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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 arsenic at former coking works sites.

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

1.1 INTRODUCTION

Arsenic is a common contaminant encountered in soils at former coking works. However, the generic assumptions and input parameters used to derive Generic Assessment Criteria (GAC), such as UK Soil Guideline Values, may not reflect the conditions normally found at former coking works and this may result in GAC that under or over-estimate human exposure at such sites. Here we have considered some input parameters used to derive GACs for arsenic and considered their applicability to the conditions normally encountered at former coking works and subsequently, as an example, we have derived Coking Works Assessment Criteria (CWAC) for the residential land use that may better reflect the risks posed by arsenic at such sites.

To produce such generic criteria we have used similar reasonably cautious assumptions relating to building and soil characteristics to those assumed by the Environment Agency in deriving the Soil Guideline Values (*i.e.* small terraced house and a sandy loam soil). However, due to the nature of former coking works, it is likely that the soils at such sites will mainly be made ground whose composition is dependent in part on the local geology and from where the material has been sourced. It is likely that such materials will be low in natural organic matter contents (although significant amounts of organic contamination may be present).

Although we have attempted to derive generic assessment criteria for use at most coking works, there is still significant uncertainty relating to several site-specific factors, including soil and building type. However, the discussion of input parameters below can also be used to inform site-specific detailed quantitative risk assessments, which take these factors into account.

1.1.1 Coking works – what are they?

Coking works were a subset of the UK coal carbonisation industry. Coal carbonisation (pyrolysis) involved the heating of coal in an oxygen deficient atmosphere to produce a number of solid, liquid, and gaseous products including coke, coal gas, coal tar, ammoniacal liquor and sulphur (Department of the Environment, 1995). The primary function of coking works was to produce coke, a solid residue that principally comprises carbon. However, the other products and by-products were also often utilised to improve the efficiency of the process.

Historically, coke was used in large quantities during the production of iron and steel. This was because coke is a major ingredient used in blast furnaces, where the pure carbon produces carbon monoxide which reduces iron ore (*i.e.* iron oxides) to iron metal. Consequently, coking works were often present at iron and steel works to provide a suitable supply of coke.

A second use of coke from at least the 1920s was in the manufacture of smokeless fuels. This use increased from the 1950s following the implementation of clean air legislation, which required many homes in industrial Britain to stop using coal and move to alternative clean-burning fuels instead. As coke is primarily carbon with many of the impurities present in coal removed, it burns relatively cleanly to produce carbon dioxide and very little smoke. However, coke is typically small, brittle and porous making it bulky to transport. Consequently, smokeless fuels are usually made from powdered coke reformed into briquettes using pitch or other binders. The manufacture of smokeless fuels, using the 'Coalite' or 'Rexco' processes for instance, was conducted at lower temperatures than other carbonisation plants, which reduced the generation of coal gas and yielded more coal tar containing higher levels of volatile organic compounds. Consequently, at coking works that manufactured smokeless fuels, a significant element of the production process involved the refining and utilisation of coal tar products (Forth & Beaumont, 1999).

In line with the decline of the UK steel industry and the move away from solid-fuel to heat UK homes, coke production has declined significantly from its peak in the mid 1950s. Coke production in the UK attained a peak production of some 30 million tonnes per annum in 1956 declining to some 8 million tonnes in 1984 (Forth & Beaumont, 1999). By 1986 there were just 16 sites still producing coke in the UK and this fell to only 4 by 1995 (Department of the Environment, 1995), and the majority of these have closed subsequently.

1.1.2 What is Arsenic?

Elemental arsenic (CAS No. 7440-38-2) occurs in two forms under ambient conditions – a steel grey coloured brittle metallic solid or a dark grey amorphous solid (ATSDR, 2007; Environment Agency, 2009c). Although commonly described as a heavy metal, arsenic is in fact a metalloid (Environment Agency, 2009c).

Arsenic is often identified at elevated concentrations in soils at former coking works (Forth & Beaumont, 1999). This is largely because arsenic is present in coal which is used in the production of coke (USGS, 2005). Iron sulphides, such as pyrite and marcasite, are common inorganic constituents of coal, composing anywhere from a negligible amount to about 5% by weight. Other than iron and sulphur, arsenic is generally the most abundant element in pyrite and marcasite

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(USGS, 2005). As such, arsenic may be encountered at elevated levels in soils and made ground in areas which comprise either coal fragments or coal combustion products (USGS, 2005). These may include former process areas, former coal storage sites, and areas used for the disposal of spent oxides and / or other process residues.

