Society of Brownfield Risk Assessment

SOCIETY OF BROWNFIELD RISK ASSESSMENT
SUMMER WORKSHOP REPORT 2010

HUMAN HEALTH RISK ASSESSMENT
AND
POLYCYCLIC AROMATIC HYDROCARBONS

PUBLICATION

This report summarises key technical issues relevant to the human health risk assessment of polycyclic aromatic hydrocarbons as presented and discussed at a SoBRA (Society of Brownfield Risk Assessment) workshop in June 2010.

Whilst every effort has been made to ensure the report is an accurate account of workshop proceedings, neither SoBRA nor the authors of the report accept any liability whatsoever for any loss or damage arising in any way from its use or interpretation, or from reliance on any views contained herein.

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PREFACE

The Society of Brownfield Risk Assessment (SoBRA) was established in December 2009 with the principal aim of promoting technical excellence in land contamination risk assessment in the UK.

As part of achieving this aim, SoBRA undertook to host regular conferences and workshops on technical subjects of interest to UK risk assessors.

SoBRA's first summer workshop was held on 30th June 2010 at the Merchant Taylors Guild Hall in York. The workshop addressed the human health risk assessment of polycyclic aromatic hydrocarbons (PAHs) in soil. The morning session was structured around a series of expert presentations on four themes as follows: 1) human toxicology; 2) chemistry and site analysis; 3) exposure assessment; and 4) bioaccessibility and plant uptake. Morning presentations were followed by afternoon workshops on the same four themes in which all workshop delegates participated.

The workshop attracted over sixty delegates and was judged by most to be a resounding success. As such, the PAH workshop was a very encouraging start to what is intended to be many 'signature' SoBRA events, all of which will aim to engage, inform and establish consensus amongst, practitioners on key technical issues.

This report fulfils an undertaking given by SoBRA to produce a formal record of the proceedings of the PAH workshop. The report summarises the expert presentations given on the day, records current views on the main technical issues within each subject area and describes the challenges identified by risk assessors in dealing appropriately with PAH contamination. The report also sets out a number of recommendations on how progress on some of these challenges might be made.

In documenting the outcome of the PAH workshop, it became evident that practitioners consider there is a need for further research to support good risk assessment practice. Various recommendations have been made regarding the need for new or revised guidance and continued review of the technical literature on specific topics, and for the collation, review and analysis of empirical data on PAHs in the environment.

Workshop delegates were not specifically asked to consider how these various recommendations might be delivered. However, in the current economic climate, where central and local government budgets are highly constrained and are likely to remain so for the foreseeable future, and where private sector resources are also scarce, it is pertinent to ask how this necessary research can be initiated and sustained over the coming years.

In addition to adding to the UK's store of technical knowledge on the risk assessment of PAHs, it is hoped that this report will encourage constructive debate amongst practitioners about the mechanisms that will be needed in the future to support progress in the most important field of land contamination risk assessment.

ACKNOWLEDGMENTS

SoBRA wishes to thank the following individuals for their considerable assistance in the successful delivery of the SOBRA summer workshop, whether as expert speaker, workshop facilitator, workshop rapporteur, report author/editor or a combination of these roles.

Tayo Adedeji	Atkins
Sarah Bull	Health Protection Agency
Chris Collins	University of Reading
Simon Firth	Firth Consultants Ltd
Liz Hart	Environment Agency
Rob Ivens	Grey Zone Ltd and Mole Valley District Council
Seamus Lefroy-Brooks	LBH Wembley Geotechnical & Environmental
Yolande Macklin	Health Protection Agency (formerly London Borough of Tower Hamlets)
Mike Quint	Environmental Health Sciences
Ed Stutt	WCA Environment
Mary Harris	MRH Consultants Ltd

Special thanks must also be given to Liz Hart and Yolande Macklin of SoBRA's Executive Committee for their excellent organisation and running of the event, and to Ed Henshaw of Envirorisk Solutions who, as SoBRA's treasurer, looked after financial matters.

Finally, SoBRA wishes to acknowledge the contribution to the overall success of the event made by individual workshop delegates; firstly for attending and enthusiastically participating in the day's proceedings and, secondly, for providing comments and suggestions to authors during the draft reporting stage. Workshop delegates are listed in Appendix 1 to this report.

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1 INTRODUCTION

1.1 Background

Polycyclic Aromatic Hydrocarbons (PAHs) are prevalent in most urban soils in the UK largely as a result of the historic burning of coal at both a domestic and industrial scale, and through the processing and use of petroleum hydrocarbons.

PAHs present a number of challenges for risk assessors. They comprise a large group of compounds which have different physico-chemical properties and exhibit different behaviours in the environment. The toxicological significance of individual compounds to humans also varies, and there is much uncertainty regarding the intakes at which adverse health effects are likely to occur.

In common with many other contaminants found routinely in UK soils, there is considerable debate about the actual extent of human exposure to PAHs and the human health implications of such exposure. The biological availability of PAHs in soils, to both humans and food plants, is also poorly understood.

1.2 The SoBRA Workshop

The SoBRA PAH workshop aimed to define current understanding of the key issues surrounding the human health risk assessment of PAHs in soil, to identify key uncertainties in current approaches to this group of compounds, and to establish where there is (and is not) consensus on how best to manage and resolve these uncertainties.

A specific goal of the workshop organisers was to produce a formal workshop output which summarised the proceedings, consolidated ideas and made recommendations on the work required to support risk assessment efforts in the future. This report is that written output.

1.3 Structure of the Report

Following this introduction, section 2 of the report summarises key technical issues relevant to the human health risk assessment of PAHs, as described by expert speakers. Four key themes were addressed:

- human toxicology;
- chemistry and site analysis;
- exposure assessment, and;
- bioaccessibility and plant uptake.

Sections 3 to 6 of the report summarise workshop discussions on each of these four themes. During these workshops, delegates further explored the issues, identified key uncertainties, drew conclusions and made recommendations on the direction of future research.

Section 7 of the report draws on the outcome of the workshop discussions, identifies some common issues and highlights priorities for future consideration.

Reference documents used to support presentations and workshop discussions are shown as footnotes to the text, and are collated as a complete list in section 8 of the report.

Appendix 1 gives details of the workshop groups including names of individual participants. Appendix 2 sets out a list of the abbreviations used in the report.

2 SUMMARY OF WORKSHOP PRESENTATIONS

2.1 Human Toxicology

Two of the workshop presentations reviewed the toxicological approaches used to assess PAHs. Tayo Adedeji (Atkins) provided an overview of some of the approaches currently available, while Sarah Bull (Health Protection Agency, HPA) gave a description of research being undertaken within the HPA regarding this subject. A summary of the key points from each presentation is provided below.

Assessing PAHs – Varying Approaches to Toxicology (Tayo Adedeji)

Most PAHs occur in soil in the form of mixtures. Since the environmental behaviour and toxicology of mixtures is different from that of individual compounds, there are a number of issues that make assessing PAH mixtures, rather than individual PAHs, challenging. A particular challenge relates to limitations in the experimental data that are often the basis of the toxicological criteria, such as Health Criteria Values (HCVs), which are used in risk assessment. This is largely due to the fact that experimental testing procedures are costly, and such a cost would need to be multiplied by the vast number of PAH mixtures that could potentially be found in soil in order to capture all possible combinations.

One approach is to look at PAH congeners as individual chemical entities. Advantages of this kind of approach include:

1. The ability to compare measured and modelled exposure data to HCVs directly.
2. The availability of toxicological data for individual congeners.
3. The existence of well-understood risk assessment protocols for individual compounds.
4. That it provides an assessment which does not rely on knowledge of the source of the PAH compounds.

The downsides of this approach are that it is often limited by the analytical suite, HCVs are not available for all known PAH congeners, and the approach does not include a consideration of interactions that may occur due to the presence of a mixture.

Another approach is to assess PAHs as mixtures. In this regard, the guidance available in the Environment Agency's (EA's) "Human health toxicological assessment of contaminants in soil" (SR2)[1] states that such evaluations should be based on a knowledge of the modes of toxicity of a compound, with additive effects only being assumed where the substances share a common mode of action. Three mixture-based approaches have been described in the open literature for the risk assessment of PAHs from soil. These are described below.

The surrogate marker approach adopts an indicator compound as a basis for assessing the toxicity of varying PAH mixtures. In effect, it is assumed that the risk from the PAH mixture is proportional to that of a marker compound within the mixture, such as benzo(a)pyrene (BaP). In practice, an estimate is made of the carcinogenic risk (or margin of exposure) from BaP within the context of a specific PAH mixture. The overall risk from the mixture is therefore assumed to be proportional to the risk from BaP.

[1] EA (2009). Human health toxicological assessment of contaminants in soil, Science Report Final SC050021/SR2

The comparative potency approach estimates the potency of a PAH mixture, without having to identify or quantify individual compounds. It involves extrapolating the carcinogenic potency of an unknown mixture (such as roofing tar or residue from coke ovens) in humans, based on the potency of the mixture in a bioassay. The potency of other mixtures is also used as a means of comparison in order to provide additional "lines of evidence".

A third approach involves the use of relative potency factors, also referred to as the Toxicity Equivalency Factor (TEF) approach. In order to assess PAH mixtures, an estimate of the toxicological potency of each individual PAH relative to that of another (e.g. BaP) is used to generate risk estimates, which are then added together. In practice, this can be done by either: 1) adding the BaP equivalent exposures and multiplying them by the potency of BaP; or 2) assessing the risk from each PAH and then adding the results. This approach is currently limited by the fact that it implies that the individual compounds have the same mechanism of action, which is not the case for all PAH congeners. Practical studies show that different PAHs result in tumour formation at differing sites, some by a direct genotoxic mechanism and some requiring metabolic activation to result in genotoxic effects. Due to this uncertainty, the TEF approach may under-predict the risk from a PAH mixture.

Regulatory support for the TEF approach varies widely. The following agencies have adapted or adopted it in some form over the years:

- the Committee on Carcinogenicity of Chemicals in Food, Consumer Products and the Environment (COC)[2];
- the Expert Panel on Air Quality Standards (EPAQS)[3];
- the United States Environmental Protection Agency (USEPA)[4];
- the Dutch National Institute for Public Health and the Environment (RIVM)[5]; and
- the Canadian Council of Ministers of the Environment (CCME)[6].

Conversely, both the Joint FAO/WHO Expert Committee on Food Additives (JECFA)[7] and the Scientific Committee on Food (SCF)[8] have recently concluded that the TEF approach is not appropriate due to limitations in the available data and because of different modes of action amongst different PAHs. Instead, the surrogate marker approach has been adopted by these bodies, and by the European Food Safety Authority (EFSA)[9]. Perhaps most importantly, the TEF approach is not supported by the HPA for use in evaluating PAHs in soil, the HPA preferring instead the surrogate marker approach (see below).

2 CoC (2003). Carcinogenicity of dibenzo(a,l)pyrene COC/03/S5

3 Department of the Environment Transport and the Regions (1999). Expert Panel on Air Quality Standards, Polycyclic aromatic hydrocarbons

4 USEPA (1993). Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons, EPA/600/R-/089

5 RIVM (2001). Re-evaluation of human-toxicological maximum permissible risks levels, RIVM report 711701 025

6 CCME (2008). Canadian Soil Quality Guidelines. Carcinogenic and other polycyclic aromatic hydrocarbons (Environmental and human health effects), Scientific Supporting Document

7 JECFA (2005). Sixty-fourth meeting, Rome, 8-17 February 2005, Summary and conclusions

8 SCF (2002). Opinion of the Scientific Committee on Food on the risks to human health of polycyclic aromatic hydrocarbons in food, SCF/CS/CNTM/PAH/29 Final

9 EFSA (2008). Polycyclic aromatic hydrocarbons in food, Scientific Opinion of the Panel on Contaminants in the Food Chain, The EFSA Journal, 724, 1- 114

Toxicology Behind the Scenes (Sarah Bull)

Sarah Bull from the HPA outlined the various approaches used in deriving threshold and non-threshold HCVs generally and went on to describe which approach the HPA currently advises for assessing PAHs in soil. Key considerations underlying the HPA's approach include:

1. The fact that quantitative risk assessment based on low-dose extrapolation from experimental animal data is not endorsed by the COC.
2. There is a lack of data to assess all of the individual PAHs likely to be present in complex soil mixtures.
3. The judgement that the TEF approach is not appropriate for PAHs which do not have a similar mode of action.

