CL:AIRE

RB 15

(September 2011)
ISSN 2047-6450 (Online)

research bulletin

CL:AIRE research bulletins describe specific, practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater. This bulletin describes the development of generic human-health assessment criteria for benzo[a]pyrene at former coking works sites.

Generic Human-Health Assessment Criteria for Benzo[a]Pyrene at Former Coking Works Sites

1.1 INTRODUCTION

Coking works were a subset of the UK coal carbonisation industry. Coal carbonisation involved heating coal in the absence of air to produce coke, coal gas and coal tar, and several by-products, such as ammoniacal liquors and sulphur (Department of the Environment, 1995). The primary function of coking works was to produce coke. Coke is the solid carbon residue after most of the organic components present in coal have been volatilised. However, other by-products were often also commercially exploited. From at least the 1920s coke was used in the manufacture of smokeless fuels. This use increased following the implementation of clean air legislation in the 1950s which required many homes in Britain to abandon burning coal and adopt cleaner-burning fuels.

Benzo[a]pyrene (CAS No. 50-32-8) is a yellowish crystalline solid at room temperature with a melting point of around 179ºC. Its synonyms include 3,4-benzopyrene, 6,7-benzopyrene and benzo[def]chrysene, and it is often abbreviated to BaP. Benzo[a]pyrene is a relatively high molecular weight, 5-ring polycyclic aromatic hydrocarbon (PAH) with the chemical formula $C_{20}H_{12}$ and has a low volatility and aqueous solubility. As such it is relatively persistent in the environment (Nathanail *et al.*, 2009). Benzo[a]pyrene and other PAHs occur naturally, associated with volcanoes and forest fires *etc.*, but the majority of emissions to the environment are thought to be from anthropogenic sources, such as the burning of wood or fossil fuels, foundry activities, waste incineration and motor vehicle emissions (Nathanail *et al.*, 2009). PAHs, including benzo[a]pyrene, generally occur together as complex mixtures. For example, they are significant components of crude oil and coal. However, they also account for the majority of most coal tars and pitch, which are commonly found in soils at former coking works (Nathanail *et al.*, 2009).

Benzo[a]pyrene is a typical contaminant at former coking works. The assumptions and input parameters used to derive Generic Assessment Criteria (GAC), such as the LQM/CIEH GAC for benzo[a]pyrene (Nathanail *et al.*, 2009), do not necessarily reflect typical conditions at former coking works. We have reviewed the main input parameters used to derive GACs for benzo[a]pyrene and identified values pertinent to typical conditions at former coking works. We have also derived an example Coking Works Assessment Criterion (CWAC) for the residential land use that may better reflect the risks posed by benzo[a]pyrene at such sites. We have also identified areas where site specific data are needed to avoid unnecessary conservatism due to a paucity of published data and areas where additional research would likely result in more realistic risk estimation.

In order to produce the CWAC we assumed a small terraced house and a sandy loam soil, as assumed by the Environment Agency in deriving Soil Guideline Values. It is likely that the soils at former coking works will mainly be made ground whose composition may reflect the local geology (*i.e.* may vary between clay and sandy in nature) and on site disposal or reuse of waste. It is likely that such materials will be low in natural organic matter (although significant amounts of organic contamination may be present). Consequently, in deriving the CWAC we have assumed a soil organic matter content of 1% (rather than the 6% assumed in deriving the SGVs).

We have derived CWAC for use at most coking works but there is still significant uncertainty relating to several site-specific factors, including soil and building construction. The discussion of input parameters below may be used to inform site-specific detailed quantitative risk assessments that take these factors into account.

1.2 RESIDUAL PHASE CONTAMINATION IN COKING WORK SOILS

In deriving the CWACs we have assumed that most soils at former coking works consist of natural or made ground with various coal carbonisation residues distributed through them. Coal tar, which are complex mixtures of PAHs, various hydrocarbons and other contaminants, are likely to be of particular note. Coal tar is likely to be present in a variety of forms including coatings on soil particles and discrete droplets and "tar balls" *etc.* This material does not represent "free phase" NAPL *per se,* as the soil is not saturated with them, but rather as residual NAPL contamination disseminated throughout the soil.

We have used CLEA 1.06 in the derivation of the CWACs, but SR3 (Page 53 in Environment Agency, 2009c) states that the partitioning equations used within CLEA do not take the presence of free phase contamination into account. Under such conditions, the equations used may result in predicted dissolved and/or vapour phase concentrations above theoretical saturation limits, which would result in overestimation of exposure. However, the CLEA software handbook, SR4 (Page 68 in Environment Agency, 2009a) explains that the software assumes "*that chemical concentrations and soil properties are homogenous across the site and throughout the soil profile. In reality this is not the case, and free phase contamination may occur locally at levels that on average are below the theoretical saturation limit*". This statement implies that CLEA model is suitable for use in soils containing the type of residual phase contamination envisaged to be present at coking works, but would not be suitable if soils saturated with NAPL are present. This interpretation is supported by Fig 5.1 (Page 82) within SR3 (Environment Agency, 2009c) which shows the presence of discrete "particles" of "free phase" being present within soils. The formation of such "blobs and ganglia" of residual DNAPL left in the unsaturated zone at the trailing end of a DNAPL body (*i.e.* free phase) as it migrates downwards, is also described in the DNAPL handbook (Environment Agency, 2003a).

The challenge for the contaminated land risk assessment community is to identify suitable physical-chemical parameters for the contaminant mixtures that

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make up such residual phase contamination, such as coal tar at former coking works. This is because the properties of individual contaminants within mixtures behave differently to that of the pure form. For example, it is likely that the contaminants will be significantly less mobile (*i.e.* soluble and volatile) when present in such mixtures compared to their pure state. One approach to estimating appropriate physical-chemical properties may be the application of Raoult's Law, which allows the behaviour of mixtures to be estimated based on that of the pure compound and the mole fraction of that compound within the mixture. However, there are still significant technical and scientific issues to overcome in the application of this approach as it cannot be applied directly to many of the most important algorithms within the current CLEA model that utilise parameters such as K_{aw} and K_{oc}. This document explores some of these issues but does not explicitly make use of or necessarily recommend the use of Raoult's Law in deriving the CWAC. Instead, where relevant empirical K_{oc} data exist (see Section 1.6.6), these have been used to account for some of the practical implications of Raoult's Law.

1.3 PATHWAY CONTRIBUTIONS

The "Distribution by Pathway (%)" data generated by CLEA 1.06 demonstrate that for the "Residential with home-grown produce" land use and inputs presented in Table 1 roughly 45% of exposure to benzo[a]pyrene is predicted to be via direct ingestion of soil and dust but with major contributions from outdoor dermal exposure (29%) and the consumption of home-grown produce (25%).

The inhalation of indoor dust makes only a minimal contribution (0.14%) to the exposure (Table 1). However, since the Index Dose for inhalation (ID_{inhal} 7 E-5 µg kg^{-1} body weight (BW) day^{-1}) is some 3 orders of magnitude lower than the oral Index Dose (ID_{oral} 2 E-2 µg kg^{-1} BW day^{-1}), this small contribution to the predicted exposure makes a very significant contribution to the overall CWAC (roughly 30%).

Table 1: Percentage contribution for each exposure pathway for benzo[a]pyrene as predicted by CLEA 1.06. Based on the "Residential with homegrown produce" land use (RwHGP) and a sandy loam soil with 1% SOM and using the physical–chemical inputs given in Table 2.

Pathway	Distribution by Pathway (%)
	RwHGP
direct soil ingestion	44.65
sum of consumption of homegrown produce and attached soil	25.37
dermal contact (indoor)	1.09
dermal contact (outdoor)	28.73
inhalation of dust (indoor)	0.14
inhalation of dust (outdoor)	0.00
inhalation of vapour (indoor)	0.02
inhalation of vapour (outdoor)	0.00
oral background	0.00
inhalation background	0.00
Total	**100.00**

Consequently, in deriving CWAC for benzo[a]pyrene we have had to consider the appropriateness of nearly all the input parameters, as most of the exposure pathways make a significant contribution to the resulting assessment criteria. This contrasts with benzene, for example, where it is possible to identify a limited number of dominant exposure pathways.

We have also reviewed the general appropriateness of the various parameters that influence the indoor dust exposure pathways (such as the soil-to-dust transport factor and the dust loading factor) to investigate any conservatism in these parameters. This is particularly relevant to the assessment of benzo[a]pyrene because of the apparently disproportionate contribution of indoor dust exposure to the resulting assessment criteria.

1.4 PROBABILISTIC MODELLING

LQM have developed a probabilistic model which utilises the same algorithms used within the fully deterministic CLEA (version 1.06), which has been abbreviated to PCLEA. PCLEA supports input parameters defined as independent Probability Density Functions (PDFs) rather than discrete (reasonably cautious) values. This allows the uncertainty (*i.e.* the variation present in real-world data) to be better incorporated into the model. During each model iteration a different value is selected from each PDF and the resulting exposure is calculated. Running the model numerous times results in a dataset of potential exposures, which reflects the likely range of exposures given the variability contained within the input parameter PDFs.