In addition to its presence in coal, arsenic is also present in 'bog ore' or 'bog iron ore' (hydrated ferric oxide mixed with peat) which was typically stockpiled at coking works sites for use as a catalyst and corrosion inhibitor during the coal carbonisation process due to its high content of iron hydroxide (goethite) (Department of the Environment, 1995; Groen *et al*., 1994). For example, Groen *et al*., (1994) reported that bog ore-containing soils in the Netherlands exhibited concentrations of inorganic arsenic of up to 500 mg kg^{-1}.

While the greatest concentrations of inorganic arsenic at former coking works sites are typically associated with storage and processing areas, arsenic is also found at relatively elevated concentrations in off-site soils surrounding former coking works due to its presence in airborne particulate matter emitted during operation of a coal carbonisation plant (Lambert & Lane, 2004).

Arsenic occurs naturally in the environment, however rarely in its elemental form (Environment Agency, 2009c). Over 200 arsenic-containing minerals have been identified with approximately 60% being arsenates, 20% sulphides and sulphosalts, and the remaining 20% including arsenides, arsenites and oxides (Environment Agency, 2009c). In the soils of former coking works sites, arsenic is likely to occur predominantly in association with iron oxides and hydroxides present in both coal (as magnetite) and bog-ore (as goethite).

The main valence states of arsenic in the soil environment tend to be As[V]$^-$ under oxidising conditions and As[III] under reducing conditions.

1.2 TOXICITY

The toxicity of arsenic has been reviewed by Environment Agency (2009b). The review suggests that long term exposure to inorganic arsenic is carcinogenic to humans, producing lung tumours following inhalation and a range of cancers from ingestion in water, most clearly cancer of the skin, bladder and lung. Exposure to arsenic may also have other effects including hyperkeratosis, peripheral vascular disease, cardiovascular effects, diabetes, and developmental effects, however the public health assessment is driven by the cancer risks. Although the biological mechanisms of arsenic-induced cancers are unclear, inorganic arsenic is demonstrably genotoxic and expert groups have assumed arsenics dose-response will not exhibit a dose threshold.

1.2.1 Health Criteria Values

Health criteria values (HCVs) for exposure to inorganic arsenic via oral and inhalation routes are recommended by the Environment Agency (2009b) for use in deriving assessment criteria with the CLEA model. The HCVs take the form of Index Doses (IDs) to reflect the non-threshold dose-response curves expected for inorganic arsenic carcinogenicity in humans following exposure by oral and inhalation pathways.

In the case of inhalation exposure, an ID_{inhal} of 0.002 μg kg^{-1} bw day^{-1} was recommended (Environment Agency, 2009b). Exposures at this magnitude were expected to pose an excess lifetime cancer risk of 1 in 100,000 (*i.e.* 1×10^{-5}). In the case of oral exposure, an ID_{oral} expected to pose the same excess lifetime cancer risk (1×10^{-5}) was identified to lie in the range 0.0006 to 0.003 μg kg^{-1} bw day^{-1} (Environment Agency, 2009b). However, the UK drinking water standard (DWS) for arsenic is 10 μg L^{-1} (HMSO, 2000), which is equivalent to an intake of 0.3 μg kg^{-1} bw day^{-1}, assuming a 70 kg adult drinking 2 L of water per day. Therefore, in order to avoid disproportionately targeting exposures from soil, the Environment Agency (2009b) recommended that the intake derived from the DWS (*i.e.* 0.3 μg kg^{-1} bw day^{-1}) was used as the ID_{oral}, which was thought to be associated with an excess lifetime cancer risk of 40 – 400 in 100,000.

Because of the different levels in cancer risk at the proposed ID_{inhal} and ID_{oral}, inhalation exposure is unlikely to make a significant additional contribution to cancer risk under the standard land use exposure scenarios described by Environment Agency (2009b). Therefore, the current SGVs for arsenic are derived by considering exposure via oral pathways only (Environment Agency, 2009c). However, as the ID_{oral} represents an exposure that is higher than that which would be considered to pose a minimal risk, the likelihood that an exceedance of this ID_{oral} would represent a *significant possibility of significant harm* is much greater than if the ID_{oral} was based solely on health-based considerations of minimal risk (Environment Agency, 2009b; 2009c).

In deriving CWAC for inorganic arsenic, it is reasonable to adopt the HCVs recommended for arsenic by the Environment Agency (2009b).

1.2.2 Background Intake

The background intake of inorganic arsenic by humans from air, food and drinking water has been reviewed by the Environment Agency (2009b). For adults, background inhalation exposure to inorganic arsenic from its presence in ambient air was estimated to be approximately 0.014 μg day^{-1} (Environment Agency, 2009b). The background oral exposure from its presence in food and drinking water was estimated to be much higher at 5 μg day^{-1} (Environment Agency, 2009b). While these data are useful for comparison with the HCVs, they have not been used in deriving CWAC as inorganic arsenic exhibits non-threshold dose-response.