In the light of the above, the HPA considers that the surrogate marker approach is the most appropriate means of assessing PAH exposure to soil. This approach is not without its complexities, however, and questions exist in terms of:

- whether BaP is present in all soils;
- whether there are suitable toxicological data to assess PAH mixtures in soil (the HPA recommend the use of the Culp *et al*[10] study on coal tar mixtures);
- whether the soil profile of PAHs from different areas of the UK is similar;
- whether the soil PAH profile is similar to the profile of mixtures used in toxicology studies;
- whether the relevant dose-response curve for PAH mixtures in soil is linear.

In order to address the first, third and fourth bullet points above, the HPA has considered soil data from 52 sites spread across the UK. It found that not only is BaP present at all of the sites considered, but also the ratio of BaP to other PAHs is similar in all samples, even though the absolute concentration of BaP is variable. In addition, it was found that the PAH profile in the soils examined is similar to the profile in the toxicity study selected for use as an indicator of PAH mixture potency.

Sarah informed the audience that the research described is being considered by the EA in developing revised guidance for assessment of PAHs in soil.

2.2 Chemistry and Site Analysis

Ed Stutt of WCA Environment gave a presentation on the chemistry of PAHs which covered: their chemical structure and composition; sources of PAHs - both generally and in contaminated soils; the rationale for the selection of particular PAH compounds for study in land contamination applications; the physico-chemical properties of PAHs; and the behaviour of PAHs in the soil environment.

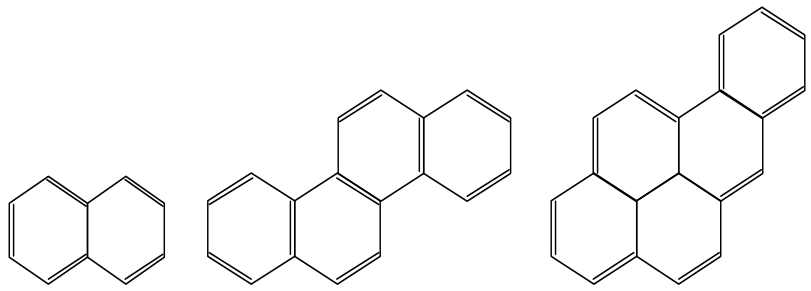
There are several hundred PAH compounds although the environmental analyses of PAHs is often confined to just a handful of substances. Chemically, PAHs consist of 2 or more aromatic hydrocarbon rings fused together, or with other hydrocarbon rings (see Box 1), and they often occur in complex mixtures.

Sources of PAHs include:

- incomplete combustion or pyrolysis of any organic matter;

[10] Culp, S.J., Gaylor, D.W., Sheldon, W.G., Goldstein, L.S. and Beland, F. A. (1998). A comparison of the tumors induced by coal tar and benzo[a]pyrene in a 2-year bioassay. Carcinogenesis, 1998, 19(1), 117-124

Box 1: Chemical structure of selected PAHs



Naphthalene Chrysene Benzo(a)pyrene

- fossil fuels such as coal, crude oil and tar deposits.

Sources of PAHs in contaminated soils include:

- atmospheric deposition of combustion particles;
- ash fill and clinker from industrial processing;
- coal tar from gasworks;
- fuel oil (diesel, heating oil, lube oil);
- asphalt;
- industrial processing of oil and coal tar derivatives.

The composition of PAH mixtures also varies depending on the source (Tables 1 and 2).

Table 1: Composition of PAHs - petroleum source [11]

PAH	% Composition of fuel (ratio to BaP)		
	Diesel	Heating Oil	Lube Oil
Chrysene	4.5×10^{-5} (0.2)	6.9×10^{-2} (16)	3.5×10^{-3} (2.1)
Benzo(a)pyrene	2.2×10^{-4}	4.4×10^{-3}	1.7×10^{-3}
Benzo(a)anthracene	9.6×10^{-5} (0.44)	5.5×10^{-2} (12.5)	6.3×10^{-3} (3.7)
Benzo(b)fluoranthene	$3.1 \times 10^{-5*}$ (0.14)	$4.4 \times 10^{-2*}$ (10)	1.5×10^{-3} (0.88)
Benzo(j)fluoranthene			
Benzo(k)fluoranthene	$3.1 \times 10^{-5*}$ (0.14)	$4.4 \times 10^{-2*}$ (10)	
Dibenzo(a, h)anthracene			
Benzo(g,h,i)perylene	1.2×10^{-5} (0.05)		2.8×10^{-3} (1.6)
Indeno (1,2,3-cd) pyrene	1.6×10^{-5} (0.05)	1.0×10^{-2} (2.3)	4.0×10^{-3} (2.4)
Total	0.36 (PAHs)	34 ('total aromatics')	22 ('total aromatics')
%BaP(relative to G9)	52	2.4	10

*Note to Table: * Combined concentration given for benzo(b+k)fluoranthene*

[11] TPHCWG, Total Petroleum Hydrocarbon Criteria Working Group Series (1998). Volume 2, Composition of petroleum mixtures

Table 2: Composition of PAHs - combustion residue

PAH	Composition (ratio to BaP)			
	Coal Tar 1 (mg/kg) *Culp et al*	Coal Tar 2 (mg/kg) *Culp et al*	Combustion Ash 1 (% of PAHs) *Joa et al*[12]	Combustion Ash 2 (% of PAHs) *Joa et al*[12]
Chrysene	2379 (1.3)	2960 (1.1)	8 (0.9)	10 (1.0)
Benzo(a)pyrene	1837	2760	9	10
Benzo(a)anthracene	2374 (1.3)	3340 (1.2)	10 (1.1)	8 (0.8)
Benzo(b)fluoranthene	2097 (1.1)	2890 (1.1)	10* (1.1)	8* (0.8)
Benzo(j)fluoranthene				
Benzo(k)fluoranthene	699 (0.4)	1010 (0.4)	10* (1.1)	8* (0.8)
Dibenzo(a, h)anthracene	267 (0.15)	370 (0.13)		
Indeno (1,2,3-cd) pyrene	1353 (0.74)	1990 (0.72)	8 (0.89)	8 (0.8)
Total PAHs				
%BaP(relative to G8)	17	18	20	23

*Note to Table: * Combined concentration given for benzo(b+k)fluoranthene*

Ed pointed out that the inclusion of individual PAHs in any environmental risk assessment project should take into account:

- the toxicology of the compound;
- occurrence of the compound in soil/land being considered;
- the fate and behaviour of the compound;
- analytical methods.

The rationale for the selection of individual PAHs in the so-called 'USEPA 16' priority list of compounds (Keith & Tellard, 1979[13]) was explained. In the UK, this group of PAHs is often included in the laboratory testing of contaminated soils. Amongst the criteria for inclusion of particular PAH compounds in the 16 PAH list was whether the compound featured in the original Toxic Pollutant List (i.e. those pollutants subject to regulation and effluent limitations) and whether the compound was listed in at least one chemical supply catalogue. Chemical production data were also taken into account when prioritising compounds for inclusion on the list.

Ed questioned whether, on close examination, this rationale was entirely relevant to a consideration of PAHs in a risk assessment context. It was suggested that other PAHs, not included in the USEPA 16 list, might also be considered for assessment including:

- benzo(j)fluoranthene - a commonly occurring compound which is a known genotoxic carcinogen and which co-elutes with benzo(b)fluoranthene;
- benzo(e)pyrene - a potential genotoxic carcinogen?;
- dibenzo(a,l)anthracene - a more potent genotoxic carcinogen than benzo(a)pyrene;

[12] Joa, K.. Panova, E., Irha, N., Teinemaa, E., Lintelmann, J. and Kirson, U. (2009). Determination of polyaromatic hydrocarbons (PAHs) in oil shale processing wastes: Current Practice and New Trends. Oil Shale, 2009, Volume 26, No. 1, 59-72

[13] Keith, L. H. and Telliard, W.A. (1979). Priority pollutants, I - A perspective view. Environmental Science and Technology, 13, 4, 416-424

- heterocyclic forms (containing nitrogen and sulphur) especially in asphalt/tars;
- branched/alkyl substituted forms - especially in diesel.

Ed presented a number of slides setting out the physico-chemical properties of PAHs showing that:

- as molecular weight increases, solubility, vapour pressure and air-water partition coefficient (K_{aw}) decrease, and hydrophobicity (K_{ow}, K_{oc}) increases;
- there is a cut-off point (molecular weight of 228) within the 4-ring PAH compounds that distinguishes between low and high molecular weight compounds;
- all genotoxic PAHs are comprised of 4 or more aromatic rings with a molecular weight of equal to or more than 228;
- all genotoxic compounds share common physico-chemical properties in terms of hydrophobicity, volatility and affinity for binding to soil organic matter.

Information on the environmental fate and behaviour of PAHs was also presented (see Table 3).

Table 3: Environmental fate and exposure pathways

Ring Class	Environmental Summary	Most Significant Pathways
2 ring PAHs (naphthalene) 3 ring PAHs	Significant aqueous solubility, vapour phase in atmosphere, relatively mobile in soils & higher bioavailability (plants/microbes)	• Vapour inhalation • Soil/dust ingestion • Dermal exposure • Plant uptake
4 ring PAHs	Low solubility, vapour phase & particulates in atmosphere; relatively immobile in soil	• Soil/dust ingestion • Dermal exposure • Plant uptake?
≥ 5 ring PAHs	Insoluble, non-volatile, associated with particles in atmosphere, and very strongly sorbed to soil	• Soil/dust ingestion • Dermal exposure • Dust inhalation

Ed concluded the presentation by commenting that:

- the selection of PAHs for laboratory analysis and risk assessment should be based on a consideration of the physico-chemical properties and toxicology of compounds;
- while physico-chemical properties and behaviour in the environment vary amongst PAH compounds, high molecular weight genotoxic types have similar properties;
- while BaP may be a suitable marker for the 8 to 9 genotoxic PAHs, it may not be a suitable marker for low molecular weight, non-genotoxic types or for fresh fuel/oil spills where there is some variance in PAH profile depending on source.

2.3 Exposure Assessment

Simon Firth of Firth Consultants Ltd summarised research conducted on behalf of National Grid in relation to human exposures to PAHs and the uncertainties in

exposure modelling that are important when assessing potential health risks. He also explored the scope for selecting model parameter values that may be of use when assessing risk under Part 2A of the Environmental Protection Act 1990 in the context of a "significant possibility of significant harm" (SPOSH). Simon examined the key contributors to exposure, and the key contributors to risk, when humans are exposed to BaP in soil in a residential context. The analysis of exposure was based on calculating Average Daily Exposures (ADE) for 9 exposure pathways (as defined by the Contaminated Land Exposure Assessment, CLEA, model), and for risk by comparing ADEs to HCVs. The key contributors were found to be:

For exposure:

- soil/dust ingestion;
- outdoor dermal contact.

For risk:

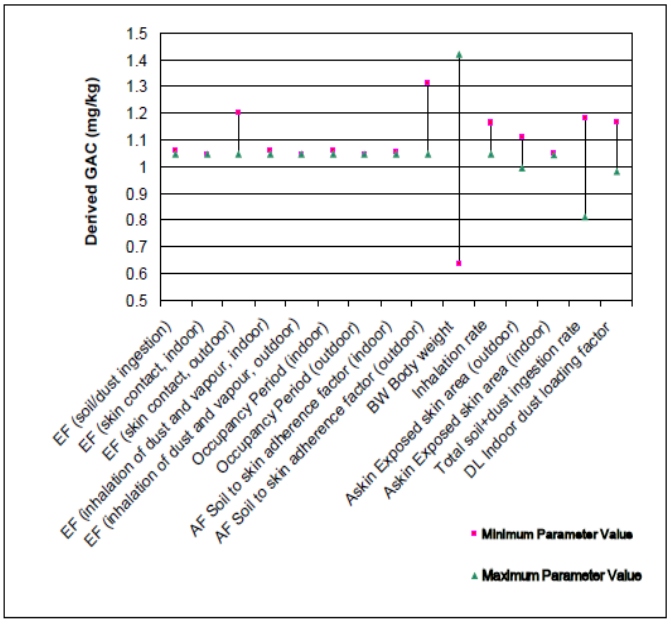
- soil/dust ingestion;
- outdoor dermal contact;
- indoor inhalation of dust.

Exposure from dust inhalation was found to be much less than the exposure from soil and dust but the risk level associated with the two pathways is comparable because the published HCV for the inhalation of BaP is 286 times lower than the published HCV for oral intake of BaP[15].

The results of an uncertainty analysis carried out for exposure to BaP in soil in a residential setting were described. In the analysis, reasonable minimum and maximum values were assigned to each of the model parameters and then Generic Assessment Criteria (GAC) were calculated using the CLEA approach by adjusting each parameter between minimum and maximum values.

The results are shown in Box 2.

