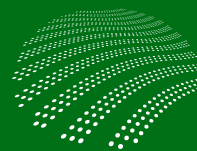


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TECHNICAL REPORT NO. 39

Risk-based management and remediation guidance for benzo(a)pyrene

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Risk-based management and remediation guidance for benzo(a)pyrene

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Executive summary

This report provides guidance on the risk-based management and remediation of benzo(a)pyrene (B(a)P)-contaminated sites. It provides information and a framework that will assist practitioners, regulators and site owners in effectively managing and remediating B(a)P-contaminated soil and groundwater. In particular, the guidance has the potential to promote best practice and reduce costs, uncertainty, and the risk to human health and the environment. Consideration has been given to accounting for site-specific variables such as bioavailability and bioaccumulation, and for providing more reliable screening criteria for determining when ecological effects might occur.

The key findings and conclusions of the report are:

- B(a)P is a ubiquitous environmental contaminant, particularly in urban areas. It tends to be of greater concern in soil and sediment matrices than groundwater or surface water, due to its very low solubility. B(a)P is persistent in the environment and does not readily degrade, and B(a)P contaminated soils and sediments are difficult and costly to remediate.
- Human health and ecological screening criteria are available in Australia for B(a)P (NEPM HILs and ESLs respectively).
- With respect to the HSLs, this guidance document has not sought to assess and revise the values that are listed in the NEPM for B(a)P. However, the application of these HSLs generally does not consider bioavailability, and there is concern that this may be overly conservative in many cases. It is recognised that the bioavailability of B(a)P and hence toxicity can reduce through sorption to organic material in the soil, with ageing, and with certain soil properties and other factors. However, methods have not yet been developed that can reliably measure the bioavailability of B(a)P, and using bioavailability or bioaccessibility measures to derive site-specific criteria for organic contaminants is not well established in Australia. This is likely to change in the future, as laboratory methods become validated and their use more certain and reliable. An approach currently being developed in Australia by Juhasz et al. (2016) to measure the bioaccessibility of B(a)P, individual PAHs and the sum of 16 PAHs, using a sorption-sink laboratory test is showing promise for assessing bioavailability relevant to human health. It is recommended that this be considered as a line of evidence as to the likely level of bioavailability of B(a)P.
- The NEPM ESLs are based on an older set of Canadian soil quality guidelines, which have been subsequently revised. For this guidance document higher reliability screening levels have been developed using additional and more recent information following the NEPM methodology. The derived screening levels are more than an order of magnitude greater than the ESLs previously listed in the NEPM, and more generally accord with the revised Canadian guideline levels. In the case of urban land, the revised ESLs are considerably higher than the corresponding HSLs, and are not likely to determine the requirements for remediation.
- As for the HSLs, the application of the NEPM ESLs for terrestrial ecosystems does not take into account changes in bioavailability that might apply. This may be unnecessarily conservative depending on site-specific factors. Some contaminant extraction methods are aggressive, and may overestimate the fraction of B(a)P

that is bioavailable for uptake by an organism. Currently there is insufficient information to reliably quantify the effects of aging and soil properties on bioavailability. This guidance has considered this matter, and recommends that the assessment of the bioavailability of B(a)P in soils should be undertaken using a lines of evidence approach, with the butanol (BuOH) extraction method being used to provide a measure of the bioaccessible fraction of B(a)P. Other lines of evidence that could also support the conclusion that B(a)P is likely to have reduced bioavailability to organisms include contaminant age, source and composition of contamination, and the soil properties.

- With respect to the protection of aquatic ecosystems, the ANZECC/ARMCANZ (2000) guideline values are used in Australia for this purpose. For the protection of sediments, a set of revised ANZECC/ARMCANZ sediment guideline values have been published. This guidance document has not sought to re-evaluate these values. In the case of water, the values are numerically low, and can be below standard laboratory limits of reporting. However, because B(a)P has low solubility it is usually not present in soluble form in water, and it is more often the case that B(a)P adsorbed on sediments, or contaminants other than B(a)P, will determine the requirements for remediation of aquatic ecosystems.
- Given that B(a)P is often found at concentrations that exceed the HILs or the ESLs, and does not readily degrade, remediation of B(a)P impacted soil and sediment (and to a lesser extent waters) may be indicated. In understanding the implications of the exceedances of the screening values, and the risks posed by B(a)P contamination to human and ecological receptors, it is important to develop a site-specific CSM. The CSM should detail the source, potential receptors, exposure pathways by which receptors may come into contact with B(a)P, and the likelihood that B(a)P may be present in less bioavailable form. Guidance on developing a site-specific CSM is provided.
- For situations where there is a requirement for remediation of B(a)P contaminated media, this guidance document provides general guidance on developing a remediation strategy. Typically, response actions will include no action, re-use, in-situ or ex-situ treatment, containment or institutional controls, or excavation (soil)/extraction (groundwater) and offsite disposal. Because of the recalcitrance of B(a)P in soil, treatment options can be limited, and it can be difficult to reach the low concentrations indicated by the HILs, or the ESLs in the case of land with high ecological significance. Consideration of the lines of evidence regarding the level of bioavailability that is likely to apply at a site may support the conclusion that the B(a)P poses a low risk to human health and the environment, and may allow concentrations higher than the HSLs and ESLs to remain on site.

Abbreviations

ANZECC	Australian and New Zealand Environment and Conservation Council
ASLP	Australian standard leaching procedure
BuOH	Butanol
B(a)P	Benzo[a]pyrene
CEC	Cation exchange capacity
CRC CARE	Cooperative Research Centre for Contamination Assessment and Remediation of the Environment
CSM	Conceptual site model
CT	Contaminant threshold
DCM	Dichloromethane
EEA	European Environment Agency
EIL	Ecological investigation level as per the NEPM
EPA	Environment Protection Authority
ESB	Equilibrium sediment benchmark
ESL	Ecological screening level as per the NEPM
GIL	Groundwater investigation level
HIL	Health investigation level as per the NEPM
HSL	Health screening level as per the NEPM
HPCD	hydroxypropyl-beta-cyclodextrin
IWRG	Industrial waste resource guidelines
K _{ow}	Octanol/water partition coefficient
LOR	Laboratory limit of reporting
MAHs	Monocyclic aromatic hydrocarbons
NAPL	Non aqueous phase liquids
NEPM	National Environment Protection (Assessment of Site Contamination) Measure (NEPM) 1999 (as amended 2013)
NHMRC	National Health and Medical Research Council
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NOEC	No observed effect concentration

PAH	Polycyclic aromatic hydrocarbon
PBET	Physiologically based extraction tests
PNEC	Predicted no-effect concentration
POP	Persistent organic pollutant
RAP	Remediation action plan
SQGV	Sediment quality guideline value
SSD	Species sensitivity distribution
SWL	Standing water level
TCLP	Toxicity characteristic leaching procedure
TDS	Total dissolved solids
TEF	Toxicity equivalence factors
TEQ	Toxic equivalent quotient
TOC	Total organic carbon
US EPA	US Environmental Protection Agency

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1. Introduction

1.1 Background

Benzo(a)pyrene (B(a)P) has been identified by CRC CARE as a first tier priority contaminant in Australia (CRC CARE 2014a). It is one of 28 polycyclic aromatic hydrocarbons (PAHs) classified by the US EPA as priority pollutants due to its carcinogenicity (US EPA 2008).¹ B(a)P is a common contaminant throughout Australia, ubiquitous in the urban, and to lesser extent regional environments. It is a persistent organic pollutant (POP), characterised by low aqueous solubilities, low vapour pressures, lipophilic properties, and an extended half-life in soil (Rostrami & Juhasz 2011).

Although numerical screening levels for human health and the environment are available in Australia, they are stringent due to the limited toxicity data used to derive them and are often exceeded. The screening levels do not account for variations in the bioavailability of B(a)P, and bioavailability can vary considerably depending on factors such as the presence of other PAHs and hydrocarbons, the soil matrix and properties, and the age of contamination. If bioavailability is not accounted for, the screening levels may at times lead to unnecessarily low remediation targets. It is difficult to directly measure bioavailability, and to date it has generally not been possible to vary the screening levels to account for reductions in B(a)P bioavailability.

In terms of management and remediation of B(a)P contamination, available technologies such as physical-chemical, chemical and thermal treatments are generally well understood. There is uncertainty regarding the effectiveness and applicability of bioremediation and stabilisation, and this is an area of research. Despite there being a general understanding of remedial options, there is currently no standardised and accepted approach to the risk-based management and remediation of B(a)P contaminated sites in Australia.

To address these knowledge gaps, the intent of this guidance is to provide an overview of risk-based management and remediation strategies for B(a)P-contaminated soil and groundwater that accounts for site-specific variables such as bioavailability, bioaccumulation, and likely exposure. It is intended that this guidance assist practitioners, regulators and site owners to effectively manage and remediate B(a)P-contaminated soil and groundwater, allowing more targeted remediation and potentially reducing the cost of managing contamination while continuing to protect human health and the environment.

It should be noted that although this guidance is primarily focused on B(a)P, it is recognised that B(a)P is usually not present in isolation. Other PAHs can have a similar mode of effect on human health, and it is usual to consider these other PAHs in combination with B(a)P in terms of their toxic equivalent. As a result, the assessment of B(a)P and PAHs has complications not relevant to individual chemicals, such as composition, toxicity of mixtures, and differences in bioavailability and bioaccessibility of the different components in the mixture. It is important that the implications of PAH

¹ Priority pollutants are a set of chemical pollutants that US EPA regulates, for which EPA has published analytical test methods (water.epa.gov/scitech/methods/cwa/pollutants-background.cfm).

mixtures be considered when applying this guidance and determining remediation and management strategies for a site.

1.2 Scope of the document

This guidance is aimed at regulators, industry, environmental consultants, remediation practitioners, owners and operators of contaminated sites in Australia. It provides a framework for developing a B(a)P conceptual site model and developing a management and remediation strategy for a B(a)P-contaminated site.

It is intended to work within the extent of the framework covered by the *National Environment Protection (Assessment of Site Contamination) Measure 1999* as amended 2013 (herein referred to as the NEPM), and will complement the National Remediation Framework which is currently being prepared by CRC CARE. This guide provides alternative soil ecosystem criteria to the NEPM, based on updated information available. It does not provide alternative soil and groundwater human health screening criteria to the NEPM, but does provide an outline of how site-specific factors such as bioavailability and bioaccessibility could be considered in determining the risk profile associated with B(a)P contamination.

2. B(a)P and the environment

2.1 Sources

PAHs, including B(a)P, are ubiquitous environmental contaminants, formed primarily from (US EPA 2006, Juhasz & Naidu 2000, CRC CARE 2014b, Duan et al. 2015b:

- incomplete combustion of organic materials such as the processing of coal
- coke production
- carbon black and asphalt production and use
- crude oil
- combustion of natural gas
- refuse
- vehicle emissions (exhaust condensate and particulates, tyre particles, lubricating oils/greases)
- heating
- cooking
- tobacco/cigarette smoking
- as by-products of industrial processes, and
- natural processes, including carbonisation.

Bonfire smoke has been reported as containing up to 70 parts per million of B(a)P, approximately 350 times the concentration in cigarette smoke (Juhasz & Naidu 2000).

Food is considered the primary source of human exposure to PAHs, due to the formation of PAHs during cooking or from atmospheric deposition of PAHs on grains, fruits and vegetables (Rostami & Juhasz 2011, CRC CARE 2014b). The main non-dietary source of B(a)P exposure is through ingestion of contaminated soil (Rostami & Juhasz 2011).

Throughout Europe, B(a)P in particulate matter is of concern, with widespread exposure particularly in central and eastern Europe. In Europe, particulate emissions of B(a)P increased by 21% between 2003 and 2012, driven by a 24% increase in emissions from domestic combustion (EEA 2015). It is estimated that, in 2012, a quarter of the EU urban population was exposed to B(a)P concentrations above the EU target value of 1 ng/m³, and up to 88% of the population were exposed to concentrations above the WHO air quality guidelines reference level of 0.12 ng/m³ (EEA 2015).

There are an estimated 160,000 contaminated sites in Australia of which 60% are hydrocarbon-contaminated sites (Duan 2014). The number of sites contaminated with PAHs is unknown, though it can be assumed that all former gasworks sites are contaminated with PAHs (among other contaminants). Sites where ash from wood fires has been disposed of historically will also contain PAHs.

2.2 Typical concentrations in the Australian environment

Attempting to define a typical concentration range for B(a)P-contaminated material (soil, sediment, groundwater, surface water) in Australia is difficult and subjective, given the broad range of potential sources and ubiquitous nature of contamination. CRC CARE (2014b) has noted that B(a)P tends to increase in abundance near urban

centres, likely being the result of historic disposal of ash from wood fires or from industrial processes such as gas manufacture. The same trend could be inferred for existing and historical industrial centres. The concentration of B(a)P in environmental matrices may also be subject to seasonable variability (e.g. increased concentrations in airborne particulate matter during winter through widespread use of combustion heating). Workplace exposure is also an issue, with B(a)P concentrations in workplace air potentially several orders of magnitude greater than in ambient air (Juhasz et al. 2010).

Typical concentrations of B(a)P in groundwater have not been identified, but are typically very low because of its limited solubility and high K_{ow} , unless there is another solute (e.g. monocyclic aromatic hydrocarbons) that causes B(a)P to be present (such as may occur in dissolved form in oil micelles²). In this instance, the other contaminants would be likely to be limiting, and remediation of these would also address the B(a)P contamination (Ng et al. 2009).

Due to the hydrophobic nature of B(a)P, it has a tendency to accumulate in fine grained sediments, partitioning to carbonaceous material. Sediments can act as reservoirs for PAH (including B(a)P) accumulation, with a range of contributing sources such as atmospheric deposition, industry effluent, sewage discharge, boating or petroleum production/transportation/spills (Juhasz et al. 2000).

CRC CARE (2014b) provided a summary of B(a)P concentrations in environmental matrices across Australia and internationally. This is reproduced in table 1, together with information based on experience from GHD. This information is general in nature and indicative of the ranges involved, and is not specific to particular sites.

2.3 Physico-chemical properties

B(a)P is a five-ring PAH, which is sparingly soluble in water, non-volatile (exists in the atmosphere entirely in the particulate phase) and sorbs strongly to soil constituents such as clays and organic material (CRC CARE 2014b). Its tendency to sorb onto organic material reduces B(a)P bioavailability, biological activity and degradation.

Sorption is influenced by soil properties (e.g. organic matter, clay content), as well as environmental factors such as pH, temperature, and the nature of solutes in the surrounding solution (Duan et al. 2014). Concentrations in water are typically very low due to its low solubility, and as indicated above B(a)P accumulates in fine-grained sediments, and partitions to organic matter present in soils due to its hydrophobic nature (CRC CARE 2014a).

PAHs such as B(a)P that contain more than four fused benzene rings are classified as recalcitrant (Duan 2014). They are not easily degraded and are therefore difficult to remediate in contaminated soils and sediments. Biodegradation half-lives of B(a)P in soils varies considerably, with estimates ranging from 60 days (agricultural soil, degradation via co-metabolism) to 420 days (agricultural soil amended with sewage sludge), and ≤ 2 years (Rostami & Juhasz 2011, Duan et al. 2015b). In practice, B(a)P will often be found remaining in fill material (such as that contaminated with waste from

² an aggregate of molecules in a colloidal solution.

former gasworks sites, ash from wood fires, or bitumen) and in the vicinity of contamination sources after many decades.

Table 1 Typical ranges of benzo(a)pyrene concentrations in environmental matrices (CRC CARE 2014b, Nadebaum 2016)

Environmental matrix	B(a)P concentration	Locations
Air	0.0001 – 4.32 ng/m ³	Europe, Russia, UK, USA
	0.038 – 2.02 ng/m ³	Australia
Soil	14 – 536 mg/kg	Superfund sites USA
	2.9 – 90.3 mg/kg (median 17.6 mg/kg)	Australia
	0.5 – 5 mg/kg	Australia – widespread across older urban areas with a history of industrial use
	0.5 – 1,000 mg/kg	Australia – former gasworks sites
Sediment	<0.1 – 1,100 mg/kg	Canada, Europe, USA
	<0.01 – 6,800 µg/kg	Australia

Reporting degradation in terms of a half-life may be misleading and may underestimate persistence, as with time the rate of degradation may reduce and result in an increase in the apparent half-life. For example, experimentally determining half-lives by spiking fresh B(a)P into the soil may reflect the relatively available and relatively rapid degradation of this form of B(a)P, compared with the less available historical, aged and weathered B(a)P contamination present on many sites which degrades relatively slowly. The less available form of aged and weathered B(a)P may also not be to be extracted in laboratory analysis to the same degree as freshly spiked B(a)P, and in the short term this may result in a greater apparent loss of B(a)P with time than has occurred. The use of radio-labelled PAH coupled with complete combustion and trapping of radio-labelled compounds can provide a more quantitative estimate of the rate of degradation (Violante et al. 2002).

The primary physical properties of B(a)P are summarised in table 2, and the chemical structure is shown in figure 1.

Table 2 B(a)P physical properties (CRC CARE 2014a)

Property	Value
CAS number	50-32-8
Molecular formula	C ₂₀ H ₁₂
Solubility (µg/L at 25 °C)	3.8
Vapour pressure (mm Hg at 25 °C)	5.6 x 10 ⁻⁹
Henry's Law constant (atm/m ³ /mol)	4.9 x 10 ⁻⁷
Boiling point (°C)	310–312
Melting point (°C)	179
Log octanol-water partitioning coefficient (K _{ow}) *	6.04–6.35
* Measure of hydrophobicity, has a direct relationship with organic matter partitioning. PAHs with log K _{ow} >4 tend to sorb strongly to soil (Duan 2015).	

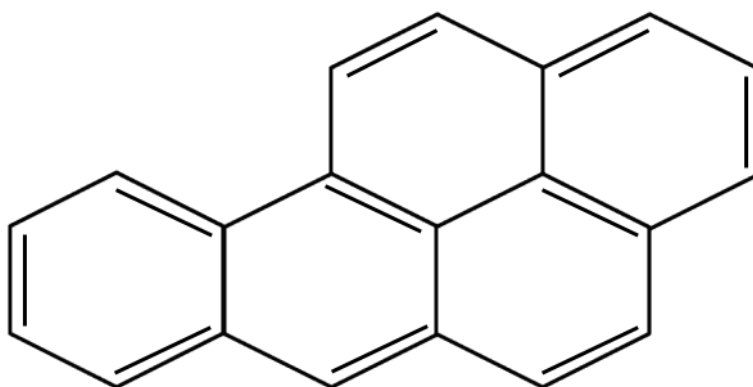


Figure 1 Chemical structure of B(a)P (CRC CARE 2014b)

2.4 Transport mechanisms and exposure pathways

The primary transport mechanisms and potential exposure pathways for B(a)P in the environment are summarised in table 3.

Table 3 B(a)P transport mechanisms and exposure pathways

Transport mechanism	Potential exposure pathway	Comment
Airborne particulate matter	Inhalation of airborne particulates (ingestion and inhalation pathway) Ingestion of contaminated soil at point of deposition Dermal contact with contaminated soil at point of deposition	Ingestion of contaminated soil can be a significant exposure pathway where contaminated soil is present, for example at gasworks and petroleum sites, and where fill containing ash from combustion is present. Inhalation of B(a)P in vapour form is not a significant exposure pathway, because B(a)P is not volatile. Inhalation of B(a)P as airborne particulate can be a significant exposure pathway, for example where airborne particulate matter results from combustion. Continued discharge of B(a)P-contaminated particulate matter can result in B(a)P-contaminated soils.
Contaminated soil leaching to groundwater and/or surface water	Ingestion of contaminated groundwater Dermal contact with contaminated groundwater	B(a)P has very low solubility, therefore does not readily leach into groundwater or aquatic environments (CRC CARE 2014b).
Surface water runoff of contaminated sediments to marine or freshwater environments (e.g. stormwater)	Ingestion of contaminated sediments Dermal contact with contaminated sediments	B(a)P has a tendency to accumulate in fine grained sediments because of its hydrophobic nature, arising for example from transport in rainfall runoff of particulate matter from contaminated areas, atmospheric deposition, seepage of petroleum hydrocarbons to surface waters, offshore petroleum production/transportation, or sewage disposal.