The assessment criteria are defined as the soil concentration at which 95% of all the predicted exposures are equal to or less than the relevant health criteria value.

Previous versions of the CLEA model, such as CLEA2002 (Defra & Environment Agency, 2002b), were also partly stochastic. The use of stochastic modelling as part of a Detailed Quantitative Risk Assessment (DQRA) is widely used within other fields of exposure modelling and risk assessment (*e.g.* GasSim and landfill gas risk assessment; ConSim and hydrogeological risk assessment). Justification for the applicability of stochastic modelling as part of a DQRA within a contaminated land setting is also provided by the Environment Agency: "Stochastic techniques are useful in analysing and characterising uncertainty within complex multimedia models" (Environment Agency, 2009b, page 25). The Agency went on to report that "These [techniques] have been used along with other techniques to produce a comprehensive [though still unpublished] sensitivity analysis of the CLEA model" (Environment Agency, 2009b, page 25).

1.5 TOXICITY

The toxicology of benzo[a]pyrene has been reviewed by Defra and the Environment Agency (2002a) and subsequently by the Health Protection Agency (HPA, 2008; HPA, 2010) to inform the selection of health criteria values.

1.5.1 Health Criteria Values

Defra and Environment Agency (2002a) recommended an oral Index Dose (ID_{oral}) of 0.02 µg kg^{-1} BW day^{-1} and an inhalation Index Dose (ID_{inhal}) of 0.00007 µg kg^{-1} BW day^{-1} for benzo[a]pyrene. These values were used to derive the LQM/CIEH GAC for benzo[a]pyrene (Nathanail *et al.*, 2009).

Oral

The ID_{oral} is reportedly based on the WHO drinking water guideline for benzo[a]pyrene of 0.7 µg L^{-1}, which represented an excess lifetime cancer risk of 10^{-5} (WHO, 2003). This was primarily based on the work of Neal & Rigdon (1967). It is also consistent with more recent reports such as that of Culp *et al.* (1998).

Neal & Rigdon (1967) exposed CFW mice (male and female) on diets containing 0.001, 0.01, 0.02, 0.03, 0.04, 0.045, 0.05 or 0.25 mg of pure benzo[a]pyrene per gram of food. The aim of the research was to identify the concentration of benzo[a]pyrene exposure needed to induce gastric tumour within 115 days.

In contrast, Culp *et al.* (1998) investigated the tumorigenicity of two coal tar mixtures compared with that of benzo[a]pyrene alone. This study involved female mice exposed to coal tar mixtures (composites of coal tars from several "coal gasification plant waste sites") at doses of between 0 and 1% in the diet. Mice were separately exposed to benzo[a]pyrene at doses of 0.5, 25 and 100 mg kg^{-1} in the diet. The Culp *et al.* study was the basis for benchmark dose modelling for benzo[a]pyrene by EFSA (EFSA, 2008) and JECFA (JECFA, 2005) resulting in $BMDL_{10}$ values of 0.07 and 0.1 mg kg^{-1} BW day^{-1} (HPA, 2010).

Although the study of Neal & Rigdon (1967) was based on benzo[a]pyrene alone, the work of Culp *et al.* (1998) appears to demonstrate that the resulting risk estimates are likely to be representative of coal-tar contamination. Consequently in deriving the assessment criteria for use at coking works, we have adopted the ID_{oral} within Tox2 of 0.02 µg kg^{-1} BW day^{-1} (Defra & Environment Agency, 2002a).

Inhalation

Defra and the Environment Agency (2002a) recommended an ID_{inhal} of 0.07 ng kg^{-1} BW day^{-1}, which has subsequently been endorsed by the HPA (2010). The ID_{inhal} was derived from the UK Expert Panel on Air Quality air quality standard for PAHs of 0.25 ng BaP m^{-3} (EPAQS, 1999), which was based on an epidemiological analysis of workers at a Canadian aluminium smelter exposed to Coal Tar Pitch Volatiles containing PAHs and other carcinogens (Armstrong *et al.*, 1994 cited in Defra & Environment Agency, 2002a). However, it should be noted that the Expert Panel on Air Quality have not subsequently considered any of the supplementary publications by Armstrong, which extend and augment his analysis (Armstrong & Gibbs, 2009). Although this is the largest known epidemiological study of the lung cancer risk relating to PAH inhalation, the latest publications still acknowledge uncertainty regarding the dose response relationship involved (Armstrong & Gibbs, 2009). While it seems clear that the inhalation of PAHs increases the risk of developing lung cancer, and that the dose response curve appears to be steep at low exposures, the dataset still appears to be relatively poor at quantifying risks in anything other than relative terms (for example no excess lifetime cancer risk estimates have been documented).

The recommended ID_{inhal} is 286-times lower than the ID_{oral} and consequently plays a dominant role in constraining the magnitude of assessment criteria in scenarios involving inhalation exposure (SoBRA, 2011). We also note that the EU air quality target for PAHs (expressed as concentration of BaP) due to be implemented in December 2012 (*i.e.* 1 ng m^{-3}) would be equivalent to a four-fold increase over the recommended ID_{inhal}. However, in the absence of a UK estimate other than that proposed by EPAQS, we have adopted the value 0.07 ng kg^{-1} BW day^{-1} in deriving the CWAC.

Dermal

Although there have been many studies of the carcinogenicity of BaP via dermal exposure, there are currently no authoritative reviews of this literature that have resulted in a quantitative risk estimate for BaP via this exposure route. However, a recent document from the Canadian Council of Ministers of the Environment stated that "Health Canada is currently in the process of developing a dermal slope factor for benzo[a]pyrene" (CCME, 2008). If and when such a value becomes available, it may help refine the estimates of risk posed from contaminated soils in the UK, although it will be difficult to use such a value in CLEA 1.06.

1.5.2 Background Intake

Benzo[a]pyrene is considered to be a genotoxic carcinogen displaying non-threshold toxicity. UK policy regarding non-threshold toxicity recently reiterated by the Environment Agency in a land contamination context (Environment Agency, 2009b) considers that any level of exposure represents some degree of risk and therefore exposure via any given route should be "as low as reasonably practicable" (ALARP). Consequently, in assessing risks from benzo[a]pyrene in soils it is not necessary to consider background exposure.

Table 2: Summary of the physical-chemical parameters for benzo[a]pyrene used to derive the LQM/CIEH GAC (Nathanail *et al.*, 2009).

Parameter	Units	Value
Air-water partition coefficient (K_{aw})	dimensionless [a]	1.76 E-6
Diffusion coefficient in air (D_{air})	m^2 s^{-1} [a]	4.38 E-6
Diffusion coefficient in water (D_{water})	m^2 s^{-1}	3.67 E-10
Relative molecular mass	g mol^{-1}	252.31
Vapour pressure (P_v)	Pa [a]	2.0 E-8
Water solubility (S)	mg L^{-1} [a]	3.8 E-3 (25°C)
Organic carbon-water partition coefficient (K_{oc})	Log (cm^3 g^{-1})	5.11
Octanol-water partition coefficient (K_{ow})	Log (dimensionless)	6.18
Dermal absorption fraction (ABS_d)	dimensionless	
Soil-to-plant concentration factor for green vegetables	mg kg^{-1} plant (FW or DW) per mg kg^{-1} soil (DW)	Model
Soil-to-plant concentration factor for root vegetables	mg kg^{-1} plant (FW or DW) per mg kg^{-1} soil (DW)	Model
Soil-to-plant concentration factor for tuber vegetables	mg kg^{-1} plant (FW or DW) per mg kg^{-1} soil (DW)	Model
Soil-to-plant concentration factor for herbaceous fruit	mg kg^{-1} plant (FW or DW) per mg kg^{-1} soil (DW)	Model
Soil-to-plant concentration factor for shrub fruit	mg kg^{-1} plant (FW or DW) per mg kg^{-1} soil (DW)	Model
Soil-to-plant concentration factor for tree fruit	mg kg^{-1} plant (FW or DW) per mg kg^{-1} soil (DW)	Model
Soil-to-dust transport factor (TF)	g g^{-1} DW	0.5
Sub-surface soil to indoor air concentration factor	dimensionless	1

[a] at 10°C; FW - fresh weight; DW - dry weight

1.6 PHYSICAL-CHEMICAL CHARACTERISTICS

The parameters relating to the physical-chemical characteristics of BaP used in deriving the LQM/CIEH GAC (Nathanail *et al.*, 2009) are presented in Table 2 and were mainly based on the recommendations presented in SR7 (Environment Agency, 2008). The parameters in SR7 are superficially intended to represent benzo[a]pyrene as an isolated, pure compound. However, at a coking works, BaP is likely to be one component of various complex mixtures such as coal tars, distillates and condensates. In such mixtures, the physical properties of component substances differ from those of the pure substances. Consequently, dependent on the sources of the information underpinning the SR7 recommendations (Environment Agency, 2008), the physical-chemical properties of BaP at a coking works may differ significantly from those used to derive the LQM/CIEH GAC for 'pure' BaP.