1.3 EXPOSURE ASSESSMENT

The Environment Agency (2009c) presents an exposure assessment for inorganic arsenic under the standard residential land use exposure scenario utilised within the CLEA 1.06 model (Environment Agency, 2009e). It is shown that the ingestion of soil and dust exposure pathway contributes most to the total human exposure (*i.e.* 79.9%). This is followed by dermal contact with soil and dust accounting for 12.3% of total exposure and the consumption of home-grown produce accounting for 7.5% of total exposure. Finally, inhalation of dusts contributed least to total human exposure (*i.e.* 0.3%).

As part of the exposure assessment, the Environment Agency identifies two soil-specific factors that may have a substantial influence on estimates of total human exposure at different types of sites (Environment Agency, 2009c). These are: (i) the bioavailability of soil-bound inorganic arsenic within the gastrointestinal system for uptake into the blood following ingestion; and (ii) the bioavailability of soil-bound inorganic arsenic within the rhizosphere for uptake by the roots of produce-bearing crop plants.

The bioavailability of soil-bound inorganic arsenic within the gastrointestinal system of humans in the standard residential land use exposure scenario is assumed to be 100% (Environment Agency, 2009a). This assumption may be overly cautious for many soil types because a large proportion of inorganic arsenic may be tightly bound within the soil / substrate matrix and pass through the gastrointestinal system without being released or taken up by the body. This is in contrast to inorganic arsenic present in drinking water (*i.e.* the medium of exposure used to derive the ID_{oral}), which is taken up by the body within the gastrointestinal system to a much greater extent (Environment Agency, 2009c). While the bioavailability of soil-bound inorganic arsenic within the human gastrointestinal system cannot be measured directly, the past decade has seen substantial advancements in *in vitro* testing of oral bioaccessibility (an estimate of bioavailability within the human gastrointestinal system) on a commercial basis for use in human health risk assessment (Environment Agency, 2002a; 2002b; 2006). One analytical method, known as the Physiologically Based Extraction Test (PBET), simulates the conditions of the human gastrointestinal tract to assess the human bioaccessibility of elements, including arsenic, by ingestion (Ruby *et al.*, 1996). More recently, the Bioaccessibility Research Group in Europe (BARGE) has agreed a method (termed the Unified BARGE method) to assess human bioaccessibility of elements that reflects the strengths of several different test methods developed or applied across Europe (Caboche, 2009; Wragg *et al.*, 2009). As such, there is a growing dataset of bioaccessibility measurements for inorganic arsenic bound within the matrix of different soil types within the published literature (see Section 1.3.1).

The bioavailability of soil-bound inorganic arsenic within the rhizosphere for uptake by produce-bearing plant roots is represented within the CLEA 1.06 model by the soil-water partition coefficient (K_d) (Environment Agency, 2009e). The K_d, given in units of $cm^3\ g^{-1}$, is the ratio of the chemical concentration sorbed to soil to the concentration in aqueous solution, and can vary widely for a single chemical between soil types (Environment Agency, 2009e). It is used as an input parameter within the PRISM model (which is incorporated into CLEA 1.06) to calculate soil-to-plant concentration factors (CF) for edible plant parts in the case that empirically derived CFs are unavailable (Environment Agency, 2009e). The standard residential land use exposure scenario assumes a K_d for inorganic arsenic of 500 $cm^3\ g^{-1}$ (Environment Agency, 2009d). This value was taken from the Food Standards Agency (2005) who suggested a reference K_d for inorganic arsenic of 500 $cm^3\ g^{-1}$ for sand, loam, and clay soil types within a possible range from 5 – 50,000 $cm^3\ g^{-1}$. Importantly, this value may be overly cautious for soil types with a high inorganic arsenic sorption capacity, thus under-estimating the amount of inorganic arsenic which remains sorbed to the soil matrix and over-estimating the amount available in solution for uptake by roots of produce-bearing plants (see Section 1.3.2).

1.3.1 Oral Bioaccessible Fraction

Oral bioaccessible fractions (BAFs) for arsenic determined using the PBET have been reported in the published literature by several authors for various material types at sites located in the UK (Environment Agency, 2002b; Nathanail *et al.*, 2004; Nathanail *et al.*, 2006; Palumbo-Roe *et al.*, 2005) and elsewhere (Meunier *et al.*, 2010). Furthermore, Land Quality Management Ltd (LQM) have undertaken a number of site investigations which have involved characterisation of BAFs for arsenic in soils and made ground (LQM, 2006; 2007; 2010a; 2010b). These material types and their reported range of BAFs for arsenic are given in Table 1.