2.5 Fate in the environment

In air, B(a)P exists entirely in the particulate phase and is physically removed by wet and dry deposition to the ground surface (soil or water). Particulate B(a)P may degrade in the atmosphere by reaction with photochemically-produced hydroxyl radicals or

oxidant gases (NO_2 , O_3 , and SO_3). B(a)P may also photolyse directly but this can be impeded by sorption to some substrates.

In soil, B(a)P has a tendency to sorb to organic soil fractions (Mahmoudi et al. 2013). This tends to reduce B(a)P's bioavailability, biological activity and degradation, and hence biodegradation in soil is a slow process. The predominant mechanism for removal is through microbial activity (Mahmoudi et al. 2013). Sorption is influenced by soil properties and environmental factors including pH, temperature, the amount of organic matter in soil, and the nature of solutes in the surrounding solution (CRC CARE 2014b). Soil residence time also influences sorption; as residence time increases and the B(a)P ages, diffusion into soil micropores and partitioning onto organic matter increases (Mahmoudi et al. 2013). Factors influencing bioavailability of B(a)P to ecological and human receptors are discussed further in sections 3.4.3.4 and 4.1.4 respectively.

Volatilisation of B(a)P from soil is not expected to be an important fate process based on its estimated Henry's Law constant. In water, B(a)P can migrate overland in surface run-off (primarily adsorbed to sediment particles) and affect stormwater quality. Discharge of stormwater to receiving environments can result in contaminated sediment, and benthic organisms in the sediments can then be exposed to B(a)P.

B(a)P has a very low solubility in water, and generally low concentrations of B(a)P are observed in water environments. Upon discharge to the aqueous environments, B(a)P will adsorb very strongly to sediments, particularly to the organic fraction, due to its solubility and high $\log K_{OW}$. B(a)P therefore will tend to accumulate in fine-grained sediments (CRC CARE 2014b). B(a)P will not hydrolyse due to the lack of hydrolysable functional groups. Volatilisation from water will not be an important fate process based on its estimated Henry's Law constant. B(a)P has been shown to undergo metabolism by microorganisms, however this degradation process is very slow (CRC CARE 2014b). Aquatic organisms which lack metabolic detoxification enzyme systems tend to accumulate PAHs, whereas organisms such as fish show low levels due to monooxygenase detoxification enzyme activity (CRC CARE 2014b).

Because of its low solubility B(a)P will not readily leach to groundwater unless dissolved by an organic phase. It is generally not found in drinking water and, because B(a)P is typically associated with particulate material, it is readily removed in the commonly applied drinking water treatment processes (coagulation, flocculation and filtration).

B(a)P is potentially bioaccumulative in the food chain, and can occur where organisms are exposed to B(a)P. The degree of uptake by plants has not been adequately assessed (Sverdrup et al. 2002). If it is deemed that herbivorous organisms could be impacted together with their predators or consumers of their products, plant uptake may need to be considered in ecological risk assessments (see section 3.4 in relation to bioavailability and bioaccessibility factors).

The recalcitrance of PAHs to microbial degradation increases proportionally with molecular weight and $\log K_{OW}$ (Juhász & Naidu 2000). A number of bacteria, fungi and algae have been found to degrade B(a)P, with varying success depending on conditions and additives. The production of carcinogenic byproducts (metabolites) such as epoxides and dihydrodiols should be considered (Juhász & Naidu 2000). The success of organisms in degrading B(a)P when present as part of a complex PAH

mixture is uncertain. B(a)P degradation can be influenced by the presence of essential nutrients or growth substrates, soil clay and humic content, temperature, oxygen availability or soil pH (Juhasz & Naidu 2000). Where B(a)P has low bioavailability, it can reduce accessibility to microbes and hence degradation. The use of surfactants is commonly applied to assist in solubilising B(a)P and increasing its bioavailability and hence rates of degradation (Li & Chen 2009, Reddy, ZI-Hamdan & Ala 2011).

3. Human health

3.1 Toxicity and exposure pathways

B(a)P toxicology in humans is well understood. The International Agency for Research on Cancer has classified B(a)P as Group 1 (carcinogenic to humans). B(a)P has been shown in animal studies of many species to be carcinogenic via numerous routes of exposure (NEPM, CRC CARE 2014a). B(a)P is an indirect carcinogen, where carcinogenicity results from its metabolites as opposed to B(a)P itself (NEPM).

B(a)P is primarily absorbed through the gastrointestinal tract and the lungs, with the rate of absorption increasing with increased intake of polyunsaturated fatty acids (NHMRC 2011, Barhoumi et al. 2014). Several different types of tumours have been observed as a result of exposure to B(a)P, with tumour development closely related to route of administration, (dermal application induces skin tumours and oral administration induces gastric tumours). Exposure to B(a)P causes disruption to cellular genetic material, in particular DNA adducts are formed as a result of exposure, and B(a)P is considered to be a genotoxic carcinogen. A US EPA (2005) report concluded that B(a)P acts via a mutagenic mode of action and has potential to cause developmental toxicity in children, including the development and function of the immune system, and reduced fertility in offspring during adulthood following B(a)P exposure during pregnancy.

In addition, B(a)P has been demonstrated to be a skin irritant (rash and/or burning sensations) and dermal sensitiser, repeated exposure can cause thickening or darkening of the skin, and dermal exposure can be a significant contributor to total exposure (NJDH 2007, Turkall et al. 2009). Adults may be exposed dermally to contaminated soil through work-related activities (e.g. waste-disposal operations, accidental releases), while children can be exposed through play activities (Turkall et al. 2009).

3.2 Investigation levels and landfill acceptance criteria

3.2.1 Soil HILs and HSLs

The NEPM provides health investigation levels (HILs) for B(a)P and PAHs, as summarised in table 4 Table 4 (NEPM Sch B7, Appendix A2).

Table 4 Health investigation/screening levels (B(a)P, total PAHs and health screening levels (naphthalene) for soil (NEPM Schedule B1, Table 1A(1) and Table 1A(3))

Chemical	Health based investigation/screening levels (mg/kg)			
	Residential A	Residential B	Recreational C	Commercial/industrial D
B(a)P TEQ	3	4	3	40
Total PAHs	300	400	300	4,000
Naphthalene – vapour intrusion	3	3	Not limiting	Not limiting
Naphthalene – direct contact	1,400	2,200	1,900	1,100

In table 4, residential A, B and C, and commercial/industrial D indicate different levels of access to soil. Residential A indicates a garden or accessible soil, and ingestion of < 10% homegrown fruit and vegetables (no poultry). It also includes childcare centres,

preschools and primary schools. Residential B is for minimal opportunities for soil access and includes dwellings with fully and permanently paved yard space such as high-rise buildings and apartments. Residential C encompasses public open spaces such as parks, playgrounds, playing fields (e.g. ovals), secondary schools and footpaths. This does not include undeveloped public open space where the potential for exposure is lower and where a site-specific assessment may be more appropriate. Finally, commercial/industrial D includes premises such as shops, offices, factories and industrial sites.

The B(a)P toxic equivalent quotient (TEQ) in table 4 is based on 8 carcinogenic PAHs (benzo(a)anthracene, benzo(a)pyrene, benzo(b+j)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene) and their toxicity equivalence factors (TEFs) (potency relative to B(a)P) (CCME 2008, NEPM Schedule B7). The B(a)P TEQ is calculated by multiplying the concentration of each carcinogenic PAH in the sample by its B(a)P TEF, and summing these products. Significant exposure pathways in the derivation of HILs for total PAHs comprise soil ingestion, dermal contact and inhalation of particulates.

The total PAHs are based on the sum of the 16 PAHs most commonly reported for contaminated sites (NEPM). The application of the total PAH HIL should consider the presence of carcinogenic PAHs and naphthalene (the most volatile PAH). Carcinogenic PAHs reported in the total PAHs should meet the B(a)P TEQ HIL. Naphthalene reported in the total PAHs should meet the relevant HSL. Significant exposure pathways in the derivation of HILs for B(a)P comprise soil ingestion, dermal contact and inhalation of particulates.

Naphthalene direct contact values are for incidental soil ingestion, dermal or inhalation exposure pathways, which are generally not the risk drivers for the same contamination source as the HSLs for vapour intrusion (Friebel & Nadebaum 2011, NEPM, schedule B1 s 2.4.2).

Key considerations involved in the development and application of the HILs and HSLs are:

- **B(a)P toxic equivalent quotient (B(a)P TEQ) HIL:** the TEQ approach accounts for PAH-containing mixtures, and incorporates toxicity equivalence factors (TEFs) for eight potentially carcinogenic individual PAHs (including B(a)P). The toxicities of the eight PAHs (including B(a)P) are related to the toxicity of B(a)P, and given a TEF. The B(a)P TEQ is calculated by multiplying each of the individual PAH concentration with its TEF, and summing the results for all eight PAHs. The TEFs adopted have been applied for all exposure routes.
- **Total PAHs HIL:** the sum of concentrations of 16 PAHs most commonly reported for contaminated sites (NEPM). This HIL is protective of non-cancer toxicity endpoints. Carcinogenic PAHs reported in total PAHs should also meet the B(a)P TEQ HIL, and naphthalene (which is not one of the carcinogenic PAHs and is not included in the B(a)P TEQ), should meet the relevant HSL (see below).
- **Naphthalene HSL:** naphthalene is the primary PAH where volatile exposure can be significant. It is not considered carcinogenic³, and so is not included in the B(a)P TEQ. HSLs that consider exposure through inhalation of vapour were developed by CRC CARE for petroleum hydrocarbon contamination, and consider

³ US EPA classifies naphthalene as category C (possible human carcinogen)

the conditions that affect volatility, including soil type, source depth and building construction type (Friebel & Nadebaum 2011).

For the purpose of this document which focuses on B(a)P, only the B(a)P TEQ and total PAH HILs will be considered further.

The HILs for B(a)P TEQ account for oral ingestion, dermal contact and dust inhalation exposure pathways:

- For residential (HIL-A, HIL-B) and recreational (HIL-C) land use, combined child through to adult exposure is considered, as the risk is based on the incremental lifetime risk of cancer.
- For low density residential (HIL-A), dermal exposure contributes approximately 54% of the risk, while oral exposure contributes approximately 46%. This ratio changes for different land uses (HIL-B ingestion 17%, dermal 83%, HIL-C ingestion 29%, dermal 71%, HIL-D ingestion 18%, dermal 82% (NEPM, Schedule B7). The contribution of risk through dust inhalation was determined to be negligible (<1%) compared to the other two pathways for all land uses.
- The exposure pathway of plant uptake was not considered in the HIL derivation, as plants grown in PAH-contaminated soils have only a limited ability to take in and translocate anthropogenic PAHs to the plant biomass, especially higher molecular weight PAHs such as B(a)P which strongly sorb to the soils. Even if plant uptake was considered, this would contribute <1% to the HIL.
- The B(a)P TEQ HILs are based on an incremental lifetime cancer risk of 1 in 100,000.
- Oral bioavailability is assumed to be 100%, as bioavailability is highly site- and source-specific, and insufficient data are available to support and define a value of less than 100% bioavailability. Considerations surrounding the measurement and application of bioavailability in assessing the toxicity of B(a)P contamination are discussed further in sections 3.5, 3.6 and 3.7.
- Dermal bioavailability is assumed to be 6% for all source types.
- The contribution of risk through dermal exposure is based on systemic toxicity (i.e. absorbed in blood stream) not skin cancer risk. Some studies suggest that the risk of skin cancer is significantly higher than systemic toxicity, however none of the primary health organisations (e.g. NHMRC, WHO, ATSDR, USEPA) have included these skin cancer risk considerations in the derivation of their guidance and toxicity reference values, and the NEPM HIL has not included this consideration.
- The total PAH HILs are based on an arbitrary factor of 100 on the derived cancer-based B(a)P HILs. This HIL allows for the effects of the non-cancer causing PAHs if there is an absence of carcinogenic PAHs.
- Naphthalene is considered a special case due to its volatile nature and toxicity and should be compared with the naphthalene HSLs.

The calculations of the HILs are presented in the HIL calculator spreadsheet, available in the ASC NEPM toolbox. Schedule B7 of the NEPM outlines the derivation and assumptions of the HILs for PAHs (and phenols).

3.2.2 Groundwater investigation levels (GILs)

The NEPM (Schedule B1) presents groundwater investigation levels (GILs) for drinking water, and fresh and marine aquatic ecosystems based on the *Australian water quality*

guidelines 2000 (ANZECC/ARMCANZ 2000), *Australian drinking water guidelines 2011* (NHMRC 2013) and *Guidelines for managing risk in recreational waters 2008* (NHMRC 2008). The GILs apply at the point of groundwater use. GILs for other environmental values – agricultural use (stock watering and irrigation) and recreational use – are typically specified in ANZECC/ARMCANZ (2000), but no GILs have been specified for PAHs or B(a)P for these environmental values.

The drinking water GIL (0.01 µg/L) is based on the limit of determination. This is precautionary and is less than the value derived on the basis of an incremental lifetime cancer risk of 1 in 1,000,000 (which is the risk level adopted in the *Australian drinking water guidelines* for genotoxic carcinogens). Selecting the acceptable risk level is a policy-based regulatory decision (Naidu et al. 2013). In the case of water supplies the occurrence of B(a)P is very uncommon and adopting a precautionary approach does not result in a significant regulatory burden. In addition, in the case of drinking water supply systems the exposed population can be in the millions, compared with contaminated sites where relatively few people are likely to be affected, and this supports a precautionary approach for drinking water supplies.

The drinking water guideline value is typically adopted to protect the beneficial use of recreation (e.g. swimming, boating). Where ingestion is expected to be the dominant route of exposure, criteria can be derived by multiplying the drinking water guideline value by a factor of 10–20, to account for the limited ingestion of water that can occur during recreation compared with the amount allowed for in drinking (NHMRC 2008). A more conservative approach should be adopted for contaminants that might absorb via dermal exposure (such as can occur in the case of dissolved organics). In the case of B(a)P, it is likely to be present adsorbed on particulate material, and is less likely to be in a form that would be readily absorbed through the skin. If skin absorption is considered to be a concern, a site-specific risk assessment would need to be undertaken to determine what allowance should be made for absorption.

There is no recognised guideline value for agricultural use of groundwater (irrigation use). Given the low solubility of B(a)P in water and limited uptake by plants, this is unlikely to be a limiting risk pathway in human health risk assessments.

In the case of use of groundwater for stock, guideline levels for B(a)P have not been developed in Australia for stock water. In the absence of other information, ANZECC/ARMCANZ 2000 recommends that drinking water guidelines for human health be adopted for organic contaminants, although in many cases this will provide a very conservative outcome. As a comparison, the American Petroleum Institute (API) provides stock drinking water risk-based screening levels for PAHs that are protective of the health of livestock (API 2004). The API guidelines consider both high and low molecular weight PAHs, and for higher molecular weight PAHs (≥4 rings) that include B(a)P, the criteria range from 0.4 mg/L for calves, to 2.1 mg/L for horses.

3.2.3 Landfill acceptance criteria for B(a)P contaminated soil

Landfill acceptance criteria for contaminated soils differ significantly with each state and territory. Table 5 provides a summary of the relevant policies and criteria set in each jurisdiction for B(a)P and PAHs.

Table 5 Landfill disposal requirements for B(a)P and PAH contaminated soils in Australia

State	Relevant policy documents	Criteria	
		Total PAHs	B(a)P
VIC	EPA VIC 2009, <i>Industrial waste resource guidelines – soil hazard categorisation and management</i> , Publication IWRG621.	Total \sum_{16} PAHs Fill (no restriction on use): <20 mg/kg Category C: ≤ 100 mg/kg Category B: ≤ 400 mg/kg Category A: >400 mg/kg	Fill (no restriction on use): <1 mg/kg Category C: ≤ 5 mg/kg, ASLP ≤ 0.001 mg/L Category B: ≤ 20 mg/kg, ASLP ≤ 0.004 mg/L Category A: >20 mg/kg, ASLP >0.004 mg/L
NSW	NSW EPA 2014, <i>Waste classification guidelines part 1: Classifying waste</i> .	Total \sum_{16} PAHs ¹ Soil concentration only (no leachable)² General solid waste: ≤ 200 mg/kg Restricted solid waste: ≤ 800 mg/kg Hazardous waste: >800 mg/kg Specific contaminant concentration and leachable concentration when used together: General solid waste: ≤ 200 mg/kg, TCLP N/A Restricted solid waste: ≤ 800 mg/kg, TCLP N/A Hazardous waste: >800 mg/kg, TCLP N/A	Soil concentration only (no leachable) General solid waste: ≤ 0.8 mg/kg Restricted solid waste: ≤ 3.2 mg/kg Hazardous waste: >3.2 mg/kg Specific contaminant concentration and leachable concentration when used together: General solid waste: ≤ 10 mg/kg, \leq TCLP 0.04 mg/L Restricted solid waste: ≤ 23 mg/kg, \leq TCLP 0.16 mg/L Hazardous waste: >23 mg/kg, <TCLP 0.16 mg/L
QLD	Dept. of Environment and Heritage Protection 2015, <i>Model operating conditions – ERA 60 – Waste disposal</i> .	ERA 60 provides max. contaminant levels in soil that can be disposed of to landfill. Each landfill also specifies acceptance criteria (these are generally based on the levels in ERA 60) Total PAHs ⁴ Max. contaminant level for clay-lined landfills: 500 mg/kg, Max. contaminant level for double lined landfills: 1000 mg/kg	Soil: not specified TCLP: Allowable leaching contaminant levels for clay-lined landfills: 0.002 mg/L Allowable leaching contaminant levels for double-lined landfills: 0.02 mg/L
SA	SA EPA 2010, <i>EPA 889/10: Waste disposal Information sheet, Current criteria for the classification of waste – including industrial and commercial waste (listed) and waste soil</i> . ³	Total PAHs ⁴ Waste fill (no restriction on use): ≤ 5 mg/kg, ASLP not specified Intermediate waste: <40 mg/kg, ASLP not specified as long as not above criteria for soil Low-level contaminated waste: <200 mg/kg, ASLP not specified as long as not above criteria for soil High-level contaminated waste: >200 mg/kg (must be treated and remediated prior to disposal to landfill).	Waste fill (no restriction on use): ≤ 1 mg/kg, ASLP not specified Intermediate waste: <2 mg/kg, ASLP not specified as long as not above criteria for soil Low-level contaminated waste: <5 mg/kg, ASLP <0.001 mg/L High-level contaminated waste: >5 mg/kg and ASLP >0.001 mg/L (must be treated and remediated prior to disposal to landfill).

