussed in Section 6. Additional site characterisation work products, examples and tools are provided in the appendices.

Due to the broad scope of the guidelines, it is not possible to provide full details on all relevant subjects and at times the reader will therefore be referred to further information. Throughout the document these key references will be highlighted as shown in the example below:

API LNAPL Interactive Guide (API 2004)

This useful guide in electronic format provides substantial background information on petroleum hydrocarbons and their behaviour in the subsurface, in addition to a number of tools to evaluate LNAPL. It can be downloaded for free at **www.api.org/lnapl**.

2. Overview of petroleum hydrocarbons

Petroleum is the complex liquid mixture of substances found in the Earth, which were formed over millions of years from compression and heating of deposited marine organic materials. The majority of petroleum is made up of a multitude of hydrocarbons, in addition to smaller amounts of other organic compounds containing oxygen, nitrogen, sulfur andsome inorganic constituents. The actual composition of the petroleum will vary depending on its origins. Petroleum is extracted from the ground in the form of crude oil (in addition to natural gas), which then undergoes refining and blending processes to derive petroleum fuel mixtures and single component hydrocarbon products (petrochemicals). Fuel mixtures may also include chemical additives introduced during the refining and blending process to impart particular properties such as anti-knock agents or anti-oxidants, and more recently bio-fuel additives such as ethanol.

Individual hydrocarbons and the various mixtures each have unique properties that affect their behaviour in the subsurface and therefore impact on efforts to characterise petroleum hydrocarbon releases. Once released, compounds may also partition into several phases and are also subject to degradation ('weathering') that can alter the substance and lead to the creation of new compounds. An understanding of the main petroleum hydrocarbon types, their properties and behaviour is therefore crucial to effective site characterisation and these aspects will be discussed in this section. Common petroleum hydrocarbon facilities, sources and releases will also be covered. The American Petroleum Institute (API) has also published a compendium of information on investigating petroleum hydrocarbon-contaminated sites titled the *API LNAPL Interactive Guide* (API 2004).

> **API LNAPL Interactive Guide (API 2004)**
>
> This useful guide in electronic format provides substantial background information on petroleum hydrocarbons and their behaviour in the subsurface, in addition to a number of tools to evaluate LNAPL. It can be downloaded for free at **www.api.org/lnapl**.

2.1 Introduction to petroleum hydrocarbons

Individual petroleum hydrocarbons compounds can be divided into two broad groups, aliphatics and aromatics. Aliphatics include: alkanes, which are straight or branched chains of carbon atoms surrounded by hydrogen atoms; cycloalkanes, where carbon atoms form cyclic structures (rings); and alkenes, which are similar to alkanes except there are double bonds between one or more carbon atoms. Aromatics are ring structures, with alternating single and double bonds between carbon atoms. The simplest aromatic is benzene, a ring of six carbon atoms and six attached hydrogen atoms. Benzene is a mono-aromatic (containing only one ring); aromatic hydrocarbons with multiple fused rings are termed polycyclic aromatic hydrocarbons (PAHs).

The properties of petroleum hydrocarbons are determined by their chemistry. For example, the longer carbon chains in higher carbon number compounds result in higher boiling points and lower solubility (and therefore greater persistence and lower mobility in the environment).

2.1.1 Types

The primary petroleum hydrocarbons relevant to these guidelines are crude oil and several refined fuel products of the crude oil. Crude oil is largely refined through the process of distillation, where the oil is heated and separated into fractions based on the number of carbon molecules in the fraction. The main fractions, in ascending order of boiling point (and therefore carbon number) are (TPHCWG 1998):

1. Low-end distillates:
   a) gases such as propane and butane, which can be liquefied to form petroleum gas (LPG)[1]
   b) straight run gasoline/petrol which is blended to form automobile petroleum.
2. Middle distillates – including kerosene, jet fuels, diesel and light fuel oil.
3. Heavy end distillates – motor and lubricating oils and heavy fuel oil.

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[1] Gases and LPG are not contaminants of concern in petroleum hydrocarbon releases and will not be discussed further.

4. Residuals – bitumen (or asphalt) is left after other fractions have been distilled.

Further details on the petroleum hydrocarbons that may be commonly released into the subsurface are provided herein.

Crude oil

As discussed above, crude oil is the raw product that is extracted from the ground and used as the feedstock in the refining process. The composition and appearance of crude oil varies greatly depending on its origin, and it can range from a pale yellow liquid to a heavy black sludge. Crude oil typically contains high concentrations of straight chain alkanes and cycloalkanes, with lower concentrations of mono-aromatics and branched alkanes and very low concentrations of PAHs (TPHCWG 1998).

Petrol (gasoline)

Petrol comprises approximately 44% of the product from crude oil distillation in Australia (AIP 2005) and includes the fraction with a boiling point between 35 degrees centigrade (°C) and 210°C. In addition to use in automobiles some types of petrol may also be blended for use in aviation. Petrol is largely made up of C_4 to C_{12} aliphatics, and mono-aromatics including benzene, toluene, ethyl benzene and xylenes (BTEXs) as well as other mono-aromatics and additives (additives are further discussed in Section 2.1.2). PAHs are not present in significant concentrations in petrol.

Kerosene and jet fuels

Kerosene and kerosene based jet fuels are distilled in the boiling point ranges of approximately 150°C to 300°C and are predominantly made up of alkanes in the C_9 to C_{16} range. Concentrations of BTEXs and PAHs are very low in kerosene and jet fuel (TPHCWG 1998). Kerosene is used widely for heating and for blending into jet fuels. The most common commercial jet fuel blend in Australia is known as 'Jet A-1', and approximately 13% of refinery output in Australia is used for jet fuel (AIP 2005). Military aircraft often use specially designed blends to cope with the high altitudes and speeds at which these aircraft may operate.

Diesel and light fuel oils

Diesel fuel and light fuel oils are middle distillates with boiling points between 170°C and 360°C, predominantly comprised of straight chain alkanes in the range of C_9 to C_{21}. These types of petroleum hydrocarbons usually also contain significant quantities of aromatics, including PAHs, though have low concentrations of BTEXs (ATSDR 1999). Diesel fuel is used to power diesel engines in automobiles, and a range of transport, earthmoving, industrial vehicles and ships, and in power generation and represents approximately 32% of Australian refinery production (AIP 2005), while light fuel oils are used in domestic and industrial heating, though not widely in Australia.

Heavy fuel oils

Heavy fuel oils, also known as residual fuel oils, are formed by blending the residual oil left after light and middle distillates have been extracted. They have a boiling range of 350°C to 700°C and contain alkane chains and cycloalkanes with carbon numbers greater than C_{12}, significant concentrations of aromatics including PAHs, and low concentrations of BTEXs (TPHCWG 1998). Heavy fuel oils have previously been used in a range of industrial burners, including powering ship engines and in power generation, though their use has declined recently.

Lubricating oils

Lubricating and motor oils have a boiling point range of approximately 325°C to 600°C and contain high concentrations of branched alkanes and cycloalkanes (from C_{18} and above) with very low concentrations of BTEXs and PAHs (TPHCWG 1998). Used lubricating oils are likely to have a different composition to new oils due to their close contact with the engine and may contain higher concentrations of PAHs and metals (ATSDR 1997).

2.1.2 Fuel additives

A number of additives have been historically, and currently, added to fuels to improve performance. There are two main groups of additives that have been used: oxygenates, still in use for boosting the octane rating and cleaner burning; and lead, for anti-knock purposes and associated lead scavengers, which are no longer used in Australia.

Oxygenate additives include: ethanol; methyl-tertiary-butyl ether (MTBE); tertiary-butyl alcohol (TBA); and diisopropyl ether (DIPE). Ethanol is currently the most widely used additive in Australian fuels, with 10% by volume (v/v) blends (the maximum permissible under current Australian fuel standards – DEWHA 2001a) now common in many retail service stations. MTBE has been used extensively in the United States of America (US), though it has not been commonly used in Australia. TBA is a degradation product of MTBE that may also be used as an oxygenate additive and DIPE has also been used. MTBE, TBA and DIPE are each limited to a maximum of 1% v/v in Australian fuels under current regulations (DEWHA 2001a).

The use of leaded petrol for automobile use in Australia was phased out completely by January 2002, and its use had been declining since unleaded petrol was first introduced in 1985. The lead in leaded petrol was in the form of lead alkyl compounds that were used as anti-knock agents. Lead scavengers were also required to be added to remove lead deposits from engines, and these included ethylene dibromide and ethylene dichloride.

Knowledge of potential additives used in petrol is important in characterising a site, as in addition to some of the additives being potentially toxic, they may also influence the solubility of other fuel components and impact degradation rates. Potentially toxic oxygenate additives such as MTBE and TBA can be significant groundwater contaminants due to their solubility and persistence. It was for this reason that the State of California required that MTBE be phased out of use between 1999 and 2002 (LLNL 2001) and its use is limited in Australia. Ethanol, while not toxic in itself (at the concentrations that would likely result from a spill or leak), can still have consequences for soil and groundwater contamination, by increasing the solubility of other fuel components (Niven 2005) and potentially impeding the natural attenuation of petroleum hydrocarbons, including BTEXs (LLNL 2001).

2.1.3 Fuel properties

Regulated Australian standards

In Australia, the Department of Environment, Water, Heritage and the Arts (DEWHA) has established standards for petrol and diesel quality under the *Fuel Quality Standards Act 2000*. Both environmental and operability standards have been implemented and pertinent standards for both petrol and diesel fuel are shown in Table 1. It should be noted that as these standards have been progressively introduced since 2002, they may not be relevant for sites where historical releases have occurred. For example, until 2006 up to 5% v/v of benzene was permitted in petrol. From 2006 the limit for benzene has been 1% v/v.

Table 1. Australian Standards for automotive fuel (DEWHA 2001a, 2001b)

Parameter	Petrol standard (max. allowable)	Date of effect	Diesel standard (max. allowable)	Date of effect
Sulfur	150 ppm (ULP) 50 ppm (PULP)	01-Jan-05 01-Jan-08	50 ppm 10 ppm	01 Jan 06 01 Jan 09
Distillation (final boiling point)	210°C	01-Jan-05	360°C	01 Jan 06
Alkenes (olefins)	18% v/v	01-Jan-05	–	–
Aromatics	45% v/v	01-Jan-05	11% PAHs by mass	01 Jan 06
Benzene	1% v/v	01-Jan-06	–	–
Lead	0.005 grams per litre (g/L)	01-Jan-02	–	–
Ethanol	10% v/v	01-Jan-03	–	–
MTBE	1% v/v	01-Jan-04	–	–
DIPE	1% v/v	01-Jan-02	–	–
TBA	0.5% v/v	01-Jan-02	–	–
Density	–	–	0.82 to 0.85 grams per cubic centimetre (g/cm^3)	01 Jan 06
Kinematic viscosity	–	–	2.0 to 4.5 centi-Stokes (cS) at 40°C	01 Jan 02

ppm – parts per million
ULP – unleaded petrol
PULP – premium unleaded petrol

Physical and chemical properties

The properties of petroleum hydrocarbons, in combination with the characteristics of the environment that the product is released into, govern their behaviour in the subsurface. Density and viscosity are key properties in the mobility of a hydrocarbon, as can be seen in the difference in behaviour between a plume of denser, more viscous fuel oil, and a less dense and less viscous petrol plume (API 2004). The petrol plume will spread much more rapidly and will also dissolve into groundwater more readily, as further discussed in Section 2.4. Other important properties include boiling point, solubility, volatility and interfacial tension. Table 2 provides properties for the main petroleum hydrocarbons products, individual compounds and additives. Due to the range of compounds that make up the petroleum products, ranges may be given for some properties.

Table 2. Properties of petroleum hydrocarbon products, compounds and additives

Product/compound	Boiling point (°C)	Density (g/cm³) at 15°C	Dynamic viscosity (centipoise – cP) at 15°C	Solubility in water (mg/L)
Petrol	35 – 210	0.715 – 0.76 [a]	0.4 – 0.6 [b]	–
Kerosene/jet fuel (A–1)	150 – 300	0.775 – 0.84 [c]	2.0 – 2.3 [b]	–
Diesel	170 – 360	0.82 – 0.845 [d]	2.7 [b]	–
Heavy fuel oil	350 – 700	0.96 – 0.99 [b]	~ 45,000 [b]	–
Lubricating oil	325 – 600	0.83 – 0.90 [b]	~ 100 – 200 [d]	–
Benzene	80.1	0.8787	0.65 (at 20°C)	1780 [b]
Toluene	110.8	0.867	0.58 (at 20°C)	515 [b]
Ethylbenzene	136.2	0.868	0.68 (at 20°C) [e]	180 [b]
Xylenes	138.4 – 144.4	0.86	0.79 (at 20°C)	175 [b]
MTBE	55.2	0.745	0.35 (at 20°C)	48,000 [f]
Ethanol	78.4	0.789	1.2 (at 20°C)	Miscible

[a] *Shell 2007a*
[b] *API 2004*
[c] *Shell 2005, 2007b*
[d] *EC 2006*
[e] *Castro et al.*
[f] *ATSDR 1996*

The data provided in Table 2 is intended as an indicative guide only, and more detail on hydrocarbon properties can be found in API (2004) and TPHCWG (1997). It should be noted that as products weather following their release, their physical and chemical properties will be altered. In addition, the solubility values given for the individual compounds represent solubility in the pure form, and may be misleading when dealing with actual releases. This is because most incidents of contamination involve a mixture of compounds, in the form of a petroleum product (or several products), and in these circumstances the solubility of a single compound is generally much lower (in a mixture the 'effective' solubility[2] is related to the mole fraction of the compound in the product). API (2004) provides the pure phase and effective (mixed) solubilities of the main constituents of several petroleum products. Benzene solubilised from fresh petrol (gasoline) may be as low as 2% of the pure phase solubility, while in weathered petrol it is as low as 1%.

[2] Effective solubility $C_W = x_O \, S$
C_W = Effective solubility
x_O = mole fraction (of chemical in fuel)
S = solubility

2.2 Petroleum hydrocarbon sites

The manufacture, storage, distribution and use of petroleum hydrocarbons is widespread and they may therefore be found as contaminants at a large variety of sites. This section focuses on the more common sites that are potentially impacted by hydrocarbons and features at these sites that should be targeted by investigations.

2.2.1 Typical sites

The main sites which are likely to be impacted by petroleum hydrocarbons are mainly associated with the 'downstream' petroleum industry, and include:

- refineries
- bulk storage and distribution terminals
- airport storage terminals
- distribution depots
- transport, fleet and government refuelling depots
- commercial and agricultural sites with refuelling facilities
- retail service stations.

In 2004 there were seven active refineries in Australia, 26 ports with bulk terminals, and approximately 6500 service stations, down from 8000 in 2000 (AIP 2005) and some 20,000 in the early 1970s (NSW EPA 1994). This rationalisation of service station sites has required site characterisation of many decommissioned facilities in recent years.

In addition to the sites noted above, distribution networks also have the potential to cause hydrocarbon impacts to the subsurface. Pipelines may be used to distribute fuels from refineries to storage terminals and airports. At most large airports a 'hydrant' system is also used to deliver fuel to aircraft, where a network of underground pipes links each gate to the airport bulk storage (Chevron Corp. 2006).

Sites not associated with the petroleum industry but which use and store petroleum hydrocarbons include sites associated with the petrochemical and manufacturing industries including paint and pesticide manufacture.

2.2.2 Contamination sources

Contamination sources can be generally defined as those originating from a loss of containment or release from either underground storage tanks (UST), aboveground storage tanks, transfer systems (pipelines and hydrants), and surface spills at transfer points (loading gantries, bowsers and pumps) and drum storage areas.

Largely due to the number of service stations relative to other petroleum hydrocarbon sites, leaks from underground storage tanks (UST), underground petroleum storage systems (UPSS) and their associated pipework are probably the most widespread source of hydrocarbon product releases to the subsurface. Historically, UST have been installed that are susceptible to corrosion, or have been improperly installed and are therefore liable to leak. Due to the buried nature of the tanks and pipes the leaks could go undetected for many years. In response to these potential contamination risks, improvements in the management and regulation of UPSS have been implemented in recent years (for example NSW DECC 2008).

Leaks from aboveground storage tanks (AST) are another common source, and while they are generally more easily detected than leaks from UPSS, an AST release from an elevated tank may result in more penetration of LNAPL to the subsurface than a leak at the surface of comparable volume. A surface release will typically spread before slowly entering into the deeper soils, whereas an AST release from height penetrates quickly downward due to the large vertical gradient, which is sufficient to overcome entry-head pressures (API 2004). A release from transfer systems such as pipelines can be significant depending on the size of the line and how quickly the release is able to be detected, and for underground systems this is particularly pertinent.

In general, long duration slow leaks (such as those from a pipe, valve, flange or tank) will penetrate the subsurface in a deeper and narrower profile than a spill, which will typically spread wide and may not penetrate very deeply into the subsurface. Establishing the nature of a release at a site, where possible, is therefore an extremely important part of the site characterisation process.

While far less numerous than service stations, the huge quantity of petroleum hydrocarbons stored and distributed at refineries and bulk terminals brings the greatest potential for large scale contamination of the subsurface. It is for this reason that these sites typically have the most sophisticated spill detection and containment systems; though historically this was not always the case.

2.3 Potential impacts and effects

The need for these guidelines is driven by the fact that when petroleum hydrocarbons are released into or onto the ground, they have the potential to impact detrimentally on human health and the environment. Both petroleum product mixtures and individual compounds are potentially toxic. A summary of potential human health and environmental effects are further discussed herein, to allow an understanding of the basis for characterising hydrocarbon impacts at sites. However, for more detail reference should be made to CRC CARE (pending).

2.3.1 Human health

Health effects from exposure to petroleum hydrocarbons will vary depending on the types of chemical compounds in the product, the length of exposure and the concentration of the compounds one was exposed to. The assessment of health effects is made difficult by the lack of adequate toxicological data, despite petroleum hydrocarbon use and contamination being widespread. For example, the TPHCWG (1997b) noted that of an approximate 250 individual compounds identified in petroleum, toxicity data existed for only 95, and reliable data for as few as 25. Potential impacts are further complicated by the weathering process undergone by products when released, resulting in composition changes and meaning that exposure data for products such as petrol or jet fuel may not be accurate to the fractions humans may be exposed to at a contaminated site.

The many compounds in petroleum hydrocarbons impact on human health in differing ways. Compounds such as BTEXs and n-hexane can affect the central nervous system and if exposures are high enough, could result in death (ATSDR 1999). Petroleum hydrocarbons have also been shown to affect the blood, immune system, renal and respiratory organs and can be irritating to the skin and eyes. Some petroleum compounds have the potential to cause cancer, with benzene and benzo(a)pyrene in particular recognised as Class 1 human carcinogens (IARC 1987, 2008), benzene having been shown to cause leukaemia in humans.

The toxicity of petroleum products generally increases as the content of low boiling point, unsaturated and aromatic compounds increases, and toxicity is also seen to increase in ascending order of alkanes, alkenes and aromatics (MfE 1999). It is for this reason that recently developed human health based screening levels for petroleum hydrocarbons have been based on fractions grouped according to carbon number and aliphatic/aromatic content (such as those provided in NEPC 1999).

The various additives that may be included in petroleum products, such as MTBE, TBA and DIPE, can also affect human health. While not considered as toxic or carcinogenic as petroleum hydrocarbons such as benzene, these compounds can cause eye, throat and skin irritation and affect the nervous system in high doses. People exposed to MTBE while pumping petrol also reported headaches, nausea, dizziness, and MTBE also has an unpleasant odour (ATSDR 1996).

Exposure to petroleum hydrocarbons at a contaminated site can be through direct contact with contaminated soil or groundwater, ingestion of soil or groundwater, or inhalation of vapours.

2.3.2 Environmental

Similarly as for human health impacts, determining ecological impacts from petroleum hydrocarbons is difficult due to the complex mixture of substances and the changes in composition due to weathering.

For releases in soils, eco-toxicological effects have been reported in plants, microbiota and invertebrates. However, the persistence of a substance in the environment has a large bearing on the potential impacts it may have on ecological receptors. For example releases of petroleum hydrocarbons into surface or near surface soils will be subject to weathering, and the generally more toxic and bioavailable light fraction components will be lost. The less soluble components remaining are more likely to sorb to soils, particularly those with higher organic content and finer particle sizes and will be less bioavailable. Lansdell and McConnell (2003) also indicate that, in general, bioaccumulation of petroleum hydrocarbons is not considered to be significant in plants, invertebrates or mammals.

It is noted that studies of the eco-toxicity of petroleum hydrocarbons in water have largely been limited to releases of products directly to waterways, whereas this document provides guidance for characterising subsurface (groundwater) impacts. The concentrations of contaminants found in groundwater at a site are likely to be significantly higher than resultant concentrations at a waterway receptor. This is due to weathering processes such as volatilisation, dispersion, sorption, dissolution, oxidation and biodegradation (see Section 2.4.3 for more information). Low concentrations of hydrocarbons released into waters can stimulate algal

growth and biodegradation processes; however, at higher concentrations crude oil, diesel and petrol have all been reported to have lethal and sub-lethal effects on invertebrates and fish (ANZECC/ARMCANZ 2000).

2.4 Behaviour of hydrocarbons in the subsurface

An understanding of the behaviour of petroleum hydrocarbons in the subsurface following their release is fundamental to successful site characterisation. This section provides a summary of the main processes that are undergone when a product is released. A more detailed discussion can be found in API (2004) and Mayer and Hassanizadeh (2005).

> **Soil and Groundwater Contamination: Nonaqueous Phase Liquids** (Mayer & Hassanizadeh 2005)
>
> A good text on the basics of NAPL contamination (it discusses both LNAPL and DNAPL) and processes associated with migration and distribution, characterisation and remediation.

Figure 1 depicts a typical scenario of a product release and associated subsurface migration, which is further discussed in the following sections.
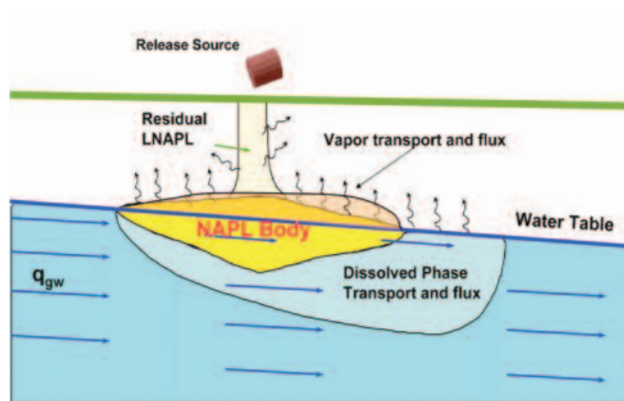
Figure 1. Depiction of petroleum hydrocarbon release (ASTM 2006)

2.4.1 Phases

Petroleum hydrocarbons may be present in the subsurface in four different phases: as the largely immiscible liquid product (LNAPL); dissolved in groundwater as the aqueous phase; volatilised into gas or vapour; and adsorbed to soil particles in the solid phase. It is necessary to conceptualise petroleum

hydrocarbon releases in terms of these 'multiphase' relationships in order to understand the migration and distribution of the contaminants.

An LNAPL in the subsurface may be present as: free product moving down through the unsaturated zone and/or 'pooling' at the capillary fringe or low permeability zones; residual product in the unsaturated zone; or trapped residual product in the saturated zone. As the LNAPL moves through the subsurface some molecules may partition into the solid phase by adsorbing to particles of soil. When groundwater comes into contact with LNAPL, or adsorbed contaminants, a low percentage of the product also dissolves into the aqueous phase. As discussed in Section 2.1, the solubilities of different products and compounds vary significantly. BTEX compounds and additives such as MTBE are more likely to dissolve into groundwater and result in contaminant plumes. Partitioning of contaminants into the gaseous phase is possible whenever air comes into contact with either LNAPL, dissolved contaminants in groundwater, or contaminants adsorbed to soils.

It is notable that after a product is released it may undergo multiple phase changes; the same molecule may adsorb to a solid soil particle, subsequently dissolve into water and then be volatilised. All four phases may be present in the unsaturated zone, while in the saturated zone contaminants will not be present in the vapour phase (US EPA 1995) as water has displaced air from soil pores.

2.4.2 Migration processes and dynamics

The main factors contributing to the distribution and migration of petroleum hydrocarbons in the subsurface are:

- characteristics of the product(s) released
- nature of the release (i.e. point source, ongoing etc.)
- hydrogeological conditions at the site.

In a 'typical' release of a product to the subsurface, as depicted in Figure 1, the LNAPL will migrate downwards under the force of gravity, with some lateral spreading. During this migration, a significant proportion of the LNAPL will be retained as residual in the unsaturated zone by capillary forces. This residual product can remain a long-term source of contamination to groundwater through a fluctuating water table or infiltration, and can also be a source of vapour. If the release is sufficiently large in volume, mobile product will continue through the unsaturated zone until it encounters a barrier, such as a low permeability layer, or the capillary fringe of the water

table. At the capillary fringe, buoyancy forces resist gravity forces and the LNAPL will begin to accumulate and migrate laterally, typically more so in the direction of the groundwater gradient. As the amount of product builds up, a head of LNAPL will develop and penetrate the capillary fringe and the water table, displacing water. Once the product release has ceased, the head will dissipate quickly and downward migration of the LNAPL will end, with water displacing the product that penetrated the saturated zone (Mayer & Hassanizadeh 2005). Some residual product will remain in the saturated zone and this residual LNAPL acts as a potential long-term source of groundwater contamination.

As indicated above, product released into the subsurface may be present as mobile or immobile/residual LNAPL. Mobile LNAPL refers to connected portions of product that are able to coalesce and migrate. Immobile LNAPL refers to the disconnected films and droplets left behind by migrating LNAPL in the unsaturated zone, and disconnected 'blobs' of LNAPL that have been cut off by water in the saturated zone. Figure 2 and Figure 3 depict LNAPL in the saturated zone in a mobile and residual (trapped) state respectively. It is important to note that water acts as the wetting fluid and is in contact with the soil pores, as shown in the figures. LNAPL will not typically act as the wetting fluid, even in the vadose zone, where LNAPL is an intermediate wetting fluid between air pores and water attached to the soil pores.

As mobile LNAPL migrates in the subsurface more of it is trapped in soil pores and becomes immobile LNAPL (the quantity of LNAPL left trapped in soil pores is termed the 'residual saturation'). As noted by API (2004), this results in LNAPL plumes being 'spatially self limiting', unless there is an ongoing source. It is for this reason that contaminants dissolved in groundwater or volatilised in the gaseous phase, which have the potential to migrate significant distances, often represent the greatest potential risk to human health or the environment.