Box 2: Results of parameter value sensitivity analysis



- Order of importance in terms of sensitivity:
  - Body weight
  - Soil and dust ingestion rate
  - Soil to skin adherence factor outdoors
  - Indoor dust loading factor
  - Exposure frequency for dermal contact outdoors
  - Exposed skin area outdoors
  - Inhalation rate

The analysis showed that the most sensitive model parameters were body weight followed by soil and dust ingestion rate, and the soil-to-skin adherence factor outdoors.

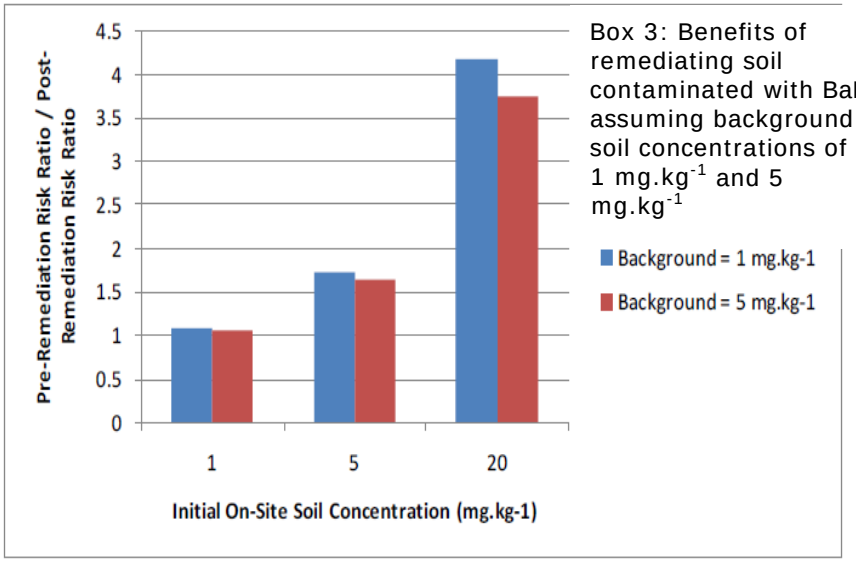
It was noted that a mixture of central tendency and upper bound values have been used in the CLEA model for the derivation of published Soil Guideline Values (SGVs). It was suggested that use of central tendency (most likely) values for exposure modelling may be more appropriate in Part 2A applications and, accordingly, the following changes were proposed:

- soil and dust ingestion rate - 70 mg/day as opposed to 100 mg/day to account for the fact that not all soil ingested will come from the site being assessed;
- soil-to-skin adherence factor - use the central tendency value rather than the 95th percentile value;
- exposure frequency for outdoor dermal contact - use 180 days/year as opposed to 365 days/year;
- exposed skin area outdoors - currently arbitrarily assumed that one third of the exposed skin area is covered with soil - possibly a lower value should be used;
- respiration rate - use recent USEPA guidance[14] which has lower values.

Use of such parameter values results in a doubling of the GAC for residential land uses routinely derived for BaP using the CLEA model, i.e. from a value of 1 mgkg^{-1} to 2 mgkg^{-1}.

The outcome of further modelling work was described which assessed the contribution to overall intakes from exposure to BaP in soil in a residential context relative to contributions from other background sources, such as soil and dust off-site, food and water, and background air.

The results of this analysis suggested that remediating soil containing 1 mg.kg^{-1} BaP confers only a negligible reduction in the overall risk to health presented to humans exposed to BaP in soil (see Box 3).



Box 3: Benefits of remediating soil contaminated with BaP assuming background soil concentrations of 1 mg.kg^{-1} and 5 mg.kg^{-1}

[14] USEPA (2008). Child-specific Exposures Factors Handbook, Report EPA/600R/R-06/096F

Simon concluded his presentation by commenting that:

- the current CLEA approach recommends using a mixture of central tendency parameter values and upper-bound estimates;
- consistent use of central tendency values may be more appropriate when assessing whether conditions on the land are such that there is a "significant possibility of significant harm" as required under Part 2A of the Environmental Protection Act 1990;
- some parameter values are subject to greater levels of uncertainty than others - further research could help to reduce uncertainty for some of these parameters;
- remediation of garden soils containing BaP at concentrations of 1 $mg.kg^{-1}$ results in only a negligible reduction in the overall risk from BaP.

2.4 Bioaccessibility and Plant Uptake

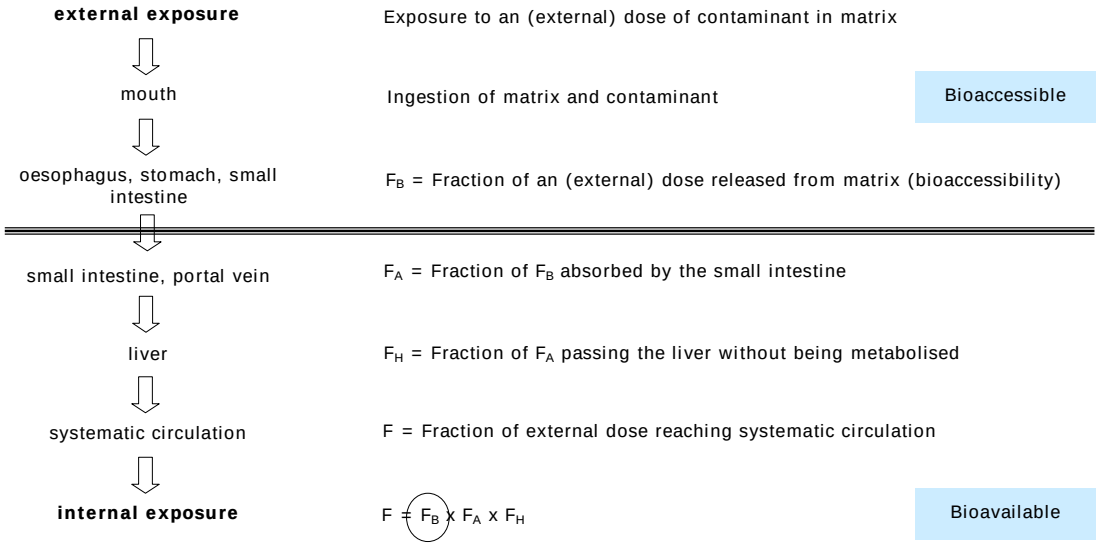
Dr Chris Collins of the University of Reading presented on the development of a simple, robust technique for determining the bioaccessibility of organic pollutants in soil.

Chris set out the definitions of key terms:

- relative bioavailability - the extent of absorption of the chemical from soil compared with its absorption from the media used in the critical toxicological or epidemiological study;
- oral bioaccessibility - the fraction of the chemical released into the gut solution from the soil during digestion.

He also described the process whereby a chemical in soil may enter the human body and reach the systemic circulation (see Box 4).

Box 4: Schematic of bioacessibility/bioavailability



While the bioaccessibility of inorganic contaminants, such as arsenic, is relatively well understood, understanding of the bioaccessibility of organic contaminants in soil is less well developed. Research funded by the Natural Environment Research Council (NERC) and the University of Reading is designed to address this gap in understanding.

The aims of the research are to develop an *in vitro* system for testing the bioaccessibility of organic substances in soil and to improve the PBET (Physiologically Based Extraction Test - simulates the stomach and small intestine) by addition of a colon phase (CEPBET - colon enhanced PBET).

The objectives of the research are to:

- characterise the experimental system;
- determine incubation times;
- evaluate different incubation media;
- investigate the effect of microbial inoculum in the colon phase.

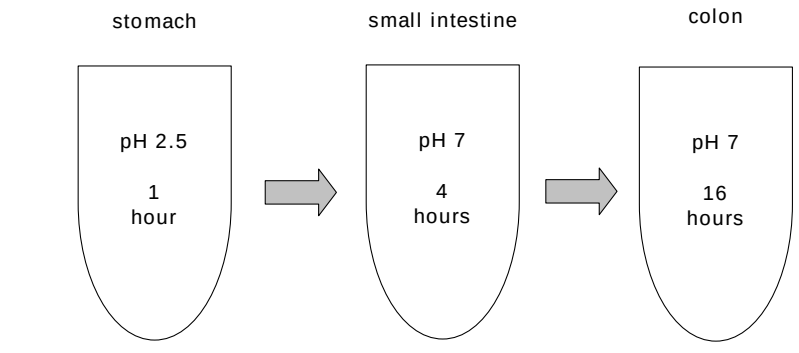
The technical basis and physical configuration of the experimental system developed during the research were described, together with the parameterisation of various system components (e.g. gas flow rate, colon incubation time, microbial effects) using a PAH mixture as the experimental medium.

The main elements of the 'simple' CEPBET system are shown in Box 5.

Chris concluded his presentation by commenting that:

- a simple robust system for the determination of bioaccessibility of organic pollutants has been developed;
- the largest losses from the soil are observed if all components [of the system] are used sequentially;
- all components need to be in the 'fed' state;
- active microbes do not increase losses.

Box 5: Colon Enhanced PBET (CEPBET) system



1.2 g of OECD soil spiked with PAH added to stomach medium (pepsin, NaCL, HCL)

Add bile, pancreatin, adjust pH

Sample centrifuged & supernatant taken for analysis, colon medium added to soil pellet. Can be frozen.

Future research needs are considered to include:

- validation with other systems (involving human or pig studies, or at least comparison with other in-vitro systems);
- testing the repeatability of the method, i.e. variation between laboratories who adopt the protocol;
- further investigation of the relevant metabolic processes;
- further investigation of the influence of the pollutant on bacterial composition, although this is considered less important for conservative risk estimation.

3 HUMAN TOXICOLOGY WORKSHOP

3.1 Introduction

The toxicology workshop was designed to encourage discussion of the various issues associated with the toxicological aspects of human health risk assessments involving PAH contaminated soil. It was facilitated by Tayo Adedeji and Mike Quint.

Prior to the day, the following reference materials were circulated for consideration by the participating delegates:

- DEFRA & EA TOX2[15]
- HPA CLCN 1[16]
- HPA CLIS[17]
- HPA Chemical Profile[18]
- COC CC/06/20[19]
- COC CC/07/14[20]
- JECFA 2005[7]
- EFSA 2008[9]
- USEPA 2010[21]

The contents of each of these documents were summarised by the facilitators at the beginning of the workshop, with various points being highlighted, including:

- TOX2 is the document which the majority of contaminated land professionals have referred to as a primary source of information on the toxicology of BaP. This document presents Index Doses of 0.02 µg/kg-day and 0.00007 µg/kg-day for ingestion and inhalation, respectively. Of note is that the ingestion Index Dose is based on a drinking water guideline value produced by the World Health Organisation[22], which is itself based on the low-dose extrapolation of excess lifetime cancer risk (ELCR), using fore-stomach tumour data from rat studies.
- The HPA's CLCN1 presents the HPA's current opinion on the use of ECLR estimates. It explains how the use of such estimates is not recommended if they are based on experimental data from animal studies, which is important since some UK risk assessors have used this approach to assist with contaminated land decision-making.

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15 DEFRA & EA (2002). Contaminants in soil: Collation of toxicological data and intake values for humans. Benzo[a]pyrene

16 HPA (2008). Contaminated Land Clarification Note No. 1, Benzo(a)pyrene – use of excess lifetime cancer risk estimates (HPA-CLCN-1)

17 HPA (2010). Contaminated Land Information Sheet (v5). Risk assessment approaches for polycyclic aromatic hydrocarbons (PAHs)

18 HPA (2008). Compendium of chemical hazards. Polycyclic aromatic hydrocarbons (Benzo[a]pyrene)

19 CoC (2006). Comparative risk assessment: Application of the MOE approach for communicating the risks of exposure to genotoxic carcinogens – CC/06/20

20 CoC (2007). Further consideration of the MOE approach - CC/07/14

21 USEPA (2010). Development of a Relative Potency Factor (RPF) approach for polycyclic aromatic hydrocarbon (PAH) mixtures. In support of summary information on the Integrated Risk Information System (IRIS)

22 WHO (1996). Guidelines for drinking water quality, 2nd Edition, Volume 2, Health criteria and supporting information

- Various toxicity criteria are reported for BaP in the JECFA, EFSA and CC/06/20 documents. The COC report presents a $BMDL_{10}$ value of 2.0 mg/kg-day, while JECFA and EFSA present values of 0.1 and 0.07 mg/kg-day, respectively. It should be noted that the value presented in the COC report is derived from experimental data involving exposure to BaP only, while the comparatively lower $BMDL_{10}$ values presented by both EFSA and JECFA are based on exposure to a mixture of PAHs, with BaP used as a surrogate.
- The USEPA has recently published an "external review draft" of a document which describes a possible approach to assessing PAH mixtures using a relative potency factor (RPF) approach[21]. This approach is similar to the TEF methodology previously described and the document provides suggested RPFs for more PAHs than have been considered under similar approaches in the past.

