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 benzene at former coking works sites.

Generic Human-Health Assessment Criteria for Benzene at Former Coking Works Sites

1.1   INTRODUCTION

Benzene is a common contaminant at former coke and coal tar processing works. However generic assumptions and input parameters used to derive Generic Assessment Criteria (GAC), such as UK Soil Guideline Values (SGV), may not reflect the conditions normally found at such works and this may result in GAC that under or over-estimate human exposure at such sites. We have considered the applicability of the main input parameters used to derive GACs for benzene to the conditions normally encountered at former coking works and, as an example, have derived Coking Works Assessment Criteria (CWAC) for the residential land use that may better reflect the risks posed by benzene at such sites. Where differences to the methodology used to derive GAC have been employed they have been justified by use of relevant empirical or scientific information to allow a more robust approach for coking work sites.

The soils at former coking works will mainly be made ground whose composition depends on the local geology (*i.e.* may vary between clayey and sandy in nature) and anthropogenic deposits of various sorts. It is likely that such material 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 more cautious soil organic matter content of 1% (rather than the 6% assumed in deriving the SGVs).

Coking works were a subset of the UK coal carbonisation industry. Coal carbonisation involved heating coal in the absence of air (Department of the Environment, 1995) to produce coke, coal gas and coal tar, and several by-products, such as ammoniacal liquors and sulphur. The primary function of coking works was to produce coke, the solid, predominantly carbon, residue of the carbonisation of coal after most of the organic components present in coal have been driven off.

Benzene (CAS No. 71-43-2) is a naturally occurring aromatic hydrocarbon, which is also widely used industrially. Its synonyms include benzine, benzol, benzole, benzol coal naphtha, mineral naphtha, motor benzol, phenyl hydride and pyrobenzole. Pure benzene is a colourless volatile liquid at room temperature, with a distinctive sweet smell. It is highly flammable and boils at around 80 °C. It is sparingly soluble in water (1780 mg L^{-1} at 25°C) but easily miscible with most organic solvents (ATSDR, 2007; WHO, 1993).

Benzene is reported to occur naturally in emissions from volcanoes and forest fires and is a constituent of crude oil (ATSDR, 2007). However, most releases to the environment are from anthropogenic sources, such as the spillage of petroleum products. It is a significant component in petrol, along with toluene, ethylbenzene and xylenes, which are often collectively referred to as BTEX. It is also present in other hydrocarbon mixtures including coal tars and other residues commonly associated with coking works (ATSDR, 2007; WHO, 1993). It is produced in large quantities world wide as an intermediate in the formation of other chemicals, such as styrene, cyclohexane and chlorobenzenes. Historically, benzene was also widely used as a solvent, in paint, adhesives and as a degreaser (ATSDR, 2007; WHO, 1993).

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 tars, 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, 2009e) 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 (p82) within SR3 (Environment Agency, 2009e) 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, 2003).

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

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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} information exists (see Section 1.5.7), this has been used to account for some of the practical implications of Raoult's Law.

1.3 PROBABILISTIC MODELLING

The Environment Agency Contaminated Land Exposure Assessment (CLEA) model uses generic assumptions about contaminant fate and transport and human behaviour to estimate exposure to contaminants in soil (Environment Agency, 2009e). CLEA 1.06 is a deterministic model. For generating generic assessment criteria reasonably cautious input parameters generally tend to be assigned to ensure the criteria are applicable for screening a wide range of sites but with the limitation that the product of combining numerous low-probability input values is a highly unlikely (or even infeasible) predicted output.

There is considerable uncertainty and variation in many of the input parameters used in the model. To account for this uncertainty LQM developed a probabilistic model which utilises the same algorithms used in CLEA 1.06; this has been abbreviated to PCLEA. PCLEA enables a number of the input parameters to be defined as independent Probability Density Functions (PDFs) to allow uncertainty to be better incorporated into the model.

In determining example assessment criteria, we have adopted a cautious approach of determining the soil concentration at which 95% of all the predicted exposures are equal to or less than the relevant health criteria value. This was also the percentile used by the Environment Agency to generate the first generation of SGVs using the probabilistic CLEA2002 model.

A probabilistic approach has only been used to investigate the influence of the chemical-specific parameters upon the output of the model (see Sections 1.5, 1.6 and 1.7); all other inputs (receptor characteristics, soil properties and building type, etc.) have been modelled deterministically using the inputs recommended in SR3 (Environment Agency, 2009e). Therefore, it is likely that the true uncertainty in exposure would be higher given the variability in human characteristics such as body weight, etc. In addition, this approach assumes that the likely uncertainty in the selected chemical-specific parameters will be generically applicable across a range of different coking works sites.

Within stochastic modelling the issue of co-dependency or correlation of input parameters can be a problem (*e.g.* ConSim accounts for this by allowing for correlation between user inputs). Within the context of the CLEA model two such co-dependent input parameters are K_{oc} and K_{ow} and can be related using empirical relationships (for example see SR7 Table 2.12, (Environment Agency, 2008)). However, within this work such a correlation (between K_{ow} and K_{oc}) was not considered appropriate since the K_{ow} applied to the plant uptake algorithms effectively assumes that the pure substance is present in the system, although variation in reported literature values has been incorporated. Other inter-related parameters (such as vapour pressure and solubility) are effectively single user or deterministic values.

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, 2009e, 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, 2009e, page 25).