WA	WA DEC 2009, <i>Landfill waste classification and waste definitions 1996 (as amended December 2009)</i>	Acceptance criteria ⁵ C1: Soil ≤100 mg/kg, ASLP N/A C1: Soil ≤100 mg/kg, ASLP N/A C3: Soil ≤1000 mg/kg, ASLP N/A C4: Soil ≤4000 mg/kg, ASLP N/A C5: Soil >4000 mg/kg, ASLP N/A	Acceptance criteria ⁵ C1: Soil ≤5 mg/kg, ASLP ≤0.0001 mg/L C2: Soil ≤ 5 mg/kg, ASLP ≤0.0001 mg/L C3: Soil ≤50 mg/kg, ASLP ≤0.001 mg/L C4: Soil ≤200 mg/kg, ASLP ≤0.001 mg/L C5: Soil >200 mg/kg, ASLP >0.001 mg/L
TAS	EPA TAS 2012, <i>Classification and management of contaminated soil for disposal</i> , Information bulletin no. 105.	Total PAHs ⁴ Fill material (no restriction on use): ≤20 mg/kg, TCLP not specified Low level contaminated soil: ≤40 mg/kg, TCLP ⁶ ≤ 0.0005 mg/L TEQ (toxic equivalent quotient, 16 PAHs) Contaminated soil: ≤ 200 mg/kg, TCLP N/A Contaminated soil for remediation: >200 mg/kg, TCLP N/A	Fill material (no restriction on use): 0.08 mg/kg, TCLP not specified Low level contaminated soil: ≤2 mg/kg, TCLP ⁶ ≤ 0.0005 mg/L Contaminated soil: ≤20 mg/kg, TCLP ≤0.005 mg/L Contaminated soil for remediation: >20 mg/kg, TCLP >0.005 mg/L
NT	NT EPA 2013, <i>Guidelines for the siting, design and management of solid waste disposal sites in the Northern Territory</i> .	Composite liner upper limits: Total (\sum_{16}) PAHs ¹ 100 mg/kg, ASLP N/A Double liner upper limits: Total (\sum_{16}) PAHs ¹ 400 mg/kg, ASLP N/A	Composite liner upper limits: 5 mg/kg, ASLP 0.001 mg/L Double linter upper limits: 20 mg/kg, ASLP 0.004 mg/L
ACT	Environment ACT 2000, <i>Environmental standards: assessment & classification of liquid & non-liquid wastes</i> .	Contaminant threshold (CT) values for waste classification of non-liquid wastes without doing the leaching test Total \sum_{16} PAHs ¹ : not applicable Total concentration and leachable concentration (TCLP) values for non-liquid waste classification Inert waste (CT1): ≤200 mg/kg, TCLP N/A Solid waste (CT2): ≤200 mg/kg, TCLP N/A Industrial waste (CT3): ≤800 mg/kg, TCLP N/A	Contaminant threshold (CT) values for waste classification of non-liquid wastes without doing the leaching test Inert waste (CT1): ≤0.08 mg/kg Solid waste (CT2): ≤0.8 mg/kg Industrial waste (CT3): ≤3.2 mg/kg Total concentrations and leachable concentration (TCLP values for non-liquid waste classification Inert waste (CT1): ≤0.1 mg/kg, TCLP ≤0.004 mg/L Solid waste (CT2): ≤0.10 mg/kg, TCLP ≤0.04 mg/L Industrial waste (CT3): ≤23 mg/kg, TCLP ≤0.16 mg/L
¹ US EPA priority pollutant PAHs. ² If a waste's specific contaminant concentration value exceeds the contaminant threshold value set for general solid waste (CT1), further assessment using the TCLP test may be used. Where the contaminant threshold value set for restricted solid waste (CT2) is exceeded, a TCLP test must be carried out to determine the leachable concentration of that contaminant and the class of waste. ³ Revised guidance due to be released in 2015. ⁴ Individual PAHs comprising total not specified. ⁵ Acceptance criteria defined by landfill class: C1 inert landfill, C2 putrescible landfill, C3 putrescible landfill, C4 secure landfill, C5 intractable landfill (for waste that is not suitable for disposal at a class 1, 2, 3 or 4 landfill (e.g. significantly contaminated soils, industrial sludges). ⁶ TCLP pH 5 extract.			

3.2.4 Trade waste acceptance criteria

Generally water authorities have not set criteria for B(a)P in trade waste, or have set a very low limit that would trigger further consideration if B(a)P is present. It is concluded that discharges of effluent containing measurable concentrations of B(a)P to a sewerage system may not be acceptable given the very low aquatic ecosystems and drinking water guidelines available (refer to sections 3.2.2 and 4.2.4), and would require consideration on a case by case basis. B(a)P is likely to accumulate in biosolids, and this could be the limiting factor that determines the acceptability of disposal of the resulting biosolids. In assessing such effects, consideration can be given to the ratio of the mass of B(a)P discharged to the mass of biosolids produced, to determine if the discharge would be significant in terms of the concentration of B(a)P in the biosolids. Generally the concentrations of B(a)P in sewage will not be enough to significantly affect the biological processes of the sewage treatment system.

3.3 Bioavailability and bioaccessibility of B(a)P

The use of oral bioavailability in human health risk assessment is well established for metals, and has regulatory acceptance in the US (US EPA 2007). The US EPA encourages the use of site-specific bioavailability data in place of default exposure and toxicity factors. In Australia, the NEPM allows for consideration of bioavailability, but, in the case of B(a)P, there is currently no widely accepted, practicable method of measuring bioavailability B(a)P in soils, and this has precluded the bioavailability of B(a)P being taken into account.

The definitions of bioavailability and bioaccessibility can vary substantially between scientific disciplines and aspects being considered, such as environmental bioavailability, toxicological bioavailability, or bioremediation bioavailability (amongst others) (Juhasz et al. 2013). The terms bioavailability and bioaccessibility are often used interchangeably (Harris et al. 2013). At a receptor, contaminant and site-specific level, considerations will differ when evaluating the bioavailability of contaminants to humans or to ecosystems and the impacts this may have to the toxicity of contaminants and risk posed to receptors. Tests to measure bioavailability also vary considerable across disciplines, and can include microbial, soil invertebrate, amphibian, and plant tests from an ecological perspective, and in-vivo tests (carried out with living organisms) or in-vitro tests (carried out in a laboratory vessel) for humans (Juhasz, Smith & Naidu 2003).

The most widely accepted definitions with respect to human health, and those adopted in this guidance, are as follows:

- **Bioaccessibility:** the fraction of a compound that is soluble in the gastrointestinal tract, and is therefore potentially available for absorption into systemic circulation (US EPA 2007, Rostami & Juhasz 2011, EnHealth 2012, Harris et al. 2013, NEPM Schedule B4). The bioaccessible fraction of a contaminant will always be higher than, or equal to the bioavailable fraction, as the bioaccessible fraction is the theoretical maximum concentration that can enter systemic circulation. The bioaccessible fraction of B(a)P is more toxic than the non-bioaccessible (non-absorbable) fraction because of the downstream formation of toxic and carcinogenic metabolic products (Harris et al. 2013).

- **Bioavailability:** the fraction of a dose (received through ingestion, inhalation or dermal exposure pathways) that reaches systemic circulation (Rostami & Juhasz 2011, EnHealth 2012). It is expressed as the ratio or percentage of the absorbed (systemic) dose to the administered dose (EnHealth 2012). Various subsets of bioavailability are also discussed in the literature, such as oral bioavailability.

The NEPM (Schedule B4) provides definitions of subsets of bioavailability in the context of human health risk assessment:

- Bioavailable fraction – ‘the fraction of a compound that is absorbed into the body (systemic dose) following exposure via all pathways (administered dose).’
- Absolute bioavailability – ‘the fraction of a compound which is ingested, inhaled or applied to the skin that actually is absorbed and reaches systemic circulation.’
- Relative bioavailability – ‘the comparative bioavailability of different forms of a chemical or for different exposure media containing the chemical.’ For the purposes of contaminated land risk assessment this is the ratio of the absorbed fraction from the exposure medium (e.g. soil) to the absorbed fraction from the dosing medium used in the critical toxicity study.

Although discussions regarding bioaccessibility and bioavailability in humans are typically focused on the ingestion exposure pathway (i.e. through the gastrointestinal tract), in the case of B(a)P it is important to also consider the influence of bioaccessibility and bioavailability on dermal absorption.

Current risk assessment methodologies assume that B(a)P is 100% bioavailable and that all of the contaminant is solubilised in the gastrointestinal tract and absorbed into systemic circulation as there is insufficient information available to define an alternative percentage (Rostami & Juhasz 2011). However, in reality the gastrointestinal (and dermal) system can only mobilise a fraction of strongly hydrophobic organic contaminants such as B(a)P that are bound onto soil particles (Guoliarmou et al. 2013). Therefore, basing risk assessment on total concentrations of contaminants and assuming 100% bioavailability can overestimate, at times greatly, the risk that B(a)P contamination poses to human health (Alexander 2000, Rostami & Juhasz 2013). This can lead to unreasonably low clean-up goals, and unnecessary remedial works and management controls. As an example, the current HILs for B(a)P (refer to section 3.2.13.2.1) assume 100% bioavailability and are at times difficult to meet, particularly in an urban setting.

Generally, the bioavailability and bioaccessibility of B(a)P in soils have been found to be less than 100%, although estimates have varied widely. The variability in estimates may be due to inherent differences in bioavailability and bioaccessibility, but may also be because of the difficulties in obtaining an accurate measurement of these parameters at low concentrations under a laboratory setting. Some reported values may therefore not represent true B(a)P bioaccessibility or bioavailability (discussed further in section 3.5.3.5). Duan (2014) conducted in vivo bioavailability studies using swine models (considered to provide the most accurate model of human bioavailability). It was found that the relative bioavailability of aged B(a)P in soil ranged from approximately 22% to 63%, except in one very sandy soil where relative bioavailability was approximately 100%. Other studies reported by Juhasz et al. (2013) indicated PAH bioaccessibility in contaminated soil ranging from 0.1–89%, dependant

on contaminant ageing, soil physicochemical properties, and the method used for its assessment.

3.4 Factors that influence bioavailability and bioaccessibility

Many factors have been shown to influence the bioavailability and bioaccessibility of POPs such as B(a)P, including age of contamination, and the organic carbon and clay content of soil. POPs may bind to soil or sediment components through hydrophobic partitioning or via physical bond formation. POPs are usually retained on the organic components of the soil including condensed humic material or soot particles. Bioaccessibility may be reduced over time through ageing, and B(a)P may be incorporated into natural organic matter, diffuse into nanopores, or adsorb to organic matter (Rostami & Juhasz 2011). These factors are applicable to both ecological and human bioavailability, as well as microbial biodegradation, though it is important to note that processes and mechanisms may differ at a cellular level (for example, degraded PAHs may be less bioavailable to bacteria, but may still be bioavailable to ecological or human receptors through an ingestion exposure pathway).

The bioassays on B(a)P that have been used to derive the ESLs in the NEPM were conducted using fresh applications of B(a)P to soils whereas for most contaminated sites the contamination is historical and has been present for many years (Sverdrup et al. 2002). Several researchers have investigated the effects of ageing on B(a)P, and it has been found that the bioavailability of B(a)P decreases over time, indicating that organisms could be exposed to higher concentrations before toxicity will be observed.

The source of contamination may also influence bioavailability of B(a)P. Grøn et al. (2007) found a low bioaccessibility of B(a)P in soils from fishnet tarring (B(a)P concentration 5.4 ± 9.1 mg/kg, bioaccessibility 5–15%). Increased bioavailability was detected for sites contaminated from urban activities such as coal and wood ash disposal, minor petroleum spills and air pollution (B(a)P concentration 3.9 ± 1.7 mg/kg and 1.8 ± 1.1 mg/kg, bioaccessibility 15%). The highest bioaccessibility at sites with traffic air pollution source (B(a)P concentration 0.22 ± 0.31 mg/kg, bioaccessibility 40%).

As discussed by Duan (2014), PAHs undergo biphasic degradation kinetics with an initial rapid phase of PAH removal due to stimulation of PAH-degrading microorganisms, and then there is a slower degradation phase. The PAHs that remain are sequestered by diffusion into micro- or nanopores within soil organic matter, and can be considered to be less bioavailable. However, this is typically applicable to lower molecular weight PAHs – B(a)P is generally resistant to microbial destruction. As noted earlier, reporting half-lives can underestimate persistence if there is a fraction that is more resistant to degradation, or is not able to be extracted and the amount remaining is underestimated. In the case of highly hydrophobic PAHs such as B(a)P in soil, when the extraction method is exhaustive the reported residual concentration of aged material will be higher, and the difference between the fast and slow phases reduced. The decrease of B(a)P concentration that occurs with ageing can become more linear with time (Paraskewich 2008).

The reduction in bioavailability with ageing is supported by the results of Alexander and Alexander (1999) who showed that the genotoxicity of aged B(a)P in soils declined

over time with little or no loss of the compound in the soil matrix. During contaminant ageing, molecules gradually move into sites within the soil matrix (micropores) that are not easily accessed by microbes (Alexander 2000). This partitioning has implications for biodegradation, and can be a limiting factor in remediating B(a)P contaminated soils (Mahmoudi et al. 2013).

In addition, several studies have indicated that organic compounds show a declining bioavailability to microorganisms, invertebrates and plants with an increased residence time in soils due to the sequestration of chemicals into inaccessible microsites within the soil matrix (Sverdrup et al. 2002). The presence of nanopores with diameters 0.3–1.0 nm can result in localised sequestration as B(a)P can diffuse into pores and voids then become trapped within soil aggregates, becoming less bioavailable to microbes and hence resistant to degradation (Mahmoudi et al. 2013). B(a)P adsorption onto soils, and hence bioavailability and toxicity, can also be affected by soil properties such as total organic carbon, pH, cation exchange capacity (CEC), organic carbon to total nitrogen ratio and clay content (Mahmoudi et al. 2013, Duan et al. 2014).

Nam et al. (1998) found that soils with an organic carbon content of 2% reduced the bioavailability and toxicity of phenanthrene after 200 days, whereas no effects were observed in soils with an organic carbon content <2%. Chung and Alexander (2002) found that there were correlations between total organic carbon (TOC), nanoporosity and CEC; however, there was insufficient information to apply these properties to predict the sequestering of PAHs. Subsequent research conducted by Duan (2014), involving test work with four different soils, showed no direct correlation in bioavailability of B(a)P with TOC or clay content after 90 days. However, a significant correlation was found between bioavailability and fine particle-associated organic carbon expressed as (silt + clay)/TOC and the soil meso-pore fraction (<6 nm), thus supporting Chung and Alexander's (2002) findings, and suggesting that soils comprising a higher proportion of fine particle size (clay, silt) and TOC have a greater ability to sequester B(a)P.

Soil microbes have the potential to degrade most PAHs, particularly in the liquid phase (Mahmoudi et al. 2013). Once the PAHs (including B(a)P) have been sequestered into the soil matrix, the microbial degradation process will only occur very slowly due to the slow rate of desorption and lack of bioavailability, and PAHs will persist in the environment.

Work undertaken using in-vivo or in-vitro models to represent human exposure support the findings of these studies. Duan et al. (2014) found that relative bioavailability of B(a)P in a swine model study was significantly reduced in soils after 90 days ageing (approximately 22–63%), except for one sandy soil where relative bioavailability remained circa 100%. Ageing has also been found to reduce dermal bioavailability (Turkall et al. 2009).

Duan et al. 2014 also found that oral bioavailability of B(a)P in swine models decreased in a clayey soil (1.4% TOC) compared with a sandy loam soil (0.04% TOC). Bioavailability in humans via dermal exposure can also be influenced by soil clay content. Turkall et al. (2009) investigated dermal bioavailability using pig skin. It was found that following direct application of pure B(a)P to skin, 76% penetrated the skin. However, when a predominantly clay/silt (22%/28%) soil contaminated with B(a)P was applied, penetration reduced by $\geq 95\%$ (compared with pure compound). The reduction in penetration was due to adsorption of B(a)P onto the soil particles, with stronger

adsorption onto soil observed in clay-dominated soils with higher surface area, compared to sand-dominated soils. A further reduction in dermal absorption was observed with ageing of contaminants.

3.5 Testing to determine bioavailability and bioaccessibility in humans

3.5.1 Bioavailability

Research into the bioavailability of inorganic contaminants such as arsenic, lead and cadmium using both in-vivo (rat, monkey and swine) and in-vitro tests has been performed (US EPA 2008, Ng et al. 2009). Adjusting clean-up targets based on the results of bioavailability laboratory tests has, and continues to gain industry and regulatory acceptance for these inorganic contaminants (Duan 2014).

In the case of organic contaminants, assessing the bioavailable fraction is more complex than for inorganics, due to the rapid metabolic transformation inside organisms (Duan 2014). It is difficult to quantify the dose that is ultimately absorbed into systemic circulation (Juhasz & Naidu 2000). The process of PAH metabolism, distribution and excretion in the human body is complex. Assessing the bioavailability of PAHs is difficult, as they may be absorbed from the gastrointestinal tract and transformed in the hepatic portal system, but may not reach systemic circulation (i.e. will not be bioavailable). Alternatively, transformed PAHs may enter systemic circulation (i.e. are bioavailable), but cannot be accounted for if only the parent compound is measured (Juhasz & Naidu 2000). The bioavailability estimates for organic contaminants in soils or sediments have varied substantially between studies, with results from different assays not directly comparable (Duan 2015). Because of species variance, use of different animals as models for humans (e.g. rats, swine and monkey) further confounds interpretation of data for the purposes of human health risk assessment, and there is currently no universally accepted in-vivo or in-vitro methodology for measuring bioavailability for B(a)P (Duan 2015).

3.5.2 Bioaccessibility

As an alternative approach, bioaccessibility measures may be used as a surrogate for bioavailability. Considering the bioaccessible fraction rather than the bioavailable fraction should be inherently conservative, as the bioaccessible fraction will always be greater than or equal to the bioavailable fraction. However, caution is required, as some studies have found that bioavailabilities of B(a)P measured in-vivo (mice studies) were actually higher than bioaccessibilities measured through in-vitro studies (Grøn et al. 2007).

Laboratory testing to determine the bioaccessibility of B(a)P in contaminated soils is generally easier than testing for bioavailability, as there are less confounding factors that require consideration (such as accounting for metabolic products, as discussed above).

While there have been many in-vivo assays developed using animal models that measure bioavailability, and many in-vitro methods of measuring bioaccessibility, there is a paucity of information validating results from different methodologies.

3.5.3 In-vivo test methods

In-vivo assays using animal models (e.g. rat and swine) to determine the bioavailability of contaminants in a specific matrix such as soil or sediment are available. In these assays an animal is given a dose of a reference/test material orally or intravenously, and bioavailability endpoints (such as concentration of POPs in blood, organs, fatty tissue, urine/faeces, urinary metabolites, DNA adducts, and enzyme induction) are measured following a specified exposure period (Rostami & Juhasz 2011). Monitoring contaminant concentrations in systemic circulation is a commonly used endpoint for some organic contaminants, but this can be difficult for contaminants such as B(a)P due to rapid partitioning from the blood to target organs and adipose tissue. B(a)P may also be rapidly metabolised to different daughter compounds when in systemic circulation, which might not be measured (Rostrami & Juhasz 2011).

Swine models are the preferred choice for bioavailability and bioaccessibility studies, given their similarity to humans, but the associated costs are usually prohibitive, and ethical considerations can be significant. Rodents (e.g. rats) are therefore popular because of ready availability, small size, low cost and ease of handling. The resultant bioavailability estimates vary considerably based on the type of animal model, endpoint measured, dose of contaminant, and method of dosing (e.g. intravenous, food, contaminated soil) (Rostrami & Juhasz 2011). Additionally, much of the data available focuses on the bioavailability of pure forms of compounds, rather than in the form of contaminated soils (Rostrami & Juhasz 2011).

While in-vivo studies are superior to in-vitro methods in determining the bioavailability of PAHs in contaminated soils, use of in-vivo models is often not practicable from a commercial perspective due to the extensive periods involved, considerable cost, and ethical constraints (Juhasz & Naidu 2000).