3.2 Key Issues

Following discussion of the documents listed above, a number of issues were identified as being relevant to the selection of appropriate toxicological criteria for the risk assessment of PAHs in soil (based on an outline provided by the workshop facilitators, as well as points raised by the workshop delegates). These were divided into four broad categories for discussion, as follows:

Approach to assessing PAHs

- should PAHs be assessed individually or as mixtures;
- should TEFs be used when assessing PAHs;
- when using the surrogate marker approach, is exposure to BaP reflective of exposure to all PAHs.

Selection of appropriate toxicological benchmark

- which toxicological benchmarks (e.g. HCVs) are most appropriate for assessing PAHs in soil;
- are ELCR estimates appropriate for use when assessing PAHs;
- which benchmark dose should be used;
- what is an appropriate margin of exposure (MOE) for use in risk assessment.

Risk evaluation

- how should the concepts of "unacceptable intake" and "significant possibility of significant harm" (SPOSH) be assessed toxicologically;
- can human biomonitoring be used to assist the risk assessment process.

PAH congeners

- how should an assessment be made of "other" PAHs, besides the USEPA 16;
- what is the most appropriate means of assessing naphthalene.

3.3 Conclusions

The above issues were discussed by the group, with the following points being noted (there is considerable cross-over between the various categories such that several of the above questions are addressed outside of their original category).

3.3.1 Approach to Assessing PAHs

It was noted that although there are a number of sources of potential PAH toxicity data and that TOX2 is still available for guidance, the data provided in the recent EFSA and JECFA reports are considered to be the most appropriate for use, based on the CLIS guidance from the HPA. As a consequence, practitioners would be expected to default to the surrogate marker approach in conducting toxicological assessments of PAHs in soil provided it can be demonstrated that the PAH profile of the site being assessed is sufficiently similar to the PAH profiles of the coal tar/soil mixtures used in the Culp *et al*[10] study from which toxicological criteria were derived. Alternative approaches utilising TEFs and ELCR estimates might be expected to need justifying on a case-by-case basis.

The group considered that the assessment of PAHs as single chemicals is likely to be inappropriate for the majority of sites, due to the fact that they are usually present in soils as mixtures. An assessment of mixtures was therefore judged to be more suitable, since it takes into account the fact that PAH mixtures have been found to be comparatively more toxic than individual PAH compounds, and a mixture assessment will therefore provide a more appropriate level of conservatism when assessing exposure to soil. Such considerations underpin the surrogate marker approach.

An important consideration relating to the mixture approach was raised with regard to whether the study by Culp *et al,* which used coal tars mixed with soil collected from gas manufacturing sites, was unduly conservative due to the nature of the test substance used. It was suggested that the coal tar evaluation might include a number of mixture components that might not be present in historically impacted soils. As a result, the use of coal tar data could increase the conservatism of such an assessment, owing to the toxicity of these additional contaminants. Notwithstanding this, it was agreed that the influence of other components within the coal tar mixture could probably not be estimated at this time.

3.3.2 Selection of Appropriate Toxicological Benchmark

It was noted that the benchmark doses from the CLIS report, when combined with an Uncertainty Factor of 10,000 (i.e. doses corresponding to a risk level of 1 in 100,000) as recommended in current guidance[1], would result in a lower HCV than the existing value within the TOX2 report. It was suggested that this could be varied on a site-specific basis, perhaps in connection with assessments of the likelihood of “unacceptable intake” or SPOSH (for Part 2A sites).

The applicability of using toxicological input criteria other than conservative $BMDL_{10}$ values, on a site-specific basis, was discussed. For example, the choice of a different “benchmark response” may be possible, as might the use of BMD rather than BMDL values and alternative BMD modelling approaches.

The participants also considered the possibility that the use of a MOE approach might not result in a toxicological benchmark which adheres rigidly to the principle of being as low as reasonably practicable (ALARP).

3.3.3 Risk Evaluation

There was a discussion about whether the use of the “lifetime exposure” setting might be appropriate when assessing BaP using CLEA, given the assumed lifetime duration of the underlying toxicological studies and benchmark dose data. It was suggested that this might be a factor for further review during the derivation of new SGVs by the EA.

Comments were made on the possibility that PAHs may cause different toxic effects, based on the route of exposure. Should this be the case, it was suggested that it might not be appropriate to integrate the route-specific soil screening criteria for PAHs. It is understood that, in response to this, both the HPA and EA are currently considering route-specific effects, as well as the implications of this when deriving SGVs.

Human biomonitoring was discussed as a potential means of providing additional information within the PAH risk assessment process, where actual exposure is thought to be occurring (e.g. in a Part 2A residential setting). A considerable amount of scientific research has been conducted on potential biomarkers of exposure, such as PAH metabolites in urine and DNA adducts[23].

3.3.4 PAH Congeners

The group discussed how PAH mixtures often contain a number of individual compounds which are not routinely assessed within the existing analytical suites for PAHs. Since a number of these individual congeners may be of greater toxicity than BaP, there is the potential for an underestimation of the risk from PAHs if using the TEF approach. This would be addressed, however, by the use of the surrogate marker approach.

A view was put forward that, as naphthalene is assessed as a component of one of the TPH fractions, it may not be necessary to evaluate it separately since there is the possibility of double-counting risk whenever this is done.

3.4 Recommendations

Following the discussion, it became apparent that there are several issues that may warrant further consideration with regard to the toxicological aspects of assessing PAH contaminated soil, as follows:

1. Official publication of the HPA's CLIS report would clarify the situation vis a vis TOX2 (note the HPA CLIS is now available on the HPA website)[17].
2. Notwithstanding the HPA's position on TEFs outlined in the CLIS document, it was suggested that the US EPA's recent document[21] might be worthy of consideration and a possible response from the HPA.
3. Assuming that a surrogate marker approach is preferred, with $BMDL_{10}$ values as described in CLIS, more work might be helpful to consider data from other PAH mixtures, aside from coal tar. It might also be appropriate to provide more extensive data for PAH profiles in UK soils, as a means of validating the data on which the HPA had assessed these profiles.
4. In the event that the CLIS approach is used with the CLEA model as it is currently configured, the resulting "minimal risk" soil screening values (e.g. SGVs) will likely be exceeded in large areas of the UK. This could prove to be a challenge to decision-making under planning and Part 2A.
5. Guidance on using toxicological input criteria other than conservative $BMDL_{10}$ values would be useful and might be applicable on a site-specific basis. Such guidance could, for example, focus on the choice of "benchmark response", the use of BMD rather than BMDL values and the use of alternative BMD modelling approaches.

[23] ATSDR (1995). Toxicological profile for polycyclic aromatic hydrocarbons, US Department of Health and Human Services, Public Health Service

6. Further work is also recommended on the selection of an appropriate MOE for situations which do not require a “minimal risk” approach (e.g. under Part 2A).

7. The possibility of conducting site-specific human biomonitoring studies at locations where PAH exposure is suspected to be ongoing should be considered and a suitable methodology for doing so should be developed, if appropriate.

It was agreed that further work by the relevant government agencies (e.g. HPA and EA) and/or SoBRA would assist with the above.

4 CHEMISTRY AND SITE ANALYSIS WORKSHOP

4.1 Introduction

PAHs are ubiquitous in the environment as the products of combustion (for example in made ground that contains an ash component) or in brownfield development sites contaminated by hydrocarbons. The physical nature of the PAH mixture (i.e. its presence in the ground as either a soil ash matrix or free phase hydrocarbons), the relative proportion of the constituent parts, and the absolute amounts, are all key factors in the assessment of risk from exposure to PAHs.

This working group was tasked with considering the key issues associated with the chemistry and site analysis of PAHs as they occur in contaminated soils.

The workshop was facilitated by Rob Ivens and Ed Stutt.

4.2 Key Issues

4.2.1 General Considerations

The group began by making some general observations about the factors that typically affect the approach practitioners take in characterising PAH contamination in soils.

Working Practices

The group contained representatives with experience of a broad cross-section of brownfield projects from high profile environmental assessment and remediation schemes through to smaller scale, developer-driven projects. It was recognised that large scale, high value remediation projects routinely involve site-specific screening for all 16 (USEPA priority) PAH compounds. However, it was noted that the majority of more straightforward risk assessment projects typically use BaP as the main indicator of PAH concentrations in soils.

Technical Approach

The group discussed the HPA CLIS[17] and the basis of its approach which is to use BaP as a surrogate marker for the genotoxic components of PAH mixtures. The group considered this method as compared to the 'relative potency' approach recognising that the toxicology of individual PAH compounds has a key role in determining how PAHs in soils should be characterised.

4.2.2 Classification of PAH Compounds

The group considered the chemical properties of PAHs noting that the USEPA 16 PAHs can be broken down broadly into three main groups with distinctly different environmental and toxicological properties:

- volatile, non-genotoxic types;
- semi volatile /non volatile, non-genotoxic types;
- non-volatile genotoxic types.

The group noted that of the PAHs typically tested for in UK land contamination applications, roughly 50% are genotoxic (non threshold) and 50% are threshold substances in terms of their mode of action, with the heavier compounds being regarded as genotoxic.

Table 4 illustrates the relationship between petroleum hydrocarbon banding, number of aromatic rings, volatility and the toxicological effects of individual PAH compounds featured in the USEPA 16 list.

Table 4: USEPA priority 16 PAHs and their PHC fraction bandings

HC Aromatic Fractions	PAHs included in fraction	No. of Rings	Volatility?	Threshold / Non threshold Effects
Aro EC>10-12	Naphthalene	2	Yes	Threshold
Aro EC>12-16	Acenaphthene	3	Semi volatile	Threshold
	Acenaphthylene	3	Semi volatile	Threshold
Aro EC>16-21	Anthracene	3	No	Threshold
	Fluorene	3	No	Threshold
	Phenanthrene	3	No	Threshold
	Pyrene	4	No	Threshold
	Chrysene	4	No	Non-threshold
Aro EC>21-35	Fluoranthene	4	No	Threshold
	Benz(a)anthracene	5	No	Non threshold
	Benzo(a)pyrene	5	No	Non threshold
	Benzo(b+j) fluoranthenes	5	No	Non threshold
	Benzo (k)fluoranthene	5	No	Non threshold
	Dibenzo(a,h)anthracene	5	No	Non threshold
	Benzo(g,h,i)perylene &	6	No	Non threshold
	Indeno(1,2,3 cd)pyrene	6	No	Non threshold

4.2.3 Volatile and Low Molecular Weight PAHs

Naphthalene is the only compound to have any substantial volatility and this compound, together with other low molecular weight PAHs, may be a risk driver where the inhalation of vapours is possible. Therefore provision should be made to test for naphthalene as a separate entity.

Naphthalene is also mobile in the water environment and should be considered separately where water bodies could be at risk.

The mobility of naphthalene in the water environment means that plant uptake might be a particularly sensitive pathway in certain circumstances. In this case, assessors should carefully consider the conceptual model to establish the relative location of the PAH mixture in relation to any likely food sources growing on the site. Other highly lipophilic PAHs are only likely to be an issue for root vegetables where the edible component is in direct contact with PAH-contaminated soil.

Whilst 3 ring PAHs, such as acenaphthene and acenaphthylene, are considered to be semi-volatile and may be indicated as potential risks using modelling, experience with soil vapour monitoring points suggests they are not usually significantly volatile in practice.

The group considered that good practice site characterisation in cases where potentially volatile PAHs may be present should involve:

- reference to appropriate guidance, such as the VOC Handbook[24] for advice on vapour measurement;
- measurement of soil vapour at relevant points in the soil profile;
- assessment of soil properties since these will influence vapour transport;
- consideration of factors, such as soil oxygenation and the potential for biodegradation in the soil profile; and

[24] Construction Industry Research and Information Association (2009). The VOCs Handbook, Report C682

- direct use of soil vapour measurements in CLEA or comparable exposure models to reassess risk, or alternatively direct comparison with appropriate HCVs such as quality standards for ambient air.

4.2.4 Non-genotoxic PAHs

The group noted that these PAHs tend to comprise the low molecular weight compounds listed in Table 4 (2-4 aromatic rings). It was also noted that the impact of these compounds can be underestimated where significantly elevated concentrations exist and the water environment is potentially at risk, if an assessor focuses exclusively on the genotoxic compounds such as BaP. The group agreed that the low molecular weight compounds should be addressed either by:

- considering each compound individually, or;
- using a ring class or TPH (Total Petroleum Hydrocarbon) banding approach and identifying marker compounds for each ring class or hydrocarbon band.