1.6.1 Raoult's Law

Raoult's Law states that in mixtures such as coal tars the effective vapour pressure and solubility of each component compound (*i*) depends on the vapour pressure or solubility of pure *i* and the mole fraction of *i* within the mixture. The mole fraction can be calculated as (Environment Agency, 2010):

$$x_i = MF_i \times \frac{MW_o}{MW_i}$$

Where:

x_i = mole fraction of compound i in a mixture
MF_i = mass fraction of compound i in a mixture
MW_i = molecular weight of compound i (g mole^{-1})
MW_o = approximate molecular weight of the mixture (g mole^{-1})

A literature search was conducted to determine the mole fraction of benzo[a]pyrene in coal tar or other residues likely to be associated with former coking works. Only a single paper (Brown *et al.*, 2005) was identified that contained the relevant details for 10 coal tar samples (see Table 3). The mole fraction of benzo[a]pyrene in these samples ranged from 0.002 to 0.030 with an average of 0.008. Consequently, we believe that a mole fraction of 0.05 should be a cautious estimate for the concentrations of benzo[a]pyrene in most types of coal tar.

Table 3: Average molecular weight and benzo[a]pyrene concentration in 10 coal tars from nine former manufactured gas plants in the eastern US (After Brown *et al.*, 2005). The calculated mass and mole fractions of benzo[a]pyrene in each sample are also presented.

Site	Average molecular weight (g mole^{-1})	Benzo[a]pyrene concentration (mg kg^{-1})	Benzo[a]pyrene mass fraction (Dimensionless)	Benzo[a]pyrene mole fraction (Dimensionless)
1	2143	678	0.000678	0.006
2	392	2610	0.00261	0.004
4M	990	1150	0.00115	0.005
4H	728	1940	0.00194	0.006
5	3213	2340	0.00234	0.030
6	621	816	0.000816	0.002
7	1099	864	0.000864	0.004
8	741	1960	0.00196	0.006
9	316	4100	0.0041	0.005
10	2303	1570	0.00157	0.014

1.6.2 Air-water partition coefficient (K_{aw})

The air-water partition coefficient is primarily used within CLEA to estimate vapour inhalation. The recommended K_{aw} at 10ºC for benzo[a]pyrene in SR7 (Environment Agency, 2008) is 1.76 E-6 based on several literature values for Henry's Law Constant at 25ºC. When corrected to 10ºC the literature values presented in SR7 range from 1.77 E-6 to 1.96 E-6. Given the minimal variation and negligible impact that this value has on the resulting assessment criteria, we have modelled this parameter deterministically using the value (1.76 E-6) recommended in SR7.

1.6.3 Diffusion coefficient in air (D_{air}) and Diffusion coefficient in water (D_{water})

The values of D_{air} and D_{water} presented in SR7 (Environment Agency, 2008) were estimated using appropriate methods from parameters relevant to pure benzo[a]pyrene. While it is possible that D_{air} may be affected by the presence of a mixture, any effect is likely to be small. Furthermore, the CLEA model is relatively insensitive to both these parameters and consequently they have a minimal influence on the resulting assessment criteria. Both D_{air} and D_{water} have been modelled deterministically using the values recommended in SR7.

1.6.4 Relative molecular mass

As expected, there is little disagreement in the literature regarding the molecular mass of BaP. Consequently, the relative molecular weight has been modelled deterministically using the SR7-recommended value (252.31 g mol^{-1}).

1.6.5 Vapour pressure (Pv) and Water solubility (S)

Vapour pressure and water solubility are not used directly in estimating exposure to organic contaminants within CLEA 1.06. They are only used to calculate soil saturation limits (C_{sat}) that indicate the potential presence of free phase contaminant.

The vapour pressure at 10ºC recommended for benzo[a]pyrene in SR7 (Environment Agency, 2008) is 2.0 E-8 Pa, which was estimated by the Grain-Watson method. Two values at 25ºC are cited in Appendix A, if corrected to 10ºC these values are equivalent to 1.38 E-7 and 6.0 E-7 Pa. Values cited in an earlier review (Environment Agency, 2003b), when corrected to 10ºC, range between 1.68 E-10 and 5.51 E-6 Pa. These values are all believed to refer to pure benzo[a]pyrene. It is likely that in a mixture, such as coal tar, the effective vapour pressure would be even lower. For example, Raoult's law would suggest that its partial vapour pressure would be roughly 1 E-9 Pa, assuming a mole fraction of 0.05.

The aqueous solubility of benzo[a]pyrene recommended in SR7 (Environment Agency, 2008) is 3.8 E-3 mg L^{-1}. This is based on literature values of 2.90E-3, 3.80E-3 and 4.30E-3 mg L^{-1}. An earlier review (Environment Agency, 2003b) reported values between 1.7 E-3 and 8.0 E-3 mg L^{-1}. In a mixture, such as coal tar, it is likely that the effective solubility, as determined by Raoult's law, would be nearer to 1.9 E-4 mg L^{-1}.

However, given that pure benzo[a]pyrene already has very low volatility and solubility, and that the contribution from the vapour inhalation pathways is therefore negligible, it seems unnecessary to try to refine these parameters, because the effect on any assessment criteria is likely to be minimal. Consequently, we have used the SR7 recommended values in deriving CWAC values.

1.6.6 Organic carbon-water partition coefficient (K_{oc})

The soil-water partition coefficient (K_d) is used in the CLEA model to predict how likely a chemical is to sorb to soil as opposed to dissolving in pore water. K_{oc} is the ratio of the amount of an organic chemical adsorbed per unit mass of organic carbon in the soil to its concentration at equilibrium in water (Lyman *et al.*, 1990). It is used as a more consistent measure of the extent to which organic chemicals partition between sorbed and dissolved phases than the K_d (Environment Agency, 2008). Ideally, K_{oc} values should be determined experimentally using methods specifically designed to determine partitioning of organics between the soils and an environmentally-relevant leachant (Environment Agency, 2000). For example, batch or column tests using simulated rainwater. However, such data are not generally available for soils contaminated with coking work wastes.

Many variables affect the partitioning of organic chemicals between soil and water. It is likely that, as with many other parameters, the K_{oc} of a chemical in a complex mixture (*e.g.* a coal tar) will differ from that of the pure compound. Furthermore, in low organic matter soils (such as much made ground), it is likely that the organic contamination present in the form of coal tar will represent the majority (or at least a significant proportion) of the organic material in the soil. Under these circumstances it will be the coal tar-water partition coefficient ($K_{ct/w}$) rather than the K_{oc} that dictates soil-water partitioning of organic contaminants.

Endo & Schmidt (2006) reviewed the, admittedly limited, available data regarding the partitioning of benzo[a]pyrene in coal tar impacted soils and identified two estimates of the log $K_{ct/w}$ for benzo[a]pyrene: 7.11 and 7.01. These values are significantly higher than the value of 5.11 recommended as the log K_{oc} in SR7 (Environment Agency, 2008). This suggests that K_{oc} values for natural soils may underestimate the actual partitioning in coal tar impacted soils.

Consequently, rather than use K_{oc} values from the literature we have used data from the former Avenue coking works to estimate the likely range of K_{oc} for benzo[a]pyrene encountered at coking works. The K_{oc} can be estimated as:

$$K_{oc} = \frac{K_d}{f_{oc}}$$

Where:

K_{oc} = organic carbon-water partition coefficient (L kg^{-1})
K_d = soil-water partition coefficient (L kg^{-1})
F_{oc} = fraction of organic carbon in soil (dimensionless)

$$K_d = \frac{C_s}{C_l}$$

Where:

C_s = Concentration of organic contaminant in soil (mg kg^{-1})
C_l = Concentration of organic contaminant in leachate (mg L^{-1})

Where data for C_s, C_l and f_{oc} are available for the same sample it is possible to derive an site-specific estimate of K_{oc} for that sample. We therefore identified suitable samples collected at the former Avenue coking works for which benzo[a]pyrene concentrations in soil and in solution (*i.e.* leachate analysis) were available, together with an estimate of the fraction of organic carbon in the soil. The fraction of organic carbon, which included natural organic matter and organic contamination, was estimated from Loss on Ignition (LOI%) data by assuming the LOI gave a reasonable estimate of the Soil Organic Matter (SOM%) ($f_{oc} \approx$ SOM%÷172) and Total Organic Carbon data ($f_{oc} \approx$ TOC÷100). In practice, only a relatively small proportion of estimates of K_{oc} used the LOI% data (18%).