3.5.4 In-vitro test methods

Because of these constraints, in-vitro methods that simulate gastrointestinal conditions in the human stomach have been developed. These have the advantage of being quick to return results, and comparatively inexpensive. They provide an estimate of bioaccessibility (rather than bioavailability), by measuring the PAH concentrations that are solubilised following gastrointestinal processes, and hence the concentrations potentially available for systemic circulation (Rostrami & Juhasz 2011, Juhasz & Naidu 2000). These methods provide an estimate of the bioaccessible fraction (concentrations available for absorption into systemic circulation) rather than the bioavailable fraction, and should provide a conservative but useful assessment in determining the risk from human exposure to B(a)P. The bioaccessible fractions of PAHs in soil can be highly variable (0.1–89%) and are dependent on soil physicochemical properties, contaminant age and assessment method used (Juhasz & Naidu 2000). Bioaccessibility in vitro tests provide a cost and time effective alternative to in-vivo studies.

However, in-vitro bioaccessibility tests are not without problems, and research is ongoing. Cave et al. (2010) noted there is still a need to develop a methodology for measuring bioaccessibility of PAHs in humans in a commercial laboratory, using standard laboratory equipment and analytical methodologies. These tests would then require validation against in-vivo soil feeding trials.

In-vitro physiologically based extraction test (PBET) assays for organic bioavailability, which involve a simulation of human gastrointestinal properties, tend to underestimate bioavailability when compared to in-vivo studies (where available) (Duan 2015). PBET tests have reported a large range of PAH bioaccessibility data (9–69%) depending on the study design (Harris et al. 2013). One commonly referenced approach, the fed organic estimation human simulation test (FOREhST) is a three-stage static in-vitro bioaccessibility test intended to simulate the physicochemical conditions in the fed state (Cave et al. 2010). It involves three stages representative of the saliva, gastric and intestinal (duodenal and bile) phases of the human gastrointestinal system. Sample collection at the end of the extraction phase represents small intestinal digestion (Cave et al. 2010). The simulator of human intestinal microbial ecosystems (SHIME) gastrointestinal model for samples containing B(a)P ranging from approximately 2–70 mg/kg has been found to give similar (albeit slightly higher) results to the FOREhST method (Cave et al. 2010). However, estimates of PAH bioavailability using the FOREhST in-vitro assay and fugacity modelling found bioavailability values up to 2000 times lower than in-vivo methods (Juhasz et al. 2014).

Other approaches, such as the mass-balance approach (ratio of toxicant mass in the original sample to recaptured toxicant fraction), while useful for inorganics, are not popular for PAHs because of the difficulty of identifying and accounting for where PAHs might be found (Harris et al. 2013).

In-vitro gastrointestinal models adopted may be static (simulated transit through the human digestive tract by sequential exposure of soil), or dynamic (mimic gradual transit of ingested toxicants) (Harris et al. 2013). Examples of other in-vitro digestion models originally developed for heavy metal-contaminated soils, but since been modified for assessing the bioaccessibility of organic contaminants such as PAHs include:

- Simple bioaccessibility extraction test (SBET) model
- German-Deutsches Institut für Normung (DIN 19738) model
- Netherlands-Rijks Instituut voor Volksgezondheid and Milieu (National Institute for Public Health and the Environment, RIVM) in-vitro digestion model
- Fugacity modelling

The outcomes of these models are influenced by many parameters, such as residence time in the gastrointestinal tract, pH of gastric liquids, experiment duration, meal or fasting state conditions, and simulation of food (Cave et al. 2010, Harris et al. 2013). As most of the methods used for accessing bioaccessibility of PAHs were originally adopted from methods used for inorganic contaminants, some of the models do not account for a lipid component (i.e. dietary fats), which is important in determining B(a)P bioaccessibility (Cave et al. 2010, Harris et al. 2013).

It is widely accepted that there is a lack of correlation between in-vivo bioavailability and in-vitro bioaccessibility models for persistent organic pollutants such as B(a)P (Rostrami & Juhasz 2011, Juhasz & Naidu 2000).

Standard practice for many in-vitro models is typically to incubate soil with a simulated digestive fluid, separate the fluid from digested soil, then calculate the bioaccessibility based on the amount of contaminant mobilised into the fluid (Gouliarmou et al. 2013). These methods only focus on the initial partitioning of the contaminant into solution, but they do not account for subsequent intestinal absorption which continually takes up PAHs from solution and therefore maintains a desorption gradient from the soil matrix.

Therefore these methods can result in an underestimate of bioaccessibility (Gouliarmou et al. 2013). Traditional in-vitro methods for assessing PAH bioaccessibility in contaminated matrices have typically found very low bioaccessibilities (in a creosote-contaminated soil, ~871 mg/kg of Σ_{16} PAHs measured <4% bioaccessibility (Juhasz et al. 2014), in B(a)P-contaminated soil (6– 270 mg/kg) had a bioaccessibility of 2–16% (Grøn et al. 2007)). Measures of bioaccessibility using traditional in vitro models may underestimate bioaccessibility due to solubility limitations (Juhasz et al. 2016).

Introduction of a sorbent material (a sink) improves the correlation of in-vitro with in-vivo data. Collins et al. 2013 added a contaminant trap (activated carbon added to silicon) to a colon extended physiologically based extraction test (CEPBET, comprising three compartments representing the stomach, small intestine and colon). The contaminant trap maintained low PAH concentrations in the gut fluid and simulated PAH absorption by the gastrointestinal tract, allowing more PAH desorption from soils, and providing much higher estimates of bioaccessibility. A drawback with this methodology is that the contaminant trap does not provide the ability to recover and quantify the bioaccessible fraction directly.

Gouliarmou et al. (2013) overcame this limitation by adding a silicone rod in to an existing in-vitro digestion model to act as a large capacity adsorption sink. The silicone rod continuously adsorbs the mobilised contaminants from the simulated gut fluid, providing near infinite sink conditions and ensuring that dissolved contaminant concentrations remain low, and the desorption gradient is maintained during the sample incubation. At completion, the contaminants adsorbed to the rod are measured by solvent extraction, providing a measure of accessible, rather than total concentrations. Sorptive extraction into silicon isolates target compounds from the solution matrix, which means no additional phase separation steps (e.g. filtration or centrifugation) were required prior to analysis of PAHs, saving time circumventing some of the uncertainties connected to whether PAH aggregate form or size contributes to bioaccessibility. Furthermore, the final extract of silicone rods contained reduced concentrations of interfering constituents originating from the soil and digestive fluids. Application to matrices such as sediment, sludge and biochar were considered possible.

Juhasz et al. (2016) have developed a laboratory test to measure PAH bioaccessibility in contaminated soils, along the lines of the sorption-sink methodology described by Gouliarmou et al. (2013). The sorption-sink test uses the org-PBET methodology, with inclusion of silicone cord as a sorption sink. The assay included a 16-hour intestinal phase, which allowed release of desorbable PAHs from the soil, and a steady state to be achieved. Measured PAH bioaccessibility varied depending on soil matrix and PAH type. Total PAH bioaccessibility ranged from 3.9% to 46.6% (n = 18; mean: 12.8%; median: 8.5%), with the highest value of 46.6% from a soil impacted with creosote. B(a)P bioaccessibility ranged from 2.5% to 36.6% (n = 18; mean: 8.4%; median: 6.6%) (Juhasz, pers. comm. 2014). In all four soils investigated, the measured bioaccessible fraction of B(a)P was far less than the total concentrations. It is understood that this test is being developed to become available on a commercial basis. Nonetheless, it may require some time for this method (or others) to become tested and accepted within the scientific community.

The sorption sink method is able to provide total and bioaccessible results for individual PAHs, the sum of 16 PAHs, and B(a)P TEQ. From this the percentage bioaccessibility can be determined for individual compounds and for B(a)P TEQ. This is an important consideration, as the NEPM HILs and human health risk assessments are based on B(a)P TEQ (refer to section 3.2.1) rather than B(a)P in isolation.

3.5.5 Conclusions

While the use of site-specific bioavailability information in establishing the risk associated with certain inorganic contaminants is accepted in Australia, acceptance for organic contaminants has not yet been achieved. It is thought that in many situations B(a)P may have low bioavailability, and measuring site-specific bioavailability may more accurately inform chemical daily intake values to account for potential differences in absorption between different exposure media (soil, water, food).

Practically applicable in-vivo and in-vitro methods for measuring bioaccessibility are yet to be established for PAH-contaminated soils. However, the development of the in-vitro sorption-sink approach by Juhasz et al. (2016), based on the methodology described by Gouliarmou et al. (2013) and Collins et al. (2013), is promising, and involves the measurement of PAH bioaccessibility in contaminated soils using the org-PBET method with inclusion of a silicone cord as a sorption sink. At this time, this method would appear to provide a practical and conservative estimate of bioaccessibility.

Internationally, the US Department of Defence research programs (Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP)) are currently undertaking a detailed study into the physical and chemical interactions between PAHs and soils, and the influence of this on the bioavailability of PAHs to humans. The study involves developing in-vivo and in-vitro methods of measuring PAH bioavailability and evaluation of bioavailability across a diverse range of soil types and contaminant sources. Further information on the scope of this work is available online (SERDP-ESTCP 2016). The US Department of Defence work will inform a broader US Interstate Technology Regulatory Council (ITRC) project which aims to develop guidance on the use of site-specific bioavailability testing (for organics and inorganics), the methods most appropriate for different situations, and the current state of science. It is understood this ITRC project is several years from completion.

As further research is undertaken into B(a)P bioaccessibility and bioavailability, and an accurate, validated and a commercially viable test becomes available for measuring bioavailability or bioaccessibility of B(a)P in soils, it is likely that application and acceptance of bioavailability on a site-specific basis will become more commonplace and more widely accepted. The timeframe within which this may occur is not known, but it is an area that should be monitored and, as advances are made, guidance relating to the consideration of bioavailability of B(a)P will require updating.

3.6 Application of bioavailability testing in site-specific risk assessment

The derivation of the HILs is described in detail in Schedule B7 of the NEPM, which presents the key assumptions, equations and exposure parameters used to derive the

HILs. With respect to PAHs, the significant assumptions are 100% oral bioavailability, and 6% dermal bioavailability (also known as skin absorption factor).

The NEPM allows for the site-specific evaluation of bioavailability. While the HILs are based on a default value for bioavailability, they may be adjusted at a site-specific investigation level by applying the measured bioavailability in the calculations. Alternatively, the measured bioavailability may be used in site-specific risk assessments to assess risk for a measured chemical concentration in soil.

In the case of B(a)P, as noted in the previous section, there are difficulties with actual measurement of bioavailability on account of chemical transformed in the hepatic portal system. However, the use of bioaccessibility to represent oral bioavailability can provide a conservative alternative, as it assumes that the body will absorb 100% of the chemical extracted from the soil media. As noted in the previous section, the sorption-sink methodology would appear to offer a practical measure of bioaccessibility, though further validation and commercialisation of this method is required before it will gain regulatory acceptance.

Unlike lead where oral exposure is the primary exposure route contributing to the HIL, with B(a)P exposure, the oral and dermal pathways both contribute significantly to the total risk and need to be accounted for. For HIL-A (low density residential) the distribution is approximately 50% for each exposure route. For the other land uses, the proportions differ (refer to section 3.2.13.2.1).

The bioaccessibility test represents the maximum possible amount of PAH that will be removed from the soil, whether within the digestive system or on the skin. In the case of skin absorption, in the derivation of the HILs for B(a)P, a default skin absorption factor of 6% is assumed. Implying that if the measured bioaccessibility is less than the default value of 6%, the skin absorption factor may be reduced to this lesser value. Note that a bioaccessibility value greater than 6% does not mean that the dermal absorption factor should be increased, as this value has been nominated as the likely maximum skin absorption factor for PAHs and considers issues such as exposure and retention time for particles in skin folds.

A simple way to derive a modified HIL with a site-specific bioaccessibility measurement is to use the NEPM HIL spreadsheet tool, which is available on the NEPC website: www.nepc.gov.au/nepms/assessment-site-contamination/toolbox#hils.

The following case examples show how bioaccessibility can be used to derive a site-specific investigation level for B(a)P, for a low density residential land use.

3.6.1 NEPM HIL-A

For low density residential land use, the NEPM health investigation level (HIL-A) for B(a)P is 3 mg/kg (2.53 mg/kg rounded to 3 mg/kg). The default assumption for dermal absorption factor (bioaccessibility) is 6% for B(a)P, while the default oral bioavailability is 100%. The NEPM HIL spreadsheet tool presents pathway specific HILs. For oral exposure (HIL_{oral}) is calculated to be 5.6 mg/kg, and the dermal exposure the (HIL_{dermal}) is calculated to be 4.6 mg/kg. The overall (combined exposure pathway) HIL is calculated as $1/HIL = 1/5.6 + 1/4.6$, resulting in a HIL of 2.53. The oral pathway contributes $2.53/5.6 = 45\%$ of the risk while dermal pathway contributes $2.53/4.6 = 55\%$ of the risk (dust inhalation contribution is small and negligible).

Case 1: This scenario assumes a measured bioaccessibility of B(a)P is 20%, and low-density residential use applies.

Using the NEPM HIL spreadsheet (HIL-A), for a measured bioaccessibility of 20%, the oral bioavailability changes from 100% to 20%, but the dermal absorption factor remains at 0.06. The resulting site-specific investigation level is 3.9 mg/kg (4 mg/kg).

The oral exposure criteria has changed from 5.6 mg/kg to 28 mg/kg (a five-fold increase) but the dermal exposure criteria remains the same at 4.6 mg/kg, resulting in a combined exposure pathway criteria of 3.9 mg/kg ($1/HIL=1/28+1/4.6$). The result is a 50% increase in criterion. The dermal exposure route originally accounted for 55% the risk, therefore the criterion could not be increased by more than a factor of two unless the dermal component changes.

Case 2: This scenario assumes the measured bioaccessibility of B(a)P is 3%, and low-density residential use applies.

Using the NEPM HIL spreadsheet (HIL-A), for a measured bioaccessibility of 3%, the oral bioavailability changes from 100% to 3%, and the dermal absorption factor changes from 0.06 to 0.03. The oral exposure criterion changes from 5.6 mg/kg to 190 mg/kg and the dermal exposure criterion changes from 4.6 mg/kg to 9.2 mg/kg, resulting in a combined exposure pathway criterion of 8.7 mg/kg ($1/HIL=1/190+1/9.2$). The result is a three to four fold increase in criterion.

Before undertaking bioaccessibility testing, an assessment of the costs versus the benefits should be undertaken. Ng et al. (2009) provides a general framework for how bioavailability and bioaccessibility might be incorporated into the risk assessment process. US EPA (2007) also provides a decision tree which includes a process of assessing the cost-benefit for undertaking bioavailability testing for metals, which can also be applied to B(a)P at such time as an accepted, commercially available method of measuring bioaccessibility is available. The following provides an outline of how bioaccessibility testing for B(a)P may be incorporated into a site-specific risk assessment.

Step 1: Estimate the cost for obtaining bioavailability data

One of the key considerations before undertaking bioaccessibility testing for PAHs is the number of samples required to obtain a representative bioaccessibility value. This will depend on the nature and distribution of the contaminant. Randomly distributed PAHs in fill will require a sufficient number of samples to represent the spread of values across the fill. Professional judgement or use of spatial geostatistical methods will be required to establish an appropriate sampling density to characterise fill. The assessor needs to consider factors such as the complexity of contamination, fill type and heterogeneity, contaminant source, and statistical analysis adopted. Localised hotspots may require fewer samples than fill, but each hotspot would then need to be considered as an individual source and would require its bioavailability to be determined. Spatial co-variance methods and variography allows an assessor to demonstrate the adequacy of site characterisation and establish whether the variance in concentration between sampling locations is dominated by spatial or random variance. The method also allows for determining the confidence that can be assigned to the spatial variation in sample concentration. These methods can support a professional judgement based approach, and increase the defensibility of a sampling and analysis approach.

Step 2: Estimate the range of bioaccessibility values that might occur

As discussed in section 3.4, many factors affect bioaccessibility of PAHs, such as source type, contaminant age, organic carbon content, and clay content. PAHs in ash and bitumen are likely to be strongly adsorbed and to have low bioaccessibility, whereas gasworks waste with liquid tars and PAHs associated with atmospheric emissions are likely to be more bioaccessible.

Step 3: Estimate the added value

In a cost benefit analysis, the added value refers to the likely cost of remediation saved. By undertaking bioaccessibility testing, a revised risk profile (such as by adjusting the HILs) is used to develop a remediation strategy and to allow the estimate of a revised remediation cost. The difference between the estimated remediation costs with and without bioaccessibility testing is the added value.

Step 4: Does the added value exceed the cost of obtaining the bioavailability data

If the added value (savings of revised estimate of remediation cost) is more than the cost of the bioaccessibility testing, then consideration should be given to undertaking the works.

The key decision point is likely to be driven by level of contamination (i.e. the extent to which the concentrations exceed the HILs) and the source of PAHs. Because the dermal absorption factor cannot be adjusted unless the bioaccessibility is less than 6%, the HIL in many cases will not be able to be increased by more than a factor of two. If the contaminant concentrations are generally higher than two times the HIL, bioaccessibility testing is unlikely to result in a cost savings, unless the source type is of a nature that is likely to result in very low bioaccessibility, such as ash.

3.7 Bioavailability conclusions

It is important to consider bioavailability in the application of the NEPM HILs, because in many situations assuming 100% bioavailability can result in unnecessary conservatism. However, methods have not yet been developed that can reliably measure the bioavailability of B(a)P, although the sorption sink approach described above has promise and may be used to provide an indicative or semi-quantitative measure of bioaccessibility. Additionally work being undertaken by US Department of Defence environmental research programs into the physical and chemical interactions between PAHs and soils, and how these interactions affect bioavailability of PAHs in soil to humans, may also provide useful information in the future.

In the absence of a reliable quantitative measure of bioaccessibility or bioavailability, it is recommended that a risk-based lines of evidence approach be undertaken, considering the following:

- **Bioaccessibility (indicative):** such as measured by the sorption sink approach or equivalent.
- **Contaminant ageing:** as discussed in section 3.4, contaminant ageing can reduce bioavailability. Contamination that has been present in soils for years or decades is expected to have a lower bioavailability.

- **Source type:** bioaccessibility and bioavailability can vary with the source and composition of the contamination (for example B(a)P arising from coal and wood ash can have a lower bioavailability than B(a)P arising from fresh coal tar or traffic air pollution).
- **Soil properties:** B(a)P is likely to be more strongly adsorbed on soils with high total organic carbon and clay content and to have lower bioavailability. Additionally, other soil properties such as cation exchange capacity (CEC), the ratio of organic carbon to total nitrogen can also affect B(a)P adsorption onto soils.

In situations where there is only a moderate exceedance of the HILs (e.g. a factor of two or three) and the available lines of evidence support the conclusion that bioavailability is likely to be low, consideration of these factors could support the conclusion that the contamination poses a low risk.

In reaching such a conclusion, consideration should be given to the relative influence of ingestion and dermal pathways (refer to section 3.6), because dermal absorption may be the limiting factor, and currently there is insufficient information to conclude that reduced bioavailability will proportionally reduce the default assumption regarding dermal absorption.

Bioaccessibility, contaminant age, source type and soil properties can be just some of the aspects that must be considered when developing an understanding of the implications of site contamination. The development of a conceptual site model (CSM) is essential to describe the pathways by which exposure can occur; this is discussed further in section 5.2.