4.2.5 Genotoxic PAHs

These are the higher molecular weight compounds which contain 4, 5 or 6 carbon rings. The group was shown data which supported the HPA's proposition that the genotoxic load contributed by BaP was relatively constant on a variety of contaminated sites.

Relative potency calculations were carried out using a simple spreadsheet using a small number of datasets from real sites. It was generally found that BaP contributed around 50% of the carcinogenic load. Facilitators and delegates were surprised to see that this seemed to be the case in both heterogeneous soils and sites with substantial fuel based hydrocarbons.

Based on the HPA evidence, and limited examination of data sets from other sites, it was agreed that BaP is a useful indicator of genotoxic load in the majority of PAH mixtures. The group also noted two key conclusions drawn by EFSA in relation to its opinion on the assessment of PAHs[9]:

- toxic equivalent factors and relative potency are not acceptable means of measuring carcinogenic load due to the *"lack of data from oral carcinogenicity studies on different PAHs and their different modes of action"*;
- that BaP, on its own, is a satisfactory measure of carcinogenicity.

However the group had reservations regarding the derivation of a benchmark dose for BaP based on the Culp *et al* toxicological study (bioassay based on coal tar mixtures), for cases where PAH mixtures are present that are NOT derived from coal tar. The group was concerned that in the experimental coal tar mixtures, the PAH compounds as measured by the USEPA 16 priority suite, contributed to only part of the toxic/genotoxic load. The group also noted the statement (see below) in the CCME's recently published review of PAH chemistry[25] (a reference to the CCME's TEF approach to PAHs) which implies that coal tar and creosote mixtures are approximately 3 times more potent than non-coal tar mixtures:

"For soil contaminated with coal tar or creosote mixtures, the calculated Benzo[a]pyrene Total Potency Equivalents (B[a]P TPE) concentration for soil samples should be multiplied by a safety factor of 3".

[25] CCME (2010). Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health, Polycyclic aromatic hydrocarbons

4.2.6 Site Sampling and Laboratory Analysis

The group agreed that for heterogeneous mixtures, sampling error was the single greatest contributor to uncertainty. However laboratory analysis was also considered to be subject to substantial error. The following key issues were identified:

Sampling

Site investigators need to ensure that the sampling strategy, throughout the soil profile, is appropriately weighted in accordance with the conceptual model. Targeted samples should be clearly identified in the sampling schedule and results to ensure they do not unduly bias the statistical assessment of data for a given zone[26].

Sufficient unbiased sampling should be carried out to enable an accurate assessment of the statistical evidence against the chosen critical concentration. Practitioners should report their level of confidence in identifying a specified size of hot spot for a given zone of the site and this hot spot size should be related to the outline conceptual model and the proposed land use.

The group also considered that for human health effects, sampling should be concentrated in the top 1m of the soil profile focusing on the top 0.5m. Specific consideration should be given to dedicated sampling of the top 300mm as this is the actual soil to which human receptors are most likely to be exposed to non-volatile contaminants.

The merits of enhanced duplicate sampling regimes, in excess of the industry standard of 10%[27], were also considered. However, it was questioned whether this provides good value for money as the uncertainties are known to be both large and significant.

Laboratory Methods

Due to the particular significance of naphthalene, and its volatility, the group agreed that practitioners should be especially careful about specifying sample preparation methods prior to PAH testing, as follows:

- the preparation method should be “as received”, and;
- extraction techniques should be standardised.

Quality assurance of laboratory data was discussed and it was agreed that practitioners should be more aware of the analytical methods being applied to obtain their results. Internal quality control was also highlighted as being an issue where understanding needed to be improved.

A wider question was raised regarding the preparation of the sample - in particular, the treatment of fines and large particles. This was expected to affect the total amount of PAH extracted from the sample and was also felt to have a bearing on risk modelling especially given the importance of the dust pathway in the CLEA model for BaP.

4.3 Conclusions

The group concluded that no single marker compound is suitable for the assessment of the entire PAH group, and the consensus was that groups of

[26] CL:AIRE/CIEH (2008). Guidance on comparing soil contamination data with a critical concentration

[27] Measurement uncertainty arising from sampling: A guide to methods and approaches (2007). A joint publication from Eurachem, EUROLAB, CITAC, Nordtest and the RSC Analytical Methods Committee, edited by M. H. Ramsey and S. L. R. Ellison

compounds should be considered. The main conclusion was that some form of tiered approach to the risk assessment of PAHs might be useful. Below are listed the suggestions generally agreed as providing the best way forward.

Volatile and Low Molecular Weight PAHs

It was agreed that when found at elevated concentrations, naphthalene should be considered as an indicator of vapour risk.

As a simple initial screen, it was also agreed that naphthalene should be considered as a preliminary indicator of the risks associated with PAHs that are mobile in the environment, particularly in the context of the water environment. Although group members dealing with the remediation of large and complex sites, where the possibility of water pollution can often be a major issue, argued for specific assessment of all individual compounds, there was strong agreement amongst group members that it would be appropriate to have a more generic approach that could be used as a screen in the initial stages of an assessment.

Non-genotoxic PAHs

As above, the consensus view of the group was that the best way forward would be to develop a generic screening approach for these lighter compounds. It was felt that the well known Total Petroleum Hydrocarbon Criteria Working Group[28] (TPHCWG) methodology could be used, with the focus on specific marker compounds or fate and toxicological properties that are representative of the PAHs within a particular fraction/carbon banding or ring class.

This work would need to consider whether ring class or a TPH carbon banding approach was the best way forward.

Genotoxic PAHs

It was agreed the PAH suite currently used seems broadly acceptable although the chemists amongst the group expressed some concerns in relation to the co-elution of some of the compounds in the suite. BaP was also considered to be a good chemical marker for total genotoxic load, However, the group noted the CCME contention that coal tar and creosote mixtures might be up to three times more potent than non-coal tar soil mixtures, and that the Canadian TEF approach allows for this using an uncertainty factor of 3. The group felt that issue would be particularly important for the assessment of risks from *soil* if the Culp *et al* paper is used to justify specific HCVs in any future revised guidance.

Site Sampling and Laboratory Analysis

The group felt that sampling plans needed to ensure sufficient unbiased coverage and should record the size of hot spot they are likely to detect. Particular effort should be made to ensure the weighting of sample within the vertical profile is consistent with the outline conceptual model. In most cases, sampling should be concentrated in the near surface. In particular, practitioners should consider sampling the interface of topsoil and any subsoil or made ground - typically this might be ~ 150-300mm. Adequate duplicate samples should also be taken and the assessor should ensure consistent and appropriate laboratory preparation of the samples.

Good practice in site sampling and analysis should increase confidence in the data set and should enable the risks assessor to make suitable generic changes to the CLEA model parameters (see section 5 of this document). The process of

[28] TPHCWG, Total Petroleum Hydrocarbon Criteria Working Group Series (1997). Volume 3, Selection of representative TPH fractions based on fate and transport considerations

controlling uncertainties associated with the site data should then reassure the regulator that any relaxations in the exposure model are appropriate.

4.4 Recommendations

The group made the following recommendations.

1. Low Molecular Weight and Non Genotoxic PAHs: Double counting of PAH and TPH fractions needs to be considered in more detail.

2. Genotoxic Compounds: A national data collection exercise should be carried out of the prevalence of the USEPA 16 PAHs and associated analytical data. Such an exercise would require a standardised data format to be agreed but the advantages would be:

    - to check and validate the HPA proposition that BaP is a representative measure of genotoxic risk from PAH compounds found on the broad range of sites encountered in practice e.g. from gasworks to old inert landfills;
    - facilitate consideration of whether the risks associated with PAHs in soils are similar regardless of the source, e.g. presence of coal tar vs presence of fuel products.

3. Site Sampling and Laboratory Analysis: The group agreed that it would be useful to produce a small number of field sampling and laboratory related documents - all to be top tier good practice guides of no more than 5-10 pages long and covering:

    - A Field Sampling Manual - this should detail the relevant considerations in achieving good site investigation coverage incorporating both unbiased and targeted sampling strategies. It should also encourage users to develop a clear sense of the spatial resolution of an investigation, taking into account considerations such as the size of an assumed hot spot and the heterogeneity of the source.
    - Assessment of available field testing kits - to include a literature review of available UK or US demonstrations of method applicability.
    - Data quality assurance (QA) - to define good practice for data transfer between the site investigator, laboratory and risk assessor. This should identify priority fields for data transfer e.g. received data, extraction date, preparation and extraction methods.
    - Laboratory QA - this should set out the generic processes followed in the laboratory and explore:
        - a hierarchical approach to checking laboratory controls;
        - whether a cost effective approach can be devised to cross check laboratory results between laboratories;
        - the most commonly available preparation and extraction methods;
        - areas of consistency and inconsistency between laboratories;
        - the accuracy with which individual chemical compounds are reported within the PAH suite especially considering the potential for the co-elution of compounds such as benzo(b)fluoranthene and benzo(j)fluoranthene.

5 EXPOSURE ASSESSMENT WORKSHOP

5.1 Introduction

This workshop was intended to look at the key issues associated with the exposure modelling of PAHs and, in particular, the uncertainties surrounding the parameter values used in human health exposure modelling.

The workshop was facilitated by Simon Firth and Seamus Lefroy-Brooks.

5.2 Key Issues

The key issues identified by the group are presented and discussed below.

5.2.1 Marker Compounds

The group agreed that, from an exposure modelling perspective, naphthalene and BaP were good surrogate markers for assessing the human health risks from PAHs: naphthalene being the most volatile PAH (and of moderate toxicity) and BaP being a good marker for assessing risk from the genotoxic PAHs. The group felt that 3 ring PAHs were unlikely to drive risk to human health.

5.2.2 Dominant Risk-driving Pathways

The group agreed to focus on the residential exposure scenario and that the dominant risk driving pathways were soil and dust ingestion, dermal contact outdoors and dust inhalation indoors for BaP and indoor vapour inhalation for naphthalene. The group agreed to focus discussions on these parameters.

5.2.3 Soil Concentration

The group discussed contaminant concentration in relation to particle size distribution (PSD). It is recognised that PAHs may be preferentially sorbed/present on smaller or larger particles. For example, Lorenzi *et al*, 2010[29] found that PAH concentrations were significantly higher in the < 250um particle sized fraction than the > 250um to < 2mm particle sized fraction for the majority of soil samples collected from a coal tar contaminated site in the UK. Li *et al*, 2010[30], assessing soil samples from a former coke oven plant in Beijing, China, found a biomodal distribution with highest PAH concentrations in the 250 to 500um and < 50um fractions. They found that PAH concentration was strongly correlated with black carbon content and suggested that particle size distribution of black carbon could have an important influence on distribution of PAHs. Several members of the group felt that for soot contamination, PAHs tend to be sorbed to the finer particles, whereas for ash/clinker contamination PAHs tend to be associated with larger particles. The majority of soil incidentally ingested will usually be the finer (clay and silt) particles and it is the concentration of PAHs in these finer particles that determines exposure. Thus, use of bulk soil concentrations may underestimate risk (in the case of soot related contamination) or overestimate risk (in the case of ash/clinker related contamination). The group agreed that sieving and particle size distribution (PSD) analysis on a sub-set of soil samples are useful techniques in supporting Detailed Quantitative Risk Assessment (DQRA).

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[29] Lorenzi, D., Cave, M. and Dean, J.R. (2010). An investigation into the occurrence and distribution of polycyclic aromatic hydrocarbons in two soil size fractions at a former industrial site in NE England, UK, using in situ PFE–GC–MS, Environ. Geochem. Health, 32, 553-565

[30] Li, H., Chena, J., Wu, W. and Piao, X. (2010). Distribution of polycyclic aromatic hydrocarbons in different size fractions of soil from a coke oven plant and its relationship to organic carbon content. Journal of Hazardous Materials, 176, 729–734

The group also agreed that protocols for dealing with stones/large particles in soil samples have not been consistent across all laboratories. One study conducted in 2006 asked six UKAS accredited laboratories about how "stones" were dealt with during sample preparation[31]. Four different methods were reported. At present, neither ISO/IEC 17025 nor MCERTS (the EA's Monitoring Certification Scheme) specify sample pre-treatment with respect to stone removal. Therefore it is important to understand what the laboratories do in this respect and adjust soil concentrations for risk assessment where necessary. The group felt that it would be useful if a 'default' preparation method could be established to be certified through MCERTS.