Table 4: Summary statistics for estimates of log K_{oc} for benzo[a]pyrene calculated for soils at the former Avenue coking works

Statistic	Benzo[a]pyrene
Minimum	3.19
Maximum	8.82
N	96
Mean	5.77
Median	5.87
SD	1.01

The resulting dataset contained 96 estimates of the log K_{oc} for benzo[a]pyrene over a significant range of contaminant concentrations and the range of material types. The dataset (see Table 4) ranges from 3.19 to 8.82 (this represents a range of some 5 orders of magnitude for K_{oc}), which suggests that there is considerable variation in the partitioning behaviour of benzo[a]pyrene across the range of materials present at the Avenue site. Although the mean value is similar to the value of 5.11 recommended for pure benzo[a]pyrene in SR7 (Environment Agency, 2008), the dataset as a whole is considered to better represent the partitioning of benzo[a]pyrene between soil and water at a coking works than a single deterministic value. Consequently, we have modelled log K_{oc} of benzo[a]pyrene using a PDF based on the Avenue coking works dataset (see Figure 1). The *best fit* distribution is considered to be a normal distribution (Mean 5.77, SD 1.01), which has been truncated at an upper (8.3) and a lower 4.0) value based on the range of values reported by the Environment Agency (Environment Agency, 2003b). Truncating the range of values (especially the lower end) was considered valid in order to avoid the effect of unrealistically low estimates of K_{oc} skewing the impact of the vapour inhalation pathway on the assessment criteria at the 95th percentile. The log $K_{ct/w}$ values cited by Endo & Schmidt (2006) fall towards the upper end of this range (*i.e.* 7.01-7.11) and so provides some justification for the upper limit.

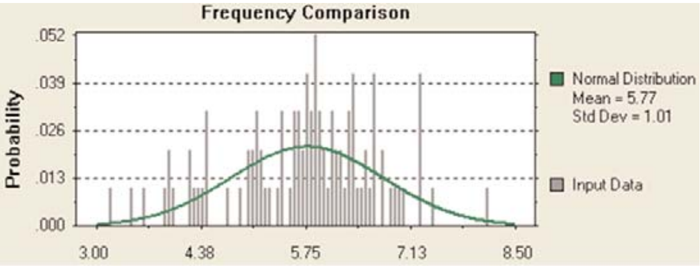

Figure 1: Probability density function for $\log_{10}K_{oc}$ for benzo[a]pyrene for coking works impacted soils (n = 96)

1.6.7 Octanol-water partition coefficient (K_{ow})

The octanol-water partition coefficient (K_{ow}) is the ratio of a chemical's concentration in octanol to its concentration in the aqueous phase of an octanol-water system (Lyman *et al.*, 1990). The K_{ow} is often used in environmental modelling as a surrogate for the lipophilicity of a chemical and its tendency to accumulate in the fatty tissues of plants and animals.

Within CLEA, K_{ow} is primarily used as an indication of contaminant lipophilicity to predict plant uptake characteristics. Logically then, it is the K_{ow} of pure benzo[a]pyrene that should be used, as the K_{ow} is not being used to model fate and transport within the source (*i.e.* coal tar) but to estimate its behaviour once taken into plants.

The Environment Agency have reviewed the K_{ow} of benzo[a]pyrene on two occasions (Environment Agency, 2003b; Environment Agency, 2008). In the former, K_{ow} values ranging between 4.05 and 8.50 were identified, whereas in the latter a consensus value of 6.18 was recommended. We have therefore adopted a triangular PDF (min 4.05, most likely 6.18, max 8.50). We have also conducted a separate assessment of the accuracy with which CLEA predicts the plant uptake of benzo[a]pyrene based on its K_{ow} (see Section 1.7).

1.6.8 Dermal absorption fraction (ABS_d)

Combined indoor and outdoor dermal exposure accounts for roughly 30% of overall exposure to BaP under the "residential with homegrown produce" land use (see Table 1). Consequently, the suitability of the default value for ABS_d recommended in SR7 (Environment Agency, 2008) for use with respect to the complex contaminant mixtures found at coking works has been evaluated.

CLEA 1.06 estimates the uptake of contaminants via the skin using a model developed by the USEPA. This takes account of the current lack of experimental data relating to the soil-to-skin permeation rates for most chemicals and other uncertainties by adopting a relatively simple "absorbed fraction per event" approach. In this approach each chemical is given a dermal adsorption fraction (ABS_d), which represents the fraction of the dose adhered to the skin that is absorbed per event. The USEPA (USEPA, 2004) have suggested suitable values for ABS_d for only a limited number of chemicals based on a review of experimental data. However, one of these chemicals is for "benzo[a]pyrene and other PAHs", where a value of 0.13 has been recommended and this value is cited in SR3 (Environment Agency, 2009c).

The value is derived from an experiment considering the percutaneous absorption of [^{14}C]benzo[a]pyrene by rhesus monkeys (Wester *et al.*, 1990). These experiments applied soil artificially spiked with pure benzo[a]pyrene to the skin of four monkeys and measured the recovery of ^{14}C in urine compared to urinary ^{14}C recovery following intravenous administration of a similar dose of radio-labelled benzo[a]pyrene. The results for a 24 hr dermal exposure indicated that 13.1%, 10.8%, 18.0% and 11.0% of the applied dose had been absorbed across the skin in each of four monkeys.

It is possible that the dermal absorption of benzo[a]pyrene from a coal-tar contaminated soil will be less than that from a soil artificially spiked with pure benzo[a]pyrene, as used by Wester *et al.* (1990). Although we have not been able to find evidence in the literature to support this hypothesis, it is of note that Stroo *et al.* (2005), as well as studying oral adsorption (see Section 1.8.3), reported dermal absorption factors for benzo[a]pyrene in gas-work soils contaminated with lampblack of between 0.14% and 1.05%. Although these values may not be directly relevant to coal-tar contaminated soils, they provide an indication that this parameter could be expected to be lower for coking works impacted soils, should data become available.

In the absence of data to support a reduced ABS_d in relation to coal tar contaminated soils, we have used a normal distribution (Mean 13.2, SD 3.3) to better represent the data presented by Wester *et al.* (1990) within the model.

1.7 PLANT UPTAKE MODELLING

1.7.1 CLEA default algorithms

Due to the limited data on soil-to-plant concentration factors for most contaminants, the CLEA model includes a number of generic plant uptake algorithms or models to predict the uptake of organic contaminants in several classes of fruit and vegetables (See Table 5). These algorithms, in general, represent simple relationships between a chemical's K_{ow} and its reported uptake by plants.

Table 5: Generic models for predicting soil-to-plant concentration factors according to produce groups (Environment Agency, 2009c)

Produce Group	Generic model	Comments
Green vegetables	(Ryan et al., 1988)	Derived from uptake data for o-methylcarbamoyloximes and substituted phenylureas by barley (log K_{ow} -0.57 to 3.7)
Root vegetables	(Trapp, 2002)	Theoretical model validated with uptake data for several PAHs
Tuber vegetables	(Trapp et al., 2007)	Theoretical model validated with uptake data for 13 PAHs
Herbaceous fruit	No suitable model identified	
Shrub fruit	No suitable model identified	
Tree fruit	(Trapp et al., 2003)	Theoretical model limited validation using data for 2 PAHs and 2 dioxins

The Environment Agency review of plant uptake algorithms (Environment Agency, 2006) concluded that the algorithms "over-predicted root concentrations by at least one order of magnitude". This is consistent with the findings of others (Samsøe-Petersen *et al.*, 2002). The result for algorithms that predict shoot concentrations was more varied with some over- and some under-predicting in comparison to empirically-derived concentration factors reported in the literature. The report also concludes that "Many plant uptake models have been poorly validated, with limited supporting studies under a range of different soil and plant conditions" and that "the literature is limited by the availability of good quality experimental data for a broad range of organic industrial chemicals".

It is therefore clear that, while the use of generic plant uptake algorithms can provide predictions of the soil-plant concentration factors for organic contaminants when these values are scarce in the scientific literature, the accuracy of these predictions is by no means guaranteed. Thus, the generic plant uptake algorithms within CLEA should be used with caution.

The CLEA model does not explicitly report the soil-plant concentration factors (CF) predicted by the various algorithms. However, CF values can be back calculated from the media concentrations for the various fruit and vegetable types that are presented in the CLEA reports using the equation:

$$CF = \frac{C_{plant}}{C_s}$$

Where:

CF = soil-plant concentration factor (mg g^{-1} FW plant per mg g^{-1} DW soil)
C_{plant} = chemical concentration in edible plant issue (mg g^{-1} FW plant)
C_s = chemical concentration in soil (mg g^{-1} DW soil). In this case, C_s is the soil concentration derived as the assessment criteria

Based on CLEA modelling for pure benzo[a]pyrene, using the default inputs in SR7, assuming a "residential with home-grown produce" land use and a sandy loam soil with 1% soil organic matter, Table 6 presents the CF values for benzo[a]pyrene predicted by the generic algorithms.