The geology in the area of a release will significantly influence the migration of product. The heterogeneous nature of most geology at the field scale results in a heterogeneous distribution of LNAPL, through processes such as pooling of product on low permeability layers, or preferential flow through high permeability layers. Product and dissolved phase contamination can travel across the hydraulic gradient where there is significant directional heterogeneity. For example in a weathered rock aquifer, bedding planes, faults, fractures, joints and cracks can cause preferential pathways. When characterising sites
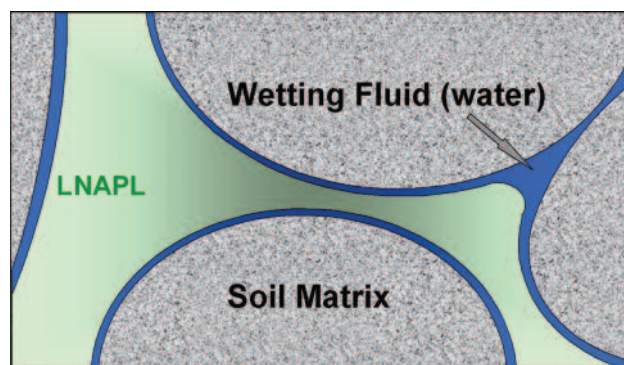
Figure 2. Depiction of mobile LNAPL in the saturated zone (courtesy of ExxonMobil)
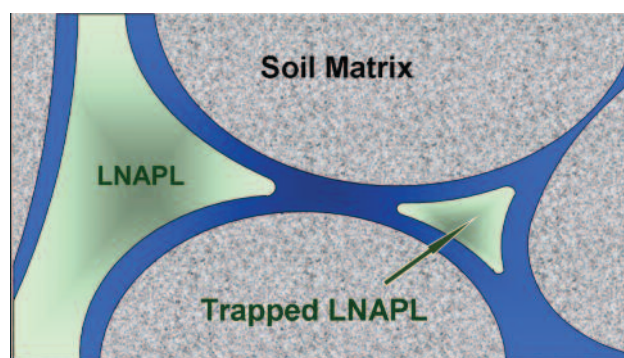
Figure 3. Depiction of residual LNAPL in the saturated zone (courtesy of ExxonMobil)

with petroleum hydrocarbon impacts it is therefore important to adequately identify and understand the site geology. Human influences at a site can also have a large impact, such as service corridors that are typically backfilled with coarse material and can therefore act as preferential pathways and transport large quantities of LNAPL.

Contaminant distribution and migration can also be influenced by the process known as 'smearing'. This occurs when accumulated mobile LNAPL is moved up or down by rises or falls in the water table. This results in product being retained in soil pores as residual, immobile LNAPL, which can be present in both saturated and unsaturated zones depending on water table movement. The effects of smearing can lead to a larger proportion of the LNAPL being trapped as residual product, which may have implications for remediation efforts targeted to product recovery.

The migration of petroleum hydrocarbons that have partitioned into groundwater is due to the physical forces of advection and dispersion. The main migration process for the dissolved contaminants is through advection,

which is essentially the transport due to groundwater flow. Migration due to dispersion includes mixing due to heterogeneities in the aquifer material, and to a lesser extent diffusion of molecules because of concentration gradients. Dispersion generally reduces the concentration of hydrocarbons in groundwater, but increases the size of the plume (API 2004). Sorption and biodegradation can be significant factors in limiting the size and extent of a hydrocarbon plume in groundwater and are further discussed in Section 2.4.3.

Hydrocarbons that have partitioned into the gaseous phase can migrate through the unsaturated zone, and have the potential to enter and accumulate in enclosed spaces such as basements, buildings and service corridors. Vapour transport is complex and influenced by several factors including soil and moisture conditions and chemical properties. Migration occurs largely by diffusion and pressure differentials, and the likelihood of vapours reaching the surface and entering enclosed spaces will depend on transport and degradation processes, ground conditions and the nature of the structure at the surface. API (2004) notes that negative ventilation conditions in some buildings can induce the flow of vapours and give rise to significant concerns.

2.4.3 Natural attenuation processes

The natural attenuation of petroleum hydrocarbons in the subsurface is discussed in detail elsewhere in the context of site remediation (CRC CARE, pending – A); however, an understanding of these processes is also important for characterisation as they will have a significant influence on the presence and distribution of contaminants. Natural attenuation, or weathering, includes physical, chemical and biological processes that act to reduce 'the mass, toxicity, mobility, volume or concentration

of contaminants in soil or groundwater' (US EPA 1999). The main natural attenuation processes for petroleum hydrocarbons are:

- Biodegradation – micro-organisms are capable of degrading many petroleum hydrocarbons, with more mobile compounds such as BTEXs, typically more amenable to biodegradation[3].
- Dilution and dispersion – under this physical process the concentrations of contaminants are reduced as they move away from the source and mix with groundwater. These processes do not destroy contaminants or cause them to change form.
- Sorption – the movement of contaminants can be significantly slowed by the sorption of the contaminants onto soil particles.
- Volatilisation – lower boiling point hydrocarbons may evaporate, and can then reach the atmosphere where the vapour can be dispersed.

When conducting a site characterisation, the effect of these attenuation processes needs to be considered. Higher solubility, lower boiling point compounds will typically be more readily attenuated and this should be taken into account, particularly for aged releases.

Significant field studies have been conducted by Parsons (1999, 2003) into the natural weathering of petrol and jet fuel releases at a number of Air Force sites in the US, in order to provide rates of LNAPL weathering that can be used in contaminant fate and transport analyses. Table 3 provides a summary of weathering rates derived in the studies. In addition to the type of product, site conditions and the age of release will impact the weathering rate, and it is therefore recommended that reference be made to the Parsons reports for specific site details to correlate with the provided ranges of weathering rates.

Table 3. LNAPL first-order weathering rates for selected chemicals (Parsons 2003)

Product type	Range for benzene (% reduction per year)	Range for total BTEX (% reduction per year)
Jet fuel (JP-4)[a]	11 to 39	4 to 28
Jet fuel (JP-8)[a]	6 to 53	10 to 35
Gasoline (petrol)	14 to 33	1.3 to 5.4

[a] *JP-4 and JP-8 are jet fuel blends used for US military aircraft, JP-4 was a kerosene/gasoline blend that has been replaced by JP-8, a kerosene based blend, similar to Jet A-1.*

[3] It is noted that biodegradation is temperature dependent (amongst other factors) and the applicability of published data, particularly from Europe or North America, to Australian sites should be carefully considered.

3. Site characterisation strategies

Davis et al. (2006) summarised the essential requirements of a successful site characterisation by noting that it must be purposeful, adequate and representative (i.e. 'on PAR'). Ensuring that characterisation efforts are purpose driven, adequate in extent and quality to meet the purpose, and provide representative site data should be the focus of the site investigation. In order to achieve these objectives it is necessary to adequately pre-plan the characterisation by clarifying the purpose, developing a CSM and identifying data gaps and data objectives. A sampling plan can then be designed to achieve the desired objectives, though it must also be flexible enough to adapt to on-site conditions.

3.1 Site management planning

3.1.1 Site end-point strategy formulation

At the front of any characterisation effort should be a consideration of the 'end-point strategy' for the site, that is, the desired end-point of the site management process, and the approach required to meet it. A draft end-point strategy will first be formulated based on information available, and the strategy will be finalised as the characterisation progresses. The driver for the site characterisation will be an important factor in formulating the site end-point strategy. For example, whether the investigation has been instigated by a spill or incident notified by the owner/operator, a community complaint, regulator requirement or a proposed land use change will influence the required outcome(s). In establishing the site end-point strategy it is desirable to identify stakeholders, as a minimum site owners and regulators/site auditors, and consult with them at an early stage. In these early discussions with stakeholders, the long-term vision for the site should be agreed upon, and goals to be achieved in reaching the vision can be set (US EPA 2005a).

> **A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquids (US EPA 2005)**
>
> This document applies to the entire site management process for LNAPL impacted sites. However, it provides useful information relevant to site characterisation efforts, particularly in relation to the early stages of the characterisation, when the end-point strategy and goals are formulated and stakeholders consulted.

In agreeing the vision and goals, the improved understanding of petroleum hydrocarbon behaviour in the subsurface must be adopted. A number of potential end-points exist and strategies to reach them should be based on an assessment of risk. Preventing unacceptable risks to human health and/or the environment must be the focus of any site management process. However, mandatory regulatory requirements that may be present in the local jurisdiction will also need to be taken into account.

3.1.2 Characterisation program to support end-point strategy

Once the draft end-point strategy for the site has been identified and agreed, the characterisation works should then be planned and implemented to support this strategy. For example, whether the characterisation is intended to show the correlation between in-well and *in-situ* LNAPL thickness; understand if a groundwater plume is migrating from the site; determine if vapours are intruding into a building; or a combination of some or all of these, will impact on the required approach (Davis et al. 2006). The characterisation should provide the required information to be used in the assessment of associated risks. It is noted that the focus of characterisation efforts may shift during as the end-point strategy is refined and this is reflected in the guidance provided in the development of the CSM and the approach discussed in Sections 3.4, 3.5 and 3.6.

3.2 Developing a conceptual site model (CSM) for hydrocarbon sites

3.2.1 CSM overview

The CSM is '*the interpretation and assimilation of all site-related information into assumptions and hypotheses regarding contamination sources, subsurface contaminant distribution, and dominant transport/fate processes*' (US EPA 1995) and can be presented in graphical and/or written form. The development of an appropriate CSM for a site is a crucial part of characterisation works. In fact, as noted by Davis et al. (2006), the aim of a successful characterisation is to produce a quality CSM that supports

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the decision-making process in regard to contaminant exposure and potential remediation/ management options. A preliminary CSM needs to be formulated as one of the very first steps in the characterisation and will be needed in the formulation of the draft site end-point strategy. The CSM should be dynamic and is revisited, revised and refined over the course of the site characterisation as more detailed information becomes available. However, it should be noted that the level of detail required in the CSM will be relative to the scale and complexity of the petroleum hydrocarbon impacts at the site.

3.2.2 CSM components

Following are the required components of a CSM for a petroleum hydrocarbon-impacted site, as provided by ASTM (2006).

Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface (ASTM E 2531 2006)

This ASTM guide describes the development of CSMs for LNAPL impacted sites, and adopts the tiered approach to characterisation described in Section 3.4. It also provides an extensive reading list, information on data collection methods and examples of how to apply the guide.

It will not be necessary to obtain detailed information for each component at all sites, the level of information required should be assessed based on the impact a lack of information will have on decision-making. It is again emphasised that the level of detail required will vary with each site.

- **Release conditions** – information on the nature of a product release, such as its source, location, age, rate and volume.
- **Dimensions of the LNAPL body** – the size and extent of the plume of product present in the subsurface (it is important to realise that the vertical dimensions of the plume are often equally as important as the horizontal dimensions).
- **Composition and characteristics of the LNAPL** – chemical composition of the product, along with its physical characteristics such as density, viscosity and solubility.
- **Hydrogeological conditions** – site geology, including distribution and properties of soil and rock, and groundwater information such as aquifer conditions and factors related to fate and transport.
- **Receptors and exposure pathways** – identifying potential receptors (human, ecological, resources) and

evaluating exposure pathways, including consideration of future scenarios due to possible land use changes.
- **Multi-phase concentrations at site boundaries or other compliance points** – the concentration or flux of contaminants in vapour or groundwater at compliance points, such as site boundaries, extraction wells, buildings.
- **Mobility/stability of plumes** – assessing whether LNAPL, groundwater or vapour plumes are stable, expanding, contracting or migrating.

3.2.3 Preliminary CSM

The preliminary CSM should be developed prior to any investigation works. It will provide a framework for identifying the data gaps to be filled by the field investigations and will be required in stakeholder negotiations regarding the vision and goals for the site.

Readily accessible information to be reviewed in preparing the preliminary CSM may include that available from desk studies (see Section 4.3) such as facility or authority records, previous investigation results, plans or databases. Initial site reconnaissance or interviews can also usually be conducted quickly and cheaply to feed into the preliminary CSM.

3.2.4 Updating the CSM

The CSM for the site can be updated many times in the course of site characterisation, even continuously with some 'real-time' investigation methods. As a minimum, the preliminary CSM will require updating based on the results of a field investigation. Data from intrusive investigations, field screening methods and laboratory analyses (see Section 4) can be incorporated into an updated and refined CSM. Depending on the type of site and the scale of the problem, supplementary investigations may be conducted to fill further data gaps, or transport and fate modelling may be required. Updating the CSM with new information is essential, as the refined CSM is used to identify remaining data gaps and inform whether additional characterisation is required or warranted.

Appendix A provides an example of a CSM certainty screening tool. The tool allows a semi-quantitative assessment of the level of uncertainty in a CSM and can assist stakeholders in making decisions on site characterisation requirements. By updating such a tool in conjunction with the CSM update, the relevance of remaining data gaps can be quantified to an extent, which will assist in agreeing requirements for further characterisation.

An example of a two-dimensional (2D) CSM graphic is shown in Figure 4.

Figure 4. Example 2D CSM for a site with hydrocarbon impacts and sand lithology

3.2.5 Data gap and uncertainty assessment

Data gap identification and uncertainty assessment are key activities in developing and refining a CSM during site characterisation, as investigation efforts should be targeted to address the uncertainty. The identification of data gaps should be conducted in a logical, structured manner, with gaps first identified, and then an assessment made of the importance of the uncertainty relative to the characterisation purpose. Achieving certainty in all areas of a conceptual model for a site is highly unlikely, and a focus should be placed on relevant data gaps.

The tool provided in Appendix A may be useful in allowing an ordered assessment of gaps and uncertainties in the CSM and their level of significance.

3.3 Data objectives (DOs) and data quality objectives (DQOs)

Setting data quality objectives (DQOs) for site characterisation is a method of systematically planning the works to ensure the data obtained meets the decision-making requirements. Existing Australian guidance (AS 4482.1 1997; NEPC 1999) promotes the use of DQOs, and they should be developed for each characterisation effort.

Guide to the sampling and investigation of potentially contaminated soil. Part 1: Non-volatile and semi-volatile compounds (AS 4482.1 1997) and *Part 2: Volatile Substances* (AS4482.2 1999)

Part 1 of this Australian Standard provides general information for soil sampling, including information on DQOs, sampling strategies and QA/QC. Part 2 provides information specific to volatile samples.

National Environment Protection (Assessment of Site Contamination) Measure (NEPC 1999)

This nationally endorsed document provides a framework for site investigation in Australia. The most relevant parts from a site characterisation perspective are Schedules B2 (Data Collection, Sample Design and Reporting) and B3 (Laboratory Analysis of Potentially Contaminated Soils).

DQOs provide a systematic approach for defining the criteria that a data collection design should satisfy. The US Environmental Protection Agency (US EPA) developed the DQO process as a seven-step iterative planning approach, to be undertaken prior to investigative work. The seven DQO steps are:

- Step 1: State the problem – summarise the potential or known contamination problem that will require new environmental data, and identify the resources available to resolve the problem.

- Step 2: Identify the decision – identify the decision that requires new environmental data to address the contamination problem, i.e. what decision drives the study?

- Step 3: Identify inputs to the decision – identify the information needed to support the decision and specify which inputs require new environmental measurements.

- Step 4: Define the study boundaries – specify the spatial and temporal aspects of the environmental media that the data must represent to support the decision.

- Step 5: Develop a decision rule – develop a logical 'if…then…' statement, or a series of such statements, that defines the conditions that would cause the decision maker to choose among alternative actions. For example, 'if contamination exceeds a specified land use criteria, then a management response is triggered'.

- Step 6: Specify limits on decision errors – specify the decision makers acceptable limits on decision errors, which are used to establish performance goals for limiting uncertainty in the data.

- Step 7: Optimise the design for obtaining data – identify the most resource-effective sampling and analysis design for general data that are expected to satisfy the DQOs.

Further detail on the DQO process can be found in US EPA (2000), which defines DQOs as '*statements that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors…*'. However, in developing DQOs there must be sufficient emphasis placed on not just 'data quality', but also 'data objectives' (DOs), the first part of the US EPA definition of a DQO. The intended use of the data provides the basis for measuring whether the data quality is sufficient to support required decisions (US EPA 2001). It is for this reason that DOs and DQOs have been discussed separately in the following sections.

3.3.1 Identification of DOs

The DOs for the characterisation, which are essentially the objectives of the study, should be clearly identified at the front of the DQO process. Establishing the DOs will require consideration of the draft site end-point strategy and the preliminary CSM. Closing the relevant data gaps identified from the preliminary CSM will be the focus of the DOs.

3.3.2 Selection of DQOs for data use

In establishing DQOs for a site characterisation, it is essential that they are appropriate for the intended use of the data. Whether data is required for risk assessment, remedial design or another purpose will result in different DQOs, even if the same site were to be investigated in each case.

For example, if the purpose of an investigation was to gather data for human health risk assessment on the one hand or alternatively to provide data for remedial design, the DQO outputs could be expected to be significantly different. Possible variations in outputs could include[4]:

- Step 1 (state the problem) – as the objectives of the investigations differ, the required resources, such as technical experts (risk assessors or remedial engineers), and stakeholders will also be different.

- Step 4 (define the study boundaries) – for a risk assessment, the study boundary may extend off-site to assess potential risks from groundwater or vapour plumes, whereas a remedial design investigation may be limited to the extent of a mobile LNAPL body.

- Step 6 (specify limits on decision errors) – in remedial design, the acceptable limits on decision errors may be highly related to cost implications, while for risk assessment they are likely to be driven by human health considerations.

3.4 Tiered approach to characterisation

The traditional approach to site characterisation in Australia has involved a staged or phased approach to investigation, whereby a site undergoes a preliminary investigation, followed by more intensive investigations in stages. While this approach allows data from each stage to be assessed and fed into planning for the next stage of investigation, it is time consuming and can be expensive. For the characterisation of petroleum

hydrocarbon-impacted sites the use of a tiered approach is considered more appropriate. This approach, as provided in ASTM (2006), involves assessing the risk and complexity of a site using the preliminary CSM and assigning a tier to the site based on the results of the assessment. A 'Tier 1' site will have the lowest complexity and will require a relatively low level of detail in the CSM to address risk and remediation issues. However, if it is identified that a site has complex issues and requires a detailed CSM for the end-point strategy, then it will be assigned a higher tier ('Tier 2' or 'Tier 3'). In this case an investigation can immediately proceed to fill relevant data gaps at the appropriate level of detail for the required CSM complexity.

A range of factors require consideration in assigning a tier to a site, some of which include (ASTM 2006):

- contaminant and hydrogeological factors – toxicity, mobility and persistence of the petroleum product(s), geological conditions/complexity, groundwater variability

- risk factors – off-site migration of plumes, land use, sensitive receptors, groundwater use, business and community considerations.

It is noted that a site initially assessed as a lower tier may require 'upgrading' to a higher tier due to more complex conditions identified during characterisation and CSM development.

3.4.1 Tier 1 investigation

A site evaluated to have low levels of complexity and potential risk is assigned as Tier 1, and an appropriate investigation can be conducted to develop a Tier 1 CSM. The Tier 1 investigation should utilise existing and historical data available for the site to the extent possible, with additional data collection as required enabling an adequate Tier 1 CSM to be constructed. Existing data that may be utilised for the Tier 1 investigation can include previous desk studies and site assessments and the operations/release history for the site. Where existing data is non-existent or insufficient, a basic site investigation including soil and groundwater sampling (and product sampling if possible), groundwater/LNAPL level gauging and an assessment of geology/hydrogeology should be conducted. A Tier 1 investigation and resultant CSM is likely to be sufficient only for basic risk assessment, with limited impacts to receptors expected, and where active complex or expensive remediation is not required to meet the objectives of the end-point strategy.

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4 Note that different outputs have only been provided for selected steps, outputs would likely differ for all seven steps of the DQO process.

3.4.2 Tier 2 investigation

A site may be evaluated as Tier 2 based on an assessment of the risk and complexity, or it may be upgraded to Tier 2 when a Tier 1 CSM is found to be inadequate to address the site complexity. A more detailed investigation will be required at these sites in order to provide sufficient data for an appropriate Tier 2 CSM to be developed and decisions on risk and remediation to be made. In addition to the standard site information noted for the Tier 1 investigation, a Tier 2 investigation will require better definition of the product type and plume dimensions and a more advanced assessment of LNAPL mobility, with some site-specific analyses (such as collection and laboratory analysis of LNAPL impacted soil cores – see Section 4.4.4). Other more advanced investigation, such as soil vapour and mass flux measurement (see Sections 4.6 and 4.8) may be introduced in a Tier 2 investigation.

3.4.3 Tier 3 investigation

A Tier 3 investigation and CSM will only be required in rare circumstances where a Tier 2 CSM is not sufficient with regard to the complexity of the site. This is likely to occur where a petroleum hydrocarbon release poses a significant risk to nearby human or ecological receptors, or where a comprehensive CSM is required as a result of other significant considerations (such as business, regulatory or community requirements or complex and expensive remediation is required to meet the objectives of the end-point strategy). Characterisation requirements to allow a Tier 3 CSM to be developed will include significant site-specific investigation techniques, testing and analysis. Complex modelling, such as a three-dimensional, multiphase computer fate and transport model is also likely to be required (see Section 4.10).

3.5 Accelerated site characterisation (ASC or 'Triad')

Site investigation activities, driven by the need for cost effective data collection, are shifting toward adaptive approaches that focus on real-time decision-making logic to guide field activities. Interest in these adaptive approaches has fostered development and evolution of the Triad approach by the US EPA. Triad is an innovative approach to decision-making for site characterisation. The Triad approach proactively exploits new characterisation tools and innovative work strategies. The Triad approach is a second-generation approach,

which has evolved from advances in field data collection and data quality, data management, and communication tools to reduce the cost and the amount of time to conduct an environmental site investigation.

The individual components of the Triad approach are not new concepts in the site investigation process. However, the Triad approach is a somewhat new package of methods to plan, implement, and improve data collection from contaminated sites. The Triad approach is an emerging tool in the site management marketplace and interest in its application is growing due to its potential cost savings. This section is intended to provide an overview of the Triad framework and its essential components.

> **US EPA Triad Resource Centre (www.triadcentral.org)**
> This website is a significant resource for information on Triad and ASC, with detailed information references and training material.

3.5.1 Background

The site management industry has long relied on formal work plans to guide investigation and cleanup of contaminated properties. Through these plans, consultants define parameters such as data needs and objectives, sampling locations, sampling methodology, sample analysis, and the data evaluation methods. These work plans often use standard sample collection techniques and fixed-base laboratories. In addition, they provide little opportunity for changes to the *prescribed* approach based on the limited amount of information learned during the field activities. This 'static' approach creates a scenario where multiple iterative cycles of sample collection, laboratory analysis and decision-making are made based on the sample results. This approach generally occurs in a linear fashion (Stage/ Phase I, II, IIA, III etc.). Since the number of iterations before characterisation or cleanup is complete is directly proportional to project costs, a decision-making framework that reduces the number of investigation cycles may offer cost savings. Preliminary evaluations suggest that incorporating the fundamentals of adaptive work planning integral to the Triad approach may offer cost savings approaching 50% over traditional approaches (Crumbling 2001). In addition, dynamic work planning allows the project to proceed more rapidly, by allowing modifications to occur in the field. It also offers the opportunity for characterisation and remediation to occur in parallel.

3.5.2 Elements of the Triad approach

The Triad approach is composed of three interconnected concepts: systematic planning, dynamic work plans, and real-time measurement technologies.

Systematic planning is the heart of a Triad process and seeks to develop a common site understanding and clear data objectives for the characterisation effort.

Dynamic work plans provide contingencies which allow for the modification of field activities quickly while the characterisation effort is proceeding.

Real-time measurements collect an appropriate level of data quality to meet data objectives and enable rapid and very adaptive execution of field activities, consistent with the dynamic work plan.

Of these concepts, systematic planning forms the backbone of the process since it serves as the framework upon which defensible site decisions can be made. Systematic planning efforts document proposed actions more clearly with the intent that every activity is performed for a clear and specific reason (Crumbling 2001).

Systematic planning

Multi-disciplinary project team

Core to systematic planning is the development of a multi-disciplinary team of environmental professionals who are capable of translating project goals established by all stakeholders (owners, regulators, communities, etc.) into clear technical objectives. Engaging all stakeholders at the beginning of the project is an essential component of the systematic planning phase. Once technical objectives are established, characterisation tools capable of fulfilling the objectives are identified by appropriate project team members.

Project teams composed of chemists, engineers and hydrogeologists have always been integral to work plan development. Within systematic planning, however, the level and complexity of interaction among the team's specialists is dramatically increased. An example of a multi-disciplinary team might include a hydrogeologist to evaluate performance of various sampling mechanisms like well installation or direct push sampling to meet the goals set by the stakeholders. A statistician may be used to convert technical objectives into a data collection schedule or means of demonstrating statistical confidence. A sampling design expert may then consult

the hydrogeologist to assess uncertainty inherent to each sample collection method. Concurrently, the project chemist would be working with the sampling design expert to select analytical methods and quality control (QC) protocols that ensure data generated is suitable for use in risk assessment. In addition, the design engineer may also be consulted to ensure that adequate data is collected to screen possible remediation alternatives. The interconnection among these professionals is high and accordingly, formal collaboration within the group is required to yield the highest quality site data at the lowest possible cost.

Uncertainty management

Managing uncertainty is also a core component of systematic planning as it helps ensure that data of known quality are collected and appropriate for the project. The development of project planning documents is the primary means by which uncertainty is controlled. Work plans, such as sampling, analysis and quality plans (SAQPs) serve to manage uncertainty in data collection. The underlying goal of these planning documents is to maximise the probability that information collected or data generated by a specific activity meets a defined decision quality. In the Triad approach, these planning documents go a step further in that they specifically identify the rationale and procedures to manage individual sources of uncertainty and its overall impact on the decision confidence and defensibility of the data collected.

Triad focuses on decision uncertainty associated with cost, fate and transport, risk, distribution and characteristics of site media, future land use, etc. Triad adopts a method known as the 'observational method.' Certain characteristics must be present for Triad to be implemented including the following:

- a considerable uncertainty exists about actual site conditions

- the uncertainty is measurable

- there is an appreciable difference in costs or risk between conditions that are favourable versus conditions that are unfavourable

- an appropriate and timely action can be taken upon receipt of the results of the measurements

- the cost of implementing the changes required to adopt a Triad approach will not exceed the savings.