The group also discussed the depth of soil contamination in relation to exposure. For non volatile PAHs (such as BaP) exposure of a zero to 6 year old child would typically be limited to exposed surface soils. Concentrations in the upper 10 cm or so of soil were therefore most appropriate for assessing risk. The group discussed the need to consider concentrations in deeper soils to account for residents digging tree pits, ponds etc. However the group felt that, in practice, this was unlikely to amount in a significant increase in long-term exposure for the vast majority of gardens – thus focus should still be on uppermost 10 cm. For planning sites, deeper soils may need to be considered to account for soil perturbation and/or if soil movements or change in level are envisaged as part of the re-development. Equally, the reduction in risk caused by import of cover soils and turf should also be considered.

5.2.4 Soil Ingestion Pathway

The key parameters for this pathway are soil concentration (see above), exposure frequency, body weight, soil ingestion rate and bioavailability. CLEA version 1.06 assumes a soil ingestion rate of 100 mg/day for the 0 to 6 year old child. Soil and dust ingestion rate studies are limited but have shown that:

- soil and dust ingestion rate can vary significantly from one child to another and from one day to the next;
- soil ingestion rates in pre-school aged children consistently average around 100 mg per day (e.g. USEPA, 2006[32] and Otte *et al*[33], 2001).

There was discussion over the assumption that a 6 month to 6 yr old child eats an average of 100 mg soil per day for 365 days per year. This was considered overly conservative as it is unlikely that all 100 mg of soil would come entirely from the property, i.e. a proportion of the 100 mg/day is likely to come from the park, nursery/school, shops etc. Furthermore, it was the group's understanding that the soil ingestion rate studies were relatively short-term (e.g. 30 days) and did not therefore account for seasonal variation in soil ingestion rate. For example, in winter it is likely that a child will ingest less soil and soil derived dust as a result of less time spent in the garden and less soil being tracked into the house from the garden.

The group recognised that there is a lack of data available for assessing soil ingestion rate but felt that there should be more scope for modifying this parameter for different conditions. It was suggested that the principles behind the delta factor in the former lead SGV report (DEFRA & EA, 2002[34]) could be

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31 Article by Mark Perrin in Ground Engineering, 2007

32 USEPA (2006). Child-specific Exposure Factors Handbook, External Review Draft, September 2006, Report EPA/600/R/06/096A

33 Otte, P., Lijzen, J., Otte, J., Swartjes, F. and Versluijs, C. (2001). Evaluation and revision of the CSOIL parameter set, RIVM Report 711701021

34 DEFRA & EA (2002). Soil Guideline Values for Lead Contamination. R&D Publication SGV10.

used for DQRA, i.e. for houses with paved gardens that were rarely used, practitioners could consider decreasing the soil ingestion rate accordingly. Note, however, that for Part 2A purposes, the effect of any change in the use of land which does not require the grant of planning permission (such as the removal of paving stones) still has to be taken into account.

5.2.5 Dermal Contact Pathway

The key parameters for this pathway are soil concentration (see above), exposure frequency, body weight, area of exposed skin, dermal adherence and dermal absorption factor. In terms of soil concentration, the same points as discussed above were considered important in that only finer particles are expected to adhere to skin. The group felt that the parameter values used in CLEA for assessing dermal exposure were more conservative than those used for the soil ingestion pathway. The estimation of exposure of soil and dust ingestion is largely based on central tendency values, e.g. average body weight and average soil ingestion rate are assumed. This is not the case for dermal exposure, especially outdoors, where:

- the child is assumed to be exposed to garden soil outdoors 365 days/year – the group considered this to be unrealistically high;
- the soil adherence factor of 1 mg/cm^2 is based on a value between the upper 95th percentile values for children playing on dry and wet soils - the group felt it may be better to use the central tendency value to be consistent with other parameters in CLEA - it was also noted that the USEPA (2004a[35]) recommend a reasonable maximum exposure value for children of 0.2 mg/cm^2;
- the child is assumed to be in shorts and T-shirt whilst outdoors 365 days/year - this was considered unrealistically conservative.

The group also discussed the recommended dermal absorption factor of 0.13 for PAHs quoted in the CLEA SR3 report[36] and questioned whether this was reasonable. This absorption factor effectively means that 13% of the PAHs sorbed to skin will enter the bloodstream per day. The SR3 report attributes this absorption factor to USEPA (2004[35]) which in turn attributes the factor to a study by Wester *et al*, 1990[37].

Wester *et al* studied the dermal absorption of C14 labelled DDT and BaP in acetone and soil using *in vitro* studies with samples of human skin with human plasma as the receptor fluid. *In vivo* studies were conducted using four female rhesus monkeys. The researchers prepared acetone solutions and soil such that they contained 10 ppm of the test compound. For the *in vivo* studies, BaP in acetone was applied to a 12 cm^2 patch of skin for 24 hours and the amount of C14 was measured in urine passed during the application period and the next 6 days. This was compared to the amount of C14 in urine when BaP was administered intravenously. This exercise was then repeated using 40 mg of soil mixed with C14 labelled BaP applied to the 12 cm^2 patch of skin (equivalent to a soil loading of 3.3 mg/cm^2).

The results showed a wide range of dermal absorption. The *in vitro* study showed that less than 0.1% of the BaP in soil entered the human plasma. The *in vivo*

[35] USEPA (2004). Risk assessment guidance for Superfund, Volume I: Human health evaluation manual (Part E, supplemental guidance for dermal risk assessment), Final Report EPA/540/R/99/005

[36] EA (2009), Updated technical background to the CLEA model, Science Report SC050021/SR3

[37] Wester, R.C., Maibach, H.I., Bucks, D.A.W., Sedik, L., Melendres, J., Liao, C. and DiZio, S. (1990). Percutaneous absorption of [14C] DDT and [14C] Benzo[a]pyrene from soil, Fund. App. Toxicol., 15, 510-516

studies indicated that between 10.8% and 18% of BaP was absorbed from soil applied to skin and that between 30.5% and 82.2% of BaP was absorbed from the acetone solution. The average absorption of BaP from soil from the *in vivo* studies was 13.2% and this is presumably the basis for the USEPA recommended absorption factor of 0.13.

The CLEA SR3 report also references a USEPA (1992[38]) report, which describes the Wester *et al* study and a study by Yang *et al* (1989[39]). Yang *et al* studied the absorption of BaP from soil using *in vitro* studies with rat skin and *in vivo* studies with rats. The researchers used soil with an organic carbon content of 1.64% mixed with crude oil such that the soil concentration of BaP was 1 mg/kg. Soil was applied to the skin in the *in vitro* study at 9 mg soil/cm^2 and 56 mg soil/cm^2 and this resulted in absorption of 8.4% and 1.3% of the BaP after 96 hours, respectively. Soil was applied in the *in vivo* study at 9 mg soil/cm^2 and this resulted in an absorption of 1.1% after 24 hours and 9.2% after 96 hours.

These two studies demonstrate a large range in absorption values, although arguably the results of the *in vivo* studies on monkeys are the most relevant to the assessment of risks to humans. However, it is also important to note that both studies share the limitation that they used soil mixed with BaP and not BaP contaminated soil from a contaminated site. The BaP in the soils used in these studies is likely to be less strongly sorbed to soil than soils where BaP has been present for many years. There are a number of more recent studies into dermal absorption of BaP from soils which conclude that the bioavailability and age of the BaP contamination can significantly reduce dermal absorption (Stroo *et al*, 2005[40], Moody *et al*, 2007[41], Turkall *et al*, 2009[42] and Abdel-Rahman *et al*, 2002[43]). It is therefore possible that the Wester *et al* study significantly over-estimates dermal absorption of BaP. The group agreed that this may be a parameter which would benefit from a thorough literature review.

5.2.6 Dust Inhalation Indoors

The key parameters for this pathway are soil concentration (see above), exposure frequency, body weight, respiration rate, soil to dust transport factor and dust loading factor (indoors). The group discussed the fact that there were uncertainties with the latter two but values were not unreasonable based on current data. Further research/data collation could help refine these parameters. The respiration rate was also discussed. The CLEA recommended value is based on central tendency values from a USEPA report[44] which has subsequently been

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38 USEPA (1992). Dermal exposure assessment: principles and applications, Office of Health and Environmental Assessment, EPA/600/6-88/005Cc

39 Yang, J.J., Roy, T.A., Krueger, A.J., Neil, W., and Mackerer, C.R. (1989). In vitro and in vivo percutaneous absorption of benzo[a]pyrene from petroleum crude-fortified soil in the rat, Bull. Environ. Contam. Toxicol., 43, 207-214

40 Stroo, H. F., Roy, T. A., Liban, C. B. and Kreitinger, J. P. (2005). Dermal bioavailability of benzo[a]pyrene on lampblack: implications for risk assessment, Environmental Toxicology and Chemistry, 24, 1568–1572, doi: 10.1897/04-240R.1

41 Moody, R. P., Joncas, J., Richardson, M. and Chu, I. (2007). Contaminated soils (I): in vitro dermal absorption of benzo[a]pyrene in human skin, Journal of Toxicology and Environmental Health, Part A, Volume 70, Issue 21, 1858 - 1865

42 Turkall, R. M., Skowronski, G. A., Abdel-Rahman, M. S. (2009). Effects of soil matrix and aging on the dermal bioavailability of polycyclic aromatic hydrocarbons in the soil, International Journal of Soil, Sediment and Water, Volume 2, Issue 1, Article 4

43 Abdel-Rahman, M. S., Skowronski, G. A. and Turkall, R. M. (2002). Assessment of the dermal bioavailability of soil-aged benzo(a)pyrene, Human and Ecological Risk Assessment: An International Journal, Volume 8, Issue 2, 429 – 441

44 USEPA (2006). Child-Specific Exposure Factors Handbook (External Review Draft) September 2006, Report EPA/600/R/06/096A

updated with lower values[14]. The group recommended updating the rate in CLEA assessments.

5.2.7 Vapour Inhalation

There was insufficient time to discuss vapour migration/inhalation in detail, other than to state that the Johnson and Ettinger model (used within CLEA) is generally conservative for petroleum hydrocarbons and that the respiration rate currently used in CLEA could be updated with more recent USEPA estimates.

5.2.8 Probabilistic Versus Deterministic Modelling

There was some discussion regarding probabilistic versus deterministic modelling. The disadvantage of deterministic modelling is that it gives one answer and can lead to a false confidence in the result. Probabilistic modelling gives a range of possible results and gives a better indication of uncertainty in the model results which can help with decision making. However, the old CLEA model (as described in DEFRA and EA, 2002[45]) was not fully probabilistic (only 4 parameters were modelled probabilistically) and therefore it underestimated the range of possible Average Daily Exposures. The group felt that deterministic modelling was easier to communicate and sufficient for most purposes but that probabilistic modelling could be considered as a research project to help define the key areas of uncertainty and the most appropriate parameter values for deterministic modelling.

5.2.9 Other Issues

The group identified several other issues that warranted discussion but time was limited on these:

- Open space/parks generic exposure parameters. The group recognised that practitioners were deriving assessment criteria for these land-uses and that values could vary significantly depending on the exact use of the site. The group felt that collating parameter values used by different practitioners would help towards agreement on appropriate ranges of parameter values for deriving GAC for these land-uses.
- Background exposure. The group felt that consideration of background exposure was important to put risk from soils in context. For example, what is risk from PAHs in soils relative to ingestion of PAHs in burnt toast, inhalation of PAHs from vehicle emissions etc.

5.3 Conclusions

The main conclusions from the discussion group are presented below:

- From an exposure modelling perspective, naphthalene and BaP were good surrogate markers for assessing risks from PAHs.
- The level of conservatism is currently inconsistent across all CLEA pathways with some based on upper 95th percentile while others use central tendency values. The main parameters of concern are considered to be:
  - soil and dust ingestion rate;
  - exposure frequency outdoors;
  - soil adherence factor;

[45] DEFRA and EA (2002). The Contaminated Land Exposure Assessment (CLEA) Model: Technical basis and algorithms

- exposed skin area outdoors;
- dermal absorption factor for PAHs;
- the respiration rate.

- Other concerns involve the distribution of PAHs within the soil in relation of particle size and the lack of consistency on sample preparation with respect to stone content.