Table 6: Media concentrations for benzo[a]pyrene predicted by CLEA 1.06 under the residential with homegrown produce land use and 1% soil organic matter. The resulting soil-plant concentration factors for each produce group has been predicted

	Predicted media concentration mg kg^{-1} FW plant	Assessment criteria (i.e. soil concentration) mg kg^{-1} DW soil	Soil-plant concentration factor
Green vegetables	2.03 E-3	0.826	2.46 E-3
Root vegetables	1.10 E-2	0.826	1.33 E-2
Tuber vegetables	7.79 E-3	0.826	9.43 E-3
Herbaceous fruit	NA	0.826	NA
Shrub fruit	NA	0.826	NA
Tree fruit	1.29 E-5	0.826	1.56 E-5

1.7.2 Plant uptake of benzo[a]pyrene

The Environment Agency (2006) suggested that dry deposition of suspended particles with subsequent permeation into plant cuticles is likely to be a major pathway of contamination for benzo[a]pyrene. This route of exposure is not explicitly included in the generic plant uptake algorithms. The Environment Agency identified case studies in the scientific literature which presented experimentally-derived CF values, and used them to examine the performance of various generic plant uptake algorithms. Several of these case studies involved PAHs, and one included benzo[a]pyrene. In general, the models over-predicted uptake of PAHs by plants and this over-prediction was greatest for the larger more lipophilic PAHs (Environment Agency, 2006).

One case study derived soil-plant concentration factors for a number of PAHs, including benzo[a]pyrene, from data presented by Kipopoulou *et al.* (1999) for vegetables grown in industrially-impacted soils. The concentration factors were derived on the basis of median soil and vegetable concentrations. For benzo[a]pyrene the concentration factors derived were: 5.42 E-3 for carrot (root vegetables); 3.33 E-3 for cabbage and 5.83 E-3 for lettuce (green vegetables). The cabbage and lettuce values are comparable to the value of 2.46 E-3 derived for green vegetables by the generic CLEA algorithm, but the value for carrot value is roughly half that predicted for root vegetables by CLEA (1.33 E-2).

We undertook a detailed search of the scientific literature to identify sources of information describing the uptake of benzo[a]pyrene from soil by plants in order to investigate the accuracy of the generic plant uptake algorithms used within CLEA with respect to benzo[a]pyrene and to identify potentially more appropriate values. We identified a number of relevant studies (Edwards, 1983; Fismes *et al.*, 2002; Linne & Martens, 1978; Sims & Overcash, 1983; Zohair *et al.*, 2006).

Of particular relevance is the work of Fismes *et al.* (2002) as this involved vegetables grown in soils collected from former gasworks in eastern France. The study looked at several tissues in lettuce, carrot and potato. Unfortunately, the soil-plant concentration factors presented are primarily for the uptake of total PAHs collectively, rather than specifically for BaP. However, the data are sub-divided into 2-, 3-, 4- and 5-6 ring PAHs. We have used this information to estimate the maximum concentration factors in the various plant tissues for BaP by making the assumption that the 5-6 ring congeners represent BaP. The most important fact highlighted by this work is an inverse relationship between soil concentration and concentration factor; soils with low concentrations of PAHs have high concentration factors (see Table 7). Such a degree of co-linearity may be expected given how the plant concentration factor is derived (*i.e.* inversely proportional to soil concentration). However, the significance of this effect is that it implies that uptake of PAHs is not a continuous linear process as assumed in the CLEA model (CLEA assumes the plant concentration is a constant proportion of that in the soil). Data provided by some of the other studies identified (see below) also indicate an inverse relationship between CF and soil concentration.

Even the highest estimates presented in Table 7 are much lower than the generic CLEA model defaults predicted for green vegetables (2.46 E-3), root vegetables (1.33 E-2) and tuber vegetables (9.43 E-3).

Zohair *et al.* (2006) present soil and plant concentration data for benzo[a]pyrene in four varieties of potato and three varieties of carrots. From this data we have estimated the soil-plant concentration factor for benzo[a]pyrene in each variety (see Table 8). Again these values are significantly below those predicted by the generic algorithms used by CLEA.

In their review of the fate of PAHs in higher plants, Sims & Overcash (1983) describe work undertaken in the former USSR using radio-labelled BaP. This work suggests BaP can be metabolised by a range of plant species, including corn, bean, alfalfa, chick pea, cucumber, pumpkin and several grass species, to form low-molecular weight organic acids. With 5-57% of radioactivity in roots and 2-62% in leaves being in the form of organic acids. The metabolism occurred primarily at the point of uptake (*i.e.* BaP taken up by the roots was mainly metabolised within the roots).

Table 8: Soil-plant concentration factors for benzo[a]pyrene (mg kg^{-1} FW plant per mg kg^{-1} DW soil) derived for 4 varieties of potato and 3 varieties of carrot. Values the mean of 3 replicates ± standard error (After Zohair *et al.*, 2006).

Vegetable (Variety)	CF$_{BaP}$	SE
Potato (Cara)	4.92E-4	7.37E-5
Potato (Valour)	2.41E-3	3.65E-4
Potato (Kestrel)	1.80E-4	2.06E-5
Potato (Desiree)	7.84E-5	8.51E-6
Carrot (Major)	8.07E-4	9.22E-5
Carrot (Nairobi)	4.01E-3	5.92E-4
Carrot (Autumn Kings)	4.03E-3	6.27E-4

1.7.3 What concentrations of benzo[a]pyrene may be expected within home grown vegetables?

In trying to derive relevant soil-plant concentration factors it is sensible to investigate the reported concentrations of benzo[a]pyrene within the relevant crop types for a range of contaminated soils consisting of a similar matrix type to soils derived from coking works wastes. Utilising data from the above literature sources it is possible to estimate likely plant concentrations to consider how this varies across plant species and soil contamination levels. The criteria used for utilising the data were: only data for food plants grown in soil or sand have been considered if BaP concentrations were presented for both soil and crop; where ranges were presented the mean has been used; where concentrations were reported as <LOD (limit of detection), the LOD has been used; all data have been assumed to be FW plant; data for plant oils have been omitted.

Figure 2 presents the literature reported or estimated (using literature reported CFs and stated soil concentrations) concentrations of benzo[a]pyrene within some of the relevant CLEA vegetable types (tubers, root vegetables and green vegetables). The data included within Figure 2 have been limited to descriptions that are similar to a generic sandy loam soil type, with the range in soil BaP concentrations ranging over 4-5 orders of magnitude (*i.e.* 2.00 E-5 to 2.99 E+2 mg kg^{-1} DW). It is clear that there is no correlation between plant concentration for any of the vegetable types and soil concentration, which contradicts the generic default situation predicted by the CLEA model (shown as a red dotted line). The literature data suggest that at higher soil concentrations (*i.e.* above those at the GAC of circa 1 mg kg^{-1}) the generic CLEA model could significantly over-predict field observations (especially for tubers). This over-prediction may be more pronounced if some of the data are excluded (*i.e.* that of Muller, 1976), as indicated within Figure 2, on the grounds that it was extracted by Edwards (1983) by estimating data from a graphical plot and it is unclear whether the plant data were presented on a fresh or dry weight basis.

Table 7: Soil-plant concentration factor data for total PAHs (CF$_{PAH}$), the estimated proportion of 5-6 ring congeners and the resulting estimate of the soil-plant concentration factor for benzo[a]pyrene (CF$_{BaP}$). Concentration factors are in units of mg kg^{-1} FW plant per mg kg^{-1} DW soil. The benzo[a]pyrene concentration in each soil (PAH1-5) is also presented. The percentage of 5-6 ring PAHs has been estimated from Fig. 2 (After Fismes *et al.*, 2002).

	Soil	Lettuce			Carrot			Potato		
	mg kg^{-1} DW	CF$_{PAH}$	% 5-6 ring	Estimated CF$_{BaP}$	CF$_{PAH}$	% 5-6 ring	Estimated CF$_{BaP}$	CF$_{PAH}$	% 5-6 ring	Estimated CF$_{BaP}$
PAH1	0.443	3.30E-3	20%	**6.60E-4**	1.34E-3	30%	**4.02E-4**	1.00E-3	25%	**2.50E-4**
PAH2	7.285	4.40E-4	40%	**1.76E-4**	5.00E-5	30%	**1.50E-5**	4.00E-5	30%	**1.20E-5**
PAH3	21.955	1.60E-4	50%	**8.00E-5**	2.00E-5	25%	**5.00E-6**	2.70E-5	50%	**1.35E-5**
PAH4	144.072	8.00E-5	55%	**4.40E-5**	7.00E-6	30%	**2.10E-6**	2.00E-6	20%	**4.00E-7**
PAH5	299.429	6.00E-5	40%	**2.40E-5**	4.00E-6	35%	**1.40E-6**	1.00E-6	50%	**5.00E-7**