1.4 TOXICITY

The toxicology of benzene has been reviewed by Defra and the Environment Agency (2003) and more recently by the Environment Agency (2009b) to inform the selection of appropriate, UK policy compliant Health Criteria Values. The Environment Agency (2009b) recommend an ID_{oral} of 0.29 µg kg^{-1} BW day^{-1} and an ID_{inhal} of 1.4 µg kg^{-1} BW day^{-1}. The health criteria values recommended for benzene are based on experimental studies involving pure benzene, rather than the complex mixtures more relevant to coking works (*i.e.* coal tars etc.).

Whilst it is likely that oral exposure at coking works is more likely to involve coal tar than pure benzene, the current documentation supporting the benzene SGV (Environment Agency, 2009d) indicates that the risk from benzene in soil is predominantly due to the inhalation of vapours. As only a minority of the components of coal tar are considered volatile, it is likely that inhalation exposure will involve far fewer compounds and possibly primarily benzene. Consequently, there appears to be little justification for changing the ID_{inhal} recommended for benzene when considering a coking works. There may be some justification for utilising an ID_{oral} based on studies of coal tar but there appear to be little, if any, such data available in the current literature. Therefore, assuming no additive, synergistic or antagonistic effects of benzene as part of a mixture it has been assumed valid to utilise the ID_{oral} proposed for pure benzene.

1.5 PHYSICAL-CHEMICAL PROPERTIES FOR BENZENE

The physical-chemical parameters of benzene used in deriving the SGV (Environment Agency, 2009c) are summarised in Table 1 and were mainly based on the recommendations presented in SR7 (Environment Agency, 2008). The parameters recommended in SR7 primarily represent pure benzene. However, at a coking works benzene is likely to be present as part 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 substance. Consequently, dependent on the sources of the information underpinning the SR7 recommendations, the physical-chemical properties of benzene at a coking works may differ significantly from those used to derive the SGV. In the sections below we have investigated the appropriateness of the various inputs recommended in SR7 with respect to coking works.

1.5.1 Pathway contributions

For the "Residential with home-grown produce" land use and inputs in Table 2, more than 65% of exposure to benzene is predicted to be via the indoor inhalation of vapours, with the majority of the remaining exposure resulting from the consumption of home-grown produce (see Table 2). If the indoor vapour inhalation linkage is broken, more than 99% of exposure results from the consumption of home-grown produce. Consequently, we have paid particular attention to those parameters which impact the indoor inhalation and consumption of home-grown produce pathways.

1.5.2 Raoult's Law

The Environment Agency (2009c), acknowledging that "key aspects of benzene's behaviour in the soil environment will be influenced by the presence of other compounds", suggest that the solubility and volatility of benzene decreases in the presence of other hydrocarbon compounds and after weathering processes have aged the original contamination. They recommend that the effects of Raoult's Law be considered when benzene is present as part of a complex mixture.

A variety of complex hydrocarbon wastes are likely to be present at coking works, including coal tars of various compositions.

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Table 1: Summary of the physical-chemical parameters for benzene used to derive the current Soil Guideline Value (Environment Agency, 2009c; Environment Agency, 2009e)

Parameter	Units	Value	Comment
Air-water partition coefficient (K_{aw})	dimensionless	1.16 E-1	Estimated from the solubility and vapour pressure (see below).
Diffusion coefficient in air (D_{air})	$m^2 s^{-1}$	8.77 E-6	Calculated estimates for pure benzene but are unlikely to differ for mixtures
Diffusion coefficient in water (D_{water})	$m^2 s^{-1}$	6.64 E-10	
Relative molecular mass	$g mol^{-1}$	78.11	
Vapour pressure (P_v)	Pa	6240	Consensus literature values for pure benzene
Water solubility (S)	$mg L^{-1}$	1780	
Organic carbon-water partition coefficient (K_{oc})	Log ($cm^3 g^{-1}$)	1.83	Estimated by linear regression from $logK_{ow}$
Octanol-water partition coefficient (K_{ow})	Log (dimensionless)	2.13	Consensus literature values for pure benzene
Dermal absorption fraction (ABS_d)	dimensionless	0.1	Default CLEA input where no contaminant-specific ABS_d is available.
Soil-to-plant concentration factor for green vegetables	$mg kg^{-1}$ plant (FW or DW) per $mg kg^{-1}$ soil (DW)	Modelled	No benzene-specific concentration factors were found in the literature. The generic algorithms were used to predict CFs based on $logK_{ow}$ of pure benzene (Environment Agency, 2009d)
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	No model currently included within CLEA but "in most circumstances these two groups will make only a small contribution to overall exposure" (Environment Agency, 2009e)
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	As for green, root and tuber vegetables above.
Soil-to-dust transport factor (TF)	$g g^{-1}$ DW	0.5	CLEA default value based on average of literature values (Environment Agency, 2009e)
Sub-surface soil to indoor air concentration factor	dimensionless	10	Based on the lower range of reported over-prediction of simple linear partitioning models (Environment Agency, 2009d)

Note: FW - fresh weight; DW - dry weight

Table 2: Percentage contribution for each exposure pathway for benzene 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 1.

Pathway	Distribution by Pathway (%)	
	RwHGP	RwHGP (minus inhalation of indoor vapour)
direct soil ingestion	0.10	0.29
sum of consumption of homegrown produce and attached soil	32.97	99.55
dermal contact (indoor)	0.00	0.01
dermal contact (outdoor)	0.05	0.14
inhalation of dust (indoor)	0.00	0.00
inhalation of dust (outdoor)	0.00	0.00
inhalation of vapour (indoor)	66.89	0.00
inhalation of vapour (outdoor)	0.00	0.01
oral background	0.00	0.00
inhalation background	0.00	0.00
Total	100.01	100.00

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 $mole^{-1}$)

Only a single paper (Brown *et al.*, 2010) was identified that contained the relevant details for 10 coal tar samples (see Table 3). The mole fraction of benzene in these samples ranged from 0.001 to 0.032 with an average of 0.012. In implementing Raoult's Law, at any former coking works site, a conservative mole fraction of 0.05 used as part of a triangular PDF (Min 0.001, Most likely 0.008, Max 0.05) to represent the range of mole fractions indicated by the data in Table 3, may be realistic (median value is 0.008). However, compositions of coal tars may vary between sites and site-specific data should be considered.

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

The air-water partition coefficient (K_{aw}) is important in estimating exposure via inhalation of ambient and indoor air. Benzene's K_{aw} in SR7 (Environment Agency, 2008) was estimated directly from the water solubility and vapour pressure of pure benzene at 10ºC. Vapour pressure and solubility of benzene in coal tars has been estimated by applying Raoult's law. However, as this effectively scales both the top and the bottom of the partitioning equation by the mole fraction of benzene, the resulting K_{aw} is the same as that for pure benzene (0.116).

We also searched the literature for measurements of the K_{aw} (or Henry's law constant) for benzene in coal-tar or coal-tar contaminated soil, but did not identify any relevant data.

Table 3: Average molecular weight and benzene concentration in 10 coal tars from nine former manufactured gas plants in the eastern United States (After Brown et al., 2010). The calculated mass and mole fractions of benzene in each sample are also presented.

Site	Average molecular weight (g mole^{-1})	Benzene concentration (mg kg^{-1})	Benzene mass fraction (Dimensionless)	Benzene mole fraction (Dimensionless)
1	2143	47.5	0.0000475	0.001
2	392	984	0.00984	0.005
4M	990	514	0.000514	0.007
4H	728	3390	0.00339	0.032
5	3213	523	0.000523	0.022
6	621	964	0.000964	0.008
7	1099	986	0.000986	0.014
8	741	1690	0.00169	0.016
9	316	1360	0.00136	0.006
10	2303	233	0.000233	0.007

1.5.4   Relative molecular mass

The molecular weight of benzene does not depend on whether or not benzene is present in a mixture. The molecular weight of benzene is well characterised and there is little variation in reported values within the literature, so the SR7-recommended value (78.11 g mol^{-1}) has been used.

1.5.5   Vapour pressure (Pv)

The vapour pressure at ambient temperature recommended for benzene (6240 Pa) in SR7 (Environment Agency, 2008) was estimated by the Grain-Watson method from data on its enthalpy of vaporisation and boiling point. Data presented in Appendix A to SR7 indicates that there is little variation in cited values for either of these parameters within the literature. While it was not possible to verify each cited value, it is believed that all the cited values relate to pure benzene.

In complex hydrocarbon mixtures such as coal tars the effective vapour pressure of benzene is likely to be lower than that of pure benzene. The vapour pressure of mixtures can be predicted using Raoult's law:

$$P_i = P_i^o \times x_i$$

Where:
P_i = partial pressure of compound i in the mixture (Pa)
P_i° = vapour pressure of pure compound i (Pa)
x_i = mole fraction of compound i in the mixture

Thus, assuming that the vapour pressure of pure benzene is 6240 Pa and that the mole fraction of benzene in coal tar is 0.05, Raoult's law predicts the effective vapour pressure (or partial pressure) of benzene in coal tar is 312 Pa.

This estimate is supported by data produced by the USEPA from an investigation of the emissions produced from coke-oven by-products (USEPA, 1979). As part of the work presented by USEPA (1979), the partial pressure of benzene was determined in 68 different samples of coke works by-products and wastes, ranging from "treated wastewater" to "heavy tar storage tank #3". The partial pressures for benzene (converted to pascals at 10°C) in the various samples ranged from 0.31 to 2693.51 Pa, but are skewed to lower partial pressures. The mean partial pressure across all 68 coke-oven by-products was 180 Pa, which would indicate that the value of 312 Pa estimated for coal tars using Raoult's law is a value suitable for most coke-oven by-products.

As the vapour pressure of benzene in a complex mixture (e.g. coal tar) will be considerably lower than that for pure benzene, intuitively the risks from vapour inhalation should also be reduced. However, within CLEA 1.06 the vapour pressure is not used in predicting inhalation exposure. This is modelled using the air-water partition coefficient (see Section 1.5.3), which does not vary with the mole fraction of benzene. Within CLEA, the vapour pressure is only used to calculate the vapour saturation limit.

1.5.6   Water solubility (S)

The reported aqueous solubility of pure benzene in SR7 (Environment Agency, 2008) is 1780 mg L^{-1}.

However, the effective solubility of benzene in a complex mixture of hydrocarbons can be estimated using Raoult's law:

$$C_i = C_i^o \times x_i$$

Where:
C_i = effective solubility of compound i in the mixture (mg L^{-1})
C_i° = water solubility of pure compound i (mg L^{-1})
x_i = mole fraction of compound i in the mixture

Thus, assuming that the aqueous solubility of pure benzene is 1780 mg L^{-1} and that the mole fraction of benzene in coal tar is 0.05, the effective solubility of benzene in water in equilibrium with a coal tar source would be 89 mg L^{-1}. This provides an illustration of the lower effective solubility of benzene in water in equilibrium to be expected within a coal tar mixture source.

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

The soil-water partition coefficient (K_d) is used in CLEA to predict how likely a chemical is to sorb to soil as opposed to dissolving into the pore water. This partitioning of organic contaminants between soil and water phases is, in reality, highly complex and subject to many variables (Environment Agency, 2009e).

The organic carbon-water partition coefficient (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 the aqueous solution (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_d values should be determined experimentally using analytical 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.

As discussed above, many variables affect the soil-water partitioning of organic chemicals and it is likely that, as with many other parameters, the K_{oc} of a chemical as part of a complex mixture (e.g. coal tar) will differ from that of the pure compound. In low organic matter soils (such as made ground), it is likely that 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 solid-media-water partitioning of organic contaminants (for example see Pollard (2008)).

There are limited data in the literature regarding partitioning in coal tar impacted soils. Endo & Schmidt (2006) reviewed the available data and identified only a single $K_{ct/w}$ value for benzene of 2.55. Lindhart et al. (1996) and Lindhart & Christensen (1996) studied the K_{tar} (i.e. the soil/water distribution coefficient normalised by the organic carbon content) of volatile components in coal tar-contaminated soils. The levels of benzene in the soil were generally too low to

calculate K_{tar}, but in soil spiked with additional benzene K_{tar} values of 2.24, 2.15 and 2.63 were reported. In general, the measured values for K_{tar} were between 3 and 11 times higher than values of K_{oc}, as predicted from its K_{ow}. This suggests that benzene and other volatile aromatic compounds sorb more strongly to soils containing coal tar than to soils containing natural organic matter. Many authors have shown this effect to be significant with free phase representing a significant sink for trace hydrocarbons (*e.g.* Pollard (2008)).

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 benzene 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})

Therefore, where data for C_s, C_l and f_{oc} are available for the same sample it is possible to derive an estimate of K_{oc} for that sample. We therefore identified suitable samples collected at the former Avenue coking works for which benzene 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 (12%).

The resulting dataset (unaffected by limit of detection issues) contained 37 estimates of K_{oc} for benzene over a significant range of contaminant concentrations and material types. The estimates of K_{oc} for benzene derived in this way are higher than the value of 1.83 recommended for pure benzene in SR7 (Environment Agency, 2008) (see Table 4). It is considered that this dataset is reasonably cautious and more likely to be representative of the partitioning of benzene between soil and water at coking works than the K_{oc} for pure benzene. It should also be noted that the $K_{ct/w}$ cited by Endo & Schmidt (2006) and K_{tar} cited by Lindhart & Christensen (1996) fall towards the centre of the range presented in Table 4.

Table 4: Summary statistics for estimates of log K_{oc} for benzene calculated for soils at the former Avenue coking works

Statistic	Benzene
Minimum	1.95
Maximum	5.13
N	37
Mean	3.20
Median	3.11
SD	0.80

We have modelled the log K_{oc} of benzene using a PDF based on the Avenue coking works dataset (see Figure 1). The *best fit* distribution which is considered to best represent the range and variability in the dataset is a normal distribution (Mean 3.20, SD 0.80).
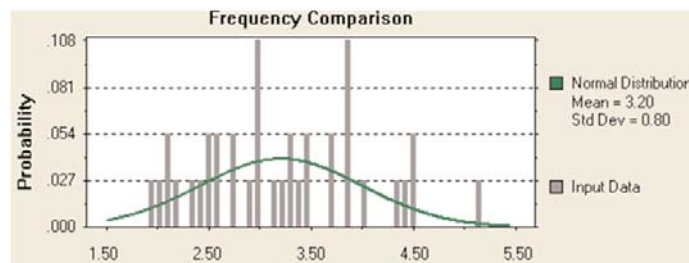

Figure 1: Probability density function for $\log_{10}K_{oc}$ for benzene for coking works impacted soils (n = 37)

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

The octanol-water partition coefficient (K_{ow}) (Lyman *et al.*, 1990) is often used 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 benzene that should be used, as plants primarily take up contaminants (and nutrients) that are present dissolved in the pore water and benzene is likely to constitute the majority of the contamination in the aqueous phase due to its high solubility compared to most other coal tar components.

The Environment Agency have reported on the K_{ow} of benzene on two occasions (Environment Agency, 2003; Environment Agency, 2008). In the former, K_{ow} values ranging between 1.56 and 2.25 were identified, whereas in the latter a consensus value of 2.13 was recommended. We have therefore adopted a triangular PDF (min 1.56, most likely 2.13, max 2.25). It should also be noted that we have conducted a separate assessment of the accuracy with which CLEA predicts the plant uptake of benzene based on its K_{ow} (see Section 1.6).

1.5.9 Dermal absorption fraction (ABS_d)

The CLEA model currently estimates the uptake of contaminants via the skin using a model developed by the USEPA. This model 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 absorption fraction (ABS_d), which represents the fraction of dose adhered to the skin that is absorbed per event. The USEPA (2004) have suggested suitable values for ABS_d for only a limited number of chemicals based on a review of experimental data.

In deriving the recent SGV the Environment Agency state that they could "not identify any studies for quantifying the dermal adsorption fraction for benzene" (Environment Agency, 2009c). Consequently, the standard default value 0.1, which implies that 10% of the applied dose is absorbed, was adopted in deriving the SGV. However, the original source of this value (USEPA, 2004) describes it as a "default dermal absorption fraction for semivolatile organic compounds" and explicitly avoids providing a default value for volatiles because "volatile organic compounds would tend to be volatilised from the soil on skin". Elsewhere, the USEPA consider the use of 0.05% as appropriate for very volatile contaminants (*e.g.* benzene; 1,1- dichloroethane; 1,1,1-trichloroethane) and 3% for other volatiles (*e.g.* ethylbenzene, tetrachloroethene, toluene, and xylenes) (USEPA, 1995). We have selected a cautious PDF based on these values (triangular, min 0.0005, most likely 0.03, max 0.1).

It is likely that ABS_d will be reduced for a contaminant present in a complex mixture because its dermal uptake is likely to be proportional to its solubility which is dependant on the mole fraction of the contaminant in the mixture (*i.e.* Raoult's law). However, as the dermal component of overall exposure to benzene is very small (*i.e.* <<1%) under most exposure scenarios, it is unlikely that changing ABS_d will result in any significant change in the overall assessment criteria for benzene.

1.6 PLANT UPTAKE MODELLING

1.6.1 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 by 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 reviewed several different plant uptake algorithms (Environment Agency, 2006) and concluded that they "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".

In the same review, the Environment Agency (2006) conclude that very little data was available concerning benzene. However, it is acknowledged that the accumulation of volatile contaminants, such as benzene, will be limited if transpiration leads to transport "to sub-stomatal tissues within leaves, from which they will subsequently be lost by volatilisation". The review also suggested that the metabolism of benzene may be significant.

Despite these observations, in deriving the Soil Guideline Value (SGV) for benzene, the Environment Agency (2009d) concluded that there were insufficient experimental data to specify benzene-specific soil-to-plant concentration factors, and so recommended that the generic plant uptake

algorithms within CLEA be used to predict plant uptake. The concentration factors predicted by CLEA for benzene for each vegetable and fruit class are presented in Table 6.

Table 6: Soil-plant concentration factors for benzene for each produce group back calculated from the media concentrations predicted by CLEA 1.06 under the residential with homegrown produce land use and 1% soil organic matter.

	Predicted media concentration mg kg^{-1} FW plant	Soil concentration mg kg^{-1} DW soil	Soil-plant concentration factor
Green vegetables	0.156	0.08	1.95
Root vegetables	0.367	0.08	4.59
Tuber vegetables	0.113	0.08	1.41
Herbaceous fruit	NA	0.08	NA
Shrub fruit	NA	0.08	NA
Tree fruit	0.266	0.08	3.33

The volatility and rapid metabolism of benzene are likely to result in the over-prediction of plant uptake of benzene by the generic algorithms used in CLEA. This over-prediction is likely to be even more pronounced where benzene is present within a mixture, as the effective solubility and partial vapour pressure of benzene within the soil will be reduced in accordance with Raoult's Law (see Sections 1.5.5 and 1.5.6). This lower solubility is likely to further reduce plant uptake of dissolved benzene via the roots. As the uptake of benzene vapour via the leaves can also be a significant uptake mechanism for benzene (Collins *et al.*, 2000), the lower vapour pressure is also likely to reduce uptake via the leaves as the release of vapour from the soil will be reduced. Consequently, the generic algorithms in CLEA are likely to be even less appropriate to the uptake of benzene from soils containing coal tars etc. than for those impacted by pure benzene.

As the consumption of home-grown produce accounts for a considerable proportion (*i.e.* >30%) of the overall exposure under the "*residential with home-grown produce*" land use (and up to 99% where indoor inhalation is excluded), this over-prediction of soil-plant concentration factors will have a significant impact on assessment criteria calculated using the generic algorithms. As the Environment Agency (2009e) recommend that the validity of the generic algorithms are evaluated "*on a substance-by-substance basis*", we have conducted a review of the uptake, volatilisation, metabolisation and accumulation of benzene by higher plants, particularly fruit and vegetables

1.6.2 Plant uptake of benzene

An extensive literature search confirms that benzene is rapidly lost from the leaves of at least one plant species (Burken & Schnoor, 1998; Burken & Schnoor, 1999) and that it is relatively easily metabolised in several species (Ugrekhelidze *et al.*, 1997). This would suggest that it is unlikely to be persistent in plant tissues or to accumulate significantly, particularly in the above-ground tissues. As none of the current generic algorithms in CLEA explicitly take account of contaminant volatility (*i.e.* vapour pressure) or biological persistence (*i.e.* its ease of metabolisation) their accuracy in predicting uptake of volatile and biologically labile contaminants (such as benzene) could be questioned. Indeed, Trapp *et al.* (2007) specifically stated that the tuber model used in CLEA is only applicable to "persistent neutral organic chemicals", which may indicate that this model is not appropriate for benzene.

However, very little data on the uptake of benzene from soils were found in the literature; most studies having investigated its uptake from the air by foliage (Collins *et al.*, 2000; Ugrekhelidze *et al.*, 1997). Despite an extensive search of

the literature, only a single paper could be identified that presented experimentally derived soil-plant concentration factors for benzene. Topp *et al.* (1986) derived relationships between K_{oc} or molecular weight and the measured uptake of 16 radio-labelled organic compounds (including benzene and various biocides and chlorobenzenes) by barley. These relationships showed a good fit for all compounds, except for benzene. Although the concentration factors are not explicitly stated, they can be estimated from graphs presented in the report. The concentration factor for benzene uptake by barley roots was roughly 0.4 µg g^{-1} FW plant per µg g^{-1} DW soil and that for whole barley plants of roughly 1.2 µg g^{-1} FW plant per µg g^{-1} DW soil. These values are much lower than the values predicted by the generic algorithms in CLEA for root and green vegetables of 4.59 and 1.95 µg g^{-1} FW plant per µg g^{-1} DW soil respectively (Table 6). The limited experimental data suggest that the actual uptake by plant roots may be around 10% of that predicted by CLEA and that of green vegetables may be close to two thirds of that predicted (62%).

The literature search did, however, find other evidence that supports the unusually low uptake of benzene by plants. Burken and Schnoor (1998; 1999) demonstrated that large amounts of radio-labelled benzene absorbed by the roots of hybrid poplar trees from hydroponic growing media was rapidly volatilised into the air via transpiration (Burken & Schnoor, 1998; 1999). Indeed of the 11 compounds studied, benzene showed the greatest losses by volatilisation; with over 90% of that translocated from the roots lost by volatilisation. Less than 10% of the benzene translocated could be detected in plant tissue at the end of the experiment (~88-180hrs). Other BTEX compounds were volatilised to a lesser extent (*i.e.* benzene>>toluene>ethylbenzene>*m*-xylene). In contrast, less than 10% of nitrobenzene, phenol, 1,2,4-trichlorobenzene and aniline were volatilised from foliage but substantial amounts of these compounds were recovered from plant tissues. It should be noted that the method of analysis for the plant tissues could not discriminate between the accumulation of benzene and the metabolism of benzene and the accumulation of its radio-labelled metabolic products. However, this work suggests that a large proportion of any benzene taken up by plants at a contaminated site would be expected to be released to the atmosphere from the leaves, and consequently would not contribute to human exposure via the diet (although outdoor inhalation exposure may be increased).

A number of other papers also suggest that benzene is rapidly metabolised within plant tissues, including the leaves. These papers primarily addressed the absorption of vapour from the air rather than uptake via the roots. However, as other research suggests that benzene is easily taken up by the roots and moves in the transpiration stream to the leaves, there seems to be little reason to assume that such metabolism is restricted to this route of entry. Ugrekhelidze *et al.* (1997) studied the metabolic fate of radio-labelled benzene using spinach leaves as a model system. Up to 77% of the benzene taken up by the leaves was metabolised to low molecular non-volatile organic acids, with 18% present as higher-molecular weight compounds (*i.e.* biopolymers) and 5% released as CO_2. It is not clear how much, if any unmetabolised benzene was recovered from the plant tissues. These data support the hypothesis that benzene metabolism in plants involves hydroxylation to form phenol and then catechol, with subsequent β-oxidation of the ring-cleavage products resulting in non-aromatic organic acids such as muconic acid (31%), fumaric acid (20.5%) and succinic acid (10.5%) (Ugrekhelidze *et al.*, 1997). These are presumably further metabolised by the standard tricarboxylic acid cycle to give CO_2, water and cellular energy.

The literature search confirms that there is little information relating to the uptake, volatilisation, metabolisation and accumulation of benzene by higher plants, possibly due to the difficulties in accurately studying uptake of such a volatile compound. However, what evidence there is suggests that the generic algorithms in CLEA do over-predict plant uptake and therefore the resulting assessment criteria may be unduly cautious. Given the importance of the consumption of the home-grown produce pathway to the assessment of benzene, this suggests that there is an urgent need for experimental studies to clarify the likely risks posed by produce from contaminated sites. It also suggests

that, where benzene is a potential risk driver (*e.g.* coking works), it may be cost effective to examine the uptake of benzene on a site-specific basis in a detailed quantitative risk assessment. Traditionally, this would involve growth trials involving produce representative of those types likely to be grown at gardens and allotments, but this is a lengthy and potentially costly process. Consequently, given that there is considerable variation in the uptake of contaminants between cultivars of the same species, it is likely that sampling existing vegetation at a contaminated site, particularly species that are related to common fruit and vegetables, may prove just as useful in indicating the likely magnitude of exposure to benzene via the consumption of home-grown produce. However, advice from a suitably qualified botanist is recommended in designing such an investigation.

Based on the findings of the literature search, we agree that there are insufficient data in the literature to derive substance-specific concentration factors for benzene. However, in deriving generic assessment criteria for coking works we have investigated the effect of the over-prediction of benzene plant uptake, which appears to be inherent in CLEA 1.06, by generating assessment criteria using concentration factors that are 100%, 75%, 50%, 20% and 10% of those predicted by the generic algorithms.

1.7 OTHER PARAMETERS

1.7.1 Soil-to-dust transport factor (TF)

Within CLEA, a default TF of 0.5 is adopted for residential land uses (Environment Agency, 2009e). This is based on the "*middle of the range*" reported by RIVM (2004) and USEPA (1998) of between 0.3 and 0.7. Consequently, we have elected to represent the TF as a triangular distribution that varies around the value of 0.5 (*i.e.* Min. 0.3, Most likely 0.5, Max. 0.7) to capture some of the reported variation in this parameter within the model.

1.7.2 Sub-surface soil to indoor air concentration factor

The SGV report for benzene (Environment Agency, 2009c) describes how modelling exposure to benzene and other volatile organics via ambient and indoor air involves a "number of simplifications and limitations". CLEA uses the Johnson & Ettinger (J&E) (1991) vapour intrusion model to predict exposure via indoor air from contamination in soils beneath the building; this involves the use of simple linear partitioning models to predict the fate and transport of contaminant vapours within the soil. The level of conservatism in the Johnson & Ettinger (1991) J&E model is discussed further in the CIRIA VOC handbook (Baker *et al.*, 2009), which concluded from limited United States case studies that the apparent over-prediction is related to the class of organic vapour being modelled (*e.g.* petroleum hydrocarbons or chlorinated solvents).

The construction design of the building being modelled is also an important consideration. The J&E model assumes a solid ground bearing slab foundation, which is the case for many houses built in the UK since the 1960s (Environment Agency, 2009e). However, many more modern homes are constructed using suspended solid floors with sub-floor voids and integral membranes to minimise gas and moisture penetration. In these circumstances the J&E model "*could significantly overestimate vapour ingress into the building*" (Environment Agency, 2009e).

There is ongoing debate regarding the reliability of the J&E model to predict indoor air concentrations (Baker *et al.*, 2009). However, there is evidence that for petroleum hydrocarbons, including benzene, it can over-predict exposure by 10 to 1000 times (Environment Agency, 2009c), possibly due to the biodegradation of these vapours in aerobic environments (DeVaull, 2007; Lahvis *et al.*, 1999). In deriving benzene SGV, the Environment Agency (2009c) selected to include a sub-surface soil to indoor air concentration factor of 10 to correct for the likely over-prediction of exposure by the J&E model.

The available literature suggests that accuracy of the J&E model is site-specific. At some sites the predicted exposure is massively over-estimated and at others is relatively accurate. There also appear to be multiple factors that affect the accuracy of the model, such as building construction, soil type, heterogeneity, availability of oxygen in the subsurface *etc*. Due to these uncertainties, much guidance in the United States now cautions against the use of model predictions and recommends the collection of site-specific data on groundwater and soil vapour concentrations for volatile contaminants.

In deriving generic assessment criteria for benzene at coking works, we have adopted the approach taken by the Environment Agency and adopted a deterministic sub-surface soil to indoor air concentration factor of 10. However, this value still contains significant uncertainty. This could be significantly reduced by the collection of site-specific soil vapour data for use in subsequent detailed quantitative risk assessment, which should also consider the applicability of the J&E model to the design of on-site buildings *etc*.

1.8   COKING WORKS ASSESSMENT CRITERIA

There appear to be a number of physical-chemical parameters used in deriving the Soil Guideline Value for benzene which assume the presence of pure benzene that may not be appropriate for assessing the risks from benzene at coking works, where benzene is likely to be present in complex mixtures (such as coal tars of various compositions). Such parameters include the vapour pressure, solubility, dermal absorption fraction, K_{oc} and the various soil-plant concentration factors predicted by the generic algorithms within CLEA 1.06.

We have selected, where feasible, input parameters that may better represent the behaviour of benzene 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 partially probabilistic model, based on the algorithms within CLEA 1.06, to represent these parameters as suitable Probability Density Functions (PDFs). The physical-chemical inputs used to derive the CWACs are summarised in Table 7; a review of the health criteria values recommended for benzene did not suggest that alternative values were available that were more appropriate for coking works contamination. This model has been used to derive examples of generic assessment criteria for coking works (CWACs) for the *residential with home-grown produce* land use assuming cautious soil characteristics (sandy loam with 1% SOM), which are presented in Table 8.

It has become common practice within the industry to specify construction methods that are presumed to break the soil vapour - indoor air linkage, and therefore derive assessment criteria that exclude a contribution from the inhalation of indoor vapour. We have, therefore, derived CWACs which both include and exclude this pathway. The risk assessor should be aware that reliance on the exclusion of the indoor pathway may not always be protective due to QA/QC procedures followed during installation of a membrane or damage following building maintenance or home improvements.

Due to the lack of certainty in the literature, it has been suggested that site-specific measurement of some parameters may be the most appropriate way to reduce significant uncertainty within the current assessment. These parameters include the sub-surface soil to indoor air concentration factor, but particularly the soil-plant concentration factors. In the case of the soil-plant concentration factors, we have investigated the effect of the likely over-prediction by CLEA 1.06 by calculating CWACs assuming varying degrees of over-prediction (*i.e.* 90%, 80%, *etc*).

Table 7: Summary of the physical-chemical parameters for benzene used to derive the Coking Works Assessment Criteria (CWACs)

Parameter	Units	Type	Values
Air-water partition coefficient (K_{aw})	dimensionless	Deterministic	1.16 E-1
Diffusion coefficient in air (D_{air})	$m^2 s^{-1}$	Deterministic	8.77 E-6
Diffusion coefficient in water (D_{water})	$m^2 s^{-1}$	Deterministic	6.64 E-10
Relative molecular mass	$g mol^{-1}$	Deterministic	78.11
Vapour pressure (P_v)	Pa	Deterministic	6240
Water solubility (S)	$mg L^{-1}$	Deterministic	1780
Organic carbon-water partition coefficient (K_{oc})	$Log (cm^3 g^{-1})$	PDF	Normal (Mean 3.20, SD 0.80).
Octanol-water partition coefficient (K_{ow})	Log (dimensionless)	PDF	Triangular (Max 2.25, Most likely 2.13, Min 1.56)
Dermal absorption fraction (ABS_d)	dimensionless	PDF	Triangular (Min 0.0005, Most likely 0.03, Max 0.1)
Soil-to-plant concentration factor for green vegetables	$mg kg^{-1}$ plant (FW or DW) per $mg kg^{-1}$ soil (DW)	modelled	Predicted value x over-prediction correction factor (between 1 and 0.1).
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	
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	0.5	Triangular (Min 0.3, Most likely 0.5, Max 0.7)
Sub-surface soil to indoor air concentration factor	dimensionless	Deterministic	10