5.4 Recommendations

The group made the following recommendations:

1. Existing (anonymous) data on PAH concentration distribution in relation to particle size should be collated. A number of practitioners have indicated that they have data on PAH concentrations in relation to particle size. National Grid also advised that they will be conducting research on PAH concentrations in soil and dust associated with remediation works. The group suggested that this would help gather an evidence base for PAH distribution on particle size.
2. Guidance should be given on the use of soil concentration data in risk assessment: e.g. depth of samples and contaminant concentration versus PSD.
3. Guidance should be given or agreement reached on the most appropriate method of soil sample preparation in relation to “stones”.
4. A review of CLEA parameter values should be carried out to ascertain whether the level of conservatism should be consistent across all pathways: e.g. should central tendency values be used for all parameters?
5. A sensitivity analysis document should be prepared which shows the range in assessment criteria produced using reasonable ranges of parameter values for exposure modelling.
6. A longer term research project should be initiated which creates a fully probabilistic version of CLEA to help determine the most suitable set of parameter values for deterministic modelling.
7. Parameter values used for the derivation of open space assessment criteria should be collated and published to show the range of parameter values applied in typical projects.
8. A literature review should be carried out of dermal absorption fraction values for PAHs in soils (including dermal bioavailability).
9. A literature review / research should be carried out into background exposure to PAHs relative to the risk from soils.

6 BIOACCESSIBILITY AND PLANT UPTAKE WORKSHOP

This workshop addressed the key issues surrounding determination of the bioaccessible fraction of organic contaminants in soils and its implications for improving the risk assessment of PAH contamination in soils. The workshop also touched on the related issue of the uptake of PAHs by plants.

The workshop was facilitated by Yolande Macklin and Liz Hart.

6.1 Bioaccessibility

6.1.1 Introduction

The current regulatory regime in the UK is based largely on the total concentration of contaminants in soils. However, the biological effects of a contaminant are not necessarily related to the total concentration since aging and weathering processes in soil can reduce the fraction of the total that is available to biological systems.

The most reliable method for determining the bioavailable fraction of a contaminant in soils is *in vivo* tests. However, there are only limited *in vivo* data for individual substances, and *in vivo* testing is costly to carry out and has ethical implications.

A number of *in vitro* tests have been developed and trialled to determine the bioaccessible fraction[46] for inorganic substances; the most widely known in the UK is the Physiological Based Extraction Test (PBET) first described by Ruby *et al* in 1993[47]. Concerns have been expressed about the PBET test in relation to reproducibility, variance in sample results, availability of reliable reference material and validation against relevant *in vivo* data.

A study undertaken across a number of UK laboratories in 2005 indicated significant variance on results from known reference material. These issues have been researched by the British Geological Survey (BGS) and the Bioaccessibility Action Research Group of Europe (BARGE) which has recommended an amended PBET test that reduces the degree of uncertainty, as discussed in a joint BARGE and BGS publication[48].

6.1.2 Key Issues

At present, there is no commercially available bioaccessibility test for organic substances in soils specifically intended for aiding human health risk assessment[49].

One method, the Fed ORganic Extraction human Simulation Test (FOREhST), which is based on a RIVM fed state model with an optimised method for PAH analysis, has been developed by BGS, National Grid and the University of

[46] Bioavailable fraction is the fraction of a substance that enters the body's systemic system. This can only be determined using *in vivo* tests and bioassays. The bioaccessible fraction is the fraction that is released during ingestion that is available for uptake. Not all the bioaccessible fraction is necessarily absorbed into the systemic system.

[47] Ruby, M. V., Davis, A., Link, T. E., Schoof, R., Chaney, R. L., Freeman, G. B. and Bergstrom, P. (1993). Development of an in vitro screening test to evaluate the in vivo bioaccessibility of ingested mine waste lead, Environmental Science and Technology, 27, 2870 - 2877

[48] BARGE/ BGS (2009). Inter-laboratory trial of a unified bioaccessibility procedure

[49] Note that ALcontrol Laboratories offer a cyclodextrin testing method for assessing the bioavailability of PAHs in soil to microbes for the purpose of assessing the potential for bioremediation but this is not physiologically based on the human gut.

Nottingham. The usefulness of this test for measuring the bioaccessibility of PAHs has been assessed in UK soils[50].

An alternative test, a modified PBET test for organic substances which incorporates an additional extraction stage in the colon is being developed by Reading University (in collaboration). This test would also be applicable for PAH assessments.

The procedure has been named the CEPBET (Colon Extended Physiologically Based Extraction Test) method and it combines the amended PBET method with an additional compartment which mimics conditions within the colon.

The colon is very conducive to the desorption of organic contaminants from soils because it is rich in a number of components, such as bile salts and carbohydrates etc., that have a high affinity for these substances. The residence time in the colon can vary from 36 to 52 hours, considerably longer than the c.4-6 hour PBET and BARGE tests. In the case of organic substances, therefore, it is particularly important to allow for extraction in the colon otherwise the bioaccessible fraction will be underestimated.

Research at the University of Reading has proved that the addition of the colon compartment increases the bioaccessibility of PAH from soils.

The CEPBET method consists of a 1 hour incubation in the acid conditions of the stomach, followed by 4 hours in the neutral conditions of the small intestine and, finally, 16 hours in the carbohydrate rich conditions of the colon. These parameters reflect the transit times and conditions in the human digestive tract[51].

To date, 12 reference soils have been analysed using the CEPBET method. *In vivo* studies are planned to verify the test methods and current results indicate that the CEPBET is as reliable as the modified PBET.

A concern raised at the workshop was the possible limitation within CLEA v1.06 when incorporating bioaccessibile fractions into risk assessments given the combined oral and dermal pathway. Clearly, bioaccessibility values are only relevant via oral exposure to contaminants.

However, the CLEA spreadsheet undertakes the exposure modelling for oral and dermal pathways separately and the bioaccessible parameter is only incorporated within the oral calculation. It is only following this exposure calculation that the two pathways are combined when both are compared against the oral HCV, in the absence of relevant dermal HCVs. This point is expanded within section 10.4 of the CLEA Handbook[52].

Further key issues regarding the use of bioaccessibility fractions within risk assessments were considered by the group including establishing appropriate supporting “lines of evidence”. The term is often used in relation to bioaccessibility testing but is not clearly defined. Clearly, a number of factors affect the bioaccessibility of a substance within soils including the soil matrix, form of carbon (to which organic contaminants are typically sorbed) and the amount of time the contaminant has been in the soil. The latter is often referred to as ‘aging’.

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50 Cave, M. R., Wragg, J., Harrison, I., Vane, C. H., Wiele, T. V. D., Groeve, E. D., Nathanail, C. P., Ashmore, M., Thomas, R., Robinson, J. and Daly, P. (2010). Comparison of batch mode and dynamic physiologically based bioaccessibility tests for PAHs in soil samples. Environmental Science & Technology, Vol. 44, 2654-2660

51 Dr Chris Collins, Reading University, test method provided by email. For more specific details contact c.d.collins@reading.ac.uk

52 EA (2009). CLEA Software (version 1.05) Handbook, Science Report SC050021/SR4

Chris Collins suggested that establishing the black carbon content of soils (a more sophisticated test than total organic carbon as reported by many UK laboratories) is an essential line of evidence for bioaccessibility testing of organic contaminants. The presence of black carbon affects the amount of PAH detected in soils, as it is frequently a rich source and therefore makes a contribution to the total PAH content. It is also a strong sink for PAH so influences the amount of PAHs that may be available to biological systems. This is discussed further by Koelmans *et al*[53]. Thus an understanding of the black carbon content is essential when considering PAH within soils whether using bioaccessibility data or not.

Although the test for black carbon is straightforward, there are currently no UK laboratories that routinely offer the test. If assessment of PAH within soil, including the use of bioaccessibility testing for organic contaminants in the UK is to advance, the contaminated land community would need to express a demand for this test from laboratories.

Other considerations relevant to the use of bioaccessibility testing more generally were discussed (see also EA report P5-062/TR/01[54]). These included the need for:

- a well designed sampling strategy and soil sampling programme;
- bioaccessibility extraction that is physiologically based and preferably validated against human or animal studies;
- a holistic approach to bioaccessibility results i.e. results should be considered in context of geochemistry, previous land use and intended land use;
- reference source material certified for total concentration to be tested with samples to provide assurance regarding final results;
- the inclusion in final reports of the results of testing for total concentrations, with bioaccessible fraction data put into context based on reference source results including details of the degree of variance.

6.1.3 Conclusions

The requirements for enabling bioaccessibility testing for PAH and other organic contaminants to become an accepted technique in UK land contamination risk assessments are likely to include:

- EA and/or industry endorsement and appropriate use;
- incorporation of the concept into the CLEA programme to advance understanding;
- a consistent and coherent approach across industry/regulators;
- recognition that the results of bioaccessibility testing may make only a modest difference to risk estimates where inhalation (particularly of dust) may be the dominant exposure pathway for some PAHs (although this can be accounted for when assessing both pathways individually);
- research/case studies on the outcome of using bioaccessibility within risk assessments;

[53] Koelmans, A.A., Jonker, M.T.O., Cornelissen, G., Bucheli, T.D., Van Noort, P.C.M. and Gustafsson, O (2006). Black carbon: the reverse of its dark side. Chemosphere, 63, 365–377

[54] EA (2002). *In-vitro* methods for the measurement of the oral bioaccessibility of selected metals and metalloids in soil: A critical review. R&D Technical Report P5-062/TR/01

- the cost of the test vs potential savings on remediation and increased understanding of the conceptual model;
- learning from previous experience in respect of arsenic bioaccessibility testing i.e. ensuring that the application and testing meet the criteria listed in the EA report P5-062/TR/01[54].

6.1.4 Recommendations

There is clearly a role for the bioaccessibility testing of organic contaminants within human health risk assessments with respect to land contamination cases.

However, some necessary steps need to be taken to allow the bioaccessibility testing of organics to be embraced by both industry and regulators. These are likely to include:

1. Clarification on the guiding principles/protocols or some form of accreditation of the test method.
2. Test data on real sites, to aid understanding of the difference/benefit bioaccessibility testing can make in risk assessments - is the outcome worth the investment?
3. A clear/consistent regulatory approach and consistent industry approach to give regulators confidence in the method.
4. Replication of test results within a reasonable variance.
5. An affordable cost for analysis.
6. Increased understanding of the availability of background concentrations of contaminants and how this fits with site characterisation.

Some progress on these issues has already been made with techniques such as FOREhST and CEPBET. Provided further evaluation of these methods is favourable, bioaccessibility testing could prove a real option for further refining risk assessments involving organic contaminants in soils.

However, uptake of the methods still hinges on regulatory and industry adoption and the publication of relevant case studies.

6.2 Plant Uptake

6.2.1 Introduction

One potential route through which humans can be exposed to contamination is via the consumption of home-grown produce, such as vegetables and fruit, which have been grown in contaminated soils. In the case of mobile, non-volatile contaminants, this often represents the most significant route of exposure.

Currently, the most common mechanism for predicting how much contamination in soils is taken up into plants is using model algorithms. The CLEA guidance notes that '*ideally, the concentration of chemicals in home-grown fruits and vegetables would be measured directly on a site-specific basis. However this is often impractical for a number of reasons including the time and cost associated with such investigations, analytical complexity and statistical variability*'[36].

In particular the analysis of fruit and vegetable samples for organic contaminants is costly and can be time prohibitive when compared to inorganic analysis. As part of the on-going review of the CLEA programme the EA undertook a detailed

review of plant uptake studies in 2006[55]. The review indicated that many plant uptake studies can be rejected because the experimental methodology is unclear and crucial information such the soil concentrations and soil conditions are not reported. Pot experiments, where plants are grown under controlled conditions in a growth chamber or indoor greenhouse, are often seen by researchers as a compromise between the necessary level of experimental control and reality. However, pot experiments have a number of known limitations including restricted soil volumes, increased leaching and/or vaporisation under optimum conditions, and potential cross contamination.

The current version of the CLEA model (v1.06) uses different approaches for predicting uptake for organic and inorganic contaminants. The model algorithms for predicting plant uptake for organic contaminants is based on the findings of the literature review undertaken in 2006. For many organic chemicals there have been very few uptake studies and generic models are the only available mechanism for prediction. The EA has concluded from the literature review that the following generic models (according to produce types) for predicting soil to plant concentration factors are the most suitable:

- Green vegetables- Ryan *et al* (1988)
- Root vegetables – Trapp (2002)
- Tuber vegetables – Trapp *et al* (2007)
- Herbaceous fruit – no suitable model
- Shrub fruit – no suitable model
- Tree fruit – Trapp *et al* (2003)

Other parameters which are key in the assessment of exposure to humans from consumption of home-grown fruit and vegetables grown in contaminated soils include:

- the fraction of produce which is home-grown;
- and consumption rates.

The consumption rates for each fruit and vegetable category within CLEA have been estimated by the Food Standards Agency (FSA) using data from several surveys including the National Diet and Nutrition Surveys 1992-2000 and the FSA INTAKE 2 model.