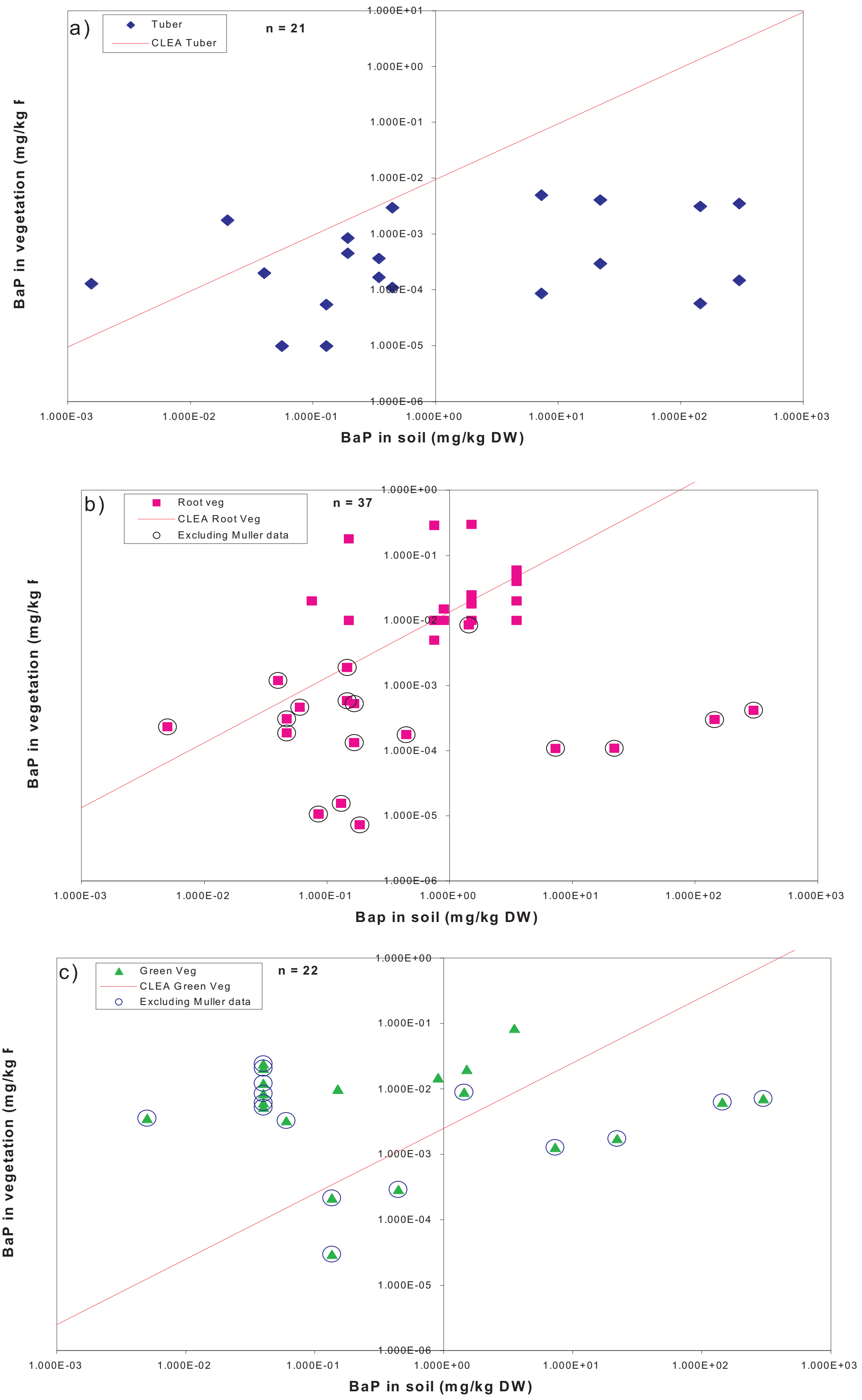

Figure 2: Variation (against concentration of BaP in soil) in the literature reported (estimated and observed) concentrations for BaP in a) tubers (pulp/core & peel), b) root vegetables (carrot (core & peel) & radish) and c) green vegetables (lettuce, cabbage, spinach, parsley, carrot tops and radish tops) (Note: logarithmic scales)

1.7.4 *How to model the plant uptake of benzo[a]pyrene?*

Given that our literature review suggests the current generic approach within the CLEA model may over predict plant concentrations significantly and that experimentally measured plant concentrations appear to be both invariant with soil concentration, but also highly variable at any particular concentration, an alternative approach can be derived.

By plotting the literature reported or estimated values of plant CFs against the reported soil concentrations for each of the main vegetable types it is plausible to derive vegetable specific relationships that incorporate these observations. The relationships observed from the identified literature sources (Figure 3) indicate that a significant amount of the variation in plant CF can be accounted for by the variation in soil concentration. The following observations are also possible:

- there are differences in concentration between the peel and core/pulp of tubers, with levels of uptake higher within the former;
- carrots generally exhibit lower uptake compared to other species of root vegetables (*i.e.* radish);
- there are limited data for green vegetable species; and
- the default generic CLEA model CF for tubers and root vegetables is much higher at typical urban concentrations of benzo[a]pyrene than may be expected from the literature, although there is reasonable agreement for green vegetables.

Linear regression (least squares) statistics were determined for the $\log_{10}$ CF versus $\log_{10}$ soil concentration plots for each of the three vegetable types for which sufficient literature data exists, which provided statistics for the equation of the form:

$$\log CF_{veg\_type} = m_{veg\_type} \cdot \log C_s + c_{veg\_type}$$

Where:

CF_{veg_type} = soil-plant concentration factor for benzo[a]pyrene in that vegetable type (mg kg^{-1} FW vegetable per mg kg^{-1} DW soil)
m_{veg_type} = slope value for that vegetable type – see Table 9
C_s = concentration of benzo[a]pyrene in soil (mg kg^{-1} DW soil)
c_{veg_type} = intercept value for that vegetable type – see Table 9

Table 9: Parameters used for predicting the soil to plant concentration factors for vegetable types for which sufficient literature data are available

Veg Type	m	SE(m)	c	SE(c)	N	r
Green Veg	-0.97162	0.13963	-2.30113	0.17666	22	0.84
Root Veg	-0.76278	0.20737	-2.55694	0.20404	37	0.53
Tuber	-0.78714	0.12278	-3.57305	0.18148	21	0.83

Note: m=slope; c=intercept; SE= standard error; N=number of observations; r= Pearson product moment correlation coefficient.

These data allow simple substance-specific formulae which are based on the available empirical data to be derived to predict soil-plant concentration factors for green vegetables, root vegetables and tuber vegetables. These formulae can be used within CLEA 1.06. However, within PCLEA we have used more complex formulae to mimic the variation in CF observed in the literature at any given soil concentration.

To achieve this, standard error estimates for parameters m and c (see Table 9) were used to estimate the uncertainty within the predicted soil-plant concentration factors at any particular soil concentration. It was assumed that uncertainty in soil concentrations was minimal relative to that in the other parameters derived. A PDF for the $\log_{10}$CF was then generated by assuming that the estimated uncertainty in $\log_{10}$CF was normally distributed about the mean fitted line with a mean of 0 and standard deviation of 1 at any particular soil concentration. This approach allows PCLEA to generate soil to plant concentration factor estimates for tubers, root and green vegetables, which follow the simple formulae described above but also allow for the variation around these lines seen in Figure 3.

The above approach for predicting soil to plant concentration factors could not be used for herbaceous, shrub or tree fruits due to a lack of literature data sourced. Therefore, the default generic approach taken for generating GACs and SGVs has been taken. This assumes that the contribution to dietary intake of contaminants from herbaceous and shrub fruits is negligible and a generic modelling approach is assumed for tree fruit (dependent upon the K_{ow}).

1.8 OTHER PARAMETERS

1.8.1 *Soil-to-dust transport factor (TF)*

Within CLEA a default TF of 0.5 is adopted for residential land uses (Environment Agency, 2009c). This is reportedly based on the “middle of the range” reported by RIVM (2004) and USEPA (1998). These reports summarise a number of sources that suggest that there is variability in the level of soil-to-dust transport (*i.e.* 30 to 70%), but the data presented do not allow a probability density function to be fully parameterised.

Consequently, we have elected to use the distribution for the fraction of soil in house dust proposed by Trowbridge & Burmaster (1997), which is a lognormal distribution (Geometric mean 0.4162, Geometric Standard Deviation 1.4424). This distribution has an arithmetic mean of 0.445, slightly below the default value used within CLEA. This approach also accounts for the uncertainty in this parameter.

1.8.2 *Dust* loading *factor*

The Dust loading factor is used in modeling indoor dust exposure within CLEA 1.06 to estimate the accumulation and resuspension of dust in indoor air. This phenomenon is the reason for indoor dust concentrations generally being higher than those found in outdoor ambient air. CLEA adopts a default value of 50 μg m^{-3} for residential properties based on the available literature (Environment Agency, 2009c). However, again the data in SR3 are not sufficient to allow a probability density function to be fully parameterised. RIVM (2004) also considered dust loading factors and present a summary of various studies reporting mean indoor dust concentrations ranging from 12.6 μg m^{-3} to 157 (± 39) μg m^{-3}, the latter represented a school environment.

We have, therefore, used data presented by Sally Liu *et al.* (2003) for the concentration of PM_{10} in indoor air during a study in Seattle between October 1999 and May 2001 to derive a PDF that represents the variation in the dust loading of indoor air at residential properties. This study is the basis of the lower indoor dust concentration cited above and is part of the data considered in SR3 (Environment Agency, 2009c). The PDF adopted is a lognormal distribution (Geometric mean 10.6, Geometric SD 1.9). The data on which this was based ranged from 0.6 μg m^{-3} to 62.2 μg m^{-3}, with a mean of 12.6 ±7.8.