4. Ecosystems

4.1 Terrestrial ecology

4.1.1 Toxicity

B(a)P may be present in soils and sediments, and usually only at very low concentrations in water. Animals can be exposed to B(a)P in soil through both dermal exposure and ingestion, and sediment-dwelling organisms can be exposed through dermal exposure, ingestion and exposure to pore water. Exposure of earthworms to B(a)P in soil can result in decreased growth and survival, an increase in antioxidant enzyme activities, an increase in cellular lipid peroxidation and DNA damage (Duan et al. 2015a).

4.1.2 Ecological screening levels for B(a)P listed in the NEPM

The NEPM provides ecological screening levels (ESLs) for B(a)P based on the Canadian soil quality guidelines (SQG):

- Areas of ecological significance: 0.7 mg/kg dry soil
- Urban residential and public open space: 0.7 mg/kg dry soil
- Commercial/industrial: 1.4 mg/kg dry soil

A review of the Canadian B(a)P SQG to assess the suitability of the guidelines for use in Australia was undertaken by Warne (2010). The Canadian guidelines for B(a)P stated that a limited toxicity data set was available including one invertebrate bioassay and two plant bioassays (Warne 2010). The limited data prevented the full use of EIL methodology as only three species were represented, but did allow derivation of a low reliability value of 88 mg/kg dry soil using the EIL assessment factor methodology (Heemsbergen et al. 2009, Warne 2010).

The Canadian guideline was based on toxicity data generated from one data point that accounts for biomagnification, resulting in a guideline of 0.7 mg/kg that is of low reliability (Van Straalen & Verweij 1991, Warne 2010). Taking a conservative approach, Warne (2010) recommended that the Environment Canada SQG values be adopted as low reliability ESLs in the NEPM.

In addition to the data used to derive the Canadian guideline (Van Straalen & Verweij 1991), other toxicity data from a study by Achazi et al. (1995) was reviewed which showed significant toxicity of B(a)P to enchytraeids (*Enchytraeus crypticus*) and earthworms (*Eisenia fetida*) (table 6). The Achazi et al. (1995) study results have not been able to be replicated (Sverdrup et al. 2007). Therefore, Sverdrup et al. (2007) recommended that these tests be repeated before the data were used for setting soil quality standards (the differences in the results of these toxicity tests are shown in table 7Table 7).

Sverdrup et al. (2007) presented data from 10 species from five taxa as shown in table 7Table 7. However, many of the data presented in table 6 and table 7 do not meet the quality assurance required to derive Australian guidelines as determined using the ecotoxicology data quality assessment method (Heemsbergen et al. 2009, Warne et al. 2014). They are included here to indicate the variability of bioassays and the resulting toxicity data.

Table 6 Data reviewed in the development of Canadian B(a)P guidelines (CCME 2008) and their revision (CCME 2010)

Organism	Effect	Endpoint	Effective concentration (mg/kg)	Exposure period (days)	Reference
<i>Cannabis sativa</i> (hemp)	Emergence	EC ₅₀	89	30	Campbell et al. 2002
<i>Lupinus albus</i> (lupin)	Growth	LOEC	>155	30	Henner et al. 1999
<i>Eisenia fetida</i> (earthworm)	Growth	EC ₁₂	10	28	Achazi et al. 1995
<i>Eisenia fetida</i> (earthworm)	Reproduction	EC ₉₁	10	28	Achazi et al. 1995
<i>Enchytraeus crypticus</i> (potworm)	Reproduction	EC ₁₈ (LOEC)	10.1	30	Achazi et al. 1995
<i>Folsomia fimetaria</i> (springtail)	Reproduction	EC ₁₀	>840	21	Sverdrup et al. 2002

Table 7 Toxicity data presented in Sverdrup et al. (2007)

Organism	Effect	Exposure period (days)	Endpoint	Effective concentration (mg/kg)	Conversion to EC ₁₀	Reference
<i>Enchytraeus crypticus</i> (potworm)	Reproduction	30	LOEC	100	40	Achazi et al. 1995
<i>Enchytraeus crypticus</i> (potworm)	Reproduction	28	LOEC	>931	372	Bleeker et al. 2003
<i>Eisenia fetida</i> (earthworm)	Growth	28	LOEC	>100	40	Eason et al. 1999
<i>Eisenia fetida</i> (earthworm)	Survival	28	LOEC	>48,000	19200	CCME 1997
<i>Oniscus asellus</i> (Isopoda)	Growth	63	LOEC	100	40	Van Brummelen & Stuijf 1993
<i>Oniscus asellus</i> (Isopoda)	Growth	329	LOEC	>316	126	Van Brummelen et al. 1996
<i>Oniscus asellus</i> (Isopoda)	Reproduction	329	LOEC	31.6	12.6	Van Brummelen et al. 1996
<i>Porcellio scaber</i> (Isopoda)	Growth	112	LOEC	>316	126	Van Brummelen et al. 1996
<i>Porcellio scaber</i> (Isopoda)	Growth	112	LOEC	100	40	Van Brummelen & Stuijf 1993
<i>Folsomia fimetaria</i> (springtail)	Reproduction	21	LOEC	>840	336	Sverdrup et al. 2002
<i>Folsomia fimetaria</i> (springtail)	Reproduction	28	LOEC	>931	372	Bleeker et al. 2003
<i>Raphanus sativa</i> (radish)	Seed emergence	14	LOEC	>23,800	9520	CCME 1997
<i>Lactuca sativa</i> (lettuce)	Seed emergence	14	LOEC	11,900	4760	CCME 1997
Soil bacteria and fungi	Community structure	>100	LOEC	>33	13.2	Park et al. 1990

4.1.3 Derivation of an Australian higher reliability ecological guideline for B(a)P

Because the ESLs in the NEPM are classified as low reliability, it is useful to consider whether there is additional and more recent information that allows higher reliability values to be estimated. Note that values derived in this way are intended to assist in informing an assessment of B(a)P following NEPM ecological risk assessment guidelines, but as they have not been developed through the NEPM review process, they should not be cited as NEPM ESLs.

EC₁₀, no observable effect concentration (NOEC), lowest observed effect concentration (LOEC) and EC₅₀ data from chronic toxicity tests using terrestrial organisms from the international literature and the quality of the results assessed using the Heemsbergen et al. (2009) assessment method were collected. These data are shown in table 8. Data for inclusion in the species sensitivity distribution (SSD) was selected using the following criteria:

- The EC₁₀ value from the most sensitive endpoint for each species were used in the SSD
- Only data derived from chronic bioassays were used, and
- Data that met the quality criteria: high quality (H = >80%) and acceptable quality (A = <80%–>50%).

In using this information, data reported as EC₅₀s were divided by a default conversion factor of five to derive an EC₁₀ value, as recommended by Heemsbergen et al. (2009). In cases where EC₅₀ and NOEC data were presented as a > value, the value was recorded as an EC₅₀ and a NOEC value respectively (i.e. the values were considered as absolute, and the > was disregarded). This will result in a conservative EC₅₀ and EC₁₀ value. To add an extra level of conservativeness, where several exposure durations were assessed, only the endpoint of the most sensitive bioassay for each species were included in the SSD calculation. This allows the EC₅₀/NOEC or EC values of fresh B(a)P to be used to provide a conservative calculation of toxicity for aged B(a)P as the toxicity of B(a)P decreases over time (Cheng et al. 2014). Cheng et al. (2014) provided three end-points for the soil bacteria, the geometric mean of the three endpoints was used in the SSD calculation.

Data used in SSD

The data shown in table 8 meet the quality assurance requirements for deriving Australian ESLs for B(a)P. The quality scores are shown in table 10 are of high quality (H = >80%) and acceptable quality (A = <80% –>50%). Any EC₅₀ values were divided by a factor of five and the NOEC or EC₁₀ values were used in the species sensitivity distribution. Due to the format of the data presented in the literature (EC₅₀, EC₁₀ and NOEC) the EC₃₀ could not be derived as raw data were not provided. Therefore, the EC₁₀ and NOEC values were used to derive a conservative ecological screening level instead of the recommended EC₃₀ (Heemsbergen et al. 2009). **Error! Reference source not found.** shows the quality assessment for the bioassays and the EC₁₀/NOEC values used in the SSD discussed in this section. As discussed previously, generally the most sensitive endpoint of each species was selected for use in the SSD, with the exception of the soil bacteria (mixed species) from Cheng et al. (2014) where the geometric mean was used.

Table 8 Data used to derive higher reliability ecological screening levels for B(a)P

Organism	Effect	Exposure period (days)	Endpoint	Effective concentration (mg/kg)	Converted EC ₁₀ /NOEC (mg/kg)	Reference
<i>Soil bacteria</i>	Growth Respiration Nitrification	28	EC ₁₀	51 22 1.3	51 22 1.3 GM = 11.3	Cheng et al. 2014
<i>Soil bacteria</i>	Nitrate production	28	NOEC	293	293	Sverdrup et al. 2007
<i>Eisenia fetida</i> (earthworm)	Reproduction	28	EC ₅₀	>128	>25.6	Hunde-Rinke & Simon 2004
<i>Enchytraeus crypticus</i> (worm)	Growth	19	NOEC	>947	>947	Sverdrup et al. 2007
<i>Folsomia candida</i> (springtail)	Reproduction	28	EC ₅₀	>128	>25.6	Hunde-Rinke & Simon 2004
<i>Folsomia fimetaria</i> (springtail)	Reproduction	21	EC ₁₀	>840	>840	Sverdrup et al. 2002
<i>Hypoaspis aculeifer</i> (mite)	Growth	19	NOEC	>947	>947	Sverdrup et al. 2007
<i>Opia nitens</i> (mite)	Reproduction	28	NOEC	1600	1600	Owojori & Siciliano 2012
<i>Brassica rapa</i> (mustard)	Growth	28	EC ₅₀	>512	>102	Hunde-Rinke & Simon 2004
<i>Avena stavia</i> (oat)	Growth	28	EC ₅₀	>512	>102	Hunde-Rinke & Simon 2004
<i>Trifolium pratense</i> (red clover)	Growth	19	NOEC	>470	>470	Sverdrup et al. 2007
<i>Brassica alba</i> (mustard)	Growth	19	NOEC	86	86	Sverdrup et al. 2007
<i>Lolium perenne</i> (ryegrass)	Growth	19	NOEC	>470	>470	Sverdrup et al. 2007

Table 9 Soil chemistry used in SSD bioassays

Reference	pH	TOC (%)	CECC (mol/kg)	Clay (%)
Cheng et al. 2014	5.16	1.0	-	-
Hunde-Rinke & Simon 2004	5.5	1.0	-	3.6
Owojori & Siciliano 2012	6.0	-	-	-
Sverdrup et al. 2002	6.2	1.6	8.14	13
Sverdrup et al. 2007	6.2	1.6	8.14	13

Table 10 Quality assurance of data used in the SSD

Taxa	Organism	% QA	Acceptability (H – high, A – acceptable)	EC₁₀/NOEC (mg/kg)	Reference
Bacteria	<i>Soil bacteria</i>	84	H	11.3	Cheng et al. 2014
	<i>Soil bacteria</i>	90	H	293	Sverdrup et al. 2007
Annelida	<i>Eisenia fetida</i> (earthworm)	72	A	25.6	Hunde-Rinke & Simon 2004
	<i>Enchytraeus crypticus</i> (worm)	90	H	947	Sverdrup et al. 2007
Hexapoda	<i>Folsomia candida</i> (springtail)	72	A	25.6	Hunde-Rinke & Simon 2004
	<i>Folsomia fimetaria</i> (springtail)	90	H	840	Sverdrup et al. 2002
Chelicerata	<i>Hypoaspis aculeifer</i> (mite)	90	H	947	Sverdrup et al. 2007
	<i>Opia nitens</i> (mite)	80	H	1600	Owojori et al. 2012
Plantae	<i>Brassica rapa</i> (mustard)	72	A	102	Hunde-Rinke & Simon 2004
	<i>Avena stavia</i> (oat)	72	A	102	Hunde-Rinke & Simon 2004
	<i>Trifolium pratense</i> (red clover)	90	H	470	Sverdrup et al. 2007
	<i>Brassica alba</i> (mustard)	90	H	86	Sverdrup et al. 2007
	<i>Lolium perenne</i> (ryegrass)	90	H	470	Sverdrup et al. 2007

The number of species shown in table 10 **Error! Reference source not found.** allows a more reliable ESL to be derived using the SSD method – with chronic data of 13 species from five taxa reported (Heemsbergen et al. 2009). The selected data for the SSD are shown in table 10, and the resulting SSD is shown in figure 2. Any data that were reported as a > value were converted to that value to provide a conservative estimate of toxicity.

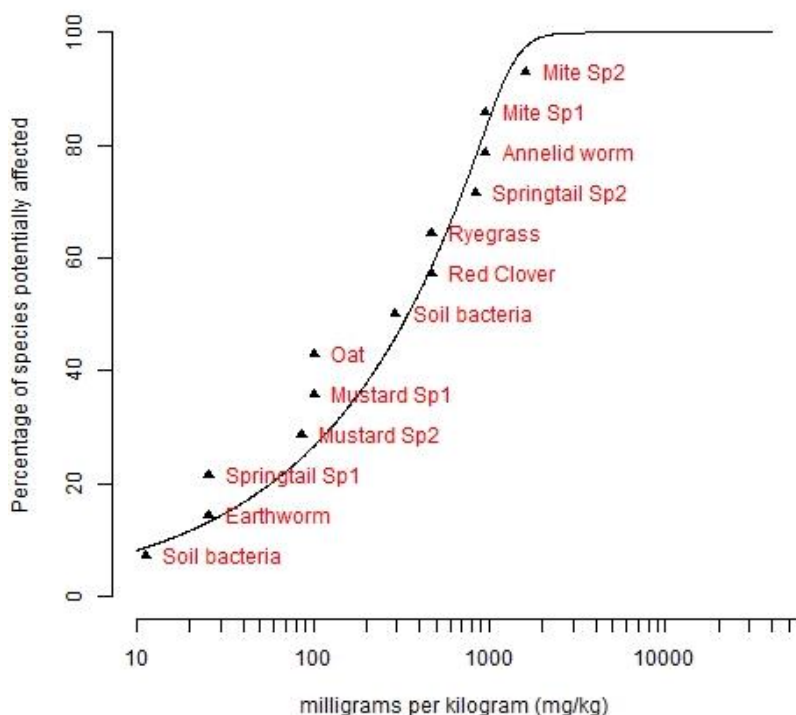


Figure 2 Species sensitivity distribution of B(a)P toxicity data using the BurrIioz 2.0 software (1% TOC-normalised data)

Table 11 shows the conservative higher reliability ecological guideline derived from the SSD for each land use for fresh B(a)P when compared to the NEPM low reliability guidelines. Given that the curve fit is good and that the database included only chronic data, the derived values can be considered to have high reliability. The standard species protection for each use has been adjusted to take into account biomagnification following Heemsbergen et al. (2009). The values shown in table 11 have been calculated from results of bioassays using fresh B(a)P and do not take into account the changing bioavailability that occurs with ageing or TOC concentration in soils.

Even using the conservative EC₁₀ values to calculate the B(a)P ecological guidelines, the values shown in table 11 are significantly higher than the NEPM low reliability ESLs for commercial and industrial and residential and open space. Importantly, the higher reliability ecological guidelines shown in table 11 using a SSD methodology uses a larger database, taking into account more species and a larger number of test results. This provides greater confidence in the derived values, and they can be considered to have a higher level of reliability for use in Australia than applying the lower reliability Canadian guidelines adopted in the NEPM for species protection.

Table 11 High reliability ecological guideline for fresh B(a)P

Land use	% protection	Derived ecological guideline (95% confidence limits) mg/kg	NEPM low reliability ESL mg/kg	Canadian SQG _E
Commercial and industrial	65	172 (57–371) (High reliability)	1.4	72
Urban residential and public open space	85	33 (21–135) (High reliability)	0.7	20
National parks/areas with high ecological values	99	0.2 (0.1–21) (High reliability)	0.7	NA
SQG _E = soil quality guidelines for environmental health (CCME 2010).				

The guidelines derived above are of a similar order of magnitude to the revised Canadian guidelines (CCME 2010). The latter guidelines list soil quality guidelines for environmental health (SQG_E) of 20 mg/kg for agricultural and residential/parkland and 72 mg/kg for ecological protection at commercial and industrial sites, as shown in table 11.

In accordance with the SSD methodology, the guideline for national parks and areas with high ecological significance is referenced as having high reliability; however, the value is a statistical extrapolation and the 95% confidence limits indicate that considerable variation in the value is possible.

4.1.4 Effects of ageing, soil properties and source type on bioavailability

As noted in section 3.4, POPs such as B(a)P may bind to soil or sediment components through hydrophobic partitioning or via physical bond formation. POPs are usually retained on the organic components of the soil including condensed humic material or soot particles. Bioaccessibility may be reduced over time through ageing, and may be incorporated into natural organic matter, diffuse into nanopores, or adsorb to organic matter (Rostami & Juhasz 2011). These factors are applicable to both ecological and human bioavailability, and the discussion on bioavailability and bioaccessibility in section 3.4 is relevant here.

For example, earthworms (*Eisenia fetida*) exposed to soil containing 3.5% organic matter, 39% clay content and 21 cmol/kg CEC exhibited a 7-day growth EC₅₀ of 66 mg/kg of B(a)P⁴, and after a 14-day exposure the EC₅₀ reduced by 2.7 fold to 180 mg/kg⁵ (Duan et al. 2015a). This decrease in toxicity may be indicative of the decrease in bioavailability and the uptake mechanism of the earthworms as oligochaetes receive the major uptake of soil contaminants through pore water rather than through ingestion of soil particles (Ma et al. 1998, Schuler & Lydy 2001).

⁴ Calculated from raw data presented in table 2 in Duan et al. 2015a

Cheng et al. (2014) also showed a reduction in toxicity related to exposure durations using microbial bioassays. The EC₁₀ for microbial growth after a 28-day exposure was 51 mg/kg compared with an EC₁₀ of 77 mg/kg after a 60-day exposure. The reduction in the toxicity of B(a)P over time was also shown by Hernandez-Castellanos et al. (2013) who reported no negative effects on earthworm populations from an oil spill that occurred 20 years prior, with concentrations of B(a)P up to 29 mg/kg in contaminated soil.

The NEPM recommends using ageing factors and toxicity relationships to determine the bioavailability and reduction in toxicity that occurs in soil in the field. This is supported by evidence of ageing reducing bioaccessibility and bioavailability of B(a)P. However, there is currently insufficient information to provide a quantitative relationship. This guidance may be updated when this information becomes available.

4.1.5 Extraction methods

As discussed in section 3.4, the threshold concentrations listed in the NEPM are based on total concentrations of B(a)P, and the assumption that the bioavailability of B(a)P is equal to the threshold concentration test results. While the bioavailability in the soils tested may not have been 100%, the tests involved soils spiked with fresh B(a)P, so the bioavailability in soils in the field will be less than in the tests due to factors such as ageing.

Soil concentrations of B(a)P are commonly measured using vigorous extraction methods which determine the total concentration in the sample, but do not account for the reduction in bioavailability that can occur with aged samples. This can lead to an overestimate of the risk of exposure.

Researchers have been advocating the use of mild extraction methods to better predict the bioaccessibility and bioavailability of PAHs in soils since the 1990s (White et al. 1997, Robertson & Alexander 1998, Tang & Alexander 1999, Schuler & Lydy 2001, Dandie et al. 2010). Harkey and Young (2000) showed that toxicity as measured by the Microtox® test system is strongly correlated with both extraction efficiency and hydrocarbon ageing.