The fraction of the produce which is home-grown is estimated from the Expenditure and Food Survey[56] with CLEA. The limitations to this data are clearly identified with the EA's guidance.

6.2.2 Key Issues

There is a great deal of uncertainty with modelling the plant uptake pathway for PAHs. The EA study in 2006 indicated that the majority of model algorithms over-predict for root concentrations whereas model predictions for shoot concentrations are variable (i.e. some over-predict and some under-predict). There was a strong feeling amongst the workshop group that the model algorithms and exposure parameters within the CLEA model on the whole tended to be over conservative and that there are insufficient data to support any of the model algorithms with

[55] EA (2006). Evaluation of models for predicting plant uptake of chemicals from soil, Science Report SC050021/SR

[56] DEFRA (2007). UK purchases and expenditure on food and drink and derived energy and nutrient intakes in 2005-2006

confidence. Workshop members felt that when it came to making a decision under Part 2A of the Environmental Protection Act 1990, it was particularly important to have robust algorithms.

The variability of uptake of PAHs into produce on a site specific basis was discussed within the workshop. It was highlighted by several members of the workshop group that in their experience the actual uptake is very variable and is highly dependent on a number of factors including the soil matrix, weather, organic content of the soil, plant type and size etc. It was felt by the workshop group that the UK would benefit from good empirical data rather than trying to collect representative site data.

Where analysis of vegetables and fruit has been undertaken at contaminated sites there are a number of factors which at the moment are not clearly defined within any guidance. This was considered to be a point of particular importance within the workshop and the correct sampling procedure and analysis of samples was considered to be key to providing meaningful robust results. The FSA is able to provide advice to local authorities on sites involving consumption of vegetables/fruit on a case by case basis. The advice that the FSA provides in terms of correct sampling includes:

- sampling root and depth should match root spread and depth;
- soil pH and soil organic matter should be determined; and
- analysis of the edible portion only of the plant should be undertaken.

Other important factors to consider when obtaining samples are the stage of growth of the vegetable/fruit being sampled as this will influence the concentration of the contaminant within the vegetable/fruit. At earlier stages of growth the concentrations of contaminants are likely to be proportionately higher than in mature vegetable/fruit.

Another key issue raised within the workshop was whether PAHs are actually taken up into leafy vegetables or fruit at all. Organic contaminants are not metabolised by plants and are not required for growth. The literature tends to support the contention that PAHs accumulate mainly in the skins of root vegetables. It was suggested within the workshop that uptake of PAHs in leafy vegetable and fruit is likely to be negligible. The risk that such uptake presents to humans through consumption is also dependent on whether the produce is washed, peeled and scrubbed as assumed by the FSA. This was discussed within the workshop and there was a strong consensus that for many vegetable types, this type of preparation is not done prior to consumption.

The CLEA model assumes that the amount of home-grown produce consumed could be grown in an area of just 20 m^2 within a residential garden. The CLEA guidance bases this assumption on the facts that 85 per cent of residential gardens in the UK are greater than 100 m^2 in size and 34 per cent are greater than 450 m^2 in size. However the workshop group felt that in their experience, the assumed productivity of the 20 m^2 plot was not a realistic estimate and perhaps did not account for the spacing between different crop types that would be required.

One area which the workshop group felt strongly would benefit from further research is the fraction of produce which is home-grown. The CLEA guidance identifies this is a subject where there is insufficient evidence to provide a robust estimate for generic exposure assessment. There was a strong opinion amongst the group that the current proportions assumed to be homegrown are too high and are therefore unrealistic.

Another issue raised was that allowable concentrations [of contaminants] in foodstuffs according to regulatory limits (Commission Regulation (EC) 1881/2006) can often be higher than the allowable concentrations calculated by CLEA. It was suggested that this is an area in which it might be possible to standardise.

6.2.3 Conclusions

It was concluded from the workshop that in order to improve the current approach to assessing the risks from PAHs via the consumption of home-grown produce, the following key issues need to be addressed:

- industry standard guidance on the procedure for sampling vegetables should be produced;
- further understanding is required on the uptake of PAHs into vegetables and fruit;
- further research is required on the proportion of home-grown produce which is consumed to allow a more realistic estimate;
- further understanding is required of the behavioural aspects of produce consumption, such as the proportion of people who peel all fruit and vegetables; and
- standardisation of regulatory limits for allowable concentrations of contaminants in foodstuffs in relation to the concentrations calculated by the CLEA software.

6.2.4 Recommendations

There is clearly a great deal of uncertainty involved in estimating exposure to contaminants via the consumption of home-grown produce. However there are a number of areas in which further research/ collaboration could be undertaken to improve risk estimation. These recommendations include:

1. The collation of measured data from UK and Europe taken from real contaminated sites to provide further verification of the model algorithms and possibly to inform default values for soil-to-plant concentration factors.
2. The development of clear guidance on sampling produce for land contamination risk assessment. This could build on guidance given to local authorities by the FSA.
3. Further UK wide research into the proportion of produce consumed by householders which are home-grown and the quantities which are grown within residential gardens and on their subsequent preparation.
4. Further research into the uptake of PAHs by plants grown in contaminated soils and understanding the mechanisms of translocation within produce.

7 CONCLUDING REMARKS

7.1 Key Priorities

It is evident from workshop discussions that while a reasonable consensus exists amongst UK practitioners on the current approach to assessing the human health risks from PAHs, there are reservations about some aspects of the approach and further work may be desirable to address gaps in understanding and/or to improve current risk assessment practice.

Some of the conclusions drawn by the workshop groups were specific to PAHs and/or the particular themes being addressed; others had a broader applicability to a number of soil contaminants or were common to more than one workshop theme. Examples of the latter were those regarding the need for appropriate sampling strategies for non-volatile contaminants, and for the standardisation of sample preparation methods, as picked up by both the Chemistry/Site Analysis and Exposure Assessment workshops.

Detailed recommendations were put forward by delegates in each of the four workshops as set out in the relevant sections of the report. However, key areas of consensus and priorities for further work specific to PAHs and individual workshop themes, were as follows.

Human Toxicology

Given that PAHs are usually present in soils in the form of mixtures, the surrogate marker approach, as proposed by the HPA, is viewed as an appropriate basis for assessment subject to:

- reservations about the toxicological study (Culp *et al*) which underpins the surrogate marker approach, especially those relating to the possibility that substances in coal tar mixtures, other than PAHs, may have contributed to observed toxic effects, and that the study may not be the most appropriate toxicological basis where PAHs are present that are not derived from coal tars;
- further consideration of more recent (USEPA) guidance, which advocates a TEF approach to the assessment of PAHs, and the extent to which this may alter current recommendations on the most appropriate approach.

It is also considered that further work is required in relation to the toxicological input criteria used in human health risk assessment, particularly in the context of Part 2A which aims to identify land which presents 'unacceptable', rather than 'minimal', risk.

Chemistry and Site Analysis

The selection of PAHs to be included in site characterisation efforts (sampling and laboratory analysis) should be based on the toxicology, physico-chemical properties and behaviours of the different compounds in line with the conceptual model developed in any particular case - this should include an assessment of the likely source of PAHs in soil.

Further work should be carried out to characterise the PAHs found in UK soils to support the proposition that BaP represents an appropriate measure of the carcinogenic potential of PAHs in soil in a range of typical site types.

Further good practice guidance, in the form of short user guides, should be developed to advise on appropriate sampling (including use of test kits), sample

handling and laboratory analysis methods (including sample preparation and extraction) for PAHs.

Exposure Assessment

The nature of soil samples (e.g. distribution of PAHs in relation to particle size) and the way in which they are collected and prepared (e.g. depth of sampling, treatment of the 'stone' content') have a bearing on the validity of exposure assessment and further work is needed to standardise soil sampling and sample treatment practices.

There are a number of uncertainties associated with the parameter values typically used to model human health risks, and the consensus is that many of the default parameters currently used in CLEA may be overly conservative. Further work is needed to:

- determine the implications of varying specific exposure parameter values;
- advise on the selection of suitable values for particular applications, such as assessment under Part 2A, and in relation to particular land uses, such as open space;
- further inform the suitability of specific values, such as the dermal absorption factor;
- establish the relative risks from exposure to PAHs from different (including background) sources.

Bioaccessibility and Plant Uptake

There is a need to further develop understanding of the availability of PAHs to biological systems, including humans and plants used for human consumption.

Methods such as FOREhST and CEPBET represent useful steps forward in improving understanding of the human bioaccessibility of PAHs in soils but further work should be undertaken to:

- develop appropriate guiding principles and protocols on the use of such bioaccessibility test methods;
- further validate the methods using *in vivo* studies and case study data for 'real' sites;
- obtain regulatory and industrial endorsement of the approach.

There are many limitations and uncertainties regarding current modelling approaches to estimating the extent to which PAHs may be taken up by food plants. Further work is required to:

- improve understanding of the mechanisms through which PAHs are taken up by, and translocated within, food plants;
- improve model estimates, including default soil-to-plant-concentration factors, using measured data from 'real' sites;
- prepare improved guidance on the collection of samples of food plants and on the preparation of samples for testing.

7.2 Delivering the Recommendations

Workshop delegates made many recommendations regarding possible future workstreams, some of which would have the specific effect of improving the knowledge base on PAHs, and others that benefit more generally the UK approach to land contamination risk assessment.

Currently there are major constraints on both public and private sector organisations in terms of the availability of personnel to carry out further research and on budgets to support it.

Delegates were not asked specifically how the relevant workstreams might be implemented. However, given current circumstances, it is pertinent to ask how necessary future research in the land contamination field can be initiated and sustained over the coming years.

While it is outside the remit of this report to answer this key question, it is hoped that, in addition to adding to the UK's store of technical knowledge on the risk assessment of PAHs, this report will encourage constructive debate amongst practitioners about the mechanisms that will be needed in the future to support progress in the important field of land contamination risk assessment.

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APPENDIX 1 - WORKSHOP GROUPS

HUMAN TOXICOLOGY WORKSHOP

Workshop Facilitators

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Workshop Members

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Andrew Gwatkin	Rodgers Leask Environmental
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Natasha Glynn (nee Dixon)	WorleyParsons
Sarah Bull	Health Protection Agency
James Lymer	Wardell Armstrong
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CHEMISTRY AND SITE ANALYSIS WORKSHOP

Workshop Facilitators

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Ed Stutt	WCA Environment

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Peter Hewitt	TerrraSolve Ltd
Adam Czarnecki	Vertase FLI ltd
Phil Hartley	Newcastle City Council
Michael Buckley	Arley Consulting
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John Muir	Jacobs UK Ltd
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EXPOSURE ASSESSMENT WORKSHOP

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BIOACCESSIBILITY AND PLANT UPTAKE WORKSHOP

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APPENDIX 2 - ABBREVIATIONS

ADE	Average Daily Exposure
ALARP	As Low As Reasonably Practicable
ATSDR	Agency for Toxic Substances and Disease Registry
BaP	Benzo(a)pyrene
BARGE	Bioaccessibility Action Research Group of Europe
BGS	British Geological Society
BMD	Benchmark Dose
$BMDL_{10}$	The lower 95th percent confidence limit on the benchmark dose producing a 10% response
CCME	Canadian Council of Ministers of the Environment
CEPBET	Colon Enhanced Physiologically Based Extraction Test
CIEH	Chartered Institute of Environmental Health
CL:AIRE	Contaminated Land: Applications In Real Environments
CLEA	Contaminated Land Exposure Assessment
CLIS	Contaminated Land Information Sheet
COC	Committee on Carcinogenicity of Chemicals in Food, Consumer Products and the Environment
DQRA	Detailed Quantitative Risk Assessment
EA	Environment Agency
EFSA	European Food Standards Agency
EPAQ	Expert Panel on Air Quality Standards
FSA	Food Standards Agency
GAC	Generic Assessment Criterion
HCV	Health Criteria Value
In vitro	[Latin] meaning *"in the glass"*
In vivo	[Latin] meaning *"in the living"*
JECFA	Joint FAO/WHO Expert Committee on Food Additives
MCERTS	Monitoring Certification System
NERC	Natural Environment Research Council
PAH	Polycyclic Aromatic Hydrocarbon
PBET	Physiologically Based Extraction Test
PSD	Particle Size Distribution
RIVM	Dutch National Institute for Public Health and the Environment
RPF	Relative Potency Factor
SCF	Scientific Committee on Food
SGV	Soil Guideline Value
TEF	Toxic Equivalency Factor
TPH	Total Petroleum Hydrocarbons
TPHCWG	Total Petroleum Hydrocarbons Criteria Working Group
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Compounds
WHO	World Health Organization