Uncertainty is managed by developing a project-specific CSM, but the CSM hypothesis can only mature if tests can be designed whereby measurements can be made. One of the things to focus on with tools and the CSM is

spatial heterogeneity (between samples [macro-scale]), and composition heterogeneity (within samples [micro-scale]).

Conceptual site model

The CSM, as previously discussed in Section 3.2, is the third element of systematic planning. The conceptual model is a powerful planning tool in that it serves to document what is already known about a site. More importantly, the conceptual model also serves to identify the specific data gaps that must be bridged to achieve the overall project goals. Once gaps are identified, field activities are tailored to answer the specific questions required to complete the conceptual model so that remediation can progress with an acceptable level of uncertainty.

The CSM is dynamic. It is 'tested' and modified (as needed) as more information becomes available from investigation and interim remedial measures. Under this approach, data is collected in support of a specific decision or question rather than the collection of general site information. Incorporating a site-specific conceptual model to the systematic planning process helps assure that only data pertinent to the required decisions is collected. This approach clearly benefits overall project financials as it minimises the collection of costly data that might not be relevant to the project goals or outcome.

Dynamic work plans

The dynamic work plan is essentially the product of systematic planning by the technical team members of the project. The plan serves as the project decision tree and it is constructed to be adaptive to site conditions and project budget constraints. For example, decision logic should not lead to the collection of more samples than allowed by the project budget. Under the dynamic work plan, operational decision points in a project may be answered by the field team based on the data that is being collected. Major decisions, however, are more likely addressed by the stakeholder team using logic defined during systematic planning.

Dynamic work plans are often directly linked to the CSM. This link fosters rapid resolution of the site model by providing necessary information or by quickly adapting field approaches to account for site-specific observations or conditions. The use of dynamic work plans is not a new concept (Robbat 1997). However, successful implementation of these plans has demonstrated the need for experienced field consultants to implement

the decision-making logic developed during systematic planning when unexpected project conditions are encountered by the team (Crumbling 2001).

Real-time measurement

The third component of the Triad approach is the use of real-time information to support rapid decision-making processes. Like the dynamic work plan, the foundation for appropriate real-time measurement technologies is laid during systematic planning. This connection assures that measurement or analytical techniques employed are the most appropriate for a given data collection task. Real-time data may be generated by many mechanisms: real-time *in-situ* sensors such as membrane interface probe (MIP – see Section 4.5.3) and laser-induced fluorescence (LIF – see Section 4.4.3), rapid off-site laboratory turnaround, an on-site mobile laboratory, or hand held instruments used in the field to evaluate discreet samples. On-site analysis tools can be cost effective options for real-time data generation (Crumbling 2001). However, effective use of these tools depends largely on the target compound and the ultimate use of the resulting data in the decision-making process.

The combination of systematic planning with real-time measurement attempts to pair the most cost-effective analytical tool with the planned use of the data collected. The use of on-site analytical techniques is generally considered screening-level. Yet, when these techniques are incorporated into a clear and defensible approach for site data collection, the results offer data more valuable than simple field screening measurements. In most instances, the use of on-site analysis will not eliminate the need for traditional laboratory analysis. However, when on-site analysis and traditional laboratory techniques are combined within the framework of a dynamic work plan, the resulting data sets are often more meaningful than data generated only through a fixed laboratory (e.g. a more complete conceptual model is prepared). Aside from lower costs, the combination of on-site analysis and traditional laboratory techniques also allows generation of data sets with high confidence since they are more representative of site conditions. This concept is directly related to the ability of on-site analytical tools to dramatically increase sampling density with little impact to the overall investigation cost. In addition, a more rapid investigation is achieved, that can be used to focus further work that may require the installation of more permanent monitoring points.

Summary

Although the individual components of the Triad approach are not new, the integrated use of systematic planning, dynamic work plans, and real-time field analysis shows promise for reducing the cost of site investigation. The uncertainty of remediation strategies may also be reduced through improved CSM development. The Triad approach also has the ability to allow for schedule compression through implementation of investigations and/or remediation along parallel paths.

Under several different acronyms, program components core to the Triad approach have been applied for several years in the US by the Department of Energy, the US Army Corps of Engineers, state agencies and commercial customers, to streamline site investigation. In Australia, the Commonwealth Department of Defence is also now advocating the use of Triad type approaches for site investigations. Application of these components to site investigation has shown measurable cost savings and improved stakeholder satisfaction (Crumbling 2001; US EPA 2000).

Interest in the Triad approach to streamline site investigation and closure is growing. The integrated approach builds on the demonstrated benefits of accelerated site characterisation and comprehensive project planning to yield a structured yet adaptable framework for data collection and site management decision-making. However, it should be noted that there remain limitations to the successful application of the Triad approach, particularly in Australia, and these are further discussed in Section 3.6.

3.6 Selecting the right approach

The nature of site characterisation is such that there can be no 'one-size-fits-all' formula for the works, even in the somewhat narrowed scope of petroleum hydrocarbon-impacted sites. Differences in site conditions, the nature of contamination, regulations and stakeholder requirements and interests require the characterisation approach to be unique for each site. This is not to say that common elements and methods, which will benefit the characterisation, do not exist. These include a CSM of sufficient detail for the tier of site and establishing DOs and DQOs, as discussed previously. As to the question of selecting investigation approaches, for example multiple site mobilisations versus an accelerated/Triad type approach, this will be assessed on a site by site basis.

The use of Triad may be desirable to allow rapid characterisation of a site and selection of management options, with associated cost savings. However, there remain constraints to this approach, particularly in Australia where accelerated and Triad-type approaches have had limited use. The systematic planning required for a successful Triad project may not be possible due to the stakeholders involved. Depending on the regulator, or potential community issues, agreement may not be able to be reached to allow on-site decision-making. This may be especially true for high profile or contentious projects (Crumbling et al. 2004). A lack of expertise, equipment and/or technology may also limit the ability of a project team to adopt Triad approaches to characterisation, though with time this is likely to be less of a constraint in Australia.

3.7 Sampling/monitoring plan design

The design of sampling/monitoring plans for the characterisation of potentially contaminated sites is a complex subject and significant guidance exists in Australia and internationally. Sampling plans must be site-specific to account for the varying site conditions, DOs and DQOs of the characterisation. It is beyond the scope of these guidelines to provide detailed information on this subject and the reader is referred to NEPC (1999) and AS4482.1 (1997) for information, particularly in designing soil sampling plans. CRC CARE (pending – A) guidance provides information on monitoring plan design for natural attenuation monitoring and API (2005) and ITRC (2007a) include guidance for the design of soil vapour sampling strategies.

The information provided herein is intended to provide summary and complementary information for sampling plan design that is largely specific to petroleum hydrocarbon-impacted sites.

3.7.1 Factors affecting sampling plan

A number of factors should be taken into account when designing a sampling plan to characterise potential petroleum hydrocarbon impacts. These important factors will influence the overall scope of the plan and primarily include:

- the tier of the investigation – a Tier 1 investigation will generally require fewer sampling/monitoring points, and may require monitoring in fewer phases than higher tier investigations

- characterisation approach adopted – if a Triad approach is adopted then the sampling plan will be required to be dynamic and able to be modified as field investigations progress based on conditions encountered

- number of sources – the sampling plan will be required to take into account multiple sources, where present, and associated complications in plume delineation and contaminant migration

- site size/shape – the size of the site requiring characterisation is likely to influence the density of sampling required to provide sufficient coverage at an acceptable level of uncertainty and the size and shape will influence sampling and monitoring with regard to boundary issues and may introduce constraints on the sampling plan

- geology and hydrogeology – the nature of soil, rock and aquifer(s) at the site will have a large bearing on the type of sampling approaches to be adopted, particularly with regard to vertical delineation of contaminants and more heterogeneous sites will typically require more sampling/monitoring points.

3.7.2 Balancing regulatory requirements with DOs/DQOs

In addition to the factors noted above, regulatory requirements are likely to influence sampling plan design at most sites. Regulatory approval, and/or review and endorsement by site auditors accredited under various state legislation and site auditor schemes, of the sampling plan will often be required, and incorporating these requirements will therefore be necessary. However, currently applied guidance by regulators may not be in line with the DOs and DQOs established for the characterisation and a balance must be struck to meet the mandatory regulatory requirements without compromising the investigation objectives. In this regard the benefit in early consultation with regulators and/or site auditors during the site end-point strategy formulation is again emphasised.

3.7.3 Plan components

A sampling plan will be required to cover the following main components:

- media to be sampled (i.e. soil, groundwater, vapour, LNAPL)

- number, location and depth of sampling points

- sampling and/or field screening methods

- types of analyses to be conducted

- frequency of sampling and analysis

- methods for analysing and interpreting data obtained.

3.7.4 Selection of investigation methods

The selection of investigation methods that are appropriate for the characterisation of a site is a key component of the sampling plan. The following section (Section 4 – Investigation methods) provides a wide array of possible sampling and screening techniques. The process of choosing which methods are appropriate at a particular site should be based upon the site conditions, data gaps that exist in the site's CSM, and the level of complexity and risk at the site (i.e. the site's tier). In general, lower tier investigations will require less complex investigation methods, for example a desk study that draws on existing information may be sufficient for a Tier 1 site. However, a Tier 3 site is likely to require significant site-specific information from complex investigations, and will likely benefit from the use of advanced techniques.

4. Investigation methods

4.1 Introduction and application of methods

A range of investigation methods that can be utilised in characterising petroleum hydrocarbon impacts are provided in the following sections. These include: sampling and field screening methods for LNAPL, soil, groundwater and vapour; an overview of fate and transport modelling techniques; and a summary of analytical methods. The methods provided are all proven, though some have not been widely adopted as yet in Australia, and there may be limitations on their use due to the availability of equipment or lack of expertise. Information on these 'newer' methods is nevertheless provided, as it is likely that their uptake in Australia will increase with time. Similarly, it is noted that the development of new investigation technologies is continual, and it is therefore not possible to capture potential future methods in these guidelines. For this reason, the list of methods provided herein should not be considered exhaustive. As new methods are developed and proven their use should be considered under the framework of these guidelines.

Care must be taken in selecting investigation methods for a site to ensure that outputs meet decision-making requirements. An assessment must also be made as to the suitability of the method, not just in regard to site conditions such as geology, but also regulatory, business and community considerations.

US Federal Remediation Technologies Roundtable (FRTR)

The FRTR website provides a comprehensive matrix of sample collection, screening and analysis methods that can be used in the selection of appropriate technologies (**www.frtr.gov/site**).

US EPA Hazardous Waste Clean-Up Information (CLU-IN)

The CLU-IN website contains an extensive section on characterisation and monitoring, which includes information on various investigation technologies and a range of publications (**http://clu-in.org/char1.cfm**).

4.2 Potential hazards of invasive sampling

There are a number of hazards associated with undertaking invasive sampling or investigation at a site that must be considered before commencing any works, and a site-specific occupational health and safety plan should always be prepared and implemented.

Potential impacts with buried services, such as electricity, gas, telecommunications (including fibre optics), water or sewerage, can result in serious injury or death, may be very expensive to repair, and can also have considerable ongoing effects for other users of the service. Petroleum hydrocarbon sites often have additional risks associated with damage to UPSS and the potential for fire or explosion due to flammable vapours that may accumulate, particularly in low-lying and poorly ventilated areas. There is also the potential to mobilise contaminants during works, allowing them to migrate and contaminate deeper intervals. Contaminant exposure to investigation workers must also be considered.

Prior to any invasive sampling, detailed plans of buried utilities, tanks, lines, etc. should be sought from the site owner or occupier. A professional cable and pipe locater should also be utilised to reduce the risk of contacting buried infrastructure. The risk of fire or explosion should also be assessed, and will depend on the nature of the site and products that are used/stored there, whether it is currently active, and the nature of the required investigation work. If there is the potential for explosive vapours, then monitoring should be conducted and works should cease when concentrations approach the lower explosive limit. Appropriate investigation techniques, and due care during works, are required to ensure that contaminants are not mobilised to uncontaminated zones, and safe work practices and personal protective equipment must be adopted to prevent contaminant exposure to workers.

4.3 Desk-based studies

Information gained from desk-based studies forms an important component of a site characterisation, particularly in the initial portion of the work. In fact, for a Tier 1 site, sufficient information may be available from a desk study of existing data to enable a Tier 1 CSM to be developed. Existing Australian guidance (NEPC 1999) should be referred to, which provides details of site information that should be established in the desk study, including relevant information sources. More specifically for petroleum hydrocarbon sites, the following information should also be sought:

- previous investigation reports for the site (in addition to contamination studies, geotechnical reports or environmental audits may also have valuable information and data)
- location and history of hydrocarbon storage or transmission infrastructure
- product inventories and records of any spills or leaks
- buried service locations (which may act as preferential pathways).

4.4 LNAPL investigation methods

4.4.1 In-well thickness

Oil-water interface probe

The 'standard' approach to measuring the thickness of an LNAPL is to utilise an oil-water interface probe. These probes generally operate through use of infrared refraction to detect differences in conductivity between aqueous and hydrocarbon-based liquid layers in the well. The tip of the probe pairs an infrared light and sensor to detect the presence and conductivity of a liquid; based on the type of liquid detected the instrument will usually emit an audible tone and light. If the liquid is a non-conductive product the signals are usually steady, whereas if the liquid is conductive such as water an intermittent tone and light are produced. When used properly, an oil-water interface probe can accurately measure the observed thickness of most LNAPLs in a monitoring well or piezometer.

Care should be taken when utilising an oil-water interface probe to accurately measure the depth at which the oil-water interface is encountered. The probe should always be lowered slowly and steadily through the interface so as to not disturb the clear separation of the two layers

of liquid. As product can coat the probe tip temporarily, the interface depth should be measured whilst moving the probe tip from the water layer into the product layer in order to minimise inaccuracies. For example when measuring the thickness of an LNAPL, after measuring the depth of the top of the LNAPL layer, the probe should be lowered carefully through the LNAPL into the water until the tip is clear of all product (based on observed tone) and then pulled slowly upwards to measure the depth of the oil-water interface.

Indicator pastes

Product finding paste is another useful method to measure the thickness of LNAPL in a monitoring well. When these pastes come into contact with petroleum hydrocarbon products they undergo a colour change. Using this method requires the application of the paste to a weighted measuring tape, which is then lowered into the well a known distance and left in place for a few seconds before retrieval. Once the tape is retrieved, the thickness of the product can be read directly from the tape as the length that underwent a colour change.

Bailer

A clean bailer can be utilised as a qualitative tool to indicate the presence of product in a well. In this technique the bailer should be lowered slowly to just below the base of the product layer (based on the oil-water interface probe anticipated thickness) and then retrieved. Observed product in the bailer and sheen on the exterior can be utilised to indicate the presence of product. It should be noted that the use of a bailer will generally be inaccurate for assessing product thickness and a specific 'product' bailer with a wider aperture and lighter gravity ball should be used where possible.

In-well thickness and relationship to LNAPL in adjacent soil

The LNAPL thickness measured in a monitoring well (or 'apparent thickness') is rarely representative of the true thickness of LNAPL in the subsurface, and usually the apparent thickness is greater (up to several times greater) than the recoverable mobile LNAPL in the subsurface. This phenomenon is due to a number of factors but most typically is related to the type of lithology encountered and the location of the well screen. For examples of the lithologic conditions that can cause this inequality between the LNAPL thickness in the well and the adjacent soils see Figure 5.
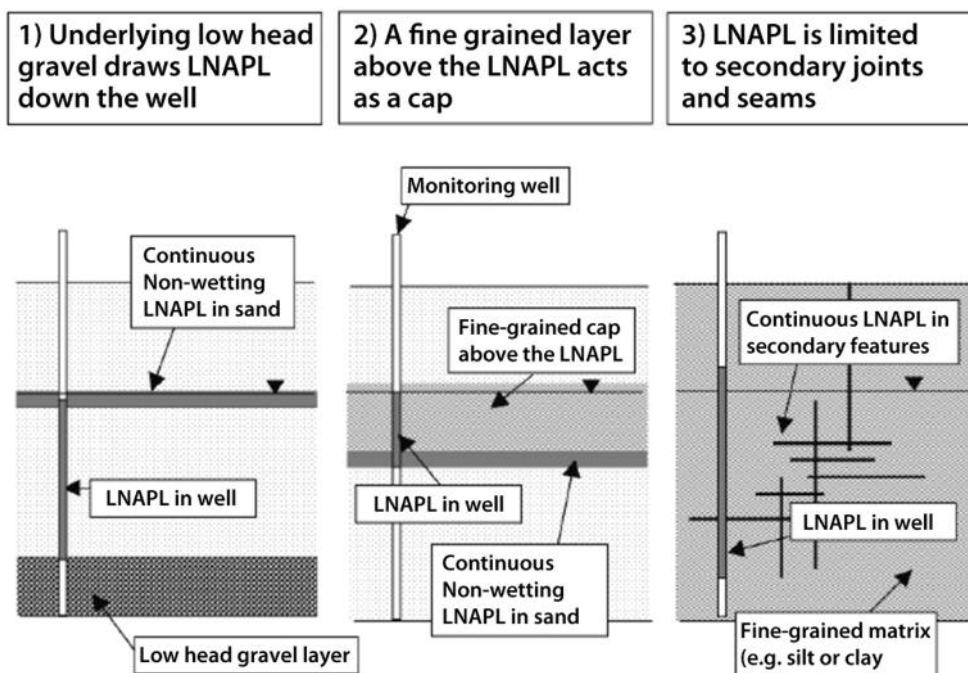
Figure 5. Conditions affecting LNAPL thickness in wells (API 2003)

In addition to these lithology factors such as layering of sediments or more porous media, other factors including LNAPL physical properties and water table fluctuations can affect the relationship between the volume of LNAPL that accumulates in a well and the LNAPL in the adjacent soil formation.

If a more specific estimation of LNAPL volume and mobility is required to evaluate LNAPL recoverability it is often necessary to conduct intact soil coring for petrochemical analysis (see Section 4.4.4), bail down tests or pumping tests (see Section 4.4.6).

In-well LNAPL thickness and relationship to groundwater elevation

LNAPL in a well will depress the groundwater, due to the weight of hydrocarbon, resulting in a need to correct the groundwater elevation for a more accurate representation of the equivalent piezometric surface. The correction is performed by multiplying the apparent LNAPL thickness measured in the well by the LNAPL's specific gravity, and adding the result to the LNAPL/water interface elevation. The LNAPL specific gravity can be determined based on literature values of the product type, or preferentially, based on laboratory results. However, caution should be applied when conducting such a correction as skewed results are possible. Therefore it is generally preferable

not to utilise groundwater elevations from wells that contain LNAPL.

4.4.2 Geophysical techniques

Geophysical techniques such as ground penetrating radar (GPR), electrical resistivity (or electrical impedance tomography [EIT]), and electromagnetic conductivity surveys are capable of detecting anomalies in the subsurface that may result from contamination such as an LNAPL. These techniques utilise the properties of the subsurface in a hydrocarbon plume such as high electrical resistivity and low relative permittivity[5] to define the contamination extent.

GPR is the most commonly used of the geophysical methods and is a good approach to define the extent of a product plume in soil or groundwater. In general, shallower plumes are more easily defined.

GPR surveys are typically conducted using a radar unit that is rolled across the site in a grid pattern recording data which is later interpreted by a computer to provide a two or three dimensional image of the results. Metal objects or subsurface features (pipes or utility corridors), and surface features close to or within the investigation area can cause noise on the measured signal; if these features are known or mapped they can be minimised during data interpretation.

[5] The material's ability to transmit or permit an electric field.

Heterogeneous changes in lithology or soil moisture can add complexity to the data evaluation. Similarly, GPR can sometimes detect a 'shadow' around an LNAPL plume that causes difficulty in interpretation of the data; this shadow is believed to be caused by the more conductive groundwater and degrading contaminants that surround the NAPL in a typical weathered plume.

Recent research has shown that in addition to characterising the lateral and vertical extent, GPR can provide information relating to the saturation, properties, and biodegradation of LNAPL by comparing the GPR signal attenuation with laboratory-based measurements of LNAPL properties (Cassidy 2007). However, this practice is not in common use.

Geophysical surveys should be conducted utilising a contractor experienced in both operating the survey equipment and interpreting the complex dataset. The survey should not be considered a stand-alone tool for site investigation and will require further sampling to determine specific contaminants and concentrations; however, the technique can be useful for large contaminated sites during the initial phases of investigation.

4.4.3 Laser-induced fluorescence (LIF)

LIF can be utilised to investigate LNAPL in the subsurface including both residual and mobile saturation levels.

The LIF equipment is typically contained in its own box and is temporarily mounted on either a direct push technology (DPT) or cone penetrometer testing (CPT) drilling rig. The LIF system consists of an ultraviolet (UV) or visible wavelength laser connected to a sapphire window mounted on the side of the DPT/CPT probe tip. Depending on the type of LIF system selected (for example: ROST™, UVOST®, TarGOST®) the LIF laser will transmit light to the window through a fibre optic cable, typically with an adjustable excitation wavelength. The laser light passes through the sapphire window and is absorbed by the petroleum product's PAH in contact with the window as the probe is advanced. This addition of energy to the PAH causes them to fluoresce; the fluorescence emitted from any encountered aromatic component returning through the sapphire window is sent through a second fibre optic cable to a detection system. The emission data resulting from the pulsed laser light is typically averaged and recorded continuously as the probe is advanced.

All commercially available LIF systems are operated to detect emitted fluorescence at multiple wavelengths, giving LIF the ability to distinguish the characteristics of different types of product. Generally, lighter (two to three ring PAH) petroleum products will emit fluorescence at shorter wavelengths and heavier four to six ring PAHs products (or more weathered older products) will emit fluorescence at longer wavelengths. Though usually, interpretations of product type will be made after comparing field data with relative percentage ratios generated by known product samples. Thus, operating LIF to detect fluorescence at multiple wavelengths both enhances the detection capabilities for LIF to detect a wide range of product types and it provides an ability to distinguish between different types of LNAPL or plumes of different fuels or detect false positives such as sea shells. The UV LIF systems (ROST and UVOST) are appropriate for light fuels up to mid-range oils, but often fail to adequately respond to heavy fuel oil, heavy crudes, coal tars, and creosotes. Visible wavelength systems, such as TarGOST, behave oppositely, detecting heavy fuel oil, heavy crudes, coal tars, and creosotes but do not respond to light fuels such as petrol and kerosene (jet fuels). It is critical to understand the difference. LIF vendors will usually test the product free of charge to ensure the appropriate wavelength LIF technology is applied.

LIF emission data is reported continuously as a total of the fluorescence intensity (as measured relative to a standard reference emitter) recorded at all wavelengths from polycyclic aromatic hydrocarbons and is typically presented as a graph of fluorescence intensity versus depth. For example, see Figure 6, where increased fluorescence (higher %Reference Emitter [%RE]), as illustrated in the first plot at seven feet and between 10 and 12 feet, indicates contamination. The 'Callouts' on the left of the figure show the wave forms of the fluorescence, which indicate the contaminant type. The electrical conductivity (EC) is also measured by a separate sensor in the LIF tool, as shown in the second plot, which allows an understanding of lithologies and likely locations where LNAPL will reside (similar to the use of EC with MIP, described in Section 4.5.3).

It should be noted that the total fluorescence intensity recorded may not correlate directly with the percent saturation of LNAPL in the subsurface. As the fluorescence intensity varies greatly depending on the type of LNAPL detected and site-specific lithologic conditions, interpretation of the extent of residual phase or mobile
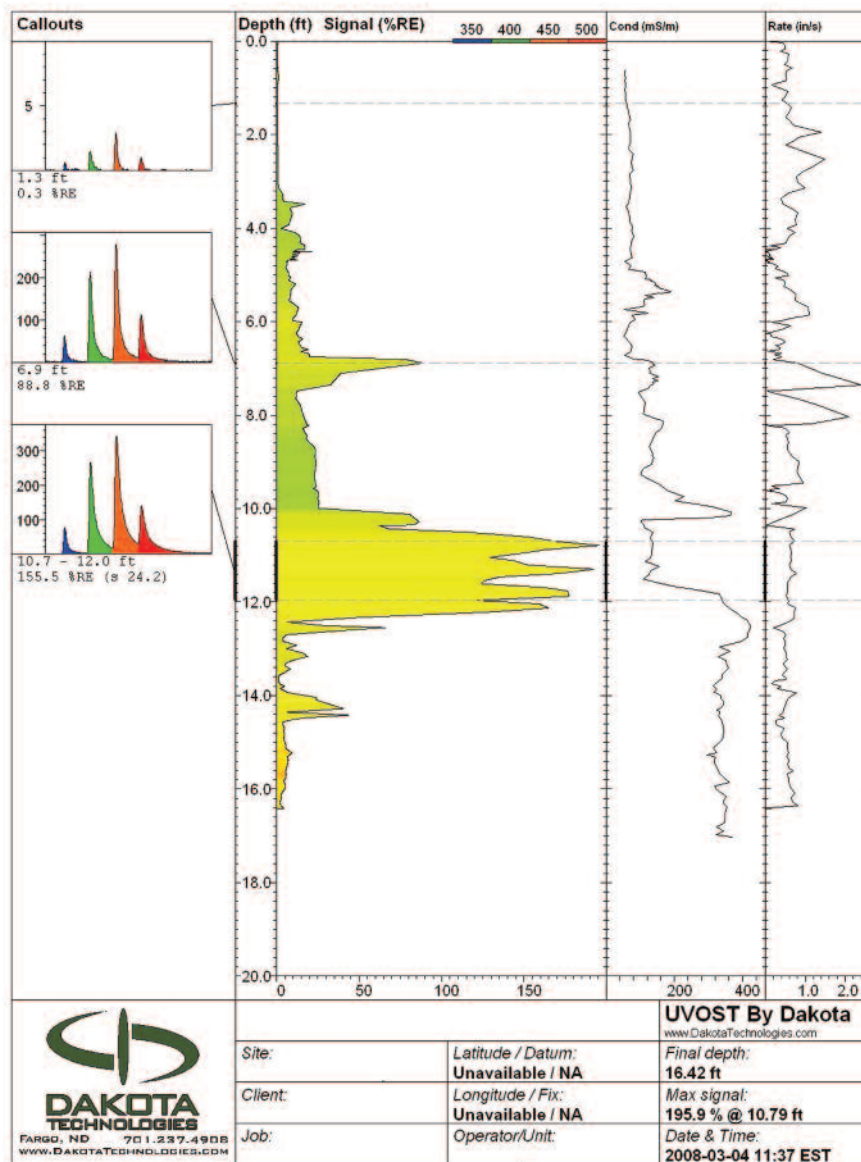
Figure 6. Example LIF fluorescence and EC versus depth plots

LNAPL is difficult based on LIF data alone. In order to utilise LIF data to make this determination, intact soil coring and/or other LNAPL or soil sampling techniques should be employed to enable calibration of the site-specific LIF data to characteristics such as LNAPL saturation and mobility and specific LNAPL types as indicated through LNAPL fingerprinting.

LIF is typically utilised in the field with an adaptive sampling approach, or in other words, the investigation typically proceeds in a step-approach with the location and depth of each subsequent boring being determined in the field based on the interpretation of the preceding borings *in-situ* LIF data.

One or more background LIF borings will typically be advanced up-gradient of each investigation area in order to determine the background LIF response. If possible, a LIF boring will usually be advanced adjacent to a well where LNAPL has been measured. This boring will be utilised to calibrate the LIF response to the product observed in the well. Additionally, if a sample of product recovered from the site is available, the product (or better yet, product saturated site soil) can be placed on the LIF probe window and the response used as an indicator of the fluorescence intensity associated with the specific type of fuel at the highest possible saturation level.

LIF data is typically validated with soil sampling to determine LNAPL properties and analytical concentrations at a few locations throughout the LIF investigation area. The analytical data and LNAPL data is then utilised together with the LIF data to develop a complete CSM for the investigation area.

With multiple boring locations and the use of data interpolation and visualisation, LIF data can enable a three-dimensional (3D) depiction of LNAPL source areas in the subsurface – in both the vadose and saturated zones (see Appendix B for information, including an example, on 3D site depictions using LIF data).

4.4.4 Intact soil coring

Intact soil coring, or the collection of undisturbed soil cores, can be a useful component in an LNAPL investigation in order to collect critical petrochemical information such as those described in Sections 4.11.4 and 4.11.5 (though not all these parameters require an *intact* soil core).

Intact soil coring would typically be conducted as one component of either a site investigation or a pre-design study for remediation implementation. It is conducted by advancing a thin-walled metal tube or Shelby tube into the boring by direct push or hammer in order to reduce sampling disturbance and increase sample recovery. Shelby tubes can vary in size and depend on the sample quantity necessary and drilling method selected. Split-spoon samplers fitted with clear acetate sleeve liners may also be used to collect soil core samples. The tube containing the sample is typically quickly packed tight, capped, labelled, and frozen on dry ice maintaining the sample in its relatively undisturbed state.

4.4.5 Soil gas sampling as a surrogate

Soil gas sampling can be utilised as a surrogate tool to LNAPL delineation as part of a tiered or comprehensive site investigation. As some soil gas sampling (see passive methods, Section 4.6) can be relatively inexpensive to collect a large number of samples on a grid basis compared with other investigation methods, and are less intrusive, soil gas sampling can be used as a screening or first phase of an investigation to identify source areas and hot spots.

Soil gas sampling as a surrogate is generally only performed at shallow depths (less than 1.5 m) and the most typical sampling is done via passive methods.

Depending on site lithology, depth to LNAPL source area, contaminant properties (volatility), and transport, this technique may have limited applicability to the site. Therefore, any information that helps estimate the efficacy of soil gas sampling prior to sample planning is of benefit.

4.4.6 LNAPL recoverability tests

Where characterisation works are required to provide specific information on potential LNAPL mobility and recoverability (typically where information is required to make remedial decisions), bail down or pumping tests can be conducted to allow the effective LNAPL conductivity and transmissivity to be calculated. The use of LNAPL recoverability testing is a relatively new concept, though it is based on established hydrogeological testing techniques (API 2004). By measuring the recovery or displacement of product after pumping, bailing or withdrawal of a slug the required parameters can be calculated.

API (2004) includes protocols for recoverability tests, by Lundy (2002) and Beckett and Lyverse (2002), which provide somewhat differing approaches and should be reviewed to determine the appropriate methods for specific sites. It is important to note that data gained from these tests is only indicative of product draining to a well due to hydraulic gradient in that locality. This does not necessarily indicate similar conditions for LNAPL mobility on a regional scale (Beckett & Lyverse 2002).

4.4.7 LNAPL investigation methods comparison

The various LNAPL investigation methods that have been discussed in this section are presented in Table 4 along with advantages/applicability and disadvantages/limitations of the techniques. It should be noted that the information presented herein is a summary comparison of the methods, the preceding sections should be referred to for full detail on the techniques and their applicability.

4.4.8 LNAPL sampling and analysis QA/QC

Standard operating procedures (SOPs) for all sampling and investigation methods should be developed. Well prepared and implemented SOPs ensure the consistency of a particular activity independent of the personnel involved.

When using an oil-water interface probe, the probe tip should be kept clean and checked frequently for a haze or scratches on the prism as these defects could cause the probe to not read properly.

For intact soil coring, correct sample handling procedures are important. Where analysis of fluid properties is required, soil cores are typically frozen in the field to preserve volatile and semi-volatile hydrocarbons during transport, and prevent fluids migrating into different portions of the core. Freezing of the soil core should occur using either liquid nitrogen or dry ice.

Where LIF tools are utilised, QA/QC procedures should be run at the beginning and end of each day to ensure accurate measurements are being made; this should include checks using a standard reference emitter solution to measure reflectance and proper laser strength. Prior to logging each LIF location, performance tests should be conducted to evaluate the sensitivity of the probe, trunk line, and detector suite to be used.

Table 4. Comparison of LNAPL investigation techniques

Technique	Advantages/applicability	Disadvantages/limitations
In-well thickness measurements		
Oil-water interface probe	Good accuracy (+/- 1 mm), simple to operate.	Product can coat probe and give erroneous readings. Should be repeated three times to confirm result.
Indicator pastes	Good accuracy (+/- 1 mm), simple to use, does not rely on equipment that may malfunction.	Pre-measurement required to know where to target paste. Can be messy and therefore best suited to measuring smaller thicknesses.
Bailers	Allow product to be viewed. Simple to use. Best suited to larger thicknesses and qualitative use.	Lower accuracy and specific product bailers required. Usually underestimate thickness, especially for smaller layers.
Other LNAPL investigation methods		
Geophysical techniques	Allow the extent of product to be established quickly without intrusive investigation. Useful for large sites in early stages of investigation.	Work best for shallower plumes. Surface and underground features, especially metal, can cause interference. Experienced operators should conduct the survey and interpret data. Is not a substitute for intrusive investigations.
LIF	Provides 'real-time' data that can be interpreted in the field to guide the next investigation location. Capable of achieving up to 100 m of vertical assessment in a day. Provides vertical spatial resolution of almost 2 cm, allowing small zones of contamination to be delineated. Allows a 3D depiction of the LNAPL plume extent.	The correct system (ROST, UVOST, TarGOST etc) must be selected for the type of product to be investigated. Data requires interpretation by experienced operators/ technologists – who may not be currently available in Australia due to the technique's limited use to date here. Requires calibration and validation with actual soil sampling results. Minerals such as calcite and naturally occurring organic matter can fluoresce, which may cause interference problems.
Intact soil coring	Testing of collected cores provides accurate data on LNAPL properties. Generally used only in higher tier investigations.	Collection and analysis of cores can be expensive and requires specialist laboratory.
Soil gas sampling as a surrogate	Relatively inexpensive method of screening a large area for potential LNAPL.	Application can be limited depending on site geology and nature of the LNAPL (i.e. not applicable to less volatile products).
Recoverability tests	Generally only required for higher tier investigations and remedial planning.	Not indicative of LNAPL mobility on a regional scale, only applicable to area around well where tests were conducted.

4.5 Soil investigation and sampling methods

Investigation and sampling methods for soils are provided herein. The methods discussed are those considered to be most useful in characterising soil at petroleum hydrocarbon-impacted sites. It is noted that other methods, such as test pit sampling, may be appropriate depending on target contaminants and site conditions (for example, where semi-volatile hydrocarbons are the contaminant of concern). However, some methods, such as sampling directly from a drill auger, are not appropriate and should not be used. Soil sampling information provided in AS4482.1 (1997) and AS4482.2 (1999) should also be referred to, which includes further detail on methods for logging soils and sampling requirements for volatile contaminants.

4.5.1 Coring

Soil coring should be utilised as the primary method of collecting soil samples for inspection and analysis. Under this method a hollow rod is driven into the ground to collect a relatively undisturbed core of soil. DPT and sonic drilling methods are the preferred techniques for collecting a soil core. It is noted that an auger and split-spoon technique may be all that is available or practicable in some situations, and while this is not preferable, it can still be effective provided appropriate QA/QC protocols are followed. Use of DPT for core sampling (also known as 'geoprobe' or 'push-tube' sampling) allows a core of soil to be collected, typically inside a disposable plastic liner, as the rod is advanced by pushing and/or vibrating. There are two main methods of soil coring using DPT: single-rod systems, where the sampling tool is advanced via one string of rods that must be removed from the hole after each sample is collected; and cased or dual-tube systems, where an outer casing remains in the hole as the inner rod is advanced and retrieved. Single-rod systems are typically more efficient at shallow depths, though cased systems prevent hole collapse and allow the installation of monitoring wells. Soil coring using DPT is generally limited to depths of approximately 30 m, and may also encounter difficulty in coarse soils (gravel and cobbles). Further discussion of DPT soil coring systems can be found in US EPA (1997).

> *Expedited Site Assessment Tools For Underground Storage Tank Sites: A Guide for Regulators* **(US EPA 1997)**
>
> This document provides further detail on a number of investigation technologies that are referred to in these guidelines, including DPT, CPT and geophysics. It can be downloaded for free at **www.epa.gov/swerust1/pubs/sam.htm**.

Once soil cores have been obtained, grab samples of specific depth intervals can then be sub-sampled from the core, or an entire core (or section of core) can be left in its liner, and preserved for subsequent laboratory analysis. Grab samples from the cores are typically used for chemical analysis to assess petroleum hydrocarbon concentrations at specific depths, whereas the intact cores may be analysed for soil physical properties to allow product mobility assessment (though the use of cores for chemical analysis should also be considered, as discussed in Section 4.5.5).

Rock-coring may also be required at sites where contamination is known or suspected to have infiltrated into consolidated materials. The collected cores can then be assessed for details of site geology and nature of fractures (density, orientation, location, character), and cores can be lab analysed for the rock matrix properties.

4.5.2 Cone penetrometer testing (CPT)

CPT is an *in-situ* form of DPT where sensors are mounted in a cone at the tip of the rods. As the cone is advanced the sensors measure the response of the soil to the force of the advancing cone and the data is fed into an onboard computer which interprets the soil stratigraphy. The technology was first developed for geotechnical purposes to measure soil stratigraphy, with sensors measuring resistance to the tip of the cone and the sleeve of the cone allowing the soil type to be interpreted. A range of additional sensors may be used with CPT, and they can often be used to measure multiple parameters simultaneously (or multiple cones may be interchanged during a single penetration using a wireline). These include pressure head transducers, allowing permeability and hydraulic conductivity assessment, conductivity probes that allow soil types and saturation zones to be estimated, nuclear and pH probes. CPT is a useful tool for providing rapid, continuous profiles of subsurface stratigraphy and can save considerable time and money, particularly at large sites with complex geology. However, CPT results require

verification with some soil coring, to calibrate the results and also to assess potential secondary soil features, such as cracks and fractures, which may significantly influence contaminant movement (US EPA 1997).

4.5.3 Membrane interface probe (MIP)

MIP technology can be utilised to investigate soil, soil vapour, and groundwater contamination in the subsurface and is an *in-situ* technique to measure volatile organic compounds (VOCs).

The MIP tool can detect the presence of VOC contamination using three detectors: an electron capture detector (ECD), photo-ionisation detector (PID), and flame ionisation detector (FID) for measurement of a wide range of VOCs. The following contaminants typically can be detected:

- straight-chained hydrocarbons (best detector is FID)
- aromatic hydrocarbons (best detector is PID)
- chlorinated hydrocarbons (best detector is ECD).

The MIP tool (see Figure 7) consists of a heated probe equipped with a semi-permeable membrane that is advanced using either a DPT or CPT drilling rig. Subsurface volatile organic contaminants diffuse across the membrane and enter into a carrier gas within the probe. The probe is heated to accelerate diffusion of contaminants across the membrane. The carrier gas sweeping behind the membrane transports the contaminants through a trunk line and to the gas-phase detectors at the ground surface for measurement. The detectors are part of a gas chromatography (GC) mobile laboratory which is typically housed in a separate vehicle to the drilling rig.

The MIP tool is usually equipped with a sensor to measure the electrical conductivity (EC) of the subsurface and can be used to discern changes in soil lithology. The EC probe uses a dipole arrangement at the tip of the MIP probe so that both conductivity and MIP detector readings can be obtained simultaneously. This enables increased understanding of the location of contaminant mass that is typically encountered trapped in finer-grained sediment layers.

The rate of MIP advancement is dependent upon the geology and presence and magnitude of contamination. To obtain an accurate *in-situ* VOC measurement, the MIP probe must remain at the depth interval for a minimum amount of time equal to the travel time of the carrier gas from the down hole membrane to the analytical detectors in the above ground mobile 'lab' (typically in the order
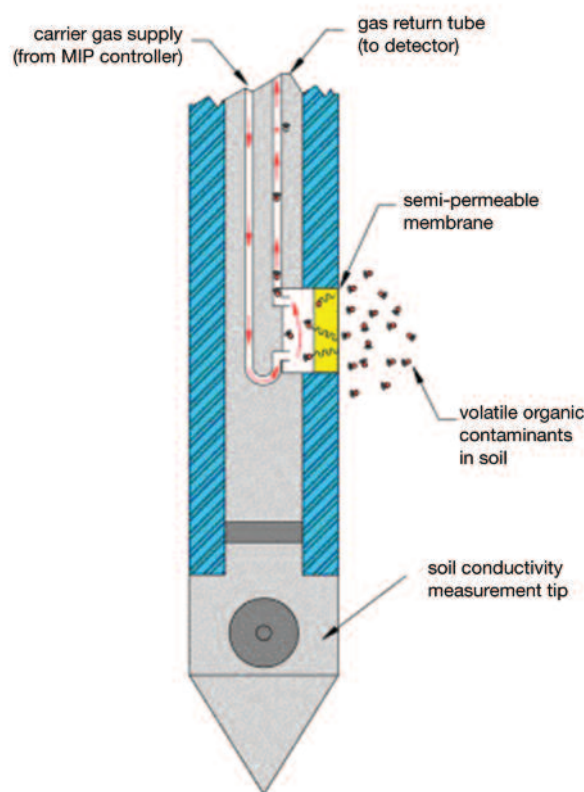
Figure 7. Schematic of MIP tool fitted with conductivity probe (US EPA 2008)

of one minute). Expediting the MIP survey includes increasing the length of the advancement intervals and focusing 'stops' only within known or suspected contaminated zones.

MIP data (ECD, PID, FID, probe temperature, EC, and probing speed versus depth) are recorded simultaneously and can be utilised together to interpret information about each borehole. Generally the detector response is recorded as a voltage and based on a calibration run of a known standard through the GC, the voltage can be equated to a relative concentration of the standard – this process enables an estimation of contaminant concentrations observed in the borehole but should not be used as a quantitative measure.

MIP is typically utilised in the field with an adaptive sampling approach, or in other words, the investigation typically proceeds in a step-approach with the location and depth of each subsequent boring being determined in the field based on the interpretation of the preceding borings *in-situ* MIP data.

One or more background MIP borings will typically be advanced up-gradient of each investigation area in order to determine the background MIP response. MIP borings

are usually located outside LNAPL source areas because the high response in these areas will flood detectors and the rate of MIP boring advancement will slow significantly. For sites containing LNAPL, MIP is typically used for the dissolved-phase groundwater and soil vapour plumes, while LIF is used to delineate the LNAPL-containing zone.

MIP data is typically validated with soil and groundwater sampling to determine analytical concentrations of specific contaminants at a few locations throughout the investigation area. The analytical data is then utilised together with the MIP data to extrapolate a better understanding of concentration and constituents observed throughout the investigation area to develop a complete CSM.

4.5.4 Composite sampling approaches

Composite soil sampling is considered to be inappropriate for the majority of petroleum hydrocarbon site characterisations. This is due to the volatile nature of many petroleum hydrocarbons, in addition to the inherent uncertainties in the data achieved from composite samples, meaning results are unsuitable for detailed assessment. In circumstances where the product released at a site is known to have low volatility (such as heavy oils, motor and heating oil) composite sampling may be adopted as a low cost method of achieving data of low quality, i.e. for broad contamination distribution information. In some cases, composite sampling may actually provide a more realistic overview of contaminant distribution (see Section 4.5.5). However, where data objectives require detailed information for risk assessment or remedial design then composite sampling will generally not be appropriate. Appendix B of AS4482.1 (1997) should be referred to for appropriate soil compositing techniques.

4.5.5 Macro-sample collection

As discussed in Section 4.5.1, samples collected for chemical analysis are typically small volume grab samples, or 'micro-samples'. However, this approach is not always appropriate, and the soil sample size must be considered against the proposed data use. For example, when seeking data representative of a bulk formation to allow mass estimates for remedial design, collecting small jars of soil from which a lab takes much smaller sub-samples, would not be appropriate. This approach may result in large variations in analytical results, depending on what the micro-sample included (e.g. if a crack or root hole acting as a product pathway is included in the

sample). Macro-size samples may be better than typical small grab samples to obtain an analytical extraction from a sample that contains the breadth of soil types present at a particular sample location. This approach can save time and money by not having to characterise to the micro-scale. Macro-samples can be collected by soil coring, larger in diameter if possible, and submitting cores to the laboratory whole. If the contaminant of concern is not volatile, then composite sampling is another valid method for collecting macro-samples.

The ability of laboratories to deal with macro-samples and extract from the whole sample is a potential limitation to this method, and discussions should be held with the project laboratory before sampling.

4.5.6 Soil investigation methods comparison

The various soil investigation methods that have been discussed in this section are presented in Table 5 along with advantages/applicability and disadvantages/limitations of the techniques. It should be noted that the information presented herein is a summary comparison of the methods, the preceding sections should be referred to for full detail on the techniques and their applicability.

4.5.7 Soil sampling and analysis QA/QC

QA/QC associated with soil sampling methods is discussed in detail in AS 4482.1 (1997), AS 4482.2 (1999) and NEPC (1999), including equipment decontamination, sample handling and QC sampling. SOPs should also be developed and implemented for each soil investigation activity to ensure consistency of approach.

QA/QC requirements for 'real-time' methods, such as CPT and MIP are not defined in current guidance. Protocols for these systems should be developed that are customised to the site-specific needs and data objectives of a project. At the beginning and end of each day, QA/QC procedures should be run on the MIP tools to ensure accurate measurements are being made; this should include checks using an appropriate reference standard solution to measure trip time through the trunk line and detector response to ensure proper system operation. Prior to logging each MIP location, performance tests with specific compounds will be conducted to evaluate the sensitivity of the probe, trunk line, and detector suite to be used. An appropriate reference standard solution should be used to test each detector

Table 5. Comparison of soil investigation techniques

Technique	Advantages/applicability	Disadvantages/limitations
Coring	Methods are generally well established in Australia, with equipment readily available. Provides cores that can be inspected and logged, and sampled for lab analysis, giving accurate information.	Does not provide 'real-time' data (other than inspection of collected cores). Laboratory testing can be expensive and can take several days.
CPT	Provides rapid continuous profile of subsurface stratigraphy.	Results require verification with some soil coring, to calibrate the results and also to assess potential secondary soil features. Not suitable for consolidated formations.
MIP	Provides 'real-time' data that can be interpreted in the field to guide the next investigation location. Best suited to dissolved and vapour plumes, where LNAPL is present then LIF would be the preferred method.	Data requires interpretation by experienced operators/ technologists – who may not be currently available in Australia due to the technique's limited use to date here. Requires calibration and validation with actual soil sampling results. Not suitable for consolidated formations.
Composite sampling	Lower cost method of collecting and analysing soil samples to provide broad contamination distribution information.	Not suitable for volatile hydrocarbons. Not suitable where detailed information for risk assessment or remediation is required.
Macro-sample collection	Useful when information on contamination in a bulk formation is required, such as for mass estimates for remedial design. Reduces potential variations in results due to 'micro' features, such as cracks or root holes.	Not widely utilised in Australia, and there may be limitations on laboratories that are able to handle the samples appropriately.

and establish the required time for vapour transport in the trunk lines. The response of the detectors can be compared to predetermined values and recorded to ensure adequate sensor performance.

4.6 Soil vapour investigation methods

4.6.1 Passive methods

Passive soil vapour methods consist of the burial of an adsorbent module in the ground, usually between 0.5 to 1.5 m below ground surface, with subsequent retrieval and laboratory analysis of the desorbed contaminants. Modules are typically deployed for between five days and two weeks, though the duration should be based on the anticipated concentrations and type of module; at locations where high concentrations are encountered the module should be deployed for a shorter duration. The

adsorbent module is generally capable of detecting a broad range of VOCs and semi-volatile organic compounds (SVOCs). Passive soil gas sampling will capture soil gas regardless of the source media – LNAPL, soil, or groundwater. Therefore, follow-on sampling to further refine the CSM with contaminant mass fractions is necessary.

Passive soil gas sampling is able to detect contaminants that migrate into the sorbent through diffusion or the 'spreading out' of volatile and semi-volatile vapour constituents from areas of high concentration to areas of low concentration. Therefore, passive soil gas sampling is not affected by processes involving the movement of contaminants in the subsurface such as advection when contaminants are transported through the most permeable zones. On sites where some of the contaminants are in diffusion-limited zones (zones of high moisture, high organic content, or suppressed permeability), passive soil gas sampling will likely provide a more comprehensive screening of the total mass distribution than active methods.

As the volume of vapour that is in contact with the sorbent is unknown, passive soil gas sampling cannot be utilised as a quantitative investigation method to determine concentrations of contaminants in soil vapour – it is only an indicator of mass of contaminants in the subsurface. Therefore, passive soil gas sampling is utilised as a screening tool to investigate a wide area of a site and determine the areas of higher mass of contaminants.

There are several different vendors of passive soil gas sampling modules on the market and varying attributes are associated with each brand. Some types of passive sampling modules (GORE™ Module) are encased in a sheath that is micro porous and hydrophobic enabling soil vapour to diffuse through, but water in liquid form is prevented from entering, thus, these modules can be deployed in areas of high soil moisture, or below the water table, without risking the saturation of the sorbent with water. Other types of passive sampling modules may not have the water protective sheath, but do claim to have superior detection of soil gas plumes through the timing of their modules' placement and have been shown through studies to correlate to the groundwater plume (EMFLUX®).

Passive soil sampling typically is employed as a screening tool at a site so a large number of samples are collected over a wide area. The density of samples should be determined to appropriately identify hotspots, or should be sufficiently dense to identify potential zones of higher mass of contaminants. Passive soil sampling would typically be implemented only once at a site as part of an initial phase of investigation.

4.6.2 Active methods

Active soil vapour methods consist of the withdrawal of the soil vapour from the subsurface and subsequent analysis of the vapour, resulting in mass/volume concentration data. Active soil vapour data can be collected and measured in real-time, enabling decisions to be made in the field (i.e. MIP or on-site lab), or may be collected in containers which are transported to the laboratory for analysis; either way, unlike passive methods, samples can usually be collected in one mobilisation to the site.

Active soil gas sampling is an advection-based method (in comparison to the diffusion-based passive methods) and will preferentially pull the sample volume from portions of the subsurface associated with the greatest potential flow. The accuracy of the results is dependent on the integrity of the soil gas collection system. If the sampling probe or tubing is installed poorly, it could result in a leak or 'short circuit' and it is possible that a sample of surface air could be collected instead of soil gas.

The objectives of an active soil gas investigation should be clearly defined prior to sampling as techniques can vary widely dependent on the type of information required. Note that if a vapour intrusion evaluation (to indoor air) is to be performed additional considerations are required that are not discussed in this guidance. It is recommended that the reader refer to ITRC (2007a) and API (2005) for guidance in this regard.

Vapour Intrusion Pathway: A Practical Guideline **(ITRC 2007a)**

A 'how-to' guideline on assessing vapour intrusion that also provides an overview of relevant information in addition to tools to complete an assessment. There is also a useful companion document *Investigative Approaches for Typical Scenarios*, which provides worked examples for six different scenarios, including an active service station. It can be downloaded for free at **www.itrcweb.org/Documents/VI-1.pdf**.

Collecting and Interpreting Soil Gas Samples from the Vadose Zone **(API 2005)**

This API guidance is targeted towards the collection of data to assess the significance of the subsurface-vapour to indoor-air migration pathway, specifically for petroleum hydrocarbon contamination.

Sampling techniques

Active soil gas samples are collected either through the installation of temporary or permanent probes:

Permanent probes are typically installed either through use of a hand auger or a DPT rig, and similar to a monitoring well, utilises a screen at the desired depth connected to the sample tubing and the borehole is sealed with bentonite. The screen usually consists of a short length (up to 20 cm) of stainless steel mesh tube. The sample tubing usually consists of a length of flexible tubing typically less than 50 mm in diameter.

Temporary probes are typically installed using hollow probe rods, equipped with either a retractable or disposable sampling tip, that are driven into the ground with a DPT rig or through use of a manual slide or electric hammer (see Figure 8). The design of the sampling system allows the sample tubing to be attached after pushing the probe rod into the ground. Once the target depth is achieved the probe rod is retracted exposing the open end of the sample tubing.
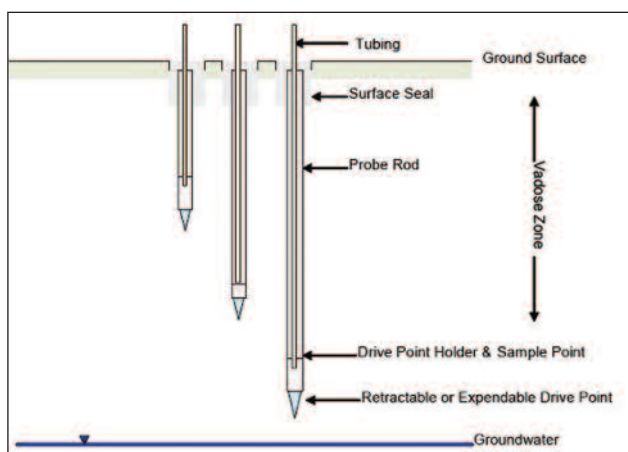
Figure 8. DPT temporary soil gas probe installation (modified from API 2005)

Regardless of the type of probe installation it is important that the sample tubing is set at the appropriate depth and the probe/tubing is well sealed to prevent leaks of surface air. Leak checks can be performed in the field to ensure the probe is properly sealed and may utilise the use of a leak check compound. Typically helium and a portable helium detector are utilised to perform the leak check which involves filling an enclosure surrounding the probe and the probe interface with the ground surface with helium, purging the sample tubing for a specified timeframe, and analysing the purged air for traces of helium. If helium is detected it typically indicates a poor seal and the probe should be reinstalled prior to sampling.

The rate of sample collection is also important in active soil gas sampling. Soil gas samples that are collected quickly, especially when a vacuum pump is utilised, may enhance the volatilisation of contaminants from media such as LNAPL resulting in contaminant concentrations that are inaccurately skewed high. The goal of sampling should be to collect the sample as slow as feasible (typically 150–200 mL/min) within a reasonable timeframe and the tolerance of the flow gauge or regulator; this will assist in minimising the potential for leakage or excess volatilisation of contaminants.

Samples are collected in various containers including: Summa® canisters, synthetic or Tedlar™ bags, or adsorbent material. For the constituents of concern at the site, it is necessary that an appropriate sample container is selected in order to meet the analytical detection limits, sample volume, storage and shipping requirements for the sampling program.

As an alternative to sample collection for later analysis, a mobile laboratory can be an affordable mechanism to analyse a large number of samples on-site with real-time data. Another *in-situ* technology for soil gas investigation is MIP (as explained in Section 4.5.3) which will detect volatile organic constituents from the subsurface regardless of their source (soil gas, groundwater, or LNAPL).

Active soil sampling typically is utilised as a finite investigation method after source areas, or the potential for vapour intrusion of contaminants into a building, have been identified. Therefore, the density of samples should be sufficiently dense to account for the variability in the subsurface lithology (and thus soil vapour transport) and preferential flow pathways over the area under evaluation. As soil vapour concentrations can be influenced by seasonal conditions, soil vapour samples should be collected on a routine frequency at contaminated sites to account for this variability.

In some cases it can be beneficial to understand the rate of contaminants diffusing to the ground surface; a flux chamber or flux hood can be utilised to determine the rate (or flux) of contaminants from the surface. The flux chamber is typically a domed chamber installed over the ground surface with a tight seal at the edges. Through tubes in the top of the chamber, clean air or nitrogen is blown into the chamber at a set flow rate, mixes inside the chamber, and air is vented out through a different tube in the chamber into the sampling container (Summa® canister, Tedlar™ bag, etc.). Following sample analysis, the flux to the ground surface can be determined quantitatively as a unit of mass (of contaminants) per unit of surface area per unit of time. Mass flux can be a useful tool to risk assessors evaluating the degree of risk posed from contaminants in soil vapour in the subsurface as it provides an indication of the rate of vapour intrusion into buildings, or the availability of contaminants at the point of exposure (above ground), without relying solely on ambient air data.

4.6.3 Soil vapour investigation methods comparison

Soil vapour investigation methods that have been discussed in this section are presented in Table 6 along with advantages/applicability and disadvantages/limitations of the techniques. It should be noted that the information presented herein is a summary comparison of the methods, the preceding sections should be referred to for detail on the techniques and their applicability.

Table 6. Comparison of soil vapour investigation techniques

Technique	Applicability/advantages	Limitations/disadvantages
Passive methods (passive sampling modules)	A screening tool to investigate a large site or wide area and identify concentrated zones for further investigation. Captures soil vapour regardless of source media (LNAPL, soil, or groundwater). Easy to use/install.	Not a quantitative investigation method and cannot be utilised to determine concentrations of vapours; provides indication of mass of contaminants. Not necessarily cheaper than active methods, but easier to install and can provide a larger coverage area.
Active soil gas sampling	Provides contaminant concentration data (mass/volume). May be collected in real-time dependent on the equipment used.	Sampling technique is more complex than passive and requires specialised equipment and experienced personnel to obtain accurate data.
Flux chamber or flux hood	A type of active sampling that enables the flux of contaminants from the surface to be measured.	Difficulties may be encountered in placing the devices in the most critical locations.

4.6.4 Soil vapour sampling and analysis QA/QC

SOPs should be developed for both passive and active soil gas sampling, so that approaches are consistent and sampling results are therefore comparable over time.

As passive soil gas sampling does not enable a real-time check of the method, QA/QC should include the analysis of method (or equipment) and trip blanks in order to verify the detected contaminants are not associated with another source or the module itself.

For active methods, important field QA/QC considerations include checking for, and minimising, leaks and using an appropriate sampling rate, as discussed above.

Laboratories should be carefully selected for vapour analyses, and they must be able to demonstrate suitable experience and/or qualifications to conduct the work, and appropriate laboratory QA/QC procedures. Pre-consultation will be required to determine appropriate sampling methods and containers and this should be formalised in the specific SOP for the sampling.

4.7 Groundwater investigation methods

Groundwater investigation and sampling methods are described herein. The methods provided include the provision for vertical delineation of contaminant concentrations in groundwater, which is important in adequately characterising a site. The location and number of groundwater investigation points will vary from site to site, depending on a variety of factors. However, the groundwater investigation should generally provide information on groundwater conditions hydraulically up-gradient and down-gradient of known or potential contamination sources. NSW EPA (1994) provides guidance on minimum groundwater investigation requirements at a typical service station site.

4.7.1 Monitoring wells

Groundwater monitoring wells are the primary means of obtaining representative groundwater samples at a fixed location over time, and they can also be used for assessing the groundwater flow regime. Monitoring wells in Australia have traditionally been installed using drilling methods similar to those used for water resource wells. When installing groundwater monitoring wells, guidance provided by the Land and Water Biodiversity Committee (2003) and in AS 5667.11 (1998) should be referred to. There is also an increasing awareness of the importance of screen length and placement (EPA Victoria 2000), and new installation methods are becoming available.

Groundwater Sampling Guidelines (EPA Victoria 2000)

Provides information on the installation of semi-permanent monitoring wells, including drilling techniques, installation and bore development, and also notes the importance of screen intervals being short and targeted to a zone of interest. Available for free download from: **www.epa.vic.gov.au/Publications/default.asp**.

Multiple wells, or wells with multiple screen intervals (discussed below) may be required to adequately characterise the vertical groundwater profile and contaminant distribution. The placement of the well screen must also be outside LNAPL areas, so that samples are representative of dissolved contamination concentrations. Where wells are screened in the smear zone, even samples that do not show evidence of LNAPL, such as a sheen, have been shown to be biased by non-dissolved contamination (Nemo 2006).

Multiple screen levels may be required to allow vertical characterisation of discrete groundwater zones and/or to prevent dilution and mixing in a longer screen well. There are several methods available for screening multiple depths, including installing multiple wells in a small area; nesting multiple wells in the same borehole; and using a pre-fabricated bundle of multi-level wells. There are cost and technical considerations with each approach. Multiple wells will typically be more expensive, but will provide confidence in results between each well and expertise is readily available. Nested wells are cheaper to install, though there are sometimes concerns that annular seals between screens are not properly installed, which may lead to cross contamination. Bundled multi-level wells (consisting of multiple small diameter tubes in a bundle) have not been widely adopted in Australia, but can provide confidence in samples at a relatively low cost, though sampling and hydrogeological assessment options in the wells are limited.

The installation of wells using DPT methods can present a rapid and cost effective approach, particularly in sandy soils. Installation of wells with this method involves either an 'exposed screen' or 'protected screen', depending on whether the well is driven directly into the ground or if a casing is used. Wells may also be installed with a 'pre-packed' screen, making them very similar to conventionally installed wells. Further details on DPT well installation methods and advantages and limitations can be found in ITRC (2006).

During the installation of any groundwater monitoring well, appropriate measures must be taken to prevent cross-contaminating underlying aquifers by creating a pathway for contaminants to migrate through.

4.7.2 Waterloo Profiler™

The Waterloo Profiler™ is a type of exposed screen DPT groundwater sampling device. It allows 'grab' sampling of groundwater from multiple depth intervals as the tool is advanced through the subsurface, without needing to withdraw the device. This allows any number of required samples to be collected and analysed and a vertical profile of groundwater chemistry to be produced. US EPA (2005b) provides details on the sampling device, which consists of a stainless-steel tool, with several drilled ports covered with fine mesh.

***Groundwater Sampling and Monitoring with Direct Push Technologies* (US EPA 2005b)**

Provides further details on DPT groundwater sampling methods, including DPT well installation and the Waterloo Profiler™. Available for free download from: **www.clu-in.org/download/char/540r04005.pdf**.

The Waterloo Profiler™ avoids potential cross contamination and clogging that affect other exposed screen devices by utilising distilled water, pumped slowly down to the ports, keeping groundwater out while it advances. When the required sampling depth is reached, the pump is reversed and groundwater is sampled. After the sample has been collected, the pump is again reversed and the tool advances to the next sample location. There are depth limitations on the device, due to the limits of the pump used, and like all DPT methods, its use is limited in very coarse soils or where there are obstructions.

The Waterloo Profiler™ has been included herein due to its widespread use in the US, and recent adoption on some Australian projects. However, it should be noted that other, similar sampling devices may be available that suit a similar purpose.

4.7.3 Sample collection methods

There are a number of methods available for the collection of groundwater samples from monitoring wells, with the sampling objective always to collect a sample representative of groundwater in the vicinity of the well. The various methods may differ in the manner of purging the well prior to sampling, the way in which the sample is collected, or both. These differences can impact on the sample, and will influence the method selected for particular site conditions and data requirements. EPA Victoria (2000) includes guidance for well gauging, field parameter measurement, purging and sampling by a variety of methods, including limitations and applicability. Some that may be appropriate at petroleum sites include disposable bailers and 'low-flow' samplers. Site-specific conditions must be taken into account in selecting the appropriate sampling method for a site. For example, the

use of bailers is generally considered inappropriate for sampling volatile contaminants, due to the disturbance of the water column.

Passive sampling devices (also known as 'no-purge' sampling devices), such as passive-diffusion bags (PDBs) and the Snap Sampler™, also may be appropriate at petroleum sites. These sampling methods do not require purging of groundwater; they are placed at a selected depth in the well screen and rely on groundwater flow through the well screen for sampling. Some advantages of passive samplers are that they do not agitate the water column, they can sample discrete depths (and can be placed in sequence to sample multiple depths) and no purge water is generated. PDBs consist of a polyethylene membrane enclosed column of distilled water, which is placed in a well and allowed to equilibrate with the groundwater (typically over a two week period). PDBs are only appropriate for sampling of volatile compounds, so will not be applicable at all sites (see Vroblesky 2001 for more information on PDBs). Passive grab samplers, such as the Snap Sampler™ have also been shown to be effective for sampling and are not limited in the type of samples they can collect. Their system of *in-situ* sealing also provides substantial data quality improvement. ITRC (2007b) includes further details on these devices.

> **Protocol for Use of Five Passive Samplers to Sample for a Variety of Contaminants in Groundwater (ITRC 2007b)**
>
> Contains protocols for the use of five different passive ('no purge') sampling devices, including passive grab samplers, diffusion samplers and diffusion/sorption samplers. It can be downloaded for free at **www.itrcweb.org/Documents/DSP-5.pdf**.

With all groundwater sampling methods at petroleum hydrocarbon sites, it is essential that only groundwater is sampled. The potential presence of LNAPL should be checked during gauging of the well, and again during sampling. Samples that exhibit signs of free product, such as a sheen will not be representative of dissolved contaminant conditions.

4.7.4 Membrane interface probe (MIP)

The MIP tool is explained in greater detail above in Section 4.5.3.

When an MIP investigation is conducted, it detects the response of VOCs regardless of their media in the subsurface – that is, a total of the concentration of VOCs from soil, soil gas, and groundwater are detected by the MIP tool. Therefore, MIP can be utilised as a versatile technology to investigate hydrocarbon contamination in both the vadose and saturated zones.

If the intent of an investigation is to focus solely on groundwater or aqueous concentrations, the MIP tool can be utilised at a depth starting at the top of the saturated zone; however, the MIP will still have the ability to volatilise and detect VOCs present in LNAPL or soil below the groundwater table (i.e. not yet dissolved). Thus, the need to calibrate a MIP survey with groundwater validation samples to determine actual aqueous phase concentrations is critical.

4.7.5 Groundwater investigation methods comparison

The various groundwater investigation methods that have been discussed in this section are presented in Table 7 along with advantages/applicability and disadvantages/ limitations of the techniques. It should be noted that the information presented herein is a summary comparison of the methods; the preceding sections should be referred to for full detail on the techniques and their applicability.

4.7.6 Groundwater sampling and analysis QA/QC

An adequate discussion of groundwater sampling QA/QC is included in EPA Victoria (2000) and will not be repeated herein. The importance of developing SOPs for sampling methods to ensure consistency is again stressed.

Passive sampling devices require additional consideration for QA/QC requirements. PDB samplers can be adjusted in length to allow additional sample volume to be collected for duplicates and other QC samples, and a trip blank PDB should be considered. This will be an additional PDB sampler that is stored and transported with the field PDB samplers from construction through to deployment in the wells. A sample from the trip blank PDB can then be collected and analysed to assess if volatiles have impacted the samples during handling and transport.

Table 7. Comparison of groundwater investigation techniques

Technique	Advantages/applicability	Disadvantages/limitations
Monitoring wells	Methods are generally well established in Australia, with equipment readily available. Allow collection of samples for lab analysis.	Does not provide 'real-time' data (other than inspection of collected cores). Laboratory testing can be expensive and can take several days. Different sampling techniques can give very different results for the same well. Care must be taken during well installation to prevent cross-contamination of underlying aquifers.
Waterloo Profiler™	Allows sampling at any number of depths to provide excellent vertical profile of groundwater conditions. Allows rapid collection of samples without the need for installing permanent monitoring wells. Circulation of distilled water minimises potential for cross-contamination.	Limited to unconsolidated aquifers. Generally cannot be used at depths greater than 30 m. Samples still require laboratory analysis after collection.
MIP	See soil investigation section.	See soil investigation section.
Sample collection methods		
Bailers	Low cost method. Simple use requires little technical expertise.	If used to purge can be time consuming. Operating the bailer can cause agitation of the water column and increase turbidity. Unable to sample discrete depths.
'Low-flow' sampling	Low quantities of purge water are generated. Minimal agitation of the water column occurs, resulting in lower turbidity and potential loss of volatiles. Allows sampling of an isolated depth interval.	Suitable only when a flow rate of 0.1 to 1.0 L/min will not cause drawdown of the well.
Passive sampling devices	Multiple samplers can be used to provide a vertical profile of groundwater conditions. Essentially eliminates purged water generation, and hence the need for disposal. Easy to use and deploy.	Passive devices rely on horizontal water flow in the well, if this is impacted by other factors then the sampling may not be successful. PDBs are not suitable for all analytes and require two mobilisations (deployment and collection) and a waiting period.

With a Snap Sampler™, planning will be required for additional samplers to be deployed so that sufficient sample quantity is obtained to allow QC sample analyses.

4.8 Mass flux measurements

An alternative method for characterising hydrocarbon-contaminated sites involves quantification of contaminant mass flux. The impetus for development of this characterisation technique has been a desire by consultants to develop more realistic remediation goals that maximise remediation efficiency by focusing on source zones that are responsible for the largest impacts to groundwater resources. Remediation of some large sites contaminated with petroleum hydrocarbons can be unrealistic and cost-prohibitive given very low concentration-based remedial goals, for example ANZECC/ARMCANZ (2000) trigger levels in groundwater. In addition, relying solely on concentration-based remedial goals may not be the most efficient means of reducing risk to down-gradient receptors. The mass flux-based approach to site assessment is a viable alternative to concentration-based approaches and can provide a basis for a risk-based approach to petroleum hydrocarbon site management. However, it is noted that appropriate toxicity data is required for the receptors at risk at a site to allow mass flux-based remediation goals to be formulated.

Contaminant mass flux *J* is generally defined as the mass of contaminant dissolved in groundwater flowing through a unit area, located perpendicular to the mean direction of groundwater flow, per unit time. The integrated mass flux or contaminant mass discharge is the spatial integration of the contaminant flux over a control plane across the dissolved contaminant plume.

Mass flux is a complex parameter that is a function of the following contaminant source zone characteristics:

- contaminant concentration in soil and groundwater
- total mass
- fractionation within various lithologic units
- three-dimensional spatial distribution or geometry
- hydrodynamic structure.

As such, measurements of mass flux integrate critical features of the source-zone architecture (Sale & McWhorter 2000) and the groundwater flow field. It is important to note that changes in a single petroleum hydrocarbon source zone characteristic may not necessarily produce an appreciable decrease in mass flux. For example, Figure 9 presents a generic range of potential results of mass flux reduction. Reduction of a small fraction of the total mass (red line) at some sites will result in large mass flux reduction. While large mass flux reduction (blue line) at some sites may result in little mass flux reduction benefit. Most sites reside closer to the 1:1 relationship.

4.8.1 Potential applications of mass flux

Estimates of contaminant mass flux have a variety of potential applications:

1. Mass flux measurements provide a metric that allows the measurement of source strength and, therefore, provides a tool with which to assess the risk posed by a site. The ability to identify high mass flux zones provides more realistic exposure scenarios to evaluate risk to human health and environment. Quantification of the contaminant flux emanating from a site enables stakeholders to make better site management decisions based on actual versus perceived risk. For example, a high groundwater contaminant concentration measured at a point can be misinterpreted as indicating a greater risk to human health and the environment than a lower contaminant concentration. However, the high concentration groundwater may be contained within low permeability zones in the aquifer, resulting in a release of total contaminant mass significantly less than that of the lower concentration groundwater.

2. Measuring the mass flux directly can provide more accurate information on the ability and effectiveness of natural processes to contain the remaining mass. In areas where no remedy is in place, differences in the contaminant flux across two control planes of the plume can be used as a basis to provide a quantitative estimate of natural attenuation.
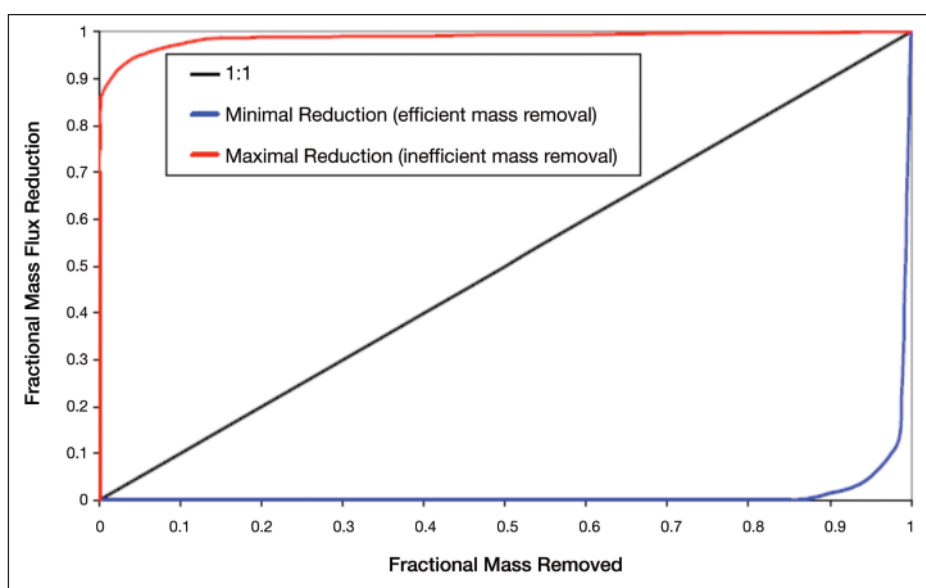

Figure 9. Mass and mass flux reduction relationship (excerpt from Brousseau 2008)

3. Measuring the mass flux directly can provide more accurate information on the risk reduction due to source depletion. Mass flux estimates can be used to evaluate the performance of a particular remedy. Monitoring mass flux both before and after the implementation of a remedial action can provide insight into the effectiveness of the remedy. In addition to evaluating the effectiveness of a remedy, estimates of mass flux can be used to optimise the design of proposed treatment systems by identifying and targeting high mass flux zones.

There is a growing consensus in the literature that estimated contaminant mass flux J or contaminant mass discharge MQ can be used to generate robust estimates of source strength, natural attenuation, and source longevity, and that mass flux can be used to evaluate the efficacy of various remedial alternatives and track remedial progress (Basu 2006; Bockelmann et al. 2003; Borden et al. 1997; Rao 2008; US EPA 1998). Additionally, consultants executing plume remediation are increasingly using contaminant mass flux measurements down-gradient of the LNAPL source, at extraction wells, and within and down-gradient of the plume to determine if remedial goals are being met and to support optimisation of the remediation process. Current findings are that although different remedial treatment technologies may achieve similar reductions in contaminant mass, they may result in significantly different reductions in contaminant flux due to the different distributions of mass remaining after treatment.

In general, when evaluating the effectiveness of different remedial options, mass flux measurements can be considered a superior performance metric to discrete, or point, groundwater concentration measurements for sites using a risk-based remediation approach. Potential benefits of measuring contaminant mass flux during the site characterisation stage include the ability to:

- improve the CSM
- prioritise sources by strength for site management decisions
- provide a measure of natural attenuation
- provide input for groundwater flow and contaminant transport modeling
- provide more realistic exposure scenarios for risk evaluation.

Some sites will receive greater benefit from a mass flux characterisation approach than others. Sites best suited for this type of analysis include those for which regulations provide for an alternative cleanup level process for active remediation where natural attenuation may be used in a treatment train approach. Other sites where mass flux analysis could be beneficial are those employing remedial actions that have a high degree of uncertainty in treatment effectiveness. Contaminant flux estimates as a function of time could track the progress of remediation and provide an indication of the effectiveness for a single remediation implementation or for a series of actions. At other sites where no remedial actions are in place, mass flux estimates could help evaluate the rate of contaminant natural attenuation and help determine whether natural attenuation is a viable remediation alternative. Finally, mass flux estimates can be a more rational metric in situations where high concentrations of contaminants are present in low permeability formations. Although contaminant concentrations are high, and may exceed relevant regulatory standards for an extended period of time, the limited groundwater discharge from the low permeability zone results in an extremely low contaminant mass flux. As such, the site may not pose a significant risk to down-gradient receptors.

4.8.2 Measurement techniques

A variety of methods have been used to estimate contaminant mass flux, as listed below. Table 8 provides a comparison of the measurement techniques.

- Groundwater transect method (control planes)
  - Mass Flux Toolkit (Farhat et al. 2006)

Mass Flux Toolkit (Farhat et al. 2006)

This toolkit allows calculation of mass flux using transects and also includes a review of mass flux concepts and methodologies. It can be downloaded for free at **www.gsi-net.com/Software/massfluxtoolkit.asp**.

- Extraction well method
  - Einarson and MacKay (2001)
- Passive flux meters
- Groundwater models[6]
  - BIOSCREEN (US EPA 1997c) / BIOCHLOR (US EPA 2000a)
  - REMChlor (US EPA 2007)

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[6] The reader is referred to the following US EPA website, which contains information on potential limitations associated with the Domenico-based BIOSCREEN, BIOCHLOR and REMChlor models: http://www.epa.gov/ada/csmos/domenico.html.

Table 8. Comparison of mass flux measurement techniques

Technique	Advantages/applicability	Disadvantages/limitations
Groundwater transect method	Uses conventional data collection techniques. Small waste volume produced. Provides spatial information on concentration distributions.	Does not estimate groundwater flux. Measurements are instantaneous. Interrogates small aquifer volumes. Data must be spatially integrated.
Extraction well method	Generates contaminant mass flows. Interrogates large volumes of aquifer. Can be used in deep aquifers.	Generates large volume of water. Requires lengthy investigation time. Does not estimate groundwater flux.
Passive flux meter (PFM)	It's a direct measurement that provides groundwater and contaminant flux. Provides vertical variation in flux. Less sensitive to daily fluctuations. Produces small waste volumes.	Data must be spatially integrated. Requires multiple wells and PFMs. Competitive and/or rate-limited sorption not considered.
Groundwater modelling	Provides a means to estimate mass flux using conventional existing data without field effort. Can be used as a means to quantify the range of uncertainty. Helpful in assessing the benefits of various remedial technologies.	It's not a direct measurement. The quality of modelling is dependent upon the quality of site-specific data (similar to the groundwater transect method). Model assumptions can significantly restrict the accuracy of the results (e.g. steady-state solutions ignore potentially significant temporal variability).

4.8.3 Limitations and complexity

Techniques for estimating mass flux can be fraught with inaccuracy and are subject to large uncertainty. Accurate determination of contaminant mass flux is difficult to achieve using concentration-based field data combined with typical methods of estimating groundwater flow. Spatial and temporal variations in both contaminant concentrations and groundwater flow, such as may occur during a rain event or rainy/drought season, can induce mass flow variations that can range by orders of magnitude at a particular site. In addition, because groundwater flow cannot be measured directly in the field, alternative methods must be used to estimate flow. These surrogate methods can introduce errors to the groundwater flow estimate, which can propagate through to the estimate of contaminant mass flux.

The number of samples needed to accurately quantify mass flux may be cost-prohibitive. Fraser et al. (2005) investigated mass flux as a function of sampling density. The standard deviation of mass discharge estimates increased greater than 50% when the sampling grid density decreased from 1.7 points per m^2 to 0.7 points per m^2. In another study, 75% of the mass flux was shown to occur within 5 to 10% of the transect cross sectional area (Guilbeault et al. 2005). In order to identify

these high concentration zones, a spacing of 15 to 30 cm was needed in some locations.

One of the most formidable challenges regarding mass flux estimates is the difficulty in incorporating transient flow conditions. Groundwater flow, and thus contaminant mass flux, can change significantly due to seasonal fluctuations in water levels and changes in pumping. A mass flux estimate is based on a single set of conditions. As water levels rise and fall, not only is the groundwater flow affected, but there is the possibility of liberating additional solute mass in the vadose zone, resulting in changes in water quality as well.

Finally, the mass flux measurements typically need to be placed into the context of concentration in order to compare the results to regulatory requirements. This generally involves the use of a mixing cell approach or spatially weighted average technique, which has its own set of assumptions. Thus, the translation from mass flux to concentration adds another layer of complexity and has the potential to introduce additional error. As a result, mass flux estimates may be most applicable to site owners who wish to use a more accurate method to track remedial progress rather than demonstrate compliance.

4.9 Geophysical techniques for locating structures

Particularly at old or abandoned sites, adequate details of underground tanks and pipes may not be available, or anecdotal evidence may indicate that drums of waste have been buried but the exact location is not known. In such circumstances, the use of geophysical techniques may be beneficial in locating and delineating these structures. As geophysical techniques (for locating structures) are non-intrusive and results can be interpreted quickly when required, they are useful when adopted early in an investigation to allow other intrusive methods to be targeted to potential contamination sources. GPR, metal detection, magnetometry and electromagnetic methods are commonly used surface geophysical techniques for locating buried objects. Further details of these techniques can be found in US EPA (1997).

4.10 Computer fate and transport models

In addition to the numerous different physical methods for investigating petroleum hydrocarbon-contaminated sites, computer models are sometimes necessary to assist in the characterisation and evaluation of these sites. This may be due to site complexities, lack of available site data, or the need to evaluate potential future impacts or remediation scenarios. The use of computer models in conjunction with reliable site-specific data allows for a thorough evaluation of potential LNAPL and dissolved-phase contaminant movement and removal scenarios.

Guidance for modelling dissolved-phase and LNAPL contaminants is available from several resources including NEPC, ASTM, API, US EPA and the United Kingdom Environment Agency.

This section seeks to discuss the various modelling options and provide references for more detailed information on LNAPL models. Discussion of the more commonly performed dissolved-phase contaminant modelling is deferred to others (ASTM 1999; Bear et al. 1992; NEPC 1999). Table 9 lists the publicly and commercially available models that accommodate LNAPL fate and transport.

4.10.1 Types and applications

Models used to assist in characterising petroleum hydrocarbon-contaminated sites can range from simple mathematical spreadsheets which solve steady-state analytical models to multi-phase, multi-component numerical codes which solve complex transient finite-element models. These models can be used to assess a variety of current, historical, or future scenarios. For example, computer models may be used to track the potential migration of a LNAPL plume, or predict the effect of a remediation system on existing LNAPL contamination. Steady-state models are often acceptable for older LNAPL plumes. More complex transient model solutions are more important for dynamic site conditions. In either case, computer models are primarily used to interpolate or extrapolate real site data to answer questions about site conditions and refine site management approaches.

General fate and transport modelling

There are numerous guidance documents and reports that describe the general use of computer fate and transport models for dissolved-phase and soil vapour contaminant fate and transport (NEPC 1999). ASTM (1995) provides a more detailed discussion of modelling specifically for petroleum hydrocarbon-contaminated sites.

This US ASTM Standard includes the following descriptions of simple analytical computer models and more complex numerical models:

'Analytical models are generally based on assumptions of uniform properties and regular geometries. Advantages include quick setup and execution. Disadvantages include, in many cases, that analytical models are so simplistic that important aspects of a given system are neglected.

Numerical models allow for more complex heterogeneous systems with distributed properties and irregular geometries. Advantages include the flexibility to simulate more complex physical systems and natural parameter variability. Disadvantages include that the approach is often very time intensive and may require much more data and information to be collected.'

Sites with limited LNAPL contamination in soil or groundwater and relatively homogeneous and isotropic conditions can usually be described using single-phase equations and simple analytical models. However, even at these relatively simple sites, modelling petroleum

Table 9. Publicly and commercially available LNAPL fate and transport models

Name	Developer	Description
ARMOS	Environmental Systems and Technology, 1988-1994 (commercially available) **www.gesonline.com/why-inn-visualization.aspx**	ARMOS, the acronym for Areal Multiphase Organic Simulator, is a numerical model to simulate the flow of water and/or hydrocarbon in an unconfined aquifer. It can simulate leak events of specified rates, durations and locations to facilitate their analysis and plan for remediation. It may be used to evaluate travel path and travel times of hydrocarbons emitted by an accident, in order to optimally locate measurement or pumping wells. ARMOS has options to evaluate only the water flow (for instance to calibrate parameters) or both water and hydrocarbon flows.
Hydrocarbon Spill Screening Model (HSSM), Version	US EPA, 1997a (publicly available) **www.epa.gov/ada/csmos.html**	Simulates flow of the LNAPL phase and transport of a chemical constituent of the LNAPL from the surface to the water table; radial spreading of the LNAPL phase at the water table, and dissolution and aquifer transport of the chemical constituent. It's one-dimensional (1D) in the vadose zone, radial in the capillary fringe, and 2D vertically averaged analytical solution of the advection-dispersion equation in the saturated zone.
LNAPL Distribution and Recovery Model (LDRM)	API, 2008 (publicly available) **www.api.org/ehs/groundwater/lnapl/**	Characterises the behaviour of LNAPL in porous media including performance of LNAPL liquid recovery technologies. It simulates the performance of proven hydraulic technologies for recovering free-product petroleum liquid releases to groundwater.
NAPL Simulator	US EPA, 1997b (publicly available) **www.epa.gov/ada/csmos.html**	Conducts a simulation of the contamination of soils and aquifers which results from the release of NAPL. The simulator is applicable to three interrelated zones: a vadose zone which is in contact with the atmosphere, a capillary zone, and a water-table aquifer zone. Three mobile phases are accommodated: water, NAPL, and vapour. A three-phase sub-model accommodates capillary and fluid entrapment hysteresis. NAPL dissolution and volatilisation are accounted for through rate-limited mass transfer sub-models. The numerical solution is based on a Hermite collocation finite element discretisation.
UTCHEM	US EPA, 1999a (publicly available) **www.epa.gov/ada/csmos.html**	A general purpose three-dimensional finite difference model for multiphase flow, transport and chemical flooding. Appropriate physical, chemical and biological process models have been incorporated into the simulator to create a 3D multiphase multi-component model capable of simulating the fate and transport of NAPLs in the saturated and unsaturated zones of aquifers. The model can be used to simulate the actual field operation of remediation activities such as surfactant remediation or bioremediation as well as laboratory experiments with large-scale aquifer models.

hydrocarbon-contaminated sites will usually, at a minimum, entail the addition of a biological degradation component due to the aerobic and anaerobic processes that significantly affect petroleum contaminants. A list of referenced ASTM standards that provide further discussion and guidance on the use of common dissolved-phase computer modelling applications is included in ASTM (1995).

Multi-phase modelling

Often at petroleum hydrocarbon-contaminated sites, additional considerations for modelling must be made based on the physical state of the contaminants. For example, a site may have contamination in the vadose zone, dissolved in the groundwater, and present as LNAPL. In these cases, typical of sites contaminated with petroleum hydrocarbons, the use of a multi-phase model is required. Again, these can range from fairly simple mathematical spreadsheets for analytical models to complex numerical codes for dynamic transient finite-element models.

Multi-phase modelling is complex and can be problematic because its myriad of parameters introduces potentially significant uncertainties to the process. Because of this, guidance on multi-phase modelling recommends relying more on field data with support from multi-phase modelling, with an appropriate evaluation of the modelling results. A detailed overview of multi-phase modelling is provided in ASTM (2006).

The simple multi-phase models use spreadsheets or simple Visual Basic® environments to address among other things, mobility and recovery of free product and longevity of dissolved-phase and LNAPL plumes at sites with high concentration source zones. The basic spreadsheet models described in Charbeneau et al. (1999), Charbeneau (2003) and API (2008) can calculate the vertical distribution of LNAPL in the subsurface given a product thickness in a well, LNAPL properties, and physical properties of the porous media. The spreadsheets can then be used to estimate LNAPL volumes in the subsurface and the amount of recoverable product under a variety of pumping scenarios. It should be noted that many literature values are based on studies from agricultural soils, and therefore may not be applicable and should be used with caution. If it is possible to obtain site-specific data then this is always preferable.

As shown on Table 5, in addition to the simple spreadsheet models, there are a number of numerical models available that provide for the more complex scenarios typically encountered at petroleum hydrocarbon-contaminated sites. Examples of these types of models include UTCHEM (Delshad 1996; USEPA, 1999a) and ARMOS (ES&T Software Ltd 1988–1994). These models are far more complex than the spreadsheet models, require additional detailed inputs, and are best run by individuals with significant experience with multi-phase flow modelling.

4.10.2 Steps required in modelling

Regardless of the complexity of a particular model, any modelling project requires a number of steps to be performed so the appropriate models are used and results are valid within the context of the data objectives. API (2004) provides a list of the more important steps to be taken during a modelling project:

- definition of objectives
- model conceptualisation
- code selection
- parameter definition
- model calibration
- predictive simulations
- results evaluation.

Further definitions and details regarding these individual steps can be found in API (2004).

4.10.3 Model selection

In general it is better to start the process with simple models and only proceed to the more complex models if necessary. Most often, an LNAPL problem statement can be narrowed down to a relatively simple set of boundary conditions and clear set of data objectives. If geologic and contaminant conditions within the reduced model domain can be considered relatively uniform, isotropic, and quasi-steady-state, then a simple analytical model may be applicable. If the geology of the model domain is dynamic and complex, then numeric models may be a prudent choice. In either case, the modeller needs to carefully consider the amenability of the site to simplifying assumptions used by models and if amenable, then weigh the costs and benefits, in terms of reducing the uncertainty in the CSM, prior to proceeding with modelling. Additional details on selection of a model are discussed in ASTM (1999).

4.10.4 Uncertainty and sensitivity in modelling parameters

One of the more important steps required in computer modelling is the selection or definition of physical and chemical input parameters. These are best obtained from site-specific sampling efforts. However, some parameters necessary for more complex models are simply unattainable from standard sampling techniques. Required physical and chemical parameters can also be obtained from appropriate literature values typical for similar materials or site conditions. To assist individuals attempting to generate representative values for their model, API produced *Methods for Determining Inputs to Environmental Petroleum Hydrocarbon Mobility and Recovery Models* (API 2001), and *Light Non-Aqueous Phase Liquid (LNAPL) Parameters Database, Database and Guide for Data Retrieval* (API 2006). Both these products are available free-of-charge at www.api.org/lnapl. Use of a literature database for modelling purposes should be for screening purposes only. Models are highly site-specific and selection of representative parameters based on conventional analytical (i.e. soil boring logs and soil and groundwater chemical analysis) is fraught with error. Therefore, a 'range of values' approach can be most beneficial to observe the effects of various assignments (similar to a sensitivity analysis). In a 'range of values' approach, the user selects a reasonable range of possible site-specific parameter values (high, best estimate, low) and runs the model with all three values to observe the potential range of results. Modelling in this manner quantifies the range of uncertainty and the compound effects of uncertainty on complex model results.

As part of model calibration and simulation runs, a sensitivity analysis should always be performed to determine which parameter(s) have the greatest effect on the model results. In this way, the modeller can minimise model error by ensuring that highest attention is paid to assignment of the most sensitive parameter input. In general, groundwater transport models are typically most sensitive to the hydraulic conductivity of the subsurface media and the sorption properties of the contaminants (i.e. retardation factor). For multi-phase flow models, the capillary properties of the soil are critical to the model calibration, and are usually the most sensitive parameter to the model results. However, the most sensitive parameters to a particular model may be different than these examples due to the model's ultimate purpose. As such, a sensitivity analysis on each input parameter should be part of every model calibration, and these sensitivity analysis results should be used to assess the

validity of the model results. More information regarding performing a sensitivity analysis on computer models can be found in ASTM (1994) and ASTM (1995). Table X2.1 in ASTM (2006) presents a list of common multi-phase modelling parameters and provides information on each parameter's potential sensitivity in the model.

4.10.5 Model limitations

The success and validity of computer fate and transport models for petroleum hydrocarbon-contaminated sites will be governed, similar to any model, by the validity of the model assumptions and representativeness of the input parameters used to describe the modelled system and components. The sensitivity analyses performed on the model parameters will assist in determining the limitations of a particular modelling effort. However, as stated above, computer model results should always be checked against real site-specific data prior to publication.

4.10.6 Summary

As described above, there are a number of useful tools for evaluating and predicting the fate and transport of dissolved-phase and LNAPL contaminants associated with petroleum hydrocarbon-contaminated sites. These tools range from simple mathematical spreadsheets to complex multi-phase, multi-component numerical simulators. Ultimately, the selection of the most appropriate model will usually be governed by the suitability of site conditions to simplifying modelling assumptions and the objective of the particular analysis. As such, a good first step in the modelling process is to resolve exactly what the objectives are for the given task. This should be followed by development of a conceptual model for the site that helps to define critical site conditions so that a proper set of defining characteristics can be assembled for model selection. Once the objectives are clearly defined and a conceptual model has been developed, then selection and application of a fate and transport model can be completed. In general it is better to start the process with simple models and only proceed to the more complex models if necessary.

4.11 Summary of analytical methods

While several field investigation methods have been discussed, laboratory analysis will almost always be required at some point in a site characterisation. A

summary of methods and their application is provided herein.

Laboratories selected for the analyses must demonstrate an appropriate level of QA/QC (NEPC 1999 details required laboratory QA/QC measures). This will whenever possible include National Association of Testing Authorities (NATA) accreditation for the analysis conducted and/or participation in a laboratory proficiency program and the use of established quality assessment techniques such as matrix spikes, laboratory duplicates and surrogate recovery. Analysis methods and techniques must be recognised, consistent and comparable with regard to the objectives of the assessment. Where 'niche' analyses that are unlikely to be NATA accredited (such as fingerprinting) are required, the selected laboratory should have access to an appropriately qualified expert to adequately peer review the results.

4.11.1 Selection of methods consistent with data use

As with the selection of any investigation methodology for a site, the selection of analytical methods must be adequately planned to ensure that the methods provide information consistent with data objectives and the tier of investigation. Conducting a total petroleum hydrocarbon (TPH) screening analysis will be insufficient for a detailed risk assessment, where data on specific chemical concentrations is likely to be required. Conversely, TPH fractionation into aliphatic and aromatic components and detailed soil property and LNAPL mobility analysis may be unnecessary at a Tier 1 site.

4.11.2 Chemical-specific analyses

Specific chemical components of petroleum are often the most toxic and chemical specific analyses are therefore required in most site characterisations to allow an assessment of risk. The most important chemical analyses at Australian petroleum sites will typically be BTEXs and PAHs, with the likely presence of these compounds dependent on the product type (e.g. a petrol release will be likely have BTEXs present and a diesel release will likely have PAHs). Analysis for additives such as MTBE, DIPE, TBA and lead is less likely to be required, unless desk study information indicates their potential presence (for example if the release is found to be imported product, or an historical release). Laboratory analytical methods should be in accordance with NEPC (1999) and should be conducted at a laboratory that is NATA accredited for the specific analyses to be conducted.

4.11.3 Total petroleum hydrocarbons

Analyses for TPH are the most common laboratory analyses conducted at petroleum hydrocarbon sites. However, there are an array of different analytical methods and ways in which to report results, from a basic TPH screening through to aromatic/aliphatic analysis and various carbon number fractions. The most important consideration with TPH analyses is to ensure that the analysis selected fits with the data requirements. For example, if the site is to be assessed against known regulatory limits with particular carbon fractions, then the TPH analysis must be selected to provide fractions in agreement with the regulatory limits.

A screening analysis for TPH provides useful information on the bulk concentration of petroleum hydrocarbons in soil or groundwater. More detailed TPH analysis, with fractionation, or splitting between aliphatic and aromatic components will generally be required for comparison to screening levels, identification of likely products and almost certainly for a detailed assessment. It is beyond the scope of these guidelines to recommend appropriate chain lengths for TPH fractionation, though for human health screening levels, reference should be made to recent work by CRC CARE (pending).

4.11.4 LNAPL fluid properties and chemical analyses

Due to weathering and possible product mixing, fluid properties of fresh product are likely to differ from the properties of LNAPL that has been released to the subsurface. Analysis of field collected samples is therefore necessary to obtain accurate fluid properties for estimating product migration and recoverability.

The actual analyses required will vary depending on the data objectives for the site. Laboratory analyses of LNAPL may include the following (ASTM 2006):

- density – used in capillary relationships
- viscosity – important for recovery and phase movement (and as it can vary greatly between hydrocarbon types its measurement is more important than density)
- interfacial tensions – LNAPL/air, LNAPL/water, air/water, used to scale capillary relationships, interfacial tension can be significant in estimations of mobility and recoverability.

Analysis of fluid properties should be conducted at temperatures as close as possible to ground temperatures. At sites with large variations in ground temperature, analyses may be required at multiple temperatures (this is likely to be less of a consideration in Australian climates than in northern hemisphere locations). API (2004) provides a range of methods for measuring LNAPL fluid properties.

Chemical analysis of LNAPL will generally be required where it has been identified at a site. In addition to standard analyses for chemical composition (which can often be inferred from soil analysis results without the need to analyse LNAPL), more advanced chemical testing can provide information on the type, age and even source of the product. So called 'fingerprinting' relies on high resolution gas chromatography (GC) to analyse a sample of product and the output is examined to provide the type of product, or mixture of products present. Further examination of samples, including biomarkers, fuel additives, sulfur content and comparison to standards can yield information on the likely age of the product and weathering processes that it has undergone. Stout et al. (2002) note that fingerprinting is best conducted in a tiered fashion, which allows flexibility to gather as little, or as much, information as necessary up to the point where investigation questions have been addressed. This is in accordance to the approach to site characterisation promoted in Section 3.4.

Fingerprint analysis at complex sites with multiple potential sources, or potential off-site sources, can therefore be useful in identifying or confirming the contaminant source. However, it should be noted that fingerprinting is not an exact analytical method and due to the specialist knowledge and data interpretation required laboratory selection is crucial to achieving satisfactory results.

4.11.5 LNAPL mobility analyses

Evaluating LNAPL mobility will generally be required at sites where the characterisation is required to provide data for remedial design (other than 'dig and dump'). Laboratory LNAPL mobility analyses can be expensive and a number of parameters are available from literature values; however, as the complexity of the site increases and the tier of investigation and CSM increases, the benefit of site-specific data will outweigh the costs of analysis. Intact and undisturbed soil cores are required for LNAPL mobility analyses.

Properties related to product mobility that may be analysed include (API 2001):

- grain size
- porosity
- soil drainage/imbibition capillary properties (LNAPL and water)
- pore fluid saturation (NAPL, water, and air)
- LNAPL mobility
- pore size distribution
- soil bulk density
- relative permeability to water and LNAPL.

Further information and details on specific analytical techniques can be found in API (2001; 2004). A specialist laboratory will be required for some of the mobility analyses.

5. Data presentation and reporting

The collection of site characterisation data is of limited benefit unless the information can be conveyed to stakeholders effectively. Stakeholders require information to be presented in a logical format that will enable them to make decisions regarding the site. In presenting and reporting data, the objectives of the characterisation are again imperative considerations. Should the characterisation be focused on collecting detailed information for remedial design, then data presentation can likely be aimed to an audience with a high level of technical understanding. However, if characterisation of a site is required due to business or community requirements, then data should be presented accordingly. In addition there may be regulatory requirements (e.g. NSW EPA 1997) for reporting in particular jurisdictions, which must be taken into account.

5.1 Report of findings

In addition to the information provided herein, reference should also be made to NEPC (1999) guidance for general requirements on data presentation (such as borehole and test pit logs and results tables) and statistical analysis.

5.1.1 Figures and graphical presentations

The use of accurate figures and graphics to present characterisation data is considered essential, especially as plume behaviour is typically of great interest at petroleum hydrocarbon-impacted sites.

There are two main approaches for presenting sampling and monitoring results graphically, with the first being the display of individual results at sample locations on a plan of the site. This is generally most useful for showing significant results, such as locations where a concentration in soil or groundwater exceeds a screening criterion. Attempting to show too many results on a plan is likely to result in cluttering and it therefore may be preferable to have separate layers for different contaminants.

The second approach involves plotting contamination contours onto a plan of the site (i.e. an isopleth plan of contaminant concentrations). This method is very useful for showing the inferred dimensions of an LNAPL or dissolved contamination plume, and showing concentration gradients (for dissolved plumes). At sites where characterisation includes multiple monitoring events over time, contour plans can illustrate changes in plume dimensions and concentrations between events and with time. Some caution must be exercised in the preparation and interpretation of contour plots, as when there is limited data the methods used to extrapolate can influence the results (NEPC 1999). When preparing data versus time plots possible differences in monitoring conditions and therefore results must be taken into account. This could include seasonal variations, such as water table fluctuations influencing LNAPL plume dimensions and thickness, or issues unique to a particular event, such as an equipment problem (Nielsen 2006).

Geographical information systems (GIS) are increasingly used, and can be very useful for presenting the various data collected during a characterisation. Using GIS allows information gained from investigations to be presented along with site information such as buildings, waterways and topography. The data can be presented in layers that can be switched on and off to allow a focus on certain aspects.

It is important to note that the hydrogeological information obtained during characterisation is typically of equal importance to contamination data in the assessment of risk and remedial design. In addition to borehole and test pit logs, preparing a graphical representation of the CSM allows this information to be displayed and is of benefit at most sites. The complexity should be relative to the site's tier, with a basic two-dimensional cross-section often adequate for low tier sites, grading into detailed three-dimensional CSMs at high tier sites. An example of a 2D CSM is provided in Figure 4, while an example 3D CSM generated by modelling software is shown in Appendix B.

Other important forms of data presentation that are likely to be beneficial in the reporting of findings include:

- cross sections with lithology and contaminant concentrations shown along primary groundwater flow alignment – providing an easily referenced indication of contaminant zones related to lithology
- trend graphs of historic data (where available) – graphically representing the trends will allow for stakeholders to readily understand the data and facilitate required discussion.

5.1.2 Statistical analysis

Statistical analysis of data can be used in the assessment of soil results, such as in determining critical hot spot size, the upper confidence limit (UCL) of the arithmetic average, or the proportion of an area that is contaminated (see NSW EPA 1995). The behaviour of plumes can also be evaluated using statistical methods to identify significant trends and changes in data. Data collected over time can be analysed and plume stability can be assessed quantitatively, providing information for likely risks or requirements for remediation. When using statistical analysis, the confidence level (the acceptable probability of an error) must be appropriately defined based on the data objectives for the site. A 95% confidence level is commonly adopted; however, where data requirements are less sensitive to error it may be appropriate to adopt a lower confidence level. For example, at a site without nearby sensitive receptors that is proposed to be redeveloped for industrial use a 90% confidence level may be appropriate (NSW DEC 2006).

When using statistical methods to identify trends and evaluate plume behaviour it is important to note that statistical significance does not always imply real-world significance. The output of statistical analysis needs to be related back to the actual problem in the field to assess whether the results are meaningful (Nielsen 2006).

Further details on statistical assessment can be found in Gilbert (1987) and US EPA (2006).

> **Data Quality Assessment: Statistical Methods for Practitioners (US EPA 2006)**
>
> This is a comprehensive guide to the statistical review of data, including tools for statistical analysis and presentation of results. It can be downloaded for free at **www.epa.gov/quality/qs-docs/g9s-final.pdf**.
>
> **Pro UCL**
>
> This US EPA software is also a very useful tool for conducting statistical analysis. It can be downloaded for free at **www.epa.gov/esd/tsc/software.htm**.

5.2 Report discussions

In addition to presenting the results and data from a characterisation effort, it is important to include a discussion of the information gained in the context of the site and its current and proposed land use(s). NSW EPA (1997) refers to this section of a report as 'Site Characterisation', noting that it should include an assessment of the type and extent of soil and groundwater contamination, chemical degradation processes and possible exposure routes for human and ecological receptors. The findings of relevant previous investigations and details of works (for example excavations or building developments) conducted at the site that may influence the characterisation should also be discussed.

The CSM should be used as the focal point for the discussion as it is the assimilation of all the relevant information obtained during the characterisation. By discussing the site impacts as they relate to the CSM the investigation findings are presented as an overall picture of the site, making it easier to convey the required information.

In the discussion it is especially important to consider the objectives of the characterisation and the audience, so that the findings are explained in an appropriate manner to be of use to stakeholders.

5.3 Conclusions and recommendations

The outcome of a site characterisation effort will lead to a refined CSM and conclusions being drawn about the contamination and risk status of the site, and recommendations being made for further works that may be required to define the site end-point strategy. Ideally the characterisation efforts close the major data gaps so that an end-point strategy may be confidently defined immediately upon completion of the characterisation effort. The conclusions should include a summary of the investigation findings, along with any assumptions used and where uncertainties have been identified (NSW EPA 1997).

Conclusions drawn as to the status of the site and recommendations for further work must be explained and justified, and should be based on an assessment of risk. The presence of petroleum hydrocarbons in the subsurface at a site will not necessarily trigger a requirement for further investigation or management if there are no completed pathways to receptors. However, it is noted that regulatory authorities may impose requirements on a site, and these should be assessed and included in conclusions and recommendations where applicable.

If recommendations for a site are to be made they are likely to fall into one of the following three categories.

5.3.1 No further action

Where a site characterisation is deemed to have provided sufficient information for required decisions to be made regarding a site, and unacceptable risks are not present, no further action may be recommended. When making such a recommendation, the CSM for the site must be free of significant (as related to the objectives and goals of the characterisation) data gaps to allow risks to be adequately assessed.

5.3.2 Additional investigations

The intent of these guidelines is that characterisation efforts are adequately planned with the site end-point strategy in mind, and an appropriate tier of investigation selected, such that additional mobilisations are minimised. Though it is acknowledged that constraints (such as budget or schedule) on the characterisation will necessitate additional works at times. If there are unacceptable uncertainties or data gaps in the CSM then additional investigations should be recommended. The requirement for further investigation should be appropriately justified by noting the uncertainties in the CSM, how they relate to the objectives for the site, and how the additional works will address these gaps. In recommending additional investigations, the benefit of further works and possibly upgrading the tier of the investigation should be weighed against potential site management options. In some circumstance (depending on stakeholder requirements) while adopting site management to address risks at an earlier stage may result in higher remediation costs, the overall benefit of returning the site to use earlier may be higher.

5.3.3 Site management

If the site characterisation has identified unacceptable risks to human or ecological receptors, then site management options may be recommended. It is beyond the scope of these guidelines to discuss site management in detail; however, any recommendations for site management should be based on addressing identified risks, in addition to applicable stakeholder requirements (including mandatory regulatory requirements) and the principles of sustainable development. At the conclusion of the site characterisation process, sufficient information should be available to fully define the site end-point strategy and commence remedial planning and design. Site management requirements for a site will also typically require additional documentation in the form of a site management plan or remedial action plan. Potential site management options could include:

- on-site treatment, such as: bioremediation, soil vapour extraction, air sparging (a range of other treatment technologies are also available – refer to the US Federal Remediation Technologies Roundtable, www.frtr.gov, for other technologies)

- monitored natural attenuation

- off-site treatment after product recovery/removal (i.e. source removal)

- controls on the use of the site (such as a site management plan, or other institutional controls[7])

- 'dig and dump' strategies where other management means are not practicable or viable.

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[7] Institutional controls are mechanisms, such as legal controls, that help minimise the potential for exposure to contamination by restricting access to, or use of, a property. They may be imposed by a property owner, for example via a deed or covenant, or by government, for example by zoning.

6. How to apply the guidelines

This section discusses how to apply the contents of these guidelines to the characterisation of a petroleum hydrocarbon-impacted site. The steps in the process of a site characterisation are presented as a flowchart in Figure 10. Further detail on using the guidelines appropriately is provided in the subsequent sections, which refer to Appendix C and Appendix D that include respectively: a checklist for the minimum information typically required to complete an adequate Tier 1 characterisation; and a hypothetical applied example of a site characterisation completed in accordance with the guidelines.

The information provided in this section is intended to assist the user in applying the intent of the guidelines to a real characterisation situation. However, caution is advised, particularly when applying the checklist and applied example. Each site to be characterised will be different, with unique requirements, and therefore the user should never 'blindly' follow a checklist or example. Rather the steps promoted in the guidelines should be followed and an appropriate site-specific approach be formulated for each site. It is also noted that if there are any differences between the information provided in this section (or in the flowchart, checklist or example) and the main body of the guidelines, then the information provided in the main body should take precedence.

6.1 Steps required in the site characterisation

The flowchart shown in Figure 10 contains each of the main tasks and decisions required to adequately complete a site characterisation at a petroleum hydrocarbon-impacted site. To assist the user in identifying where desired information can be found in these guidelines, relevant sections are highlighted in the flowchart.

6.2 Minimum information requirements

The minimum information required to be obtained for a successful site characterisation is that which meets the objectives of the investigation, and allows the required decisions on risk and/or remediation to be made. As has been previously stressed, this will therefore obviously vary for each site, depending on the site-specific conditions and environment. However, there are a number of basic requirements that are typically needed for all sites. These are provided as a checklist in Appendix C.

The checklist is intended to be used as a prompter for those conducting (and reviewing) Tier 1 (i.e. generally low complexity and risk) investigations of petroleum hydrocarbon-impacted sites. The checklist should not be considered exhaustive, and conversely it may contain information that is not relevant to all sites; however, it does provide a good starting point for basic information needs.

6.3 Example use of the guidelines

Attached as Appendix D is a worked example for the characterisation of a hypothetical Tier 1 site. The reader is referred to the example for a demonstration of how a typical site, of relatively low complexity and risk, would be characterised by following the guidance in this document. It is noted that Appendix D is an example for illustration purposes only and does not include complete site details.
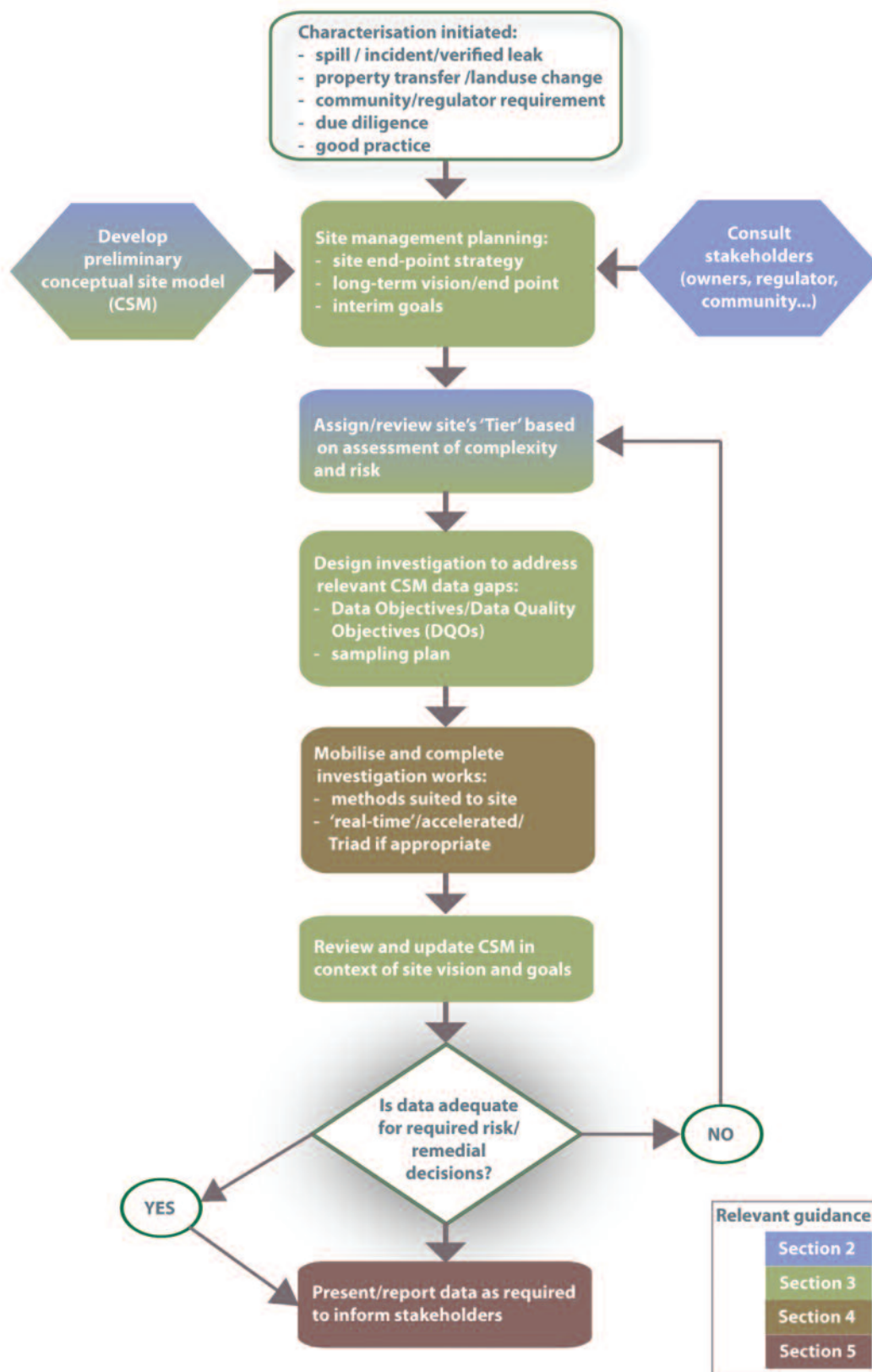
Figure 10. Characterisation flowchart for petroleum hydrocarbon-impacted sites

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APPENDIX A. CSM certainty screening tool

General LNAPL Conceptual Site Model Certainty Screening Tool

Site Name: Confidential

Purpose:

This tool is intended to assist project stakeholders in semi-quantitatively assessing the level of uncertainty present in the LNAPL conceptual site model (LCSM). It provides a list of critical technical LNAPL-specific decision-driving criteria and allows the user to assign weights and scoring values to each criteria. A total numeric score is calculated for the LCSM certainty and then judged by the stakeholders to indicate the relative certainty with which a detailed LNAPL site management strategy can be developed. After individual scoring and compilation, the project team must then collectively decide upon an acceptable level of uncertainty, with the understanding that 100% certainty is highly unlikely. This tool was designed to form the basis for the decision of whether to proceed with detailed site management planning or postpone (i.e., leave it in draft form) until more detailed LCSM analysis is completed and uncertainty is reduced to an acceptable level. It should be noted that the process prescribed in this tool is dynamic and meant to be updated as necessary to keep current with the LCSM.

Procedure:

1. Cells highlighted in yellow are the only cells to be input by the user.
2. Sub-questions are provided to aid the user in answering the primary numbered questions. Scores only need to be provided for the numbered questions.
3. Assign a relative "Weight" or degree of "Importance" to each criteria. This allows project-specific weighting to certain criteria which are more important than others. For example, if a site is pursuing Land Use Controls (LUCs) only, then understanding the detailed geometry of the LNAPL source is less important than a site pursuing active treatment of the source.
4. Provide an "Answer" to each question using the drop down menu. The number of points given, or answer value, precedes answer text. For example, if the weight-of-evidence unanimously indicates LNAPL presence, then a "4 - >90% Complete" answer should be entered for question T-2. If the LNAPL source zone is unbound on two sides, then a "2 - 30-60% Complete" should be entered for question T-3.
5. If a question is not applicable to the site conditions (i.e., there is no surface water), then a zero Weight and Answer of "0 - Not Applicable" should be assigned so that the factor is eliminated from the scoring process.

Assumptions:

1. Use of this spreadsheet is dependent upon the use of appropriate sampling and analytical procedures to derive the data upon which the criteria are scored.

Item	Criteria
Technical Factors	
T-1	**Are all above-grade and/or sub-grade contaminant release mechanism(s) identified at the site?**
	If the source of the original contaminant release is no longer in use, has it been properly decommissioned, abandoned, demolished, or removed?
	If the facility is active, are routine leak tests performed with adequate detection limits to prove that leakage is absent?
	If the facility is active, are routine accidental spills adequately contained to prevent a pathway to the subsurface?
T-2	**Is the presence of mobile- and/or residual-phase LNAPL in the vadose and saturated zones well understood?**
	Have measurements of in-well LNAPL thicknesses been made in monitoring well(s)?
	Have soil and groundwater samples been collected and physically observed for LNAPL?
	Have LNAPL indication tools (laser-induced fluorescence, ribbon sampler, Sudan IV dye, etc.) been used?
	Have contaminant partitioning equations been used to back-calculate the potential presence of free-phase LNAPL using soil and/or groundwater sample results?
T-3	**Is the source material (e.g., mobile-, residual-, or sorbed-phase contamination that emits mass to the soil gas or groundwater) geometry well characterised?**
	Has the lateral extent of source material been defined to within an appropriate tolerance?
	Has the vertical extent of source material been defined within an appropriate tolerance?
	Are inconnections of multiple sources, if present, well characterised?
	Has contaminant distribution and lithology been correlated (e.g., is the LNAPL trapped within low permeability lithology)?
	Has the mass fraction of contaminants in the LNAPL-phase been estimated?
T-4	**Is the groundwater contaminant plume geometry well characterised?**
	Have all contaminants of concern been identified?
	Has the lateral extent of the plume been defined in all principle directions including onsite and offsite areas?
	Has the vertical extent of the plume been defined?
	Is plume co-mingling, if any, well characterised?

Weight or Importance	Answer (Points)	Score	Rationale for Score	Immediate Action Items
1.0	3 - 60-90% Complete	3.00	One pipeline, extensive shallow soil sampling on all sides of leaky fitting to isolate the known source to LNAPL at this site.	Review the leak test procedure, detection limit, and recent results.
		–		
		–		
		–		
1.0	4 - >90% Complete	4.00	LNAPL has accumulated in several monitoring wells. Significant residual LNAPL is present, primarily in submerged zones. Uncertain whether mobile LNAPL is present under ambient gradients.	Conduct LNAPL mobility evaluation.
		–		
		–		
		–		
		–		
1.0	1 - <30% Complete	1.00	Previous soil sampling efforts have generally only bound the lateral and vertical extents to within 30 metres (m) and 10 m, respectively. A tighter tolerance is necessary for remedial technology screening purposes.	Conduct soil coring and UVOST™ survey to delineate the LNAPL within a lateral tolerance of 6 m and a vertical tolerance of 2 m.
		–		
		–		
		–		
		–		
0.6	2 - 30-60% Complete	1.20	Tank farm located immediately downgradient of the release hinders detailed understanding of the plume geometry. Plume is generally bound, however, within 60 m.	None at this time. Efforts are focused on source remediation and documenting plume stability.
		–		
		–		
		–		
		–		

Item	Criteria
T-5	**Are the LNAPL fate and transport mechanisms well characterised?**
	Have the contaminant migration pathways been defined from the source to the toe of the plume?
	Have the mechanisms of natural attenuation (NA) been defined and assessed with respect to its ability to control LNAPL migration and the plume?
	Have site-specific pump/slug/tracer tests been conducted to understand hydraulic parameters?
	Has site-specific fate and transport modeling been performed to predict long-term LNAPL and plume configuration?
	Has the variability of subsurface conditions been assessed with respect to its temporal impact to the LNAPL and contaminant plume?
T-6	**Is the lithology of the site well characterised?**
	Has the site heterogeneity been assessed via continuous boring logs, cone penetrometer testing, or pump testing?
	If the site consists of multiple geologic horizons, have bedding planes been assessed?
	Has the continuity of lithologic lenses been assessed?
T-7	**Are the groundwater-surface water hydraulic interactions well characterised?**
	Have temporal and spatial interactions been assessed and measured?
	Have vertical gradients adjacent to the connection been assessed?
T-8	**Has adequate exposure/risk assessment been performed to adequately understand existing and potential future human and/or ecological impacts?**
	Has an exposure and risk assessment been done for source and plume areas with an adequate set of contaminant concentration data from contaminated media with a potential exposure?
	Has adequate sampling been performed to identify contaminants of potential concern?
	Has plume stability modeling been performed to assess potential future risk under an expanding plume scenario?
	Have all existing and potential future land use scenarios been considered in the context of site zone or land use plans?
	Have all existing exposure pathways been considered including dermal, ingestion, inhalation, and indoor air vapor intrusion?
	Has leaching of vadose zone contamination been considered?
	Has connection between contaminated groundwater and surface water been considered in the risk assessment?
Total Technical Factors	
Maximum Possible Technical Factor Score	
Total Technical Factor Conceptual Site Model Certainty	

Weight or Importance	Answer (Points)	Score	Rationale for Score	Immediate Action Items
1.0	3 - 60-90% Complete	3.00	Source and plume characterisation efforts have generally provided enough information to document the fate and transport of the LNAPL. LNAPL continues to seep into MWs after bailing. Hypothesis exists on the mechanism for this transport.	Additional data needed on mechanism of continued LNAPL see page into MWs and long-term sustainability of it.
		–		
		–		
		–		
		–		
		–		
1.0	4 - >90% Complete	4.00	Many soil boring and lithologic logs form the basis of a detailed lithologic profile at the site.	None at this time.
		–		
		–		
		–		
0.0	0 - Not Applicable	0.00	Not applicable. No surface water interactions are present.	None at this time.
		–		
		–		
1.0	3 - 60-90% Complete	3.00	Exposure assessment has been completed by prior consultant and only identified potential future risk under residential use. Considering current and planned future land use is industrial/ commercial, no buildings are present over the contamination, and the plume appears stable, no risk is evident.	Close the data gap related to contamination at 3 m bgs and ensure no risk to workers is present.
		–		
		–		
		–		
		–		
		–		
		–		
		–		
		19.20		
		26.40		
		72.7%		

Criteria that are answered "1 - <30% Complete" are highlighted in RED and, if given a high importance, should be further characterised.

Criteria that are answered "2 - 30-60% Complete" are highlighted in ORANGE, and if given a high importance, should be considered for further characterisation.

TOTAL SCORE INTERPRETATION:

>90%   The site is well characterised and suitable as a basis for remedial decision making.

60-90%   The site is adequately characterised and may be suitable for remedial decision making. Increased certainty in some factors may be desired prior to remedy design.

30-60%   Site characterisation is inadequate for use as a basis for most remedial action decisions. Additional work is prudent to improve certainty.

<30%   Site is poorly understood and should not be used as a basis for remedial decision making. Additional work is required to improve certainty.

If additional certainty is required by the project team, then additional data collection must be performed in order to close data gaps.

This scoring sheet can be revisited at the end of each data collection phase to assess the level of certainty and the need for additional data.

APPENDIX B. Three-dimensional CSM

Introduction

Three dimensional (3D) models pull together a wide array of collaborative data resources to give the project stakeholders the ability to interactively view and manipulate site features which previously were not able to be viewed in such a way. A 3D Conceptual Site Model (CSM) helps to clarify complex sites by aiding in the demonstration of site characteristics, and are a valuable tool for decision-making throughout the life of the project. Further, the popularity of these models is changing how we organise and carry out site investigation and remedial design efforts. They are a great way to convey the past and present conditions at a site, and can be extremely useful for devising a path forward on a cleanup or demonstrating compliance to a regulatory agency. While it is true that these models require an initial investment, client and regulator feedback has shown that for complex sites the benefits far outweigh the costs when 3D visualisation is incorporated into the initial project work plan.

A reliable 3D CSM is valuable to both technical and non-technical observers and can be used to demonstrate the most basic or the most intricate details of a site. These models can show the relationships between surface and subsurface features, demonstrate where areas of uncertainty or concern exist at a site, and provide the ability for detailed analysis between areas of known and interpreted results. A 3D CSM has the ability to display surface features, aerial photography, lithologic layers, transient water table conditions, soil and groundwater contaminant concentration data, real-time *in-situ* measurements such as laser-induced fluorescence (LIF), changes in plumes over time, and much more. In recent years, continued improvements to 3D visualisation packages have enabled visualisation of sites with multiple chemicals, complex geology, and dynamic hydraulic conditions. The 3D modelling software allows calculation of contaminant mass, mass flux, and impacted soil and groundwater volumes. A 3D CSM has been used to delineate Light Non-Aqueous Phase Liquid (LNAPL), Dense Non-Aqueous Phase Liquid (DNAPL) and dissolved phase chemical plumes. Through the use of kriging and other interpolation methods, modellers can estimate areas of impact between points of known conditions. 3D CSMs can become an integral part of site investigation and remedial design processes by helping project teams identify data gaps during field efforts, design or augment monitoring well networks, aid in testing alternatives for remedial systems, and graphically demonstrate compliance with remedial objectives and regulatory requirements.

Environmental Visualisation System™ (EVS) Software Package

To create 3D CSMs, project teams can draw on a number of powerful modelling and visualisation packages to help interpret field data and visualise the results. One example is C Tech Corporation's Environmental Visualisation System (EVS), or in recent years, their upgraded package Mining Visualisation System (or MVS) (www.ctech.com/index.php). EVS and MVS have been used to develop numerous site-specific 3D models at sites throughout the US and abroad.

CSMs built by EVS/MVS practitioners have demonstrated site features including, but not limited to: building and roads; above ground storage tanks; aerial photography; geologic layers; potentiometric surfaces; underground utilities; soil and groundwater contaminant plumes; and results of environmental studies performed using technologies such as membrane interface probe (MIP) and LIF. The 3D modelling software has the capability to accept output from many sources and allows the project team to bring together outputs from field investigation, surveying, historic CAD drawings, GIS shape files, output from groundwater flow models, and numerous other sources to build one interactive 3D CSM. And, in recent years, these models have found greater utility as investigation tool such as MIP and LIF have become more commonplace, often generating exponentially larger data sets than conventional sampling methods. The 3D visualisation capabilities allow for results of these new technologies to be quickly and effectively visualised, often with the model being created while the field effort is still underway to aid in guiding the investigation.

Example model

The following section describes an example 3D CSM. This particular CSM was created to help visualise the results of a LIF investigation performed at a site with complex surface and subsurface features, including several geologic layers, a shallow groundwater interface, and directly adjacent surface water separated from the subsurface soil and groundwater system by a network of cement and wood boundary walls. The model was prepared to help the project team visualise the special relationships between various complex features and to identify areas of chemical impact and preferential pathways along geologic, hydrogeologic, and anthropogenic features. The 3D CSM consists of a series of slides which in the actual deliverable can be manipulated in 4D (3D plus time) using C Tech's 4D Player (www.ctech.com/index.php?page=download). In order to highlight all of the necessary features, the 3D CSM was built as a series of slides all showing various features of the site model.

Figure 1 shows a slide created for the CSM in which the surface and subsurface features are clearly visible and in which the relationship between the surface water, boundary walls, and geology is highlighted.

On the top, this figure shows the site buildings, railroad tracks, and sloping geology to the east down to the surface water. Below ground, it shows the location of the geologic contacts and the location of a historic deck platform and quay wall which extend the length of the site adjacent to the surface water body.
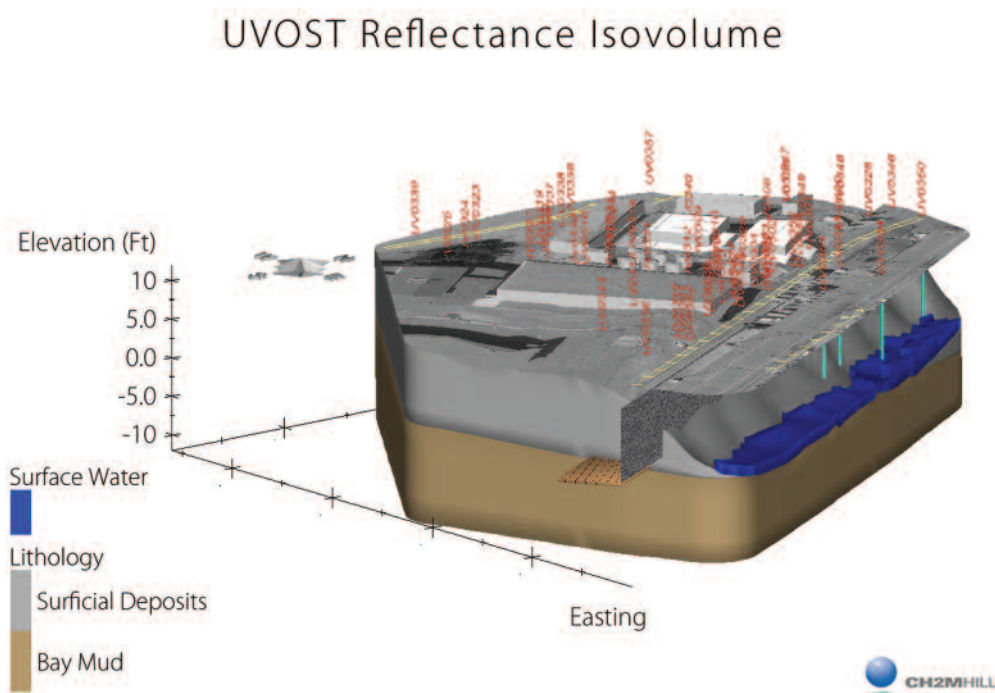
Figure 1.

Figure 2 shows the same slide in plan view.
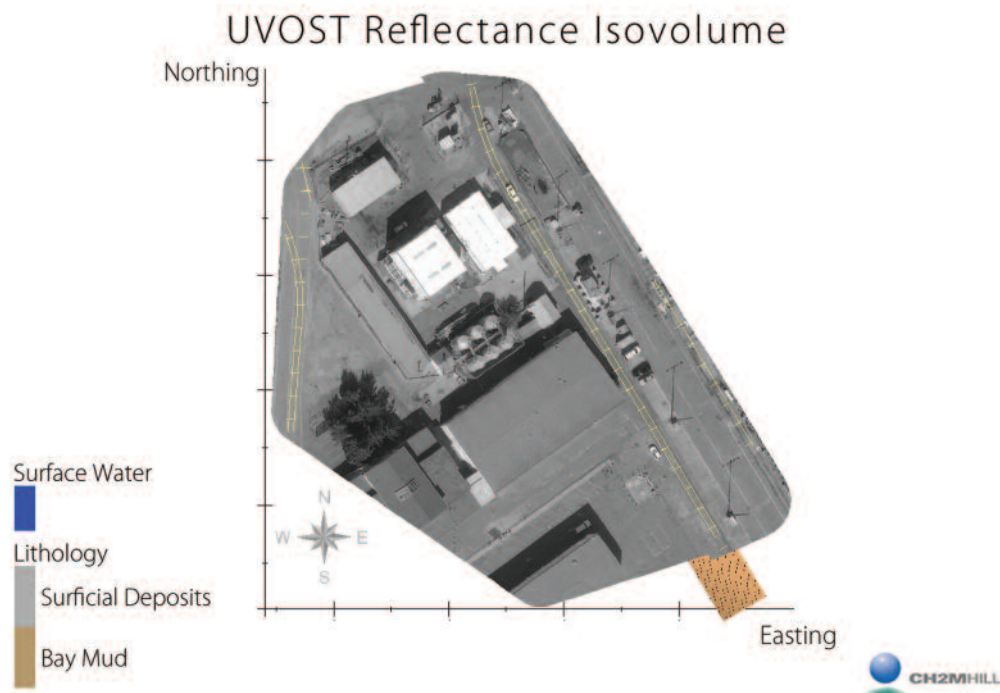
Figure 2.

In the actual CSM, the end user would have the ability to rotate the view between these two and other views of the model.

The next figure (Figure 3) shows how layers of the CSM are removed or added to highlight various features. In this example, the geologic layers have been removed (leaving behind only their outline) to reveal the location of the subsurface LIF borings and the location of the groundwater interface.
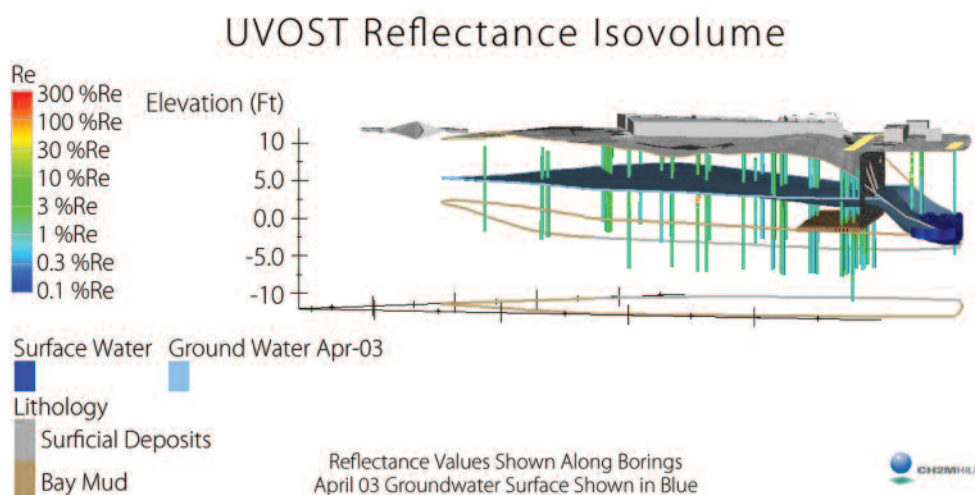
Figure 3.

In the next figure (Figure 4), the groundwater surface has also been removed (showing only the outline of the surface) to better illustrate the location of the quay wall and the LIF borings in relation to the surface features.

UVOST Reflectance Isovolume
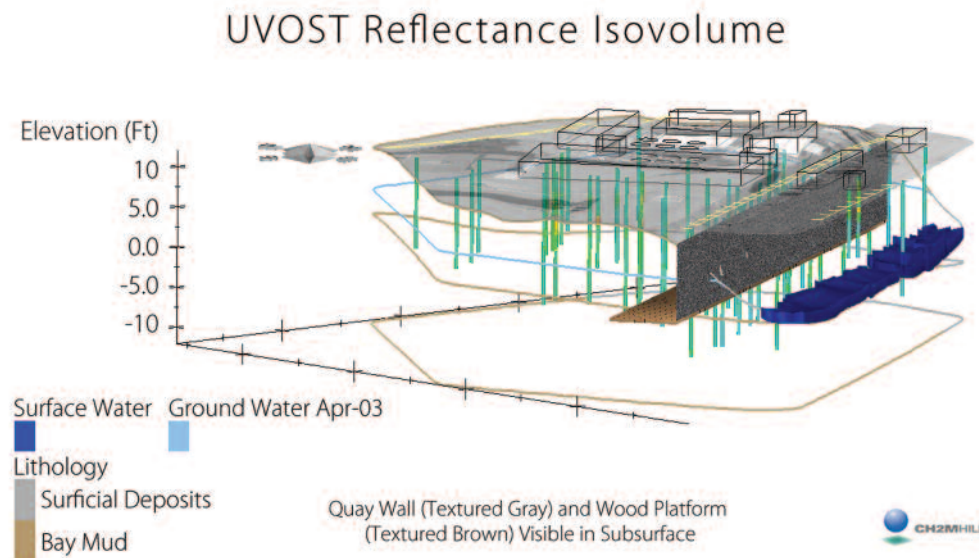
Figure 4.

In this next figure (Figure 5), the interpreted contaminant plume identified during the LIF investigation has been added to the CSM. The plume shown is the estimated area of LIF response above 5% Relative Emittance (RE) as measured by Dakota Technologies UVOST™ probe (www.dakotatechnologies.com). The interpretation of the known data to areas of unknown data was performed through a method called kriging (provided with MVS) whereby the program assigns a value (and a confidence) to nodes adjacent to areas of known concentration values. Kriging is a mathematical process recognised by the US EPA as the best and standard means for interpolation and extrapolation of measured data.

UVOST Reflectance Isovolume
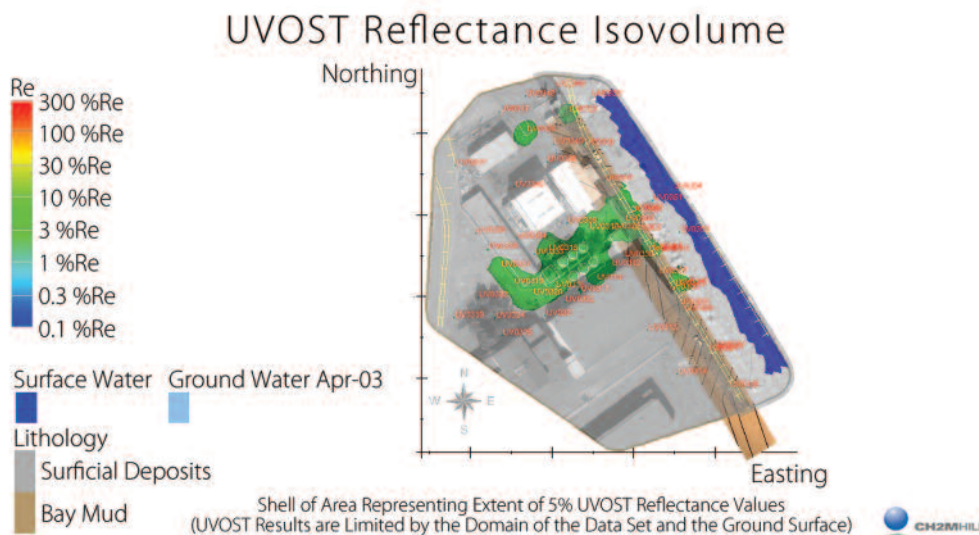
Figure 5.

The next figure (Figure 6) shows the locations of each of the LIF borings. The detections along each boring are clearly shown along each of the vertical borings, and can be interpreted when compared to the colour legend at the left of the model. This legend also corresponds to the colours for the interpreted plume area. When working with the actual model, the end user can rotate, translate, and zoom-in to better view and examine the relationship between the areas of known detected value and the interpreted plume configuration.
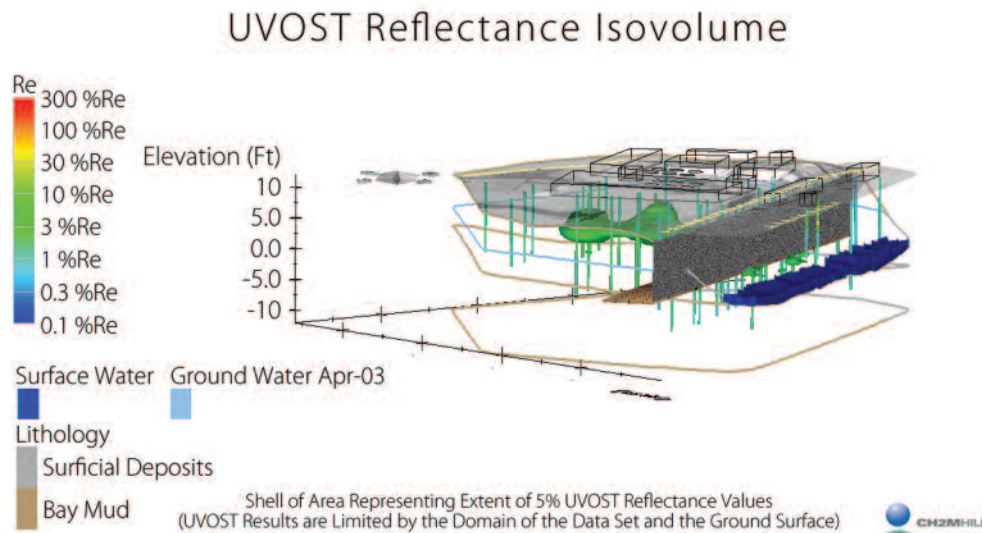
Figure 6.

The final figure (Figure 7) shows the ability of the CSM to show plumes of higher or lower detection. This particular example is from the same LIF results, but instead of the 5% UVOST™ RE plume, now shows the area of impact modeled greater than 20% UVOST™ RE.
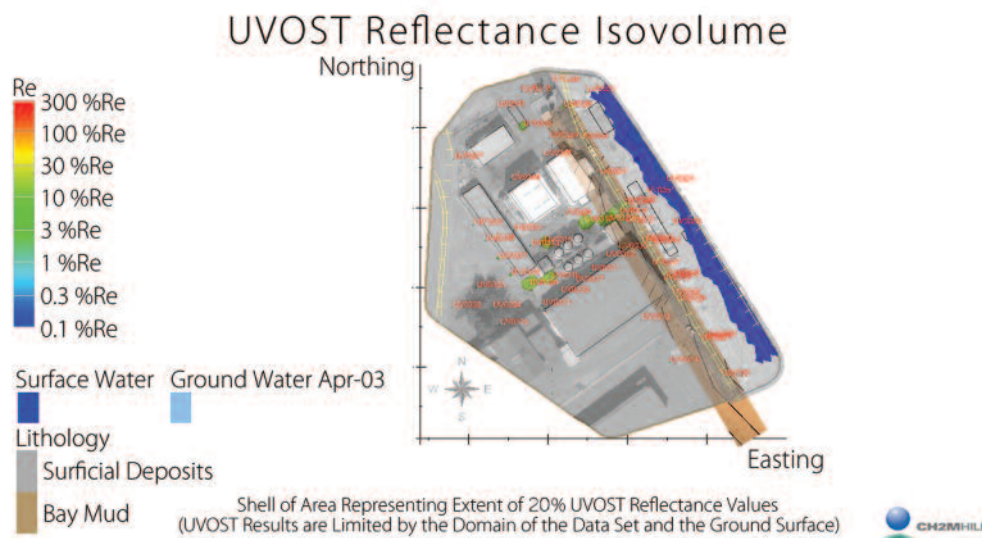
Figure 7.

Creation of a CSM

The process for creating a 3D CSM can be as easy or as complicated as is needed to meet the data needs for the particular application. In general, it is important that the project team has reliable field data organised with northing, easting, and elevation (X, Y, and Z) values for each location of known sampling and surveying data, as well as an established coordinate system, and a plan for how to model anomalous and non-detect results. Because of the need for consistency with data, the process of building an accurate 3D model will provide the project, to some degree, with a quasi-audit of the project data set. This process, while not the actual visualisation of the data, adds value to the project team in knowing that all of their data can be modelled into one space, and gaps or inconsistencies in the data set can be identified. With this in mind, it is important that the project team work closely with the model development team to ensure that components combined in the model fit together in a known coordinate system and make sense when compared to known site features. In cases where multiple coordinate systems exist, it is imperative that these data be converted to one system early in the modelling process. In addition to establishing this system, it is important that the project manager (or technical lead) provide the model creator with a detailed scope of what they are looking to incorporate into the model, and their expectations for model delivery. The modeller can then work with the project team to outline an achievable model, and provide an accurate estimate for level of effort and delivery schedule. The modeller should also make clear to the project team the expectations for data delivery from the team, and point out any areas where failure to deliver accurate and timely data may hinder model delivery. The process of creating an accurate and useful 3D CSM can be challenging and requires detail oriented discussions. However, with everyone committed to the success of the model, the entire team will be rewarded with a product that will enhance the value of the project.

Conclusions

With the vast amounts of data collected to characterise complex sites, it is prudent to provide project teams, technical specialists, clients, and other stakeholders the ability to view their sites in a 3D CSM. These 3D models are proving invaluable in conveying complex ideas in an easy to view, easy to work with, 3D visualisation, highlighting the complex processes and physical features common to complicated sites. These models, by providing a clear and concise 3D picture of the site, can lead to huge cost savings and often enhance technical and legal defensibility of site conditions. These models are designed to display surface features, aerial photos, subsurface lithology and hydrogeology, and analytical contaminant distribution. They can incorporate output from many sources and bring them all together in one place. These models are ideal for identifying data gaps during site investigations, designing or improving monitoring networks, estimating volume and mass of contamination for excavation or treatment, aiding in remedial design, and graphically demonstrating compliance with remedial objectives and regulatory requirements. Visualisation output can typically include 2D images, interactive models, and even 3D animations. 3D CSMs are becoming an integral part of remedial investigation and design processes for complex sites. They are invaluable in communicating design intent to project stakeholders and helping to cost-effectively explore a greater number of alternatives during design development.

APPENDIX C. Tier 1 characterisation information checklist

		Information obtained?	
Project:	Project No.:		
		YES	N/A
1	**SITE INFORMATION**		
1.1	Name:	❏	❏
1.2	Address:	❏	❏
1.3	Lot/DP No.:	❏	❏
1.4	Site area/dimensions:	❏	❏
1.5	Zoning:	❏	❏
1.6	Current site use:	❏	❏
1.7	Surrounding landuses (see also 3.7):	❏	❏
	- North	❏	❏
	- South	❏	❏
	- East	❏	❏
	- West	❏	❏
1.8	Driver for site characterisation (provide further detail where possible):	❏	❏
	- Spill/incident/verified leak	❏	❏
	- Property transfer/landuse change	❏	❏
	- Community/regulator requirement	❏	❏
	- Due diligence/good practice	❏	❏
	- Other (describe)	❏	❏
1.9	Key stakeholders (provide further detail where possible):	❏	❏
	- Owner/occupier	❏	❏
	- Regulatory authority	❏	❏
	- Purchaser	❏	❏
	- Community representative	❏	❏
	- Other (describe)	❏	❏
2	**SITE HISTORY**		
2.1	Previous environmental/site investigation reports:	❏	❏
2.2	Previous site landuses:	❏	❏
2.3	Previous uses of surrounding land:	❏	❏
2.4	Details of current and former ASTs/USTs:	❏	❏
	- Number and location	❏	❏
	- Capacities	❏	❏
	- Contents	❏	❏
	- Age/when removed or replaced	❏	❏
	- Construction/condition of tank	❏	❏
	- Bunding/spill control measures	❏	❏

		Information obtained?	
		YES	N/A
2.5	Product spill and loss history:	❏	❏
2.6	Historical disposal locations:	❏	❏
2.7	Local site knowledge from owner/staff/residents:	❏	❏
2.8	Known and likely contamination sources:	❏	❏
3	**SITE CONDITION AND ENVIRONMENT**		
3.1	Site and surrounding topography:	❏	❏
3.2	Regional geology and hydrogeology:	❏	❏
3.3	Site surface (i.e. sealed, unsealed?):	❏	❏
3.4	Site drainage features:	❏	❏
3.5	Presence and description of underground services:	❏	❏
3.6	Preferential flow pathways:		
3.7	Indicators of contamination (staining, odours, plant stress, bare earth, etc):	❏	❏
3.8	On site and nearby sensitive receptors (water bodies, sensitive habitats, communities, etc):	❏	❏
3.9	Site lithology/geology:	❏	❏
	- Soil stratigraphy in accordance with recognised classification (e.g. UCS)	❏	❏
	- Borehole and/or test pit logs for investigation locations	❏	❏
	- Descriptions of any observed contamination impact in boreholes/test pits	❏	❏
3.10	Site hydrogeology:	❏	❏
	- Presence and depth to groundwater	❏	❏
	- Details of the location and construction of existing/new on-site groundwater monitoring wells	❏	❏
	- Local groundwater flow direction and flow rate (hydraulic gradient and conductivity if available)	❏	❏
	- Presence of odours, sheen or free product (including thickness of any free product)	❏	❏
	- Details of off-site wells in vicinity of the site	❏	❏
3.11	Preliminary CSM:	❏	❏
4	**SAMPLING AND ANALYSIS PLAN**		
4.1	Data Objectives and Data Quality Objectives:	❏	❏
4.2	Media to be sampled (i.e. soil, groundwater, LNAPL, vapour):	❏	❏
4.3	Sampling locations and rationale (shown on a site plan):	❏	❏
4.4	Sampling/field screening methods and rationale:	❏	❏
4.5	Analytical methods and rationale:	❏	❏
4.6	Frequency of sampling/analysis and rationale:	❏	❏
4.7	Methods for analysing and interpreting data:	❏	❏
4.8	Quality Assurance/Quality Control requirements (field and laboratory):	❏	❏
5	**INVESTIGATION RESULTS AND INTERPRETATION**		
5.1	Presentation of data and findings:	❏	❏
	- Results tables	❏	❏
	- Figures and graphics (results shown on plans or as contamination contours)	❏	❏
	- Statistical analysis of data	❏	❏

		Information obtained?	
		YES	N/A
5.2	Updated CSM:	❏	❏
	- Product release conditions	❏	❏
	- Hydrogeological conditions	❏	❏
	- Dimension, composition and depth of LNAPL body (free-phase/residual saturation)	❏	❏
	- Type and extent of soil and/or groundwater contamination	❏	❏
	- Type and extent of vapour contamination in the vadose zone	❏	❏
	- Degradation processes	❏	❏
	- Potential receptors and exposure pathways	❏	❏
5.3	Comparison to Tier 1 screening criteria:	❏	❏
5.4	Potential human health risks:	❏	❏
	- Current site use	❏	❏
	- Proposed site use	❏	❏
	- Off-site	❏	❏
5.5	Potential ecological risks:	❏	❏
	- Current site use	❏	❏
	- Proposed site use	❏	❏
	- Off-site	❏	❏
5.6	Potential aesthetic issues:	❏	❏
	- Current site use	❏	❏
	- Proposed site use	❏	❏
	- Off-site	❏	❏
5.7	Other considerations (i.e. community, economic, etc):	❏	❏
5.8	QA/QC evaluation:	❏	❏
5.9	Discussion/conclusions:	❏	❏

ADDITIONAL COMMENTS

Author/title:	Signed:	Date:
Reviewer/title:	Signed:	Date:

APPENDIX D. Example application of the guidelines

Introduction

In this appendix the use of the guidelines is further illustrated by working through the characterisation of a hypothetical site with petroleum hydrocarbon impacts. The site is a fictional scenario that has been developed for the purpose of this example by drawing on the authors' experiences from a range of real sites, in addition to example sites provided in ASTM (2006). It is reiterated that the characterisation of any site will be dependent on the site-specific conditions and stakeholder requirements. Therefore the outcomes in this appendix are applicable only to the example described, and the steps provided in the main guidelines should be followed for each site to be characterised.

Example site scenario

The example site is a former railway refuelling facility that operated for approximately 40 years, between the early 1950s and the early 1990s, with a total area of approximately 4000 m^2 (50 m x 80 m). Diesel was stored in ASTs at the site and locomotives were refuelled. After the site ceased operations, the refuelling infrastructure was removed and the site has since been a largely disused area of a wider rail yard, with only occasional use of rail sidings for shunting. There are no plans for further development at this point and the site is located approximately 100 m from a tidal river. Groundwater in the area is saline and is not a water resource.

An environmental site assessment of the wider rail yard was recently conducted by the owner for due diligence purposes. This investigation included the installation of one groundwater monitoring well in the former refuelling site area. During drilling for monitoring well installation evidence of hydrocarbon contamination was noted, including a diesel-like odour at depths of 0.5 m below ground level (bgl) to 3.5 m bgl and reported observations of product at a depth of approximately 2.5 m bgl. The lithology encountered comprised a thin layer of fill, over silt and clay grading to siltstone at a depth of approximately 5.0 m bgl. Groundwater was present at a depth of approximately 2.5 m bgl, and a sample that was collected from the monitoring well reported a concentration of TPH C_{10}-C_{36} of 13,000 μg/L, with the majority of the contamination reported in the C_{15}-C_{28} range.

The site owner now wished to adequately characterise the former refuelling facility to ascertain potential risks and the requirement for remediation or management of the site.

Guidelines application procedure

The characterisation of the site will now be described, following the steps provided in the guidelines. It is noted that all aspects of the guidelines will not necessarily be utilised in this example, only those that are required for the characterisation of this site.

Site management planning

The end-point strategy for the site was first considered, in consultation with the main stakeholder, the site owner. Consultation with the local regulator was deferred until additional site information had been gathered, as there was no apparent immediate risk to human health or the environment from the identified contamination. The agreed draft end-point strategy was aimed at continued use of the site for limited rail purposes and therefore included goals of establishing the risks associated with the identified contamination, and whether remediation was required to allow the site to continue its current use.

A preliminary CSM for the site was formulated to identify data gaps and guide the characterisation effort. Based on the preliminary CSM it was identified that the most significant potential risk from the contamination was associated with potential impacts to the nearby tidal river. The characterisation program would therefore be developed with a focus on the following goals:

- establishing the extent of the contamination source
- determining whether the pathway from the source to the tidal river was complete
- if the pathway was complete, then assess the risk associated with the impact and the requirement for remediation.

Assign a Tier to the site

An evaluation of the level of complexity and risk at the site was then conducted in order to assign an appropriate Tier of investigation. Factors that were considered in the evaluation included:

- contaminant and hydrogeological factors:
  - the main contaminant is diesel, which is generally less toxic and mobile than petrol and is also not likely to generate vapours, though it is more persistent in the environment
  - the extent of the contamination is largely unknown, although the geology of the site, with silt and clay overlying bedrock in combination with the contaminant type, indicates that the contamination is unlikely to be very mobile
- risk factors:
  - the current land use is industrial and the site is only used intermittently, with no buildings or inhabited structures, therefore the potential risk of human exposure to the contamination is considered low
  - the only sensitive receptor in the vicinity of the site is the nearby tidal river
  - there are no known development or business constraints on the site, with it proposed to continue in its current use.

Based on the above assessment, the site was assigned as Tier 1, with a basic site investigation considered likely to provide adequate information to address risk and remediation issues.

Select the approach and design the investigation

In order to properly design the required investigation, the DOs and DQOs were first established. The DOs for the investigation were considered to align with the goals stated previously. The seven-step DQO process was then completed in order to define the criteria that the site characterisation effort should satisfy during data collection works. The full DQO process will not be repeated herein, Appendix IV of NSW DEC (2006) is recommended for example outputs from an adequate DQO process.

Once the DQO process was completed and the data requirements defined, the sampling plan could then be designed for the site. The sampling plan was designed to address the gaps in the preliminary CSM as they related to the site end-point strategy and goals/objectives for the

characterisation, with the type, quantity and quality of data to be collected defined by the outcomes of the DQO process. In summary the proposed sampling plan included:

- advancement of 10 DPT boreholes to assess the extent of the impact in soils through inspection of the cores, field screening and sample collection
- completion of six boreholes as groundwater monitoring wells to assess the extent of the impact in groundwater and the potential presence of mobile LNAPL
- basic permeability tests (slug tests) in selected groundwater monitoring wells
- analysis of collected soil and groundwater samples for TPH and PAH.

It is noted that the proposed sampling plan was considered flexible and subject to revision based on conditions encountered in the field. For example, if additional (or even fewer) investigation locations were considered necessary to adequately define the extent of the contamination then it was agreed with the owner that this work would be conducted in the same mobilisation, rather than having to return to the site.

Investigation results

The results of the investigation are summarised below:

- soil impacts were observed (odours and elevated concentrations) over an area of approximately 20 m x 30 m, with a maximum TPH C_{15}-C_{28} concentration of 15,000 mg/kg reported in a sample collected from near the centre of the plume
- field screening, using the shake test[8] indicated the potential presence of residual LNAPL in soil samples collected from the central 10 m x 10 m area of the plume, this area also reported concentrations of TPH greater than 1500 mg/kg
- the main impact in soils was largely confined to depth range of 1.5 m bgl to 3.5 m bgl, which is likely to represent the approximate seasonal groundwater level fluctuations over the period of the product release and to date
- groundwater gauging confirmed the assumption that the hydraulic gradient at the site was north towards the tidal river at a gradient of approximately 0.03
- permeability tests indicated that the approximate hydraulic conductivity of the aquifer was in the range of 0.02 m/d to 0.04 m/d

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[8] This involves placing a sub-sample of soil into a jar, adding water and vigorously shaking. If product or a sheen then appears on the surface of the water it can be used as an indicator of the presence of residual LNAPL in the sample.

- no LNAPL was found to accumulate in groundwater monitoring wells

- concentrations of TPH in groundwater ranged from 16,000 µg/L (near the centre of the plume) to 400 µg/L (at the hydraulically down-gradient site boundary, approximately 60 m from the centre of the plume).

Review and update CSM

With the investigation information now available, the preliminary CSM was updated and its adequacy reviewed in the context of the objectives of the characterisation. In summary, the updated CSM included:

- release conditions and source dimensions:
  - release conditions were still not fully known, though the site history indicated that the contamination was associated with ongoing minor spills and leaks of diesel during the 40 year operation of the facility, with the last release occurring at least 10 years ago
  - the dimensions of the source were considered to be the 10 m x 10 m area with soil TPH concentrations greater than 1500 mg/kg, extending to a depth of approximately 3.5 m bgl

- composition and characteristics of the source:
  - no LNAPL accumulated in monitoring wells and it was therefore inferred that the contamination was present source zone as residual LNAPL
  - the released product was only characterised by TPH fractionation analysis on soil and groundwater samples, with reported results in agreement with those that would typically be expected for a weathered diesel release, this was considered adequate for the purposes of the Tier 1 investigation

- hydrogeological conditions:
  - geology comprised silt and clay overlying siltstone bedrock at 5 m bgl
  - groundwater was present at a depth of 2.5 m bgl, with a calculated groundwater flow velocity (using Darcy's law and assuming an effective porosity of 0.1 for the clay aquifer) of approximately 0.01 m/d towards the north

- receptors and exposure pathways:
  - there were no significant human receptors for the contamination, which was located in an industrial site that was infrequently used and was not planned for land use change in the near future

  - in addition the contamination was located at depth largely precluding dermal contact and ingestion, and diesel is generally of low volatility so the vapour pathway was not considered significant
  - there was a potential off-site environmental receptor in the form of the tidal river, located 100 m hydraulically down-gradient from the site boundary

- multi-phase concentrations at boundaries or compliance points:
  - a sample collected from the groundwater monitoring well located at the down-gradient site boundary reported TPH concentrations (400 µg/L), though at significantly reduced levels from that reported in the source area
  - the background concentration of TPH in a groundwater sample collected from an up-gradient monitoring well was less than the laboratory limit of reporting (< 50 µg/L)

- mobility/stability of plumes:
  - there was a lack of historical data for the site and a complete assessment of stability of the LNAPL and groundwater plumes was therefore not possible
  - however, the lack of LNAPL migration into monitoring wells indicates that the LNAPL was in residual form, and given the lack of an ongoing release was likely to be largely immobile and stable or reducing in extent
  - the stability of the dissolved plume was uncertain, though it could be inferred that as the LNAPL was present in residual form and there was no ongoing release at the site, the dissolved plume was likely to be stabilising also
  - a rudimentary assessment of the mobility of the dissolved plume was made by reference to the calculated groundwater flow velocity, which indicated that the dissolved plume would take approximately 27 years to travel from the site boundary to the river.

Consider whether the data is adequate for required decisions

The updated CSM for the site indicated that the risk to human health from the petroleum hydrocarbon impact at the site was low, with no complete exposure pathways.

There was the potential for the nearby tidal river to be impacted by the dissolved plume resulting from the impact at the site; however, the attenuation in the

dissolved phase concentration between the source area and the site boundary indicated that an impact to the river was unlikely. This uncertainty would be closed out by addressing the remaining significant data gap in the updated CSM, namely the mobility and stability of the dissolved contamination plume at the site. Monitoring of surface water in the river for potential contamination impacts was not deemed necessary at this stage due to the likely attenuation between the source area and the river.

The Tier 1 investigation was considered adequate to address the majority of pertinent risk/remedial questions for the site and an upgrade to a higher Tier was not deemed necessary. However, in order to close out the data gap relating to the dissolved plume stability, further groundwater monitoring at key selected locations was proposed to be conducted on a six monthly basis (to assess seasonal impacts) for a period of two years. At the conclusion of this period the results were to be reviewed and an assessment made of the need for further monitoring or other characterisation/site management.

Present/report data to stakeholders

At the conclusion of the Tier 1 investigation, the collected data was compiled into an appropriate report for presentation to the site owner, complete with the detailed CSM, including graphical representations of the plume dimensions (including plan and cross-sections) and contaminant concentrations (shown as contours on a plan of the site). The report also incorporated the results from the previous investigation, which precipitated the current characterisation. The recommendation for further monitoring was presented in the report, and justified in the context of the data gap in the CSM related to the dissolved plume's long-term behaviour.