1.8.3 *Oral bioaccessibility*

The CLEA model makes the cautious default assumption that 100% of the soil contaminant is available for absorption by the body following oral exposure. It is now widely accepted that this may not be the case for many inorganic contaminants, such as arsenic (CIEH, 2009). However, the bioavailability of organic contaminants has only recently started to be addressed by the scientific community.

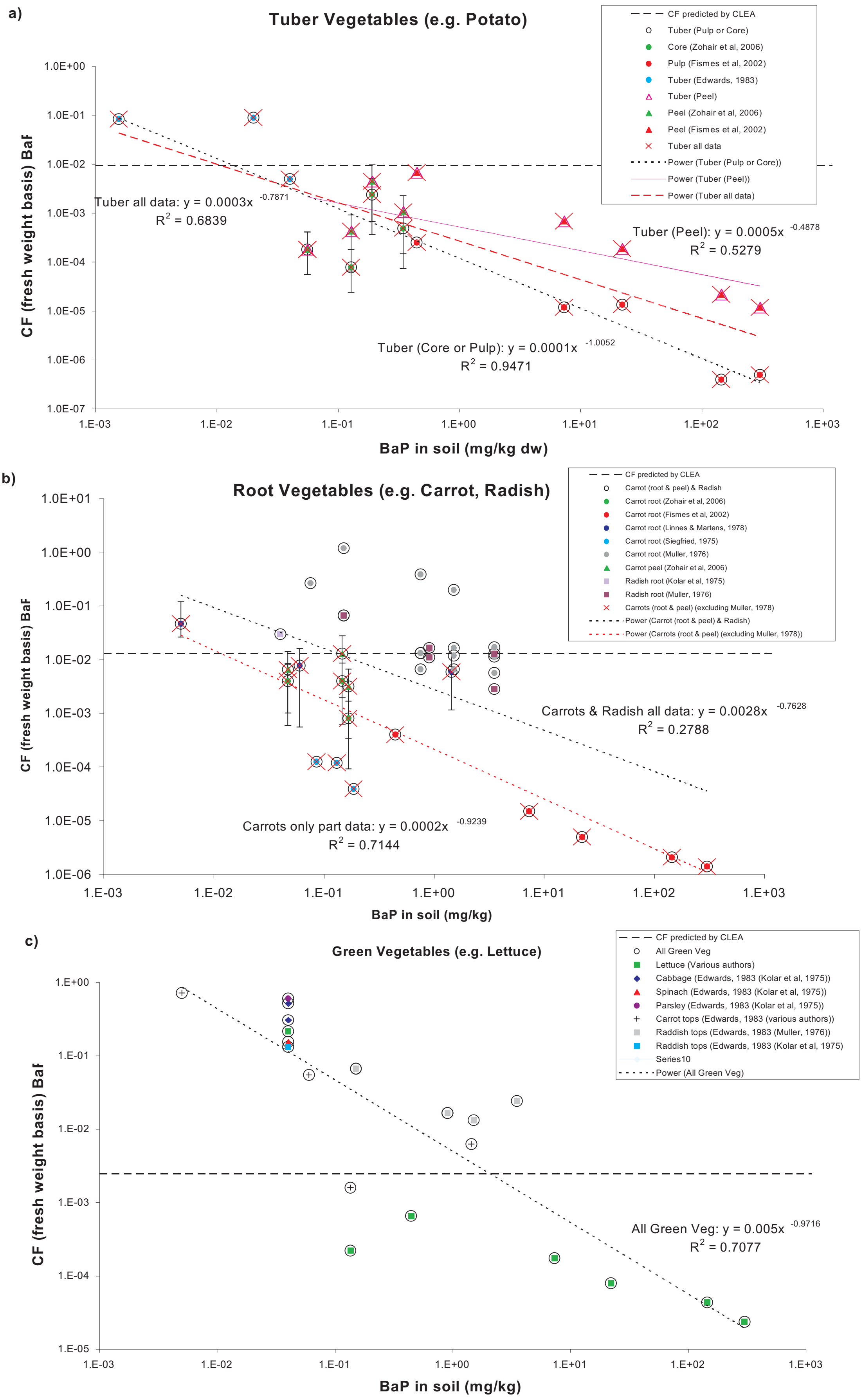

Figure 3: Literature values of BaP CF against soil concentration for a) tubers, b) root vegetables and c) green vegetables (data sources & estimated standard errors as indicated)

Researchers have recently reported both oral and dermal bioaccessibility estimates for PAHs in industrially-contaminated soils. Cave *et al.* (2010) used two experimental methods, the FOREhST and SHIME methods, to estimate the bioaccessible fraction of 6 PAHs in 11 gasworks soils (see Table 10). These results indicate that the bioaccessibility of BaP in coal tar contaminated soils may be between 17% and 50%. Weyand *et al.* (1995) reportedly obtained values as low as 11%.

Table 10: Average bioaccessible fraction of benzo[a]pyrene (n=3) ± SD in 11 different gas work soils measured using two different methods (After Cave *et al.*, 2010)

	Bioaccessible fraction %	
	FOREhST	SHIME
Soil No. 1	33.1 ± 5.9	18.2 ± 21.8
Soil No. 2	46.8 ± 0.8	51.6 ± 1.9
Soil No. 3	34.5 ± 7.0	39.9 ± 11.1
Soil No. 4	35.6 ± 8.8	25.5 ± 13.4
Soil No. 5	36.2 ± 5.2	32.3 ± 3.9
Soil No. 6	42.2 ± 5.9	31.1 ± 17.5
Soil No. 7	20.7 ± 3.5	17.8 ± 7.1
Soil No. 8	25.6 ± 8.2	24.8 ±13.0
Soil No. 9	25.6 ± 31.3	19.1 ± 3.0
Soil No. 10	46.1 ± 12.2	38.8 ± 23.9
Soil No. 11	50.4 ± 15.9	27.0 ± 6.8

Gas industry funded work on soils from oil-gas works in the United States (which converted oil rather than coal to gas) have reported oral bioaccessibilities for benzo[a]pyrene of between 0.2% and 5% in seven different soil samples (Stroo *et al.*, 2005). These studies also considered dermal absorption and reported values of between 0.17% and 1.05%. However, the contamination at oil-gas works is carbonaceous lampblack rather than coal tar at coal-gas works. Thus, such low values are unlikely to be representative of coal tar contaminated sites, such as coking works.

However, there is growing evidence that the bioavailability of organic contaminants may be less than the 100% assumed by CLEA. We have therefore derived CWACs assuming oral bioaccessibilities of 100%, 75%, 50%, 20% and 10% to indicate the impact of this potential over-prediction of exposure via the direct ingestion pathways.

1.8.4 Inhalation bioaccessibility

CLEA also has provision for the use of a bioaccessibility factor in relation to the uptake of contamination from inhaled dust within the lungs. By default a value of 100% is assumed. However, as the current ID_{inhal} is based on the relationship between occupational exposure to benzo[a]pyrene in coal tar emissions (which are assumed to be primarily in the form of particulates and dusts) and lung cancer mortality, it can be argued that bioaccessibility has already been accounted for in this study. Furthermore, there is very little research available on the measurement and verification of the bioavailability of inorganic and especially organic contaminants via the inhalation route. Consequently, at present there appears to be no justification for modification of the default value.

1.9 COKING WORKS ASSESSMENT CRITERIA

Several physical-chemical parameters for pure benzo[a]pyrene used in deriving the LQM/CIEH Generic Assessment Criteria for benzo[a]pyrene may not be appropriate for assessing the risks from benzo[a]pyrene in complex mixtures (such as coal tars of various compositions). These parameters include the K_{oc}, ABS_d and the various soil-plant concentration factors predicted by the generic algorithms within CLEA 1.06.

We have selected input parameters that may better represent the behaviour of benzo[a]pyrene within coal-tar contaminated soils, based on literature values and, where appropriate, data from an example coking works (*i.e.* the former Avenue Coking Works). However, significant uncertainty remains in the selection of several of the parameters. Consequently, we have used a probabilistic model, based on the algorithms within CLEA 1.06, to represent these parameters as Probability Density Functions (PDFs). There is also justification to model the soil-to-dust transport factor and dust loading factor probabilistically, given the relative importance that these pathways play in deriving assessment criteria for benzo[a]pyrene. The input parameters used are summarised in Table 11.

This model has been used to derive examples of coking works assessment criteria (CWACs) for the *residential with home-grown produce* land use assuming cautious soil characteristics (sandy loam with 1% SOM) and with various oral bioaccessibilities (Table 12).

1.10 LIMITATIONS AND APPLICABILITY

The CWACs are intended to be 'intervention values' that "mark the concentration of a substance in soil at or below which human exposure can be considered to represent a 'tolerable' (where the relevant health criteria value is a tolerable daily intake) or 'minimal' (where the health criteria value is an index dose) level of risk and that "exceedance can indicate to an assessor that further assessment or remedial action may be needed. Non-exceedance indicates that risk is not unacceptable and that land is suitable for its use, with regard to the contaminant in question". The CWACs do not have the same status as SGVs and should be reviewed in light of any future updated SGV or modification of CLEA 1.06. Exceedance of a CWAC does not represent *prima facie* evidence of significant possibility of significant harm or of the need for remediation under the UK's various planning regimes. Rather such exceedance should usually trigger a further detailed quantitative risk assessment where site-specific parameters (such as K_{oc}, soil vapour and plant uptake factors) are used to derive site-specific assessment criteria.