Duan (2014) discusses how the bioavailability of B(a)P is influenced by complex organism-contaminant interactions and is limited by chemical, physical or biological factors. The nature of the organic contaminant and the soil properties are important in the sorption of organic matter to soil and will influence the extractability and bioavailability over time (Duan 2014). PAHs can diffuse into micropores of soils and sediments, which can result in the PAHs being inaccessible to soil and sediment organisms, even to microorganisms. Therefore, strong extraction processes will overestimate the bioaccessibility and hence bioavailability of the selected PAH.

Duan (2014) tested four soil types (TOC 1.7%–7.5%) spiked with B(a)P to assess the use of four extraction methods in providing an indication of bioaccessibility and changes in bioaccessibility over time. The results showed that extraction declined with time after spiking for all extraction methods assessed, indicating that the B(a)P is being sequestered rapidly in the initial stages after spiking, thus limiting its bioaccessibility. For this reason, the alternative extraction methods shown in table 12 may provide a better indication of the bioaccessibility fraction of B(a)P in various soil types.

Hydrophobic compounds such as B(a)P tend to sorb strongly to the soil matrix and the physical interaction tends to increase with time resulting in a decrease in bioavailability to soil dwelling organisms. Therefore, the use of dichloromethane (DCM)/acetone extraction is likely to overestimate the amount of B(a)P that is bioaccessible. The BuOH extraction method to assist in the assessment of bioaccessible B(a)P in soils was recommended instead in conjunction with the stronger extraction process (Duan 2014).

Table 12 Bioaccessibility methods (Duan 2014, Duan et al. 2015b)

Extractant	Procedure	Justification for use
DCM/acetone (1:1 v/v) Strong extraction (85–92% of B(a)P extracted)	1.5 g of soil mixed with 3 g of anhydrous sodium sulfate and extracted three times using 10 mL of extractant, each extraction sonicated twice (40 KHz, 15 min) with vortex mixing prior to each sonication. Instead of centrifugation at 13700 g (15 min) in the original method, extractants were separated by centrifugation at 3452 g for 20 min	Used for the estimation of total PAHs in soil with high recovery rates
BuOH Weaker extraction (~45% of B(a)P extracted (Duan pers. Comm. 2016))	5.0 g of soil was extracted using 7.5 mL of BuOH by vortex mixing for 50 sec, instead of filtration, samples were centrifuged at 3452 g for 60 min.	Extracts the desorbable fraction which may represent the bioavailable fraction of PAHs to animals
HPCD	1.5 g of soil was mixed with 25 mL of 60 mM HPCD solution and the mixer was shaken on a platform mixer at 250 rpm for 20 h. The extractant was separated by centrifugation at 3452 g for 60 min.	Extracts the desorbable fraction which may represent the bioavailable fraction of PAHs
Milli-Q Water	1.4 g of soil was extracted using 35 mL Milli-Q water in an end-over-end shaker for 24 h. The extractant was separated by centrifugation at 400 g for 60 min.	Used to estimate the readily available leachable fraction thought to pose the greatest risk to groundwater

Weaker extraction methods better represent the concentration of B(a)P that was bioavailable to animals (Duan 2014). It is proposed that the concentrations reported by the weaker extraction method be included for comparison with the standard extraction method, as part of a weight of evidence approach, when assessing the ecological risk posed by B(a)P. This is consistent with NEPM guidelines.

In conclusion, it is recommended that both the standard extraction method and a weaker extraction method be used to better understand the properties of the B(a)P in particular soils.

4.1.6 Terrestrial ecology conclusions

There is insufficient information to predict an ageing or assessment factor that can be applied to the ecological guidelines to take into account changes in bioavailability based on soil properties. Because of this, it is recommended that assessment of the bioavailability of B(a)P in soils be undertaken using a lines of evidence approach, with

the BuOH extraction method being used to provide one line of evidence of the fraction of B(a)P that is bioaccessible in the soil. This should be compared with the concentrations obtained using the standard extraction method. The ecological guidelines in table 11 apply to fresh B(a)P, and the results of the standard extraction can be expected to provide a measure of fresh B(a)P (that will be more bioaccessible and extractable). The BuOH extraction results provide an indication reduction in B(a)P bioaccessibility through processes such as ageing and soil property effects. The results from the standard extraction procedure can then be compared to the ecological guidelines in table 11, following the NEPM ecological risk assessment procedure.

It is also recommended that consideration be given to other lines of evidence that would support the conclusion that the B(a)P is, or is not, likely to have reduced bioavailability. These additional lines of evidence include the extent to which material has aged, the source and composition of the contamination, and the properties of the soil (e.g. TOC, pH, CEC, particle size, clay content, meso-pore fractions, and the organic carbon to total nitrogen ratio).

This approach may be helpful in providing an indication of the bioavailable fraction of B(a)P for the purposes of an ecological risk assessment, in the absence of either an ageing factor or a toxicity reduction factor based on soil property effects.

However, currently the results of BuOH extraction have not been correlated with actual toxicity results and therefore there is uncertainty regarding the application of the suggested approach. The approach does not currently have regulatory endorsement, and will be subject to review by auditors and regulatory agencies.

4.2 Aquatic ecology

4.2.1 Aquatic toxicity

Because of the low water solubility and high K_{OW} of B(a)P, B(a)P is more likely to be found in soils and sediments, rather than in the water column. Where B(a)P is present in sediment, aquatic sediment dwelling organisms can be exposed through dermal exposure, ingestion and exposure to pore water. Penry and Weston (1998) report that 100% of the total body burden of B(a)P in fish and other aquatic invertebrates comes from dietary exposure.

4.2.2 Bioaccumulation

B(a)P has the capacity to bioaccumulate in a variety of aquatic and terrestrial organisms (CRC CARE 2014a). The uptake/bioaccumulation of B(a)P may be influenced by the presence of other PAHs (as they usually exist as complex mixtures), the contaminated matrix (i.e. bioavailability issues) and the capacity of the organisms to metabolise or transform B(a)P (CRC CARE 2014a). Table 13 shows the bioaccumulation of B(a)P in aquatic organisms as a result of exposure to water, sediment and food, with bioconcentration factors (BCF) ranging from 12 (fish) to > 134,000 (crustacean). B(a)P tends not to bioaccumulate in higher organisms, such as fish, due to their capacity to transform B(a)P as a result of cytochrome P450 monooxygenase activity (CRC CARE 2014a).

The ability of fish to metabolise PAHs may explain why B(a)P frequently is not detected or found only at low concentrations in fish from environments contaminated with PAHs

(ATSDR 1995). Lower bioconcentration factors (0.09 to 7.4) have been reported for benthic invertebrates (compared with other aquatic organisms) following exposure to B(a)P-contaminated sediment (CRC CARE 2014a). As a result of these findings, the US EPA (2007) recommended a sediment to benthic invertebrate bioconcentration value of 1.59 for B(a)P.

Feeding ecology and digestive physiology of sediment-dwelling polychaetes will affect the bioaccumulation that occurs. It has been reported that the digestive fluid of a sediment polychaete extracted 13–52% of B(a)P from sediment, and was inversely correlated to the TOC content of the sediment (Weston & Mayer 1998). This indicates that predator organisms have potential to uptake B(a)P from contaminated sediments via polychaetes.

The bioaccumulation results in table 13 show that a short-term exposure of B(a)P is sufficient for bioaccumulation to occur in aquatic organisms. However, depuration (purification) of organisms from B(a)P following exposure occurs due to elimination and biotransformation processes – this should be taken into account when the exposures occur intermittently (Jager et al. 2000).

In general, bioaccumulation of PAHs in seafood is unlikely to occur at concentrations of concern to human health through consumption of the seafood (White 2011). If there is concern that this may occur then direct monitoring of the seafood of interest should be undertaken.

Table 13 Bioaccumulation of B(a)P in aquatic organisms (CRC CARE 2014a)

Organism		Scientific Name	Exposure period	Bioconcentration factor
Insect	Midge	<i>Chironomus riparius</i>	8 h	166
	Mosquito	<i>Culex pipiens quinquefasciatus</i>	3 d	11,500
Plant	Alga	<i>Oedogonium cardiacum</i>	3 d	5,260
Crustacean	Cladoceran	<i>Daphnia pulex</i>	3 d	134,000
	Cladoceran	<i>Daphnia magna</i>	6 h	2,840
Mollusc	Snail	<i>Physa sp.</i>	3 d	82,200
	*Clam	<i>Rangia cuneate</i>	24 h	9–236
	*Oyster	<i>Crassostrea virginica</i>	14 d	242
Fish	*Northern pike	<i>Esox Lucius</i>	23 d	55
	*Mosquito fish	<i>Gambusia affinis</i>	3 d	930
	*Bluegill	<i>Lepomis macrochirus</i>	4 h	12

*Organisms with cytochrome P450 monooxygenase activity (detoxification enzymes)

4.2.3 Biotransformation

CRC CARE (2014a) provides details on the biotransformation of B(a)P in various organisms. Briefly:

- Bacterial degradation of B(a)P occurs through several oxidation stages. It has been shown to occur when PAHs that support growth (e.g. phenanthrene, fluoroanthene, pyrene) or other substrates are added to the soil. However, although it is known that bacteria have the potential to degrade B(a)P, degradation rates are generally very slow and degradation is incomplete (CRC CARE 2014a).

- Breakdown of B(a)P in fish liver can result in the formation of carcinogenic and mutagenic intermediates, which are eliminated through faeces and urine (CRC CARE 2014a).

4.2.4 Aquatic ecosystems guidelines (freshwater and marine)

The NEPM refers to ANZECC/ARMCANZ (2000) guidelines values, and low reliability values for 95% protection of aquatic ecosystems are⁵:

- Fresh: 0.2 µg/L, and
- Marine: 0.2 µg/L.

These values are based on 21 quantity structure-activity relationship-derived toxicity data and as such are considered as an interim working level. Actual toxicity data comprise four data points (fish: 42-d NOEC = 6.3 µg/L, crustacean: 96-h LC₅₀ = 5 µg/L and alga (2 species): 72-h EC₅₀ = 5–15 µg/L). Note that the interim Canadian guideline is 0.015 µg/L. The EU has a maximum annual concentration environmental quality standard of 0.27 µg/L for freshwater and 0.027 µg/L for marine waters derived by applying assessment factors of 10 and 100 respectively to toxicity data.

The ANZECC/ARMCANZ values do not account for the bioaccumulation potential of B(a)P, nor biodegradation. ANZECC/ARMCANZ (2000) recommends that if no site-specific bioaccumulation data are available, then the low reliability figure of 0.1 µg/L for 99% protection should be adopted for both marine and aquatic waters, as an interim working level. CRC CARE (2014b) noted that the lack of aquatic toxicological and biomagnification studies in the Australian context makes development of reliable aquatic ecological values difficult.

With respect to sediments, revised sediment quality guideline values (SQGV) have been prepared for PAHs, and for all sediment types the following are recommended:

- SQGV = 10 mg for total PAHs/kg (normalised to 1% organic carbon, dry weight), and
- SQG-high = 50 mg for total PAHs/kg (normalised to 1% organic carbon, dry weight) (Simpson et al. 2013).

This where total PAHs equals the sum of the 16 individual non-alkylated PAHs (also known as unsubstituted or parent PAHs (ANZECC/ARMCANZ, 2000). These are naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene.

In applying the SQGVs, the total PAH concentration is normalised to 1% organic carbon (OC) within the limits of 0.2 to 10%. Thus if a sediment has 2% OC, the '1% normalised' concentration would be the measured concentration divided by 2. For 0.5% OC, then the 1% normalised value is the measured value divided by 0.5. Or, for 0.15% OC, then the 1% normalised value is the measured value divided by the lower limit of 0.2.

Simpson et al. (2013) note that in revising the ANZECC/ARMCANZ guideline values, the values for individual PAHs were removed because, for the majority of assessments,

⁵ Low reliability guideline values based on minimal ecotoxicology data (four data points only)

the concentration of total PAHs represents contributions from a large number of individual PAHs, with each being a small percentage of the total. While it was recognised that the toxicities of the individual PAHs differ significantly, it was considered unlikely that an individual PAH will, by itself, dominate either the total PAHs concentration, or the chemistry lines of evidence within a weight of evidence framework. Consequently, the use of total PAH concentrations would be relevant for most assessments.

Simpson et al. (2013) also noted that where PAHs are likely to be the dominant contaminants of concern in sediments, the use of an equilibrium sediment benchmark (ESB) approach developed and proposed by the USEPA for mixtures of PAHs can be considered. However, while an ESB-based approach may be suitable for assessing possible toxicological effects due to PAH mixtures, it increases the complexity of the assessment and a single effects threshold based on the total PAH concentration is recommended for general guideline use.

4.2.5 Aquatic ecology conclusions

The guidelines for protection of aquatic ecosystems are listed above. The guidelines for water are low, and are likely to be below the standard laboratory limits of reporting (though ultra-trace analysis is possible which can provide limits of reporting below the guideline values). In general, noting the low likelihood of B(a)P being present in water, other contaminants (such as benzene) are more likely to determine the requirements for remediation of aquatic ecosystems.

5. Remediation and management

5.1 Introduction

Remediation and management of B(a)P-impacted media is often indicated to be required because B(a)P does not readily degrade and the residual concentrations of B(a)P that are observed will often exceed the NEPM HILs and ESLs. It has been generally not been possible to measure and account for bioavailability.

Although the HILs and EILs are not intended to be remediation goals, or even triggers for remediation, they are often adopted for this purpose. This is due to the absence of other readily available information and because many of the exposure assumptions that underlie the investigation levels will not be changed in a more detailed assessment of risk. Further, because of the persistence of B(a)P in the environment, simple methods of remediation such as natural biodegradation are not feasible.

This section provides a summary of current soil and sediment remediation methods and approaches, and provides a framework to assist in selecting an appropriate treatment option for B(a)P-contaminated soils, sediment and groundwater.

5.2 Developing a conceptual site model for B(a)P

In understanding the implications of the HILs and ESLs and determining the key requirements and drivers for remediation and management of B(a)P contaminated material, it is helpful to develop a conceptual site model (CSM). Schedule B2 of the NEPM provides an outline of how to develop a CSM. Typically, the development of a CSM for a site will involve:

1. Development of a generic CSM based on the physical and chemical characteristics of B(a)P, as detailed in section 2.3, and
2. Development of a site-specific CSM, noting that the geological, hydrogeological and receptor conditions will differ from site to site.

5.2.1 Generic CSM

The main aspects of a generic CSM are identification of the:

- **Source or sources of contaminants:** this might include gasworks waste, incinerator waste, imported fill material (e.g. from former gasworks sites), coal tar, asphalt, forest fires and other industrial waste.
- **Release mechanisms:** B(a)P is mainly released to the environment through incomplete combustion of organic material. It may also enter the environment through historical deposition of gasworks or incinerator waste as fill material, general use of the product (e.g. as bitumen), accidental spills or leaks and unauthorised disposal.
- **Impacted media and transport mechanisms:** B(a)P can impact all elements of the environment, including the atmosphere, soils, sediments and water (groundwater and surface water). Vapour phase impacts on air quality will generally not be important and will not require consideration, other than as an

aesthetic (olfactory) issue and in the context of airborne contaminated particulate matter.

- **Potential receptors:** human and ecological.
- **Exposure pathways:** the main exposure mechanisms include dermal contact, ingestion and inhalation in particulate form (dust).

Development of the CSM is an iterative process, initially developed from a preliminary site investigation, and continually refined and updated as further assessment is undertaken. An example generic CSM for B(a)P is provided in figure 3.

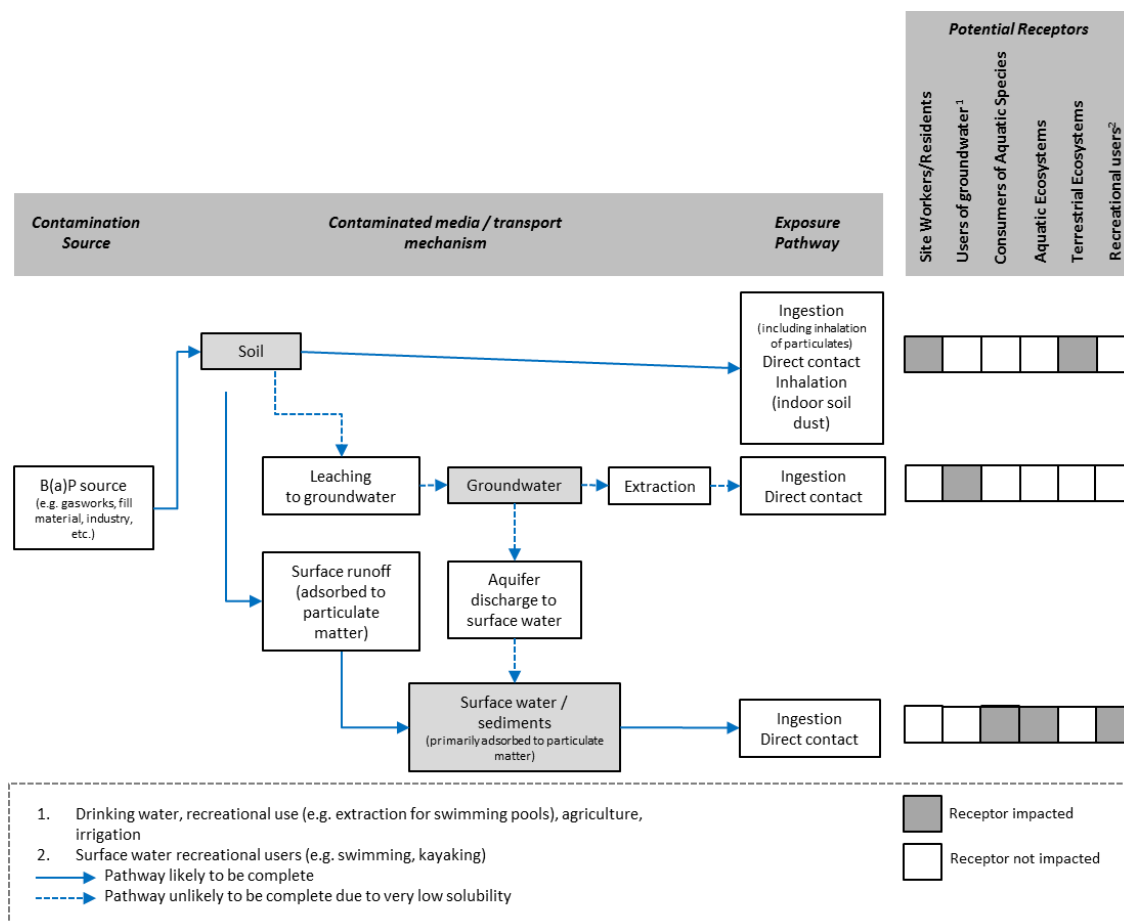


Figure 3 Example of a graphical CSM for B(a)P-contaminated site

5.2.2 Site-specific CSM

Development of a site-specific CSM involves adapting the generic CSM to include site data to consider contaminant fate and transport, and the implications of contamination both on-site and off-site. The site-specific CSM will allow for definition of the linkages between source and receptors and whether actual impacts have been identified.

The NEPM (Schedule B4) outlines factors that should be considered in developing a CSM. Table 14 provides a summary of these and other aspects, and considerations that should be made in relation to B(a)P. In developing the CSM, B(a)P should not be considered in isolation, as it is often present along with other contaminants, particularly together with other PAHs and monocyclic aromatic hydrocarbons (MAHs). Nevertheless, it is important to examine each contaminant individually, as well as holistically.