Evidently, the BAF of arsenic is highly variable within the material types identified in Table 1. However it is typically observed that maximum BAFs reported for a material are less than 100%, and indeed often less than 50%. An exception to this is provided by the bioaccessibility data for soils and made ground sampled from an allotment site located on the site of a former gas works in Nottinghamshire (LQM, 2007) (Table 1).

No studies were identified that presented BAFs measured using the PBET for soils affected by wastes which are typically present at former coking works or other coal carbonisation facilities. However, Groen *et al.* (1994) assessed the bioavailability of inorganic arsenic in bog ore-containing soils within beagle dogs following oral exposure to arsenic both as an intravenous solution and as an arsenic-containing soil (with an arsenic concentration of 339 mg kg^{-1}). They reported that the bioavailability of inorganic arsenic from the soil was 8.3 ± 2.0%.

Table 1. Arsenic bioaccessible fractions reported for different material types

Material Types	Range of As BAFs	Site Location	Reference
Soils associated with Northampton Sand	1.2 – 33%	Eastern England, UK	Palumbo-Roe *et al.*, (2005)
Allotment soils (gravelly sands and silty sands)	≤9%	Wellingborough, Northamptonshire, UK	Nathanail *et al.*, (2004)
Soils associated with Northampton Sand	<1.9%	Wellingborough, Northamptonshire, UK	Nathanail *et al.*, (2006)
Urban and rural soils (soil types not described)	5 – 45%	Cardiff, UK	Environment Agency (2002b)
Soils associated with Northampton Sand	2 – 9%	Wellingborough, Northamptonshire, UK	Environment Agency (2002b)
Mine spoil and natural soils	7 – 17%	Devon, UK	Environment Agency (2002b)
Topsoil (clay) at an allotment site on a former gas works	27 – 72% (n=10; 8 values <50%)	Bingham, Nottinghamshire, UK	LQM (2007)
Made Ground at a former gas works	20 – 99% (n=14; 11 values <60%)	Bingham, Nottinghamshire, UK	LQM (2007)
Natural ground (silt / clay) at a former gasworks	23 – 93% (n=5; 3 values ≤ 50% and 2 values >67%)	Bingham, Nottinghamshire, UK	LQM (2007)
Topsoil	6 – 54%	Barking, UK	LQM (2006)
Made Ground (mixed with ash)	1 – 47%	Barking, UK	LQM (2006)
Made Ground (ash)	9 – 47%	Barking, UK	LQM (2006)
Allotment topsoil (sandy clay with Victorian Tip wastes)	7 – 22%	Oxford, UK	LQM (2010b)
Allotment topsoil (sandy clay with Victorian Tip wastes)	8 – 15%	Oxford, UK	LQM (2010a)
Gold mine tailings and mine-impacted soils	0.1 – 49%	Nova Scotia, Canada	Meunier *et al.*, (2010)

Numerous studies examining factors affecting the bioaccessibility of arsenic in natural soils with naturally high concentrations of arsenic have been undertaken (Cave *et al.*, 2007; Wragg *et al.*, 2007). These studies have shown that in natural soils, the presence of iron oxides (*e.g.* magnetite) and hydroxides (*e.g.* goethite) is often the most important factor determining the bioaccessibility of arsenic. This is because arsenic readily adsorbs to iron oxides and hydroxides through ligand exchange mechanisms. Other factors shown to have an effect on arsenic bioaccessibility include the total arsenic concentration in soil and soil clay content.

It is known that metal oxides, including iron oxides, were employed within the coal carbonisation process as catalysts and corrosion inhibitors at former coking works sites (Department of the Environment, 1995). Furthermore, iron present in coal as pyrite (FeS_2) will undergo partial oxidation to form iron oxide (*e.g.* magnetite) (Fe_3O_4) on the surface of pyrite grains during the coal carbonisation process (Murray, 1973; Thorpe *et al.*, 1984). As such, soils in the vicinity of coking works have often been reported to exhibit elevated concentrations of iron oxides, spent iron oxides and total iron (Mansfeldt *et al.*, 2004). This is demonstrated using soil data provided for the former Avenue coking works, Derbyshire. The shallow soils and subsurface materials at this site exhibited total iron concentrations ranging from 349 to 110,000 mg kg^{-1} with a mean of ~19,000 mg kg^{-1} (*i.e.* ~1.9%).

Because iron oxides and hydroxides present in soils are known to provide sorption sites for the immobilisation of elements such as arsenic, and because soils at former coking works sites are typically characterised by high concentrations of total iron (possibly reflecting the presence of iron oxides and hydroxides such as magnetite and goethite), it is not unreasonable to hypothesise that soils affected by coking works wastes may exhibit oral BAFs for arsenic which are less than 100%. This is in contrast to the assumption of 100% bioavailability within the human gastrointestinal tract in the standard residential land use exposure scenario used to derive the inorganic arsenic SGV.

We had the opportunity as part of this project to study the bioaccessibility of one material type – the 'red shale', from the former Avenue Coking Works. Red shale is burnt colliery spoil (a sulphate-bearing material) formed by internal combustion of spoil heaps or indeed underground combustion. It is relevant to the soils that might be found in residential gardens after redevelopment of former coking works as it is often used as a hardcore fill in domestic properties in areas where coal mining and / or coke production was prevalent due to its favourable geotechnical properties. Samples of red shale were collected from the Avenue Site by LQM staff with the assistance of representatives from VSD Avenue (a joint venture comprising DEC, Sita Remediation, and Volker Stevin) and the support of the East Midlands Development Agency (emda) team and tested for total and bioaccessible arsenic by the British Geological Survey. BAFs were calculated for each sample and are presented in Table 2. The bioaccessibility testing followed the Unified BARGE method. Bioaccessible fractions were generally towards the low end of those found in the literature (0.4-12%). The data show little evidence of a relationship between total and bioaccessible inorganic arsenic (Figure 1). There is some evidence that very low bioaccessible fractions are associated with high organic matter contents as determined by loss on ignition (Figure 2).

Based on the evidence available in the literature and from Avenue, it is not unreasonable to assume that the BAF for inorganic arsenic in coking works soil lies in the range of <0.5% – 60%. This range includes all of the values measured in red shale samples obtained from the former Avenue Coking Works site while the upper limit of 60% is greater than the majority of maximum values reported for natural soils and made ground in available studies (Table 1; Figure 1). However this merely reinforces the need for site specific data if BAF<100% are to be invoked for risk assessment purposes.

Table 2. Arsenic bioaccessible fractions for red shale, Avenue Coking Works

Sample Code	Organic Matter	Soil pH	Total As	BAF As
	%		mg kg^{-1}	%
VSD BA1 1 mbgl	1.9	7.2	119	10.2
VSD BA2 2 mbgl	1.4	6.3	241	6.7
VSD BA3 1 mbgl	1.8	7.4	159	5.9
VSD BA4 2 mbgl	1.9	6.6	183	5.9
VSD BA5 1-2 mbgl	10.5	5.9	314	9.2
VSD BA6 1-2 mbgl	6.9	6.8	477	7.6
VSD BA7 1 mbgl	5.4	6.5	143	12.1
VSD BA8 3 mbgl	7.3	5.8	188	5.4
VSD BA9 3 mbgl	11.3	6.5	137	7.3
VSD BA10 3 mbgl	4.0	4.6	65.0	5.0
VSD BA11 1 mbgl	4.2	6.5	110	6.9
VSD BA12 2 mbgl	5.2	6.3	145	10.1
VSD BA13 1 mbgl	14.6	4.9	95.4	3.6
VSD BA14 2 mbgl	28.2	5.5	168	2.5
VSD BA15 1 mbgl	14.9	5.6	61.9	6.9
VSD BA16 2 mbgl	26.2	5.9	182	2.1
VSD BA17 1 mbgl	16.7	5.0	63.3	6.7
VSD BA18 2 mbgl	35.5	2.8	351	0.4
VSD BA19 1 mbgl	15.4	7.2	59.1	6.3
VSD BA20 2 mbgl	38.7	3.1	311	0.6
		Max	477	12
		Min	59	0.41

Note: Organic matter content determined by loss on ignition at 450°C

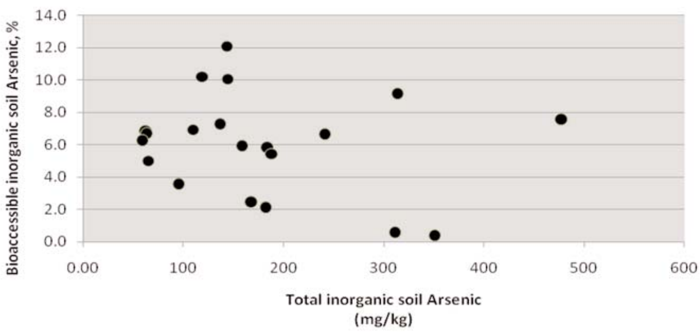

Figure 1. Total inorganic arsenic and bioaccessible fraction for red shale, Avenue

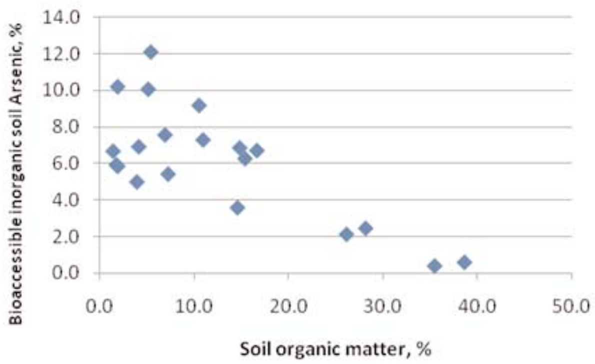

Figure 2. Soil organic matter (as determined by loss on ignition at 450°C) and bioaccessible fraction for red shale, Avenue

1.3.2 Soil-Water Partition Coefficient

Soil-water partition coefficients (K_d) for inorganic arsenic reported within the literature have been summarised by several authors (Environment Agency, 2009d; Food Standards Agency, 2005; RIVM, 2001; USEPA, 1996; USEPA, 2005). These summaries have shown that inorganic arsenic K_d values can range from 2 to 50,000 $cm^3\ g^{-1}$ across different soil types. This variation in K_d values is likely to reflect variations in both the chemical form of arsenic and the mineralogical properties of the soil.

No studies have been identified in the published literature that present inorganic arsenic K_d values for soils affected by wastes which are typically present at former coking works or other coal carbonisation facilities. However, numerous studies examining factors affecting the adsorption of inorganic arsenic within different soil types (and mineral types present within soils) were identified (ATSDR, 2007; Environment Agency, 2009c; Sakata, 1987; van der Hoek *et al.*, 1994; Zhang & Selim, 2005). Similarly to the arsenic bioaccessibility literature (Section 1.3.1), these studies have consistently shown that As[V] (the predominant form of inorganic arsenic under oxidising soil conditions) adsorbs readily to iron oxides (*e.g.* magnetite) and hydroxides (*e.g.* goethite) present in soils through ligand exchange mechanisms. As such, soils containing elevated levels of iron oxides and hydroxides may exhibit higher K_d values for inorganic arsenic (ATSDR, 2007). Waterlogged soils, which exhibit reducing conditions, may result in different patterns of arsenic adsorption, however these have not been considered as part of this project.

As discussed in Section 1.3.1, soils in the vicinity of coking works have often been reported to exhibit elevated levels of total iron, some of which may be in the form of iron oxides and hydroxides. This is due to the use of goethite in the coal carbonisation process and the partial oxidation of pyrite present in coal to magnetite during carbonisation (Department of the Environment, 1995; Murray, 1973; Thorpe *et al.*, 1984).

Because iron oxides and hydroxides present in soils provide sorption sites for elements such as arsenic, it is reasonable to hypothesise that soils affected by coking works wastes, which typically have a high total iron content, may exhibit higher K_d values for arsenic than that assumed by the Environment Agency (2009d) for the derivation of the inorganic arsenic SGV (*i.e.* 500 $cm^3\ g^{-1}$).

This is demonstrated using soil data from the former Avenue coking works. Concentrations of total arsenic in soil samples from the site ranged from <1 to 318 $mg\ kg^{-1}$ (n=2590) with a mean of 16 $mg\ kg^{-1}$, whereas concentrations in samples of soil solution ranged from <0.001 to 0.02 $mg\ L^{-1}$ (n=453) with a mean of 0.002 $mg\ L^{-1}$. Of the soil samples for which total arsenic had been measured, 436 of these samples also had corresponding measurements of inorganic arsenic dissolved in soil solution. Excluding the samples for which the arsenic concentration in soil was below the limit of detection (LOD), a total of 365 soil samples had sufficient data to calculate K_d values. Values of K_d ranged from 333 to 159,000 $cm^3\ g^{-1}$. A lognormal probability distribution was fitted to the range of K_d values with a mean of 7,274 $cm^3\ g^{-1}$ and a standard deviation of 8,313 $cm^3\ g^{-1}$. It is important to note that many of the K_d values calculated are likely to have been underestimated as many of the concentrations in soil solution were less than the LOD, and so the LOD was used in the calculation of the K_d.

Based on the evidence available, it is reasonable to assume a K_d for inorganic arsenic in coking works soils of ~**7000 $cm^3\ g^{-1}$**. This value is well within the range of K_d values reported for inorganic arsenic within the literature. However, it is important to note that substantial uncertainty is associated with this value and it would therefore require validation on a site specific basis prior to application at a site.

The current SGV for inorganic arsenic is derived using geometric mean soil-to-plant concentrations factors (CFs) for fruit and vegetable produce groups which have been derived by summarising the available CFs reported in the literature (Environment Agency, 2009b). Therefore, no use was made of the PRISM model, and hence the K_d, in calculating the inorganic arsenic SGV. Justification given for the use of literature values was that the PRISM model appeared to over-predict CFs across all produce groups, giving values which were outside the range of literature values when utilising the PRISM model input parameters for inorganic arsenic suggested by the Environment Agency (2009e). These input parameters included a soil-to-plant availability correction, δ, of 5, a root to edible plant part correction factor, f_{int}, of 0.5, and the inorganic arsenic K_d of 500 $cm^3\ g^{-1}$ recommended by the Environment Agency (2009d).

Re-parameterisation of the PRISM model using the revised Kd for inorganic arsenic at coking works sites (7000 $cm^3\ g^{-1}$), resulted in a single CF for all produce groups of **3.0E-4** (Table 3). This value falls within the range of CFs identified for each fruit and vegetable produce group reported by the Environment Agency (2009b). Furthermore, the CF based on the re-parameterised PRISM model is in the same order of magnitude as the geometric mean CFs for each produce group, with the exception of tree fruit (Table 3).

Table 3. Comparison of soil-to-plant concentration factors by produce category for a sandy loam

Dataset	Green vegetables	Root vegetables	Tuber vegetables	Herbaceous fruit	Shrub fruit	Tree fruit
Literature Review	4.3E-4	4.0E-4	2.3E-4	3.3E-4	2.0E-4	1.1E-3
PRISM model	3.0E-4	3.0E-4	3.0E-4	3.0E-4	3.0E-4	3.0E-4

Notes:
Literature review data from Environment Agency (2009b)
Input parameters values used in the PRISM model included a soil-to-plant availability correction, δ, of 5 (dimensionless); a water filled porosity, θ_w, for a sandy loam of 0.33; a soil bulk density, ρ_s, for a sandy loam of 1.21 ($g\ cm^{-3}$); a soil-water partition coefficient, K_d, of 7000 $cm^3\ g^{-1}$; and a root to edible plant part correction factor, f_{int}, of 0.5 (dimensionless).

1.4 PHYSICAL-CHEMICAL CHARACTERISTICS

The physical-chemical characteristics of inorganic arsenic which were used to derive the SGV are provided by Environment Agency (2009b). Other than the soil-water partition coefficient (K_d), the only other physical-chemical characteristic employed within the CLEA 1.06 model to derive the inorganic arsenic SGV is the aqueous solubility. However, the aqueous solubility for inorganic arsenic is used in the CLEA 1.06 model as a check to calculate the saturated soil concentration at the aqueous solubility limit and does not influence the SGV. Therefore, no further consideration was given to this input parameter.

1.5 COKING WORKS ASSESSMENT CRITERIA

Two main assumptions in the CLEA 1.06 model for the derivation of inorganic arsenic SGVs have been identified which may not be appropriate for assessing risks to human health from inorganic arsenic at former coking works. These are: (i) the assumption that the bioavailability of soil-bound inorganic arsenic within the gastrointestinal system of humans is 100%; and (ii) the assumption that soil-bound inorganic arsenic is moderately mobile in soil solution with a soil-water partition coefficient of 500 $cm^3\ g^{-1}$.

The applicability of these two assumptions for assessing risks from inorganic arsenic in soils at coking works sites can be questioned because arsenic may be more tightly bound into the soil matrix than assumed by the CLEA 1.06 model. As such, the bioavailability of inorganic arsenic within the human gastrointestinal tract for uptake into the body, and indeed the bioavailability of inorganic arsenic within the rhizosphere for uptake by plant roots, is likely to be less than currently predicted by the model at many sites.

Discussions on the use of oral bioaccessibility data as a measurement of oral bioavailability for use in human health risk assessment are given by both the Environment Agency (2009f) and the Chartered Institute of Environmental Health (CIEH, 2009). The Environment Agency state that while they are not able to recommend any specific test of arsenic bioaccessibility at this time, provided such a test is carried out in accordance with guidelines for good practice, it is considered that the results can be useful as part of a "lines of evidence approach" to evaluating site specific risk, including the sensitivity of any quantitative risk assessment (Environment Agency, 2009c). Guidance provided by the CIEH (2009) builds on the statements of the Environment Agency, indicating that bioaccessibility results may also be employed as input parameters in risk estimation tools, such as the CLEA model, provided that the results are supported by other lines of evidence (*e.g.* geological history, geochemical data, results of tests in the same geological material at other sites). The guidance goes on to state that it is usual practice to use the maximum, or a multiple of the maximum, bioaccessible test result as an estimate of bioavailability, provided that the entire range of data is examined and the relationship between total and bioaccessible concentrations is considered (CIEH, 2009).