The CWACs assume that the benzo[a]pyrene being considered is present within a soil contaminated with a complex mixture of organic contaminants typically found at coking works (such as coal tars).

We have presented CWACs that assume varying degrees of bioaccessibility for benzo[a]pyrene. The concept of bioaccessibility is now widely accepted for inorganic contaminants (*e.g.* arsenic) but its use for organic contaminants is relatively new and has not been verified using *in vivo* tests. However, it is conceivable that some organic contaminants, particularly persistent compounds with low environmental mobility (such as benzo[a]pyrene), will be far less than 100% bioavailable. However, to use assessment criteria that assume less than 100% bioaccessibility would, as a minimum, require site-specific information on the bioaccessibility of benzo[a]pyrene. This information would need to be representative of all the materials and soil types present and should be interpreted very cautiously until the community has greater experience on the meaning and relevance of bioaccessibility to the risks posed by benzo[a]pyrene.

1.11 CONCLUSIONS

Benzo[a]pyrene is a typical contaminant encountered at coking works, where it is often a risk driver due to its prevalence, persistence and high toxicity. The LQM/CIEH generic assessment criteria for benzo[a]pyrene have been derived based on the principles behind the SGVs and therefore reflect a number of cautious assumptions relevant to pure BaP. We have reviewed the various input parameters and assumptions used in deriving these GAC to determine if they are appropriate for the assessment of benzo[a]pyrene at coking works and subsequently derived example coking works assessment criteria using a probabilistic exposure model based on CLEA 1.06.

Table 11: Summary of the physical-chemical parameters for benzo[a]pyrene used to derive the current Coking Works Assessment Criteria (CWAC)

Parameter	Units	Type	Value
Air-water partition coefficient (K_{aw})	dimensionless [a]	Deterministic	1.76 E-6
Diffusion coefficient in air (D_{air})	$m^2\ s^{-1}$ [a]	Deterministic	4.38 E-6
Diffusion coefficient in water (D_{water})	$m^2\ s^{-1}$	Deterministic	3.67 E-10
Relative molecular mass	g mol^{-1}	Deterministic	252.31
Vapour pressure (P_v)	Pa [a]	Deterministic	2.0 E-8
Water solubility (S)	mg L^{-1} [a]	Deterministic	3.8 E-3
Organic carbon-water partition coefficient (K_{oc})	Log ($cm^3\ g^{-1}$)	PDF	Normal (Mean 5.77, SD 1.01).
Octanol-water partition coefficient (K_{ow})	Log (dimensionless)	PDF	Triangular (Max 8.5, Most likely 4.05, Min 6.18)
Dermal absorption fraction (ABS_d)	dimensionless	PDF	Normal (Mean 13.2, SD 3.3)
Soil-to-plant concentration factor for green vegetables	mg kg^{-1} plant (FW or DW) per mg kg^{-1} soil (DW)	modelled	Substance specific relationships (see Section 1.7)
Soil-to-plant concentration factor for root vegetables	mg kg^{-1} plant (FW or DW) per mg kg^{-1} soil (DW)	modelled	
Soil-to-plant concentration factor for tuber vegetables	mg kg^{-1} plant (FW or DW) per mg kg^{-1} soil (DW)	modelled	
Soil-to-plant concentration factor for herbaceous fruit	mg kg^{-1} plant (FW or DW) per mg kg^{-1} soil (DW)	modelled	As per CLEA 1.06
Soil-to-plant concentration factor for shrub fruit	mg kg^{-1} plant (FW or DW) per mg kg^{-1} soil (DW)	modelled	
Soil-to-plant concentration factor for tree fruit	mg kg^{-1} plant (FW or DW) per mg kg^{-1} soil (DW)	modelled	
Soil-to-dust transport factor (TF)	g g^{-1} DW	PDF	Lognormal (Geomean 0.4162, Geometric SD 1.4424)
Sub-surface soil to indoor air concentration factor	dimensionless	Deterministic	1
Dust loading factor	μg m^{-3}	PDF	Lognormal (Geomean 10.6, Geometric SD 1.9)
Oral bioaccessibility	dimensionless	Deterministic	Values of 1, 0.75. 0.5, 0.2 and 0.1

[a] at 10°C

Table 12: Example generic assessment criteria for benzo[a]pyrene at coking works for the *residential with home-grown produce* land use (assuming a sandy loam soil, 1%SOM). Criteria have been generated using a semi-probabilistic model based on the algorithms used in CLEA 1.06. The assessment criteria represent the soil concentration (mg kg^{-1}) at with the 95th percentile of predicted exposure equals the relevant health criteria value.

	Assessment Criteria (mg kg^{-1})[a]
100% oral bioaccessibility	0.90
75% oral bioaccessibility	1.00
50% oral bioaccessibility	1.10
20% oral bioaccessibility	1.25
10% oral bioaccessibility	1.40

[a] These values represent the output from 1001 iterations. At this level, approximately a 5% variation around the value stated could be expected.

This analysis suggests that the use of a probabilistic modelling approach using carefully selected probability density functions to express the inherent uncertainty within the key input parameters makes only a marginal difference to the existing assessment criteria. This is partly due to the nature of CLEA model and the specific properties of benzo[a]pyrene, which suggest that the current levels of predicted exposure via several pathways (*i.e.* direct ingestion, consumption of home-grown produce, dermal and indoor dust inhalation) are close to the current health criteria values.

In assessing the model outputs for the CWACs it is apparent that the modifications made to the soil-to plant uptake factors have typically reduced the predicted concentrations in root and tuber vegetables significantly; roughly 4- and 31-fold. However, it has increased the predicted levels in green vegetables by a factor of 2. As potatoes (tubers) constitute the majority of the home-grown produce consumed, this will significantly reduce the total estimated exposure via this pathway. Oral bioaccessibility of less than the default 100% would also reduce the predicted exposure via the direct ingestion pathway. Under these conditions the dermal contribution rises to become the dominant pathway, for example with 10% oral bioaccessibility the dermal pathway contribution is >60%.

Having reviewed the input parameters and assumptions used in modelling dermal exposure, we did not identify any obviously overly cautious inputs for BaP at coking works compared with the scenario the GAC are based on. Although the ABS_d for coal-tar-contaminated soil may be lower than suggested for benzo[a]pyrene, we could find no explicit justification for this in the scientific literature. This parameter may be worthy of further investigation, given the key role that the dermal exposure pathways appear to play in limiting the assessment criteria for benzo[a]pyrene.

The other significant issue is the apparently disproportionate impact of the inhalation of indoor dust to the assessment criteria. Even if all oral exposure routes were interrupted, inhalation of indoor dust would still limit the assessment criteria to less than 3 mg kg^{-1}. This effect is primarily due to the very stringent requirements set by the inhalation health criteria value (ID_{inhal}), whose appropriateness has not been reassessed within the current context of contaminated land risk assessment by EPAQs since 1999.

The UK appears to be the only major country to have set a health criterion value for the inhalation of benzo[a]pyrene; most countries (including the Netherlands, US and Canada) adopt route-to-route extrapolation and consider exposure via the inhalation of dusts to be additive to oral exposures. If the UK were to adopt this approach, the CWACs would range between 1.2 mg kg^{-1} (100% oral bioaccessibility) and 2.2 (10% oral bioaccessibility), with the default dermal exposure scenario limiting the derived CWAC. Therefore, a review of the current inhalation health criteria value and, in particular, the level of risk it poses and the appropriateness of the safety factors employed, would provide the opportunity for relatively large increases in the current assessment criteria.

A combination of adopting route-to-route extrapolation for the inhalation pathway, as per Netherlands, US and Canada, and assuming dermal absorption was as low as suggested at oil-gas sites (*i.e.* divide the default ABS_d value by a factor of 10) would raise the CWAC to about 10.5 mg kg^{-1} (at 10% oral bioaccessibility). Such an upper level is highly dependent upon suitable justification for the changes to the toxicology and oral/dermal bioaccessibility.

ACKNOWLEDGMENTS

The authors would like to acknowledge the unstinting help and support of Mike Fenton and George Kavvouras of the Avenue Project in formulating and supporting the work that underpins this bulletin as well as their permission to use information from the Avenue Project to augment information from the published literature.

CL:AIRE and the authors would like to acknowledge the financial support of the East Midlands Development Agency.

CL:AIRE and the authors would like to thank members of the CL:AIRE Technology and Research Group for peer reviewing and commenting on the draft bulletin on which this final bulletin is based.

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The bulletin should be cited as follows:
Ogden R & Nathanail CP (2011), Generic human-health assessment criteria for benzo[a]pyrene at former coking works sites. CL:AIRE Research Bulletin RB15. CL:AIRE, London, UK. ISSN 2047-6450 (Online)

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