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A critical evaluation of the use and 'misuse' of As and Pb bioaccessibility data in human health risk assessments

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ABSTRACT

With the now widescale reporting of oral bioaccessibility data at contaminated sites, following our investigation of three sites (one public open space and two residential) for As and Pb contamination, a critical evaluation of the application and utility of such bioaccessibility testing was undertaken to better inform future use. Mean As and Pb soil levels across the sites varied between 12.5 and 24,900 mg/kg and 149–5930 mg/kg, respectively. Using the Unified Bioaccessibility Method (UBM) for *in vitro* bioaccessibility testing the highest bioaccessible concentrations were identified in the gastric phase. At site 1, a residential urban garden site the maximum bioaccessible As was 50.2% while the maximum bioaccessible Pb was 64.8%; similarly in site 2, also a residential urban garden site the maximum bioaccessible As was 38.72% while the maximum bioaccessible Pb was 66.0%. However, at site 3, a public open space site, the maximum bioaccessible As was 29.7% while the maximum bioaccessible Pb was 38.4%. Using the appropriate soil screening values and recommended statistical testing, we highlight that the use of bioaccessibility testing was unnecessary at sites 1 and 2 (residential urban garden sites), while at site 3 the value of oral bioaccessibility testing is highlighted as part of a 'lines of evidence approach' to support the site's specific risk assessment. We need to move away from the uncritical, blanket application of oral bioacessibility testing and strategically target where the results of these data add real value to site determination.

1. Introduction

A growing public awareness of soil-borne contaminants coupled with economic drivers for greater availability of affordable housing and concerns over environmental justice has raised the profile of environmental risks to health. As and Pb are commonly encountered contaminants in our urban environments and increasing urbanisation has meant many former industrial sites have been developed as residential areas or urban parks, whilst diffuse urban Pb pollution is a well-recognised issue in many of the worlds cities (e.g. Yang and Cattle, 2015; Palmer et al., 2015; Appleton et al., 2012A, 2012B; Entwistle et al., 2019). Indeed, As and Pb are two of the most studied contaminants in the urban environment due to their considerable impact on health. (e.g. Appleton et al., 2012A, 2012B; Okorie et al., 2011; Middleton et al., 2017).

Exposure to potentially harmful elements (PHEs) in soil may lead to a significant possibility of significant harm (SPOSH) for human receptors if the substances are directly inhaled, ingested, or indirectly transferred through the food chain into the diet. The accidental or deliberate ingestion of soil is one of the primary exposure routes through which PHEs can enter into the human body. To pose a human health risk, the ingested fractions of the contaminant must be bioavailable (i.e. available for absorption into the systemic circulation) via, for example, the gastrointestinal (GI) tract. As and Pb species vary in their solubility and assumptions that overestimate bioavailability in the human body can lead to costly remediation strategies and unnecessary interventions that may impact unduly on the mental, economic and social wellbeing of residents. *In vitro* bioaccessibility studies that quantify the fraction of a contaminant in soil that is soluble and readily released during passage through the GI tract have been widely reported in the literature (e.g. Boisa et al., 2013; Denys et al., 2012; Palmer et al., 2015; Pelfrêne et al.,

Abbreviations: ABA, Absolute bioavailability; C4SLs, category 4 screening levels; CLEA, contaminated land exposure assessment; CRM, certified reference material; Cs, critical concentration; DQRA, Detailed Quantitative Risk Assessment; GI, gastrointestinal tract; GQRA, Generic Quantitative Risk Assessment; IEUBK, Integrated Exposure Uptake Biokinetic model; mbgl, metres below ground level; PHEs, potentially harmful elements; POS, public open space; RBA, relative bioavailability; SPOSH, significant possibility of harm; SSAC, site-specific assessment criteria; UBM, Unified Bioaccessibility Method.

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2015; Fernandez-Caliarni et al., 2019). *In-vitro* bioaccessibility testing simulates the human physiological condition of the GI tract and a variety of different protocols exist (e.g. Intawongse and Dean, 2006; Ruby et al., 1999). The Unified Bioaccessibility Method (UBM), as developed by the Bioaccessibility Research Group of Europe has been validated against *in vivo* bioavailability studies for As and Pb (Wragg et al., 2011; Denys et al., 2012). The first extraction stage is the gastric phase comprising simulated fluids from the mouth and stomach compartment. While, the second extraction stage is the gastrointestinal (GI) phase which consists of simulated fluids from the small intestinal compartment. This model can be used to refine site specific human health risk assessments and is especially relevant at 'grey-area' sites where marginal exceedance of soil guideline levels are observed and where a more detailed understanding of the potential release of ingested PHEs during their passage through the GI tract warrants the additional time and money.