Table 14 Inputs to site-specific CSM

Aspect	Considerations
Contaminant sources	As per the generic CSM, but refined based on site-specific details (e.g. gasworks waste as fill, incinerators, landfills and ovens). This provides an assessment of the possibility that contamination could have occurred and the likely areas of greatest impact on the site. It will be important in determining whether contamination is widespread and random in nature (e.g. from imported fill material), or attributed to point sources (e.g. incinerators) and therefore localised.
Physical and chemical properties of the contaminants, and the likely mobility in the environment.	Is B(a)P the limiting contaminant of concern, or are there other contaminants that will influence remediation and management decisions? It is important to gain a thorough understanding of the range of contaminants present, the potential interactions between contaminants, and the implications of contaminant “mixtures” on the risks posed to receptors. B(a)P has low solubility, and strong tendency to adsorb to soils, and hence has a low likelihood of migrating to groundwater. An exception might be if other contaminants are present such as MAHs, that might increase the solubility of B(a)P. B(a)P is highly recalcitrant and unlikely to naturally degrade. It may persist for many years in the environment.
Site-specific contamination analytical data	Where available, site analytical data are the most important source of information defining risk. Where absent or inadequate, this should be flagged as a significant data gap.
Type and maximum concentrations of B(a)P	Do contaminant concentrations exceed the HILs and/or ESLs?
Distribution (vertical and horizontal) of contaminants	Is contamination widespread and potentially randomly distributed (e.g. fill material), or attributed to point sources (e.g. incinerator, coal tar pit)?
Geology	Soil and rock types, stratigraphy. This information allows for an assessment of the likely migration of B(a)P through the subsurface and possible attenuation mechanisms such as sorption and biodegradation. It is also an important consideration for selection of remedial methods. Soil properties may affect the bioavailability of B(a)P (e.g. bioavailability may be higher in coarser matrices such as sand, compared with fine matrices such as clay, presence of organic matter may reduce bioavailability). B(a)P will typically adsorb strongly to sediments, with limited partitioning to water due to low solubility, and hence has a low tendency to migrate to (unless adsorbed to particulate matter which is distributed via surface water runoff, or in the atmosphere).
Hydrogeology	Depth to groundwater, aquifer type (porous or fractured rock), hydraulic gradients, hydraulic conductivity, geochemistry (TDS, pH, TOC). This information allows for an assessment of the potential for and rate of migration of the B(a)P across the site and off-site.
Potential presence of subsurface geology or structures that may act as preferential pathways for	Not usually applicable for B(a)P given its low volatility. However, other contaminants that might be present (e.g. more volatile PAHs such as naphthalene) must also be considered in developing the CSM.

migration of vapours (on and offsite)	
Beneficial uses/environmental values of groundwater	The beneficial uses or environmental values of groundwater that require protection should be identified; this will provide the framework for assessing risk and the need (or otherwise) for contaminant management. The beneficial uses or environmental values may include, for example: potable water use, maintenance of ecosystems, agriculture (irrigation and stock watering), industrial, recreation (swimming pool) use, and effects on buildings and structures.
Land uses	This will determine the adopted human health and ecological criteria.
Potential receptors	On-site and off-site. The likelihood of impact to receptors will determine the ultimate risk profile for each site. Consideration should be given to existing and potential future land uses and hence receptors, and whether complete exposure pathways (ingestion, dermal contact, inhalation of dust) exist to these receptors. Potential receptors may include: <ul style="list-style-type: none"> • Humans: site residents, utility workers, site occupants (e.g. workers or park users), users of extracted groundwater • Ecosystems: terrestrial and aquatic ecosystems directly in contact with contamination, aquatic ecosystems receiving contaminated groundwater, aquatic ecosystems exposed to contaminated sediments.
Exposure pathways: how exposure might occur and the frequency of exposure	Exposure of humans and animals to B(a)P in the environment occurs primarily through ingestion (including inhalation of contaminated dust) and dermal contact. Frequency will depend on factors such as site usage (e.g. park users may be subject to a lower exposure than site residents). As the occurrence of significant concentrations of B(a)P contamination in groundwater and surface water bodies is unusual because of the low solubility of B(a)P, migration of B(a)P will generally be restricted to transport in particulate form (such as in stormwater).
Bioaccumulation	This property of B(a)P can result in small concentrations of B(a)P accumulating in organisms, and giving rise to adverse effects higher in the food chain than would occur through direct exposure.
Bioavailability/bioaccessibility	The bioavailability/bioaccessibility of B(a)P can significantly affect whether contamination will have an adverse impact. Consideration should be given to whether the bioavailability/bioaccessibility is likely to be low, and whether it is practical to obtain a measure of these parameters and therefore include this factor in the management and remediation decision-making process.
Jurisdictional controls	State and Federal legislation, local authorities, EPA. These controls may require certain site owners to assess and report on contamination status of their sites. They may also require remediation should unacceptable risks be identified.

The CSM should be presented in graphical or in tabular format and should be accompanied by a cross section or series of cross sections indicating source-receptor linkages. Such cross-sections are excellent methods for explaining the complexities of contamination to stakeholders. An example graphical site-specific CSM is provided in figure 4. Note this is an example only and does not cover all contamination scenarios or possible source-pathway-receptor linkages.

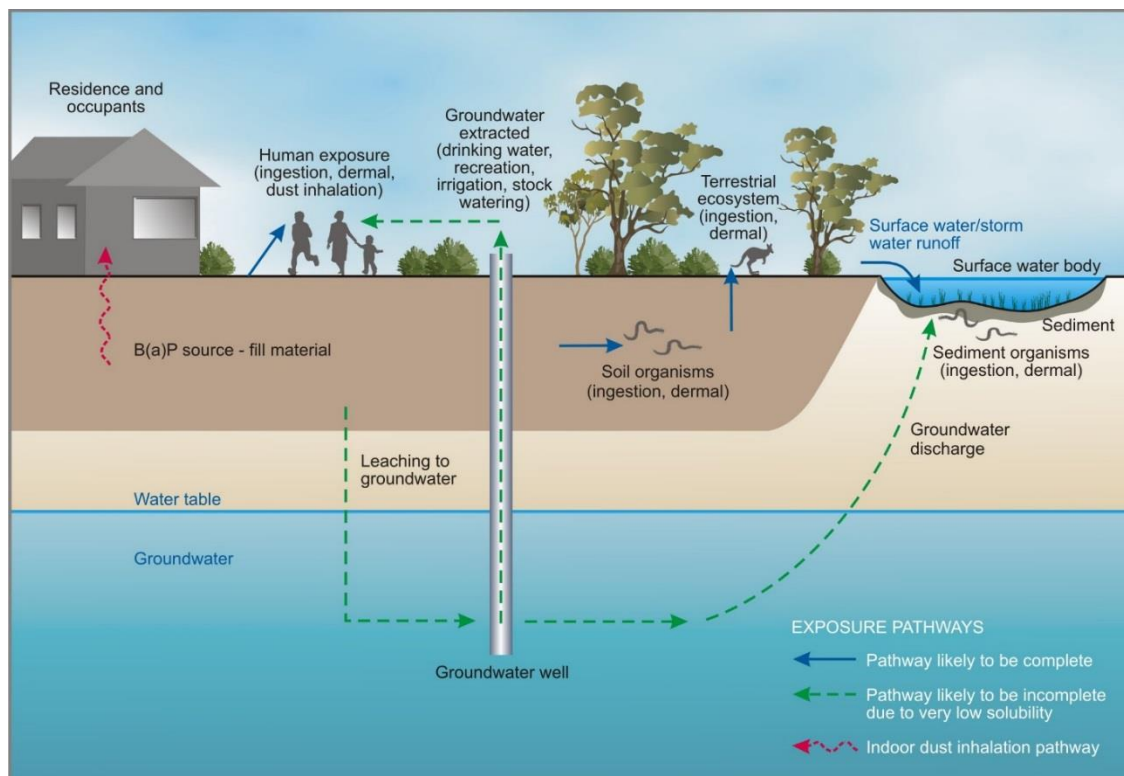


Figure 4 Example of a graphical site-specific CSM for B(a)P-contaminated site

The CSM should provide information on the following:

- **Do the site analytical data exceed HILs?** Consideration must be given as to whether comparison of total B(a)P concentrations against the HILs is appropriate, given the possibility that less than 100% of the total concentration may be bioavailable.
- **Do the site analytical data exceed ESLs?** As for the HILs, consideration must be given to the bioavailability of B(a)P. Additionally, based on updated information available there are grounds for accepting higher ecological guidelines, as discussed in section 4.1.3.
- **Is there an imminent or future risk to receptors?** Is there a complete exposure pathway (e.g. ingestion, dermal contact, inhalation of dust) between the B(a)P contamination and receptors?
- **Is further data required to determine remediation processes and how would this be obtained?** Do the current data provide an accurate representation of the contamination at the site? Is additional information required to assist in determining firstly whether remediation is warranted (e.g. bioavailability/bioaccessibility information) or to assist in determining the most appropriate remedial method (e.g. soil and/or aquifer properties)?

Once these questions are answered, the remediation objectives can be defined and technology selection can proceed. Management and remediation options are discussed further in section 5.6.

5.3 Requirements for remediation

The NEPM toolbox includes a section on *Key principles for the remediation and management of contaminated sites* (draft for public consultation). This indicates that a key goal of remediation is to result in a site that is acceptable and safe for long-term continuation of its existing or proposed use, and to maximise to the extent practicable the site's potential future uses.

In general, it is preferred to avoid the need for unnecessary remediation. Assessment of the contamination involving a sufficient level of detail to resolve uncertainties may achieve this. The information provided in this guidance document can assist in undertaking such an assessment.

In the case of B(a)P, the requirement for remediation has often been based on the total concentrations of B(a)P measured at a site, and whether those concentrations exceed the HILs and/or EILs. This is a simple and inherently conservative basis for decision making, as it does not consider the actual risk at the site posed by contamination to human health or the environment, taking into account site-specific considerations such as bioavailability. Where the concentrations of B(a)P in soil at a site only marginally exceed the HILs and/or ESLs, adopting a conservative approach may result in unnecessary remediation. There may be advantage in taking factors such as bioavailability/bioaccessibility into account to determine the acceptable concentrations of B(a)P that may be safely retained on a site.

5.4 Preferred remediation hierarchy

Where the assessment has shown action is required, the NEPM Toolbox provides the following preferred hierarchy of remediation and management options (NEPM 2014):

1. On-site treatment of the soil to either destroy the contaminant, or reduce the associated hazard to an acceptable level.
2. Off-site treatment of excavated soil to either destroy the contaminant, or reduce the associated hazard to an acceptable level so that it the soil can be returned to the site.

If neither of these options is possible, then further options for consideration include:

3. Removal of contaminated soil to an approved site/facility, and replacement (as necessary) with clean fill.
4. Isolation of contamination on-site in an appropriated designed and managed containment facility (i.e. cap and contain).
5. Adopt a less sensitive land use (to reduce risk associated with contamination), or undertake partial remediation. If there is no immediate risk to the environment or community, and the site has appropriate management controls in place, it may be possible to leave contamination in-situ.

When considering remediation approaches, there may also be a preferred waste-management hierarchy stipulated by the regulatory agency that should be considered.

These may need to be modified from a waste-management perspective to be relevant to a situation where contamination exists.

5.5 Remediation decision making processes

The decision-making process associated with remediation determines the need for remediation and informs the technology selection process (section 5.6), validation and monitoring. It is based on a modified DQO process (as outlined in NEPM Schedule B2) and involves six steps, outlined below.

5.5.1 Step 1: state the problem

This includes a statement of what media (soil, sediment, groundwater, surface water) is impacted by B(a)P.

The impact to soil could be defined by a diagram showing B(a)P concentrations (as contours if sufficient information is available) that exceed the screening criteria (refer to section 3 and 4). This will identify soils that may be harmful to human health and those with a potential impact on the environment.

The impact to groundwater would be defined by a diagram showing B(a)P contours (concentrations exceeding the screening criteria for waters, as discussed in section 3.2.2).

5.5.2 Step 2: identify the decision/goal of the remediation

The overall goal is likely to be safe use of the site, or to restore the use of the site. This may be achieved through various approaches, such as treating or removing contamination, or breaking source-receptor linkages. The concentrations of contaminants in soil that can be exposed should be reduced to below the HILs or ESLs, or to below risk-based criteria appropriate for the desired land use, that are developed through a process of risk assessment. Specific measures of ecological and human health bioavailability could be undertaken at this point to inform the risk assessment. For example, if it can be shown that bioavailability of B(a)P contamination is less than 100%, this may result in site-specific human health and/or ecological criteria that are substantially greater than the standard HILs and ESLs.

In defining the goal, stakeholders may need to be consulted, and a consultation plan developed.

Decisions about what measure is required to meet the site criteria, such as the 95% UCL, maximum/mean/median concentration, or other, are required.

In the case of B(a)P, the main goals of remediation might typically be:

Soils

- To avoid unacceptable levels of exposure to site occupants, workers or visitors. This may include capping to prevent contact with contaminated soil, or removal or treatment of soil that has concentrations levels that exceed the relevant HILs or site-specific remediation criteria.
- To avoid unacceptable contamination of groundwater that may occur, for example, by leaching of B(a)P from the soil (although in the case of B(a)P solubility is low and leaching is unlikely to be a limiting requirement).

Sediments

- To avoid unacceptable impacts to ecological systems from contamination that is present in sediments; this should include consideration of the potential for transport of sediments, and bioaccumulation. In the case of sediments, the limiting consideration is likely to be the risk to ecosystems, rather than human health (since PAHs are generally metabolised in fish, PAHs are unlikely to limit human consumption of fish).

Groundwater

- To protect human health, such as where groundwater may be used for drinking water, or for recreational use (such as make-up of swimming pools).

To protect local ecosystems where there is a real or potential risk to ecological receptors, which may arise for example through discharge of groundwater through a shoreline or sediments into a receiving water. In the case of B(a)P, solubility and leaching are generally low and this may not be a limiting requirement.

5.5.3 Step 3: identify the information inputs

Information gathered in the CSM is used to identify the need for remediation and the degree of remediation required. This would include the magnitude (concentrations) of contamination, and distribution (lateral and vertical extent). The CSM should be reviewed to determine whether the existing data is adequate to allow a remedial option to be selected.

Further assessment work may be required to adequately characterise the contamination and allow informed selection of remedial options. Biota surveys and sampling might be considered to provide a more direct measure of presence and effect.

5.5.4 Step 4: define the boundaries of the remediation requirements

The boundaries of the remediation requirements are both physical and jurisdictional. They include the physical site extent and receptor pathways, and may include wider impacted ecosystems and water resources. Temporal boundaries such as the period of the investigations and remediation, and seasonal variability must be considered.

Jurisdictional policies and requirements may have important implications when identifying potential remedial options, and associated restrictions and permitting requirements.

Step 5: Review and select remedial strategy

Options for achieving the objectives should then be identified. This will include various strategies that will achieve the objectives, and may include options such as treating or removing contamination, or providing barriers and controls to avoid exposure, or involving combinations of options. Information regarding the selection of particular technologies is in table 16 and table 17. The first stage of the selection process will be to assess whether potential options will meet the required objectives; if not, that option should be eliminated as a primary method. Effectiveness of technologies requires consideration; often the application of a particular strategy will have uncertainty and may not be able to achieve an appropriate outcome, and should be discarded or assigned for further evaluation.

Available remedial technologies for B(a)P contaminated soil, sediment and groundwater are outlined in section 5.6.

If this assessment identifies more than one possible remedial strategy, then the options will need to be compared. This may involve a staged or sequential comparison that checks that other important criteria will be met or whether there are clear advantages of one option over another, or certain options are deemed to not be acceptable and should not be considered further. For example, the risk perceived by various stakeholders could be a limiting factor. The risk may pertain to the risk arising from the remedial activity (i.e. in the short term), or in the long term (i.e. the risk of failure of a containment system). Stakeholder input may be gained through a consultation.

Where a number of factors need to be balanced, this comparison can be structured as a multi-criteria analysis involving, for example, various indicators of cost benefit or sustainability taking into account social, environmental and economic considerations. Table 15 provides an example of indicators that could be assessed when evaluating sustainability. Indicators relating to cost benefit and sustainability analysis are outlined in appendix C of the CRC CARE report *Guideline for performing cost-benefit and sustainability analysis of remedial alternatives*.

Consideration should be given to the likely performance of each of the remediation options being considered – how well will they meet the objectives, how will the remediation program be implemented and how will it be validated to demonstrate success? Implementation and validation of the selected remediation option/s is essential to demonstrate successful completion and will form a significant part of the remediation action plan (RAP).

Step 6: develop the plan (RAP) for obtaining data and implementing remediation technology

The selected remedial strategy should then be defined and documented in a remediation action plan (RAP). The RAP defines the remediation selection process (typically by including the matrix completed in step 5), design of the system, operation and maintenance, roles and responsibilities, validation and monitoring processes.

The RAP may be accompanied by a cost benefit and sustainability analysis to narrow the technology selection process and a remediation technical specification (RTS) to allow works to be released for tender.

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Table 15 Indicators for sustainability assessment of remediation options (adapted from CL:AIRE 2010 and CL:AIRE 2011)

Environmental	Social	Economic
<p>Impacts on air (including climate change)</p> <ul style="list-style-type: none"> Emissions that affect climate change or air quality (positively or negatively) <p>Impacts on soil and ground conditions</p> <ul style="list-style-type: none"> Changes (positive or negative) to soil conditions that affect ecosystem function such as soil and sediment quality, water filtration, soil structure and properties, erosion and drainage, geotechnical properties. <p>Impacts on groundwater and surface water</p> <ul style="list-style-type: none"> Change in water quality due to release of contaminants and nutrients, dissolved organic carbon or particulates Groundwater abstraction (changing water table or river levels) Flooding <p>Impacts on ecology</p> <ul style="list-style-type: none"> Flora, fauna, food changes Changes in ecological community structure or function Effects of disturbance (light, noise, vibration) Impacts of equipment on fauna (e.g. interrupting flight path or animal migration) <p>Use of natural resources and generation of wastes</p> <ul style="list-style-type: none"> Impacts/benefits for land and waste resources, use of primary resources, use of energy/fuels, material handling, disposal of waste, water abstraction and disposal <p>Intrusiveness</p>	<p>Impacts on human health and safety:</p> <ul style="list-style-type: none"> Long- and short-term risk management performance of project Chronic and acute risks <p>Ethical and equity considerations:</p> <ul style="list-style-type: none"> polluter pays principle Impacts/benefits of work relative to various stakeholder groups Intergenerational equity Ethical operation of contributing businesses <p>Impacts on suburbs or regions:</p> <ul style="list-style-type: none"> Dust, noise, odour, light, vibrations. Architectural conservation, changes in built environment <p>Community involvement and satisfaction</p> <ul style="list-style-type: none"> Impacts to community services Quality of communications Inclusivity and engagement in decision making, transparency of decision making Impacts on local culture <p>Compliance with policy objectives and strategies</p> <p>Uncertainty and evidence</p> <ul style="list-style-type: none"> Robustness of sustainability appraisal Quality of assessments (QA/QC) Requirements for, and methodology of validation/verification Establishment of robust site-specific risk-based remedial criteria (e.g. consideration of bioavailability of contamination, etc.) <p>Heritage (natural, historical, indigenous)</p>	<p>Direct economic costs and benefits</p> <p>Indirect economic costs and benefits</p> <ul style="list-style-type: none"> Long term or indirect costs/benefits (e.g. financing debt, internal allocation of financial resources, changes in property value) <p>Employment and capital gain</p> <ul style="list-style-type: none"> Job creation Skills development, learning and training Innovation <p>Gearing, induced economic costs and benefits</p> <ul style="list-style-type: none"> Opportunities for inward investment Funding schemes, collaboration to enhance economic value <p>Life-span, 'project risks' and flexibility</p> <ul style="list-style-type: none"> Duration of remediation Factors influencing success of remediation works (contractual, community, environmental, technology limitations) Ability to adapt to changing circumstances (e.g. discovery of additional contamination, unexpected conditions, expanding timescales) Robustness of option to climate change effects, or altering economic circumstances Ongoing institutional controls

5.6 Available remediation strategies and technologies for B(a)P

5.6.1 General response actions to contamination

General response actions are broad categories of actions for accomplishing remedial objectives and can be combined to form remedial alternatives. First, it must be established whether the contamination poses a risk to human health or ecosystems. This should be achieved through the development of a detailed site-specific CSM (refer to section 5.2.2). If it is determined the contamination does not pose an unacceptable risk to receptors, it may be concluded that no action is required, or that material could be re-used elsewhere on site where it will not pose a risk to receptors. Such reuse may be subject to stakeholder and regulatory agreement.

When contamination poses an unacceptable risk to receptors, the general response actions in general accordance with the preferred remediation and management hierarchy in the NEPM Toolbox (refer to section 5.4) include:

- Treatment:
 - In-situ treatment – injection of chemicals or biological agents or heat to stabilise, destroy or enhance mobilisation or solubility of the B(a)P.
 - Ex-situ treatment (assumes excavation) – treatment of excavated material with chemicals, biological agents or heat to stabilise or destroy the B(a)P.
- Containment or institutional controls – physical barriers to prevent access to or migration of impacted soil or groundwater, or restricts access for some or all activities.
- Disposal – excavation (soil) or pumping (groundwater) to remove contamination from a site. Removed soil may be disposed of to landfill, treated and re-used or treated and disposed of to landfills or encapsulated on-site. Removed water may be disposed to sewer, possibly after some treatment.

5.6.2 Soil management and remediation technologies

Within each general response action are a number of alternative approaches to B(a)P management. Potential remedial methods are listed in table 16.

5.6.1 Sediment treatment options

For sediments, it is likely that the most effective and practicable response is to remove the impacted sediments from the aqueous environment (e.g. by dredging) for treatment and disposal.

Initial treatment is likely to involve dewatering to remove excess water to allow for disposal. If sediment is to be stored or disposed of on land, assessment would also need to be conducted to determine the potential for acid generation. This should be assessed by sampling and analysis prior to excavation. In the event that significant acid generation can occur, then neutralisation may be required.

Most of the treatment methods for soil detailed in table 16 can apply to sediments.

5.6.2 Groundwater treatment options

In general, B(a)P has low solubility and the main mass of contaminant is likely to be adsorbed to soil and be effectively immobile. Because of this, remediation methods that address soil contamination in-situ (refer to table 16) are likely to also address

groundwater contamination. Where B(a)P is present in concentrations in groundwater that pose an unacceptable risk, this is likely to occur where other contaminants are present such as the more soluble PAHs (e.g. naphthalene) and mono aromatic hydrocarbons (BTEX), and the requirements for remediation driven by these contaminants may determine the overall requirements for remediation.

A list of potential remedial methods for groundwater are provided in table 17Table 17.

Table 16 Summary of potential soil management and remediation processes

General response actions	Remedial technology	Process options	General applicability in practice
No action	None	None – assumes acceptable risk from soil contamination.	Generally not an acceptable option, unless the risk has been assessed as acceptable.
Institutional controls	Access and use restrictions	Deed restrictions, fences, permits, licence conditions, management plans	Applied as a temporary measure at many sites. Applied at some sites as a long-term measure, perhaps in conjunction with containment, where exposure can be avoided and stakeholders accept this, particularly if stakeholders see the alternative requirements for remediation as being damaging.
Containment	Capping	Application of a clay, asphalt or concrete cover over impacted soils.	Applied at some sites where containment can avoid exposure and it is acceptable to stakeholders, particularly if stakeholders see the alternative requirements for remediation as being damaging. Requires ongoing management.
		Phytocap	Vegetated cover that controls rainwater infiltration through a water balance mechanism. Typically used as capping for landfills. Has rarely been applied in preference to other capping systems for B(a)P-contaminated soils, although may be an option where the site use is to be parkland.
	Physical barriers	Barrier walls – sheet piles, secant piles. The walls are installed in-situ to surround the impacted area to prevent contact with groundwater and reduce groundwater flux	Applied at some sites, although because B(a)P often has limited mobility other than when present with non-aqueous phase liquids (perhaps hydrocarbons present as micelles ¹), this technology would primarily be applied to contain other such contaminants.
Removal	Excavation (to the extent practicable)	Excavation with off-site disposal.	Most common approach adopted, because it provides certainty and a rapid solution, without constraints on future use. May be coupled with treatment (e.g. stabilisation) to reduce leaching levels to comply with landfill acceptance criteria. High cost of landfill disposal can make this very costly option and lead to other alternatives being adopted.
		Excavation with on-site treatment and re-use.	Common approach and generally well understood, with on-site treatment involving for example thermal desorption, which can provide for relatively complete treatment. Can be costly and may be restricted to large sites where the cost of mobilisation is acceptable.
		Excavation with beneficial re-use (i.e. as a building or road material)	Sometimes adopted where the regulatory agency or auditor accepts this option and groundwater contamination will not occur. Most applicable where there large road works form part of the project. This would need to be evaluated on a case-by-case basis, and discussed with regulatory agency. Evaluation of risks posed to potential receptors in re-use scenario (e.g. subsurface workers) should be undertaken.
		Excavation with on-site encapsulation	Sometimes adopted and generally well understood, although requires agreement by regulatory agency and stakeholders. May be coupled with stabilisation to reduce the

			potential for leaching. Ongoing management (e.g. through environmental management land requirements and intergenerational equity must be considered.
In-situ treatment	Biological	Enhanced bioremediation	<p>Soil microorganisms breakdown contaminants, reducing contaminant concentrations and associated toxicity. Sometimes adopted where the future land use is not sensitive and relatively high concentrations of B(a)P such as may remain after bioremediation are acceptable. Generally not applied for sites where the future intended use is residential, or a sensitive use of groundwater is to be protected in the short to medium term.</p> <p>B(a)P tends to be recalcitrant to microbial degradation due to a range of constraints. Microbial bioavailability and/or biodegradability can result in a residual B(a)P component that cannot be biodegraded, but can still be bioavailable (Juhasz et al. 2014). Pilot trials might be necessary, with bioaccessibility testing to establish whether residual PAH fractions pose a risk to future users of the site.</p> <p>It can be difficult to define the conditions under which bioremediation might reach the desired remediation end-point, as it is not possible to identify a single set of contaminant and soil characteristics that are predictors of bioremediation potential (Dandie et al. 2010). Studies have been undertaken into assays that show potential using bioaccessibility as a predictor of biodegradation potential for hydrocarbons (Dandie et al. 2010), but this work does not appear to have been widely tested in the field.</p> <p>Surfactants can be applied to increase solubility and enhance biodegradation; technology suppliers such as Verutek (EthicalChem) and Ivey International (the Ivey-sol™ technology) can be referred to for information on applicability.</p>
		Bioventing	Generally not applicable.
		Natural attenuation	Generally not applicable for B(a)P. B(a)P is recalcitrant and does not readily degrade under standard environmental conditions.
		Phytoremediation – the use of plants to stabilise or remove contamination from soil	Unusual to apply this technology – generally regarded as developmental and uncertain as to the effectiveness of significantly reducing the concentration of B(a)P.
	Physical chemical treatment	Electrokinetic separation	Generally not applicable.
		Surfactant/co-solvent flushing (soil flushing)	<p>In-situ flooding of contamination zone with an appropriate solution to remove the contaminant from the soil. Contaminants are mobilised by solubilisation, formation of emulsions, or chemical reaction (with flushing solutions). For hydrophobic contaminants such as B(a)P, surfactants are typically used, with the solution sometimes heated (US EPA 2014).</p> <p>Unusual to apply this technology; some work has been carried out (e.g. by Verutek (now EthicalChem) and Iveysol) but the final concentrations able to be achieved are uncertain; regarded as developmental at this time. Studies have found some limited success with removal of B(a)P from contaminated soils, however contaminant removal depends on</p>

			flushing solution affinity and selectivity towards the target contaminant (Reddy et al. 2011). Contaminant-containing solution is then collected for disposal or treatment. While extensive experimental trials have been carried out, there is limited field-based implementation (US EPA 2014). Not suitable for low permeability or heterogeneous soils, can cause spreading of contaminants, difficult to predict performance, can require extensive laboratory testing, and requires management of contaminated flushing solution (US EPA 2014).
		Solidification/stabilisation (S/S) – in-situ mixing of soils with a binding agent to reduce or prevent leaching of B(a)P from soils.	Unusual to apply this technology, although has been frequently applied overseas where the land use can be restricted (e.g. industrial). Can be uncertain as to whether the stabilisation will remain effective in perpetuity. Powdered reagents such as RemBind™ chemically fix (immobilise) contaminants through adsorption. The RemBind™ Product Overview indicates the primary constituents include activated carbon, aluminium hydroxide and kaolin clay. RemBind is applied at a rate of 2-10% w/w. Treatment at a former gas works site in South Australia found that B(a)P leachability was reduced from 0.0083 mg/L in TCLP before treatment, to 0.0013 mg/L in TCLP after application of 5% w/w (below landfill acceptance criteria in SA). The treated soil passed the Multiple Extraction Procedure (MEP), a leachability test that simulates a worst case leaching scenario (1000 years of acid rain in unlined landfill). Regulatory approval would need to be obtained on a case by case basis, but to date has been favourable in Australia. Although contaminants are immobilised and hence not bioavailable (pose low risk), contamination is still present and so consideration has to be given to ultimate fate of soils.
		Chemical oxidation – injection of chemical oxidants such as Fenton's Reagent, sodium persulphate, ozone to destroy the B(a)P	Some large-scale trial work has been carried out in Australia (e.g. by Verutek Technologies ⁶) with variable results but the process has yet to be applied for full scale clean in Australia; regarded as developmental at this time. Laboratory trials have indicated some success, with one study reducing the total PAH concentration from 2800 to <100 mg/kg (Ferrarese et al. 2008). However, optimal oxidant doses can be difficult to gauge (too low or high then oxidation does not occur). US EPA (2006) rates the amenability of PAHs to oxidation transformations from good to excellent, depending on the reagent used.
		In-situ thermal – e.g. using electrical resistance heating or steam	Has been widely applied overseas, and is being considered for application in Australia.
		In-situ smouldering	Contaminants are the source of fuel for smouldering combustion. Still in developmental stages overseas. Has not been applied in Australia on a commercial basis, although is being considered for some sites.

⁶ Tender called on 7 February 2014 by Lend Lease for remediation of the former Millers Point Gasworks in NSW, which stated the preferred remediation approach is to use SISCO and SEPR provided by VeruTEK Technologies. VeruTEK is now EthicalChem.

			Because vendors are offering this option, more definition regarding its application and limitations would be useful.
Ex-situ treatment (assumes excavation)	Biological	Land farming	Generally not applicable to B(a)P, although can significantly reduce lower molecular weight PAHs.
		Slurry phase biological treatment	As for land farming.
		Biopiles/composting	As for land farming.
		Mycodegradation – white rot fungi	As for land farming.
	Physical-chemical treatment	Soil washing – physical washing of soils with water and/or water-based compounds to dissolve or suspend B(a)P. Recovered water then treated. Can be enhanced by surfactants.	As above. Has been trialled at some sites, but has not been applied at full scale. Will result in a slurry or liquid concentrate with a high concentration of B(a)P that can be more difficult to dispose of.
		Solidification/stabilisation/sorption – contaminants are immobilised by sorption, precipitation or incorporation into crystal lattices or physically encapsulation by the addition of suitable reagent. The process is designed to reduce leaching potential and to improve soil condition.	As above. Has been applied at some sites to reduce leaching and hence make the material acceptable for landfill disposal. Consideration needs to be given as to how soil can be reused, given contamination is still present, albeit in a non-available form. Regulatory approval would be required on a case by case basis.
		Thermal desorption – wastes heated to volatilise water and organic contaminants. A carrier gas or vacuum system transports volatilised water and organics to the gas treatment system	Applied in Australia and generally well understood, particularly for larger sites where the high establishment cost can be accepted.
		Chemical oxidation – ex-situ mixing of soils with chemical oxidants to destroy the B(a)P.	Generally has not been applied in Australia; regarded as developmental; probably would not be preferred over alternative treatment methods such as thermal desorption.
		Pyrolysis – chemical decomposition is induced in organic materials by heat in the absence of oxygen. Organic materials are transformed into	Generally has not been applied in Australia and would not be expected to be preferred over thermal desorption for on-site treatment. A commercial system has now been established for ex-situ treatment of soil in Victoria.

		gaseous components and a solid residue (coke) containing fixed carbon and ash	
		Incineration – high temperatures (870–1,200 °C), are used to combust (in the presence of oxygen) organic constituents in hazardous wastes.	Generally not applied in Australia, as has been subject to community concern and thermal desorption offers a reliable alternative with less community concern.

Table 17 Summary of potential groundwater remediation processes

General response actions	Remedial technology	Process options	General applicability in practice
No action	None	None	Generally not an acceptable option, unless coupled with monitored natural attenuation (MNA).
Institutional controls	Access and use restrictions	Deed restrictions, fences, permits, licence conditions, management plans, groundwater quality restricted use zones	Is applied as an interim measure at many sites through the application of a groundwater quality restricted use zone; varies with jurisdiction. Is applied at some sites as a long-term (indefinite) measure, perhaps in conjunction with containment, where groundwater use can be avoided and stakeholders accept this, particularly if stakeholders see the alternative requirements for remediation as being damaging.
Containment	Physical barriers	Barrier walls – sheet piles, secant piles. The walls are installed in situ to surround the impacted area to prevent impacted groundwater migration and reduce groundwater flux	Is applied at some sites, although because B(a)P often has limited mobility other than when present with non-aqueous phase liquids (perhaps hydrocarbons present as micelles), this technology would primarily be applied to contain other such contaminants.
	Pumping controls	Borefield, interception trenches – groundwater is extracted and recirculated into the aquifer to control migration	Is widely applied and generally well understood.
Removal	Pumping	Pumping with off-site disposal or to sewer. Pumping with on-site treatment and disposal to sewer.	Unlikely to be successful as a removal strategy because B(a)P will remain adsorbed and will not be recovered by pumping. Pumping may be useful for the purposes of hydraulic containment. The principles of hydraulic containment are reasonably well understood.
In-situ treatment	Biological	Natural attenuation	Generally not applicable for B(a)P.
		Phytoremediation – use of plants of treat contamination in groundwater	Generally not applicable.
	Physical-chemical treatment	Chemical oxidation – injection of chemical oxidants into groundwater to destroy B(a)P via wells or trenches.	Unusual to apply this technology; some work has been carried out (e.g. by Verutek Technologies and Ivey International) but the final concentrations able to be achieved are uncertain; regarded as developmental at this time.
Ex-situ treatment (assumes pumping)	Physical-chemical treatment	Chemical oxidation – treatment of extracted water with chemical oxidants to destroy B(a)P	Generally not applicable; unlikely to be preferred over filtration and sorption.
		Filtration and sorption	Can be expected to be applicable if B(a)P is present in groundwater, although limitations in B(a)P solubility and ability to extract B(a)P containing groundwater makes it unlikely that this technology would be needed to be used, other than where B(a)P is present with other contaminants (such as hydrocarbon phase).

6. Summary and conclusions

This guidance has the objective of providing a practicable, risk-based framework for managing B(a)P-contaminated sites. In summary:

- B(a)P is a ubiquitous environmental contaminant, particularly in urban areas. It tends to be of greater concern in soil and sediment matrices than groundwater or surface water, due to its very low solubility. B(a)P is persistent in the environment and does not readily degrade, and B(a)P contaminated soils and sediments are difficult and costly to remediate.
- Human health and ecological screening criteria are available in Australia for B(a)P (NEPM HILs and ESLs respectively).
- With respect to the HSLs, this guidance document has not sought to assess and revise the values that are listed in the NEPM for B(a)P. However, the application of these HSLs generally does not consider bioavailability, and there is concern that this may be overly conservative in many cases. It is recognised that the bioavailability of B(a)P and hence toxicity can reduce through sorption to organic material in the soil, with ageing, and with certain soil properties and other factors. However, methods have not yet been developed that can reliably measure the bioavailability of B(a)P, and using bioavailability or bioaccessibility measures to derive site-specific criteria for organic contaminants is not well established in Australia. This is likely to change in the future, as laboratory methods become validated and their use more certain and reliable. An approach currently being developed in Australia by Juhasz et al. (2016) to measure the bioaccessibility of B(a)P, individual PAHs and the sum of 16 PAHs using a sorption-sink laboratory test is showing promise for assessing bioavailability relevant to human health. It is recommended that this be considered as a line of evidence as to the likely level of bioavailability of B(a)P.
- With respect to the NEPM ESLs, it is noted that the ESLs have been based on an older set of Canadian soil quality guidelines, which have been subsequently revised. For this guidance document higher reliability screening levels have been developed using additional and more recent information following the NEPM methodology. The derived screening levels are more than an order of magnitude greater than the ESLs previously listed in the NEPM, and more generally accord with the revised Canadian guideline levels. In the case of urban land, the revised ESLs are considerably higher than the corresponding HSLs, and are not likely to determine the requirements for remediation.
- As for the HSLs, the application of the NEPM ESLs for terrestrial ecosystems does not take into account changes in bioavailability that might apply. This may be unnecessarily conservative depending on site-specific factors. Some contaminant extraction methods are aggressive, and may overestimate the fraction of B(a)P that is bioavailable for uptake by an organism. Currently there is insufficient information to reliably quantify the effects of aging and soil properties on bioavailability. This guidance has considered this matter, and recommends that the assessment of the bioavailability of B(a)P in soils should be undertaken using a lines of evidence approach, with the BuOH extraction method being used to provide a measure of the bioaccessible fraction of B(a)P. Other lines of evidence that could also support the conclusion that B(a)P is likely to have reduced

bioavailability to organisms include contaminant age, source and composition of contamination, and the soil properties.

- With respect to the protection of aquatic ecosystems, the ANZECC/ARMCANZ (2000) guidelines values are used in Australia for this purpose. For the protection of sediments, a set of revised ANZECC/ARMCANZ sediment guideline values have been published. This guidance document has not sought to re-evaluate these values. In the case of water, the values are numerically low, and can be below standard laboratory limits of reporting. However, because B(a)P has low solubility it is usually not present in soluble form in water, and it is more often the case that B(a)P adsorbed on sediments or contaminants other than B(a)P will determine the requirements for remediation of aquatic ecosystems.
- Given that B(a)P is often found at concentrations that exceed the HILs or the ESLs, and does not readily degrade, remediation of B(a)P impacted soil and sediment (and to a lesser extent waters) may be indicated. In understanding the implications of the exceedances of the screening values, and the risks posed by B(a)P contamination to human and ecological receptors, it is important to develop a site-specific CSM. This should detail the source, potential receptors, exposure pathways by which receptors may come into contact with B(a)P, and the likelihood that B(a)P may be present in less bioavailable form. Guidance on developing a site-specific CSM is provided.
- For situations where there is a requirement for remediation of B(a)P contaminated media, this guidance document provides general guidance on developing a remediation strategy. Typically response actions will include no action, re-use, in-situ or ex-situ treatment, containment or institutional controls, or excavation (soil)/extraction (groundwater) and offsite disposal. Because of the recalcitrance of B(a)P in soil, treatment options can be limited, and it can be difficult to reach the low concentrations indicated by the HILs, or the ESLs in the case of land with high ecological significance. Considering lines of evidence regarding the level of bioavailability that is likely to apply at the site may support the conclusion that the B(a)P poses a low risk to human health and the environment, and may allow concentrations higher than the HSLs and ESLs to remain on site.

7. References

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