The relationship between the GAC for inorganic arsenic (based on the standard residential land use exposure scenario) and the oral BAF is shown in Figure 3. The GAC have been calculated using the toxicological and physical-chemical input parameters recommended by the Environment Agency (2009b; 2009d). However, instead of using the geometric mean soil-to-plant concentration factors (CFs) for each vegetable and fruit produce group to model plant uptake of arsenic (Environment Agency, 2009d), the PRISM model has been used to model the plant uptake of arsenic, employing a K_d value of 7000 $cm^3\ g^{-1}$ as discussed in Section 1.3.2.

Assuming that the oral BAF for inorganic arsenic in soils and made ground encountered at a typical coking works site is in the range of 20–60%, as suggested based on the available evidence reviewed in Section 1.3.1, it is possible to calculate Coking Works Assessment Criteria (CWAC) which correspond with these upper and lower oral BAFs as shown for illustrative purposes only in Figure 3. Assuming a moderate oral BAF of 20% (and the revised K_d for modelling CFs in the PRISM model), a CWAC of 101 mg kg^{-1} is estimated (Figure 3), whereas assuming a higher oral BAF of 60% (and the revised K_d for modelling CFs in the PRISM model), a CWAC of 50 mg kg^{-1} is estimated (Figure 3). The data for the red shale from the Avenue site indicate a maximum BAF of 12% (Table 2) suggesting that a CWAC in excess of 100 mg kg^{-1} may be more appropriate for that material at that site.

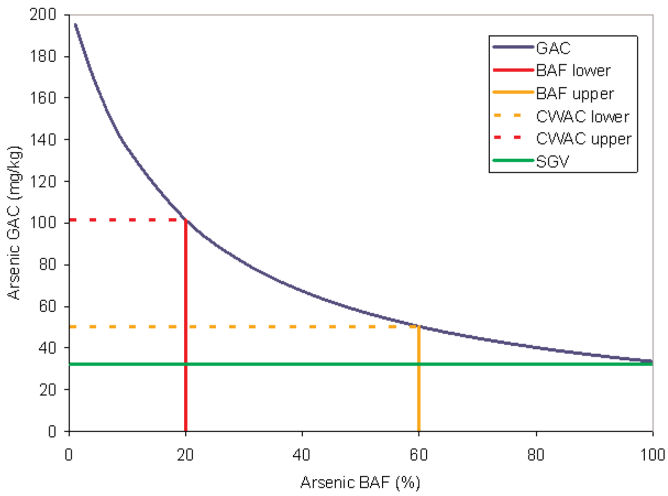

Figure 3. GAC for inorganic arsenic in the residential land use exposure scenario against arsenic oral bioaccessible fraction (BAF)

While the purpose of this bulletin is not to specify a BAF that is applicable to all materials present at all former coking works sites, it serves as a useful reminder of the value of site, and indeed material, specific information to inform the derivation of site and material specific assessment criteria within the context of a detailed quantitative risk assessment (DQRA).

It is important to re-iterate that, in following the approach of the Environment Agency (2009c), the inorganic arsenic CWAC are based on comparison of the oral and dermal exposure routes with the oral index dose (ID_{oral}) only. This approach is considered by the Environment Agency to be appropriate because of the different excess lifetime cancer risk levels associated with the oral and inhalation IDs, and the very small contribution that inhalation makes to exposure in the residential land use exposure scenario.

As described in Section 1.2.1, the ID_{oral} has been derived from the current UK drinking water standard for arsenic and does not represent an exposure at a minimal risk level. The excess lifetime cancer risk associated with the ID_{oral} has been estimated to be between 40 and 400 times higher than a minimal risk level of 1 in 100,000 (Environment Agency, 2009b). Therefore, the likelihood that exceedance of the CWAC, and hence the ID_{oral}, will represent a *significant possibility of significant harm*, is much greater than would be the case if the ID_{oral} was based on minimal risk.

The percentage pathway contributions to total human exposure for an example inorganic arsenic CWAC of 50 mg kg^{-1} are given in Table 4. Inhalation exposure from indoor and outdoor dusts is included for illustrative purposes only and has not been included in the derivation of the CWAC. The data show that the ingestion of soil and dust pathway contributes most to total exposure.

Table 4. Percentage pathway contributions to total human exposure based on a residential land use

Exposure pathways	Contribution to exposure (%)
Ingestion of soil and indoor dust	70.9
Consumption of home-grown produced and attached soil	6.9
Dermal contact with soil and dust	21.8
Inhalation of dust	0.5
Inhalation of vapour (indoor)	NC
Inhalation of vapour (outdoor)	NC
Oral background	NC
Inhalation background	NC

Notes:

The exposure scenario assumes an oral bioaccessible fraction (BAF) of 60% and a soil-water partition coefficient (K_d) of 7000 cm^3 g^{-1}

NC = Not calculated (this exposure pathway was not calculated for chemical specific reasons)

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