1.9   LIMITATIONS AND APPLICABILITY

The CWACs are intended to be 'intervention values' that "mark the concentration of a substance in soil at a former coking works, at or below which human exposure can be considered to represent a 'minimal' (since 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. (At the same time, non-exceedance will indicate that risk is acceptable and that land

Table 8: Example generic assessment criteria for benzene 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 which the 95th percentile of predicted exposure equals the relevant health criterion value.

	Coking Works Assessment Criteria (mg kg^{-1})	
	Residential *with* indoor vapour inhalation	Residential *without* indoor vapour inhalation
100% of predicted uptake (No correction factor)	0.10	0.14
75% of predicted uptake (Correction factor=0.75)	0.11	0.18
50% of predicted uptake (Correction factor=0.5)	0.13	0.26
20% of predicted uptake (Correction factor=0.2)	0.20	0.66
10% of predicted uptake (Correction factor=0.1)	0.24	1.4

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 planning regime. 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 benzene being considered is present within a soil contaminated with a complex mixture of organic contaminants typically found at coking works (such as coal tars); they are not appropriate at sites, or parts of sites, where pure or relatively pure benzene is present.

The use of assessment criteria for a highly volatile contaminant, such as benzene, that exclude the consideration of indoor vapour inhalation is only appropriate where there is demonstrable certainty that vapour intrusion will be completely prevented. In residential properties this is likely to involve the use of a multi-layered protection system, potentially including VOC-proof membranes and sub-floor ventilation, and where the installation of any membranes has been inspected and verified by a suitably-qualified and independent body.

We have presented CWACs that assume varying degrees of over-prediction of plant uptake of benzene by CLEA to indicate the magnitude of the over-estimation of benzene exposure that may result. While some degree of over-prediction is highly likely, it is not possible to determine its likely extent at any given site from the existing literature. Consequently, in order to utilise assessment criteria other than that with "no correction", it would be necessary to obtain site-specific data on plant uptake to justify the existence and degree of over prediction at the site.

1.10   CONCLUSIONS

Benzene is a common contaminant encountered at coking works, where it is often a risk driver due to its high toxicity and volatility. Existing generic assessment criteria for benzene, such as the SGV, have been derived based on a number of cautious assumptions, including that the soil is contaminated by pure benzene alone. However, at coking works this is unlikely to be the case as benzene is usually found within complex mixtures, such as coal tars. We have reviewed the physical-chemical input parameters used in existing assessments for benzene to determine if they are appropriate for the assessment of benzene

at coking works and subsequently derived example generic assessment criteria for use at coking works using a semi-probabilistic exposure model based on CLEA 1.06.

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 can allow less cautious but fully justifiable assessment criteria for benzene to be generated. However, alteration to most of the input parameters discussed above have only a minimal impact on the resulting assessment criteria (for example the SGV at 1% SOM is 0.08 mg kg^{-1} compared to the comparable CWAC in Table 8 of 0.10 mg kg^{-1}). These values are dominated by the contribution of the inhalation of indoor vapour pathway. Although we have not investigated the potential over-prediction of this pathway, there is some evidence that CLEA may over-estimate vapour intrusion of biodegradable VOCs by more than 10-fold. Therefore, problem holders may find the collection of site-specific soil vapour data could have a significant impact on assessment criteria generated at the subsequent DQRA stage.

This study also shows that selection of soil-plant concentration factors has a significant influence on the assessment criteria identified (Table 8). Where it is assumed that the concentration factors are only 10% of those predicted by the generic algorithms within CLEA (which is not unreasonable given the concentration factor for barley roots presented by Topp *et al.* 1986), a CWAC of 0.24 mg kg^{-1} is produced; this represents a significant increase from the current SGV. In addition, where assessment criteria are generated that exclude the inhalation of indoor vapour pathway (*i.e.* if suitable vapour mitigation measures will be installed), exposure via the consumption of home-grown produce accounts for the overwhelming majority of predicted exposure. Under these circumstances, assessment criteria are highly sensitive to benzene plant uptake. For example, where it is assumed that the concentration factors are only 10% of those predicted by the generic algorithms within CLEA, a CWAC of 1.4 mg kg^{-1} can be generated, which is roughly an order of magnitude increase. Therefore, under these circumstances problem holders should seriously consider obtaining site-specific plant uptake data to inform detailed quantitative risk estimates.

Finally, the nature of the CLEA model, which relies on the air-water partition coefficient (K_{aw}) to predict soil vapour concentrations means that, the decline in the vapour pressure of benzene as predicted by Raoult's Law for an ideal mixture (assuming this to be present as coal tar) does not reduce the estimated exposure to vapours. Similarly, Raoult's Law for an ideal mixture (assuming this to be present as coal tar) predicts a similar reduction in the solubility of benzene. Consideration of this phenomenon may be a useful addition to the risk assessment community during any future update to the CLEA model or alternative modelling approach.

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