With the growing use of bioaccessibility testing in human health risk assessment a critical appraisal of the role and utility of such data is timely. This paper, using a case study approach, focusses on As and Pb, and highlights the application of bioaccessibility data in three urban environments (two within a residential setting and the third an area of public open space) to illustrate where i) uncritical application of bioaccessibilty testing is at best of no to limited value and may even delay intervention or remedial actions, and ii) where bioaccessibility data can form an integral part of the 'lines of evidence' approach in the decision making process for establishing the presence, or absence, of a significant pollutant linkage. Furthermore, given the application of bioaccessibility data involves relating the *in-vitro* bioaccessibillity data to relative bioavailability the approaches to this are also reviewed.

2. Materials and methods

2.1. Soil sampling sites

Site 1 is in St. Helens, North-West England, and covers approximately 11.5 ha of a former industrial site; an alkali works which operated between 1849 and 1928. The operation of the alkali works generated chemical waste deposits on the site and it is unknown to what extent they were removed or remediated before the site was re-developed as residential housing in 1959. The sampling strategy focused on shallow depth soil (0.10–0.60 m below ground level, mbgl) and soil samples were taken from front and rear gardens (a garden is defined in this research as a piece of ground adjoining a house, in which grass, flowers, and shrubs may be grown) from 30 properties at the site where access was available. Subsequently, twelve samples were selected for bioaccessibility testing (Table 1A) due to their high pseudo-total arsenic concentrations; the term pseudo-total is used as no hydrofluoric acid was used in the digestion of the soil samples, therefore digestion is likely to be incomplete.

Site 2 is also located in St. Helens, North-West, England. The site, approximately 1.5 ha, was a former industrial site used for glass and chemical works between 1840 and 1890. The area was derelict for a long period of time before being re-developed to a residential housing estate between 1950 and 1959. The 38 residential properties comprise a mixture of semi-detached and terraced houses, with predominantly grass-covered (lawns) gardens. No specific structures or point sources of contamination were identified from the historical review and the site was treated as a single zone with non-targeted sampling locations. Shallow depth soil samples (0.10–0.60 mbgl) were taken from the front and back gardens and 10 samples were selected for bioaccessibility testing) due to their high pseudo-total arsenic concentrations (Table 1B).

Site 3 is in South Tyneside, North-East, England (approximately 4.3 ha). According to the UK Environment Agency landfill records, the site has a long history of receiving commercial and household waste since 1856. From 1921 to 1982, an allotment garden was present on part of the site, but since 1982 the area has been maintained as public recreational space. Most of the site is a level grassed open space, interspersed with overgrown grassed areas. The site is currently used for leisure, although there are no formal picnic facilities available (such as benches or litter bins) and a tarmac path crosses the site allowing access to and from surrounding residential areas and local facilities. The site is also subject to illegal 'glass bottle digging' activity, due to the historical landfill beneath, and hand and mechanically excavated 'holes' ($2 \times 2\ m^2$ and up to a couple of metres deep) infrequently appear across the site overnight. Eighteen shallow soils (0.02–0.20 mbgl) were collected from across the site using a stratified sampling grid (Table 1C).

2.2. Soil sampling

At sites 1 and 2 soil samples were collected using a hand-held auger whereas at site 3 soil samples were collected using a stainless-steel trowel. A slightly lower soil sampling depth was done at sites 1 and 2, of up to 0.60 m, to allow a representation of the type of human activity that might take place within a garden e.g. shallow digging of the soil. Whereas a soil depth of up to 0.20 m was done at site 3, as might typify the type of human-soil interaction that might occur at a recreational venue (i.e. a public open space). Sampling equipment was cleaned with acetone after each sample was collected to avoid cross contamination. The samples were transferred into suitable containers (i.e. glass jar containers at sites 1–2 and kraft geochemical sampling bags at site 3) and then transported to the laboratory for subsequent analyses. All soil samples were then subsequently dried (typically $<40\ ^{\circ}C$ for a minimum of 4 days), disaggregated and sieved through a 2 mm nylon mesh for pseudo-total analysis. Additionally, a sub-sample was then sieved through a 250 μm nylon mesh for bioaccessibility testing.

2.3. Chemicals/reagents

All chemicals used were certified analytical grade. All solutions and dilutions were prepared using ultra-pure water from a Milli-Q purifier system with a water resistivity $>18.2\ M\Omega\ cm^{-1}$ at $27\ ^{\circ}C$ (QTM Millipore, Molsheim, France). A multi-element calibration solution (100 mg/L) containing 26 elements, including As and Pb, and internal standard solutions (1000 μg/mL each) for Sc and In was supplied by SPEXCerti-Prep (Middlesex, UK). Certified reference materials (NIST SRM 2710a, GBW07401 and CRM059-50) used for instrument calibration and quality control were also obtained from LGC standards (Middlesex, UK).

For the bioaccessibility testing, a guidance material (BGS 102) was obtained from British Geological Survey (Keyworth, UK). Pepsin (porcine), bovine serum albumen (BSA), pancreatin (porcine), sodium hydrogen phosphate (NaH_2PO_4), D + glucose and urea were all obtained from Merck (Poole, UK). Uric acid, α-amylase (bacillus), lipase (porcine), bile (bovine), D-glucosamine hydrochloride, potassium thiocyanate (KSCN), mucin (porcine) were supplied by Sigma-Aldrich Co. (Gillingham, UK). D-Glucuronic acid was obtained from Fluka Chemicals Ltd, (Gillingham, UK), while ammonium acetate, ammonium chloride (NH_4Cl), anhydrous sodium sulphate (Na_2SO_4), caesium chloride (CsCl), calcium chloride dihydrate ($CaCl_2.2H_2O$), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), hydroxylamine hydrochloride, magnesium chloride hexahydrate ($MgCl_2.6H_2O$), nitric acid (70% HNO3), potassium chloride (KCl), potassium hydrogen phosphate (KH_2PO_4), sodium bicarbonate ($NaHCO_3$), sodium chloride (NaCl) and sodium hydroxide (NaOH), were all supplied by Fisher Scientific Ltd. (Loughborough, UK).

2.4. Instrumentation

An inductively coupled plasma atomic emission spectrometer (ICP-AES, PerkinElmer Optima-8000, Beaconsfield, UK) was used for analysis of samples from site 1 and 2, while for site 3 an inductively coupled plasma mass spectrometer (ICP-MS) was used (XSeries II, Thermo Electron Corp., Cheshire, UK). Acid digestion was done using either a microwave accelerated reaction system (MARS 5, CEM Corporation)

Table 1
Sample description, soil properties, total and bioaccessible concentration (mg/kg) of As and Pb, and % bioaccessibility in urban gardens (sites 1 and 2) and public open space site (site 3). (A) Site 1 residential urban garden; (B)Site 2 residential urban garden; (C) Site 3 - Public Open Space.

[b]Sample	Sample description	pH[e]	% LOI[e]	As						Pb					
				Pseudo-total	Stage 1 (gastric phase)	% BAF[c]	Stage 2 (gastric + intestinal phase)	% BAF[c]	Residual (%)[d]	Pseudo-total	Stage 1 (gastric phase)	% BAF[c]	Stage 2 (gastric + intestinal phase)	% BAF[c]	Residual (%)[d]
#UG1	Sandy soil	7.2	13.2	221 ± 7	77.3 ± 2.7	35.0	64.5 ± 4.8	29.2	174 ± 7 (78.7)	339 ± 12	121 ± 4.5	35.7	81.7 ± 4.5	24.1	273 ± 121 (80.5)
#UG2	Clayey-sandy soil	7.2	12.9	251 ± 10	126 ± 5	50.2	112 ± 1	44.6	166 ± 4 (66.1)	382 ± 7	246 ± 5.8	64.4	136 ± 5	35.6	271 ± 13 (70.9)
#UG3	Ashy soil	7.0	11.8	144 ± 2	24.1 ± 2.7	16.7	16.4 ± 1.1	11.4	131 ± 5 (91.0)	469 ± 9	126 ± 5.4	26.9	5.36 ± 0.47	1.1	447 ± 14 (95.7)
#UG4	Ash/ Clinker rich soil	6.6	8.8	126 ± 5	61.3 ± 1.8	48.7	56.0 ± 5.3	44.4	74 ± 4 (58.7)	149 ± 5	96.6 ± 7.1	64.8	52.7 ± 1.9	35.4	88.6 ± 5.9 (59.5)
#UG5	Ashy soil	6.6	11.0	169 ± 4	73.3 ± 1.4	43.4	34.8 ± 2.2	20.6	168 ± 5 (99.4)	369 ± 8	110 ± 1.8	29.8	18.7 ± 1.2	5.1	400 ± 10 (108.0)
#UG6	Ashy soil	7.4	18.2	451 ± 7	52.4 ± 3.1	11.6	42.7 ± 3.8	9.5	430 ± 12 (95.3)	385 ± 10	46.2 ± 3.4	12.0	4.37 ± 0.84	1.1	404 ± 11 (105.0)
#UG7	Topsoil	6.6	11.7	169 ± 5	74.1 ± 3.7	43.8	73.0 ± 2.3	43.2	118 ± 4 (69.8)	226 ± 7	105 ± 5.3	46.5	52.8 ± 1.8	23.4	170 ± 5 (75.2)
#UG8	Topsoil	7.1	12.0	147 ± 5	52.6 ± 3.8	35.8	41.6 ± 0.9	28.3	114 ± 2 (77.6)	345 ± 12	175 ± 13.6	50.7	13.3 ± 1.1	3.9	341 ± 19 (98.8)
#UG9	Ashy soil	6.3	7.9	530 ± 17	120 ± 6	22.6	103 ± 1	19.4	429 ± 10 (80.9)	404 ± 4	65.2 ± 2.3	16.1	35.9 ± 1.1	8.9	368 ± 10 (91.1)
#UG10	Ashy soil	7.4	16.6	911 ± 5	128 ± 4	14.1	93.2 ± 5.8	10.2	904 ± 9 (99.2)	965 ± 26	280 ± 13.2	29.0	5.29 ± 0.46	0.5	982 ± 16 (102.0)
#UG11	Ashy soil	6.5	17.3	1660 ± 43	451 ± 19	27.2	303 ± 15	18.3	1340 ± 33 (80.7)	627 ± 18	116 ± 9.5	18.5	7.09 ± 1.22	1.1	616 ± 13 (98.2)
#UG12	Galligu	6.7	11.2	364 ± 7	140 ± 6	38.5	98.6 ± 3.7	27.1	282 ± 11 (77.5)	398 ± 12	174 ± 19	43.7	9.75 ± 0.40	2.4	380 ± 6 (95.5)

(B)

[b]Sample	Sample Description	pH[e]	% LOI[e]	As						Pb					
				Pseudo-total	Stage 1 (gastric phase)	% BAF[c]	Stage 2 (gastric + intestinal phase)	% BAF[c]	Residual (%)[d]	Pseudo-total	Stage 1 (gastric phase)	% BAF[c]	Stage 2 (gastric + intestinal phase)	% BAF[c]	Residual (%)[d]
#UG13	Ashy/ clinker rich soil	5.4	13.7	5280 ± 63	1010 ± 30	19.1	814 ± 19	15.4	4810 ± 8 (91.1)	5930 ± 325	1250 ± 30	21.1	77.9 ± 7.0	1.3	5920 ± 98 (99.8)
#UG14	Lime waste	6.0	14.5	514 ± 10	199 ± 3	38.7	185 ± 7	36.0	332 ± 4 (64.6)	720 ± 26	354 ± 9.4	49.2	106 ± 3.1	14.7	618 ± 14 (85.8)
#UG15	Ashy soil	6.8	15.4	2680 ± 42	276 ± 1	10.3	251 ± 2	9.4	2420 ± 55 (90.3)	1870 ± 34	4.18 ± 0.52	0.2	7.10 ± 1.35	0.4	1830 ± 26 (97.9)
#UG16	Slag/ clinker rich soil	6.7	18.9	24,900 ± 994	4980 ± 117	20.0	3160 ± 121	12.7	23,100 ± 376 (92.8)	1980 ± 52	30.5 ± 0.3	1.5	13.1 ± 0.1	0.7	2010 ± 60 (101.0)
#UG17	Clinker	7.1	12.7	2700 ± 35	799 ± 14.8	29.6	680 ± 10	25.2	2310 ± 103 (85.6)	1530 ± 32	111 ± 3.3	7.3	15.5 ± 1.5	1.0	1430 ± 62 (93.5)
#UG18	Slag/ clinker rich soil	5.8	11.2	325 ± 28	125 ± 1.2	38.5	142 ± 4	43.7	223 ± 11 (68.6)	512 ± 2	284 ± 2.2	55.5	206 ± 6	40.2	356 ± 13 (69.5)
#UG19	Slag rich soil	5.7	8.6	287 ± 15	81.5 ± 4.1	28.4	101 ± 3	35.2	225 ± 6 (78.4)	459 ± 17	303 ± 17.6	66.0	226 ± 11	49.2	288 ± 5 (62.7)
#UG20	Ashy/ clinker rich soil	6.8	16.3	614 ± 16	150 ± 3.8	24.4	131 ± 2	21.3	554 ± 13 (90.2)	535 ± 20	177 ± 6.0	33.1	43.7 ± 6.3	8.2	548 ± 13 (102.0)
#UG21	Slag rich soil	5.2	6.1	40 ± 2	14.9 ± 0.4	37.3	21.6 ± 2.6	54.0	22.8 ± 3.7 (56.7)	193 ± 4	110 ± 1.6	57.0	76.9 ± 3.5	39.8	131 ± 12 (67.9)
#UG22	Clay soil	7.0	8.1	93 ± 4	11.0 ± 0.9	11.8	15.0 ± 0.9	16.1	85.8 ± 11.9 (92.1)	246 ± 3	2.06 ± 0.32	0.8	3.45 ± 0.17	1.4	239 ± 31 (97.2)

(C)

Sample	Soil Texture	pH[e]	% LOI[e]	As						Pb					
				Pseudo-total	Stage 1 (gastric phase)	% BAF[c]	Stage 2 (gastric + intestinal phase)	% BAF[c]	Residual (%)[d]	Pseudo-total	Stage 1 (gastric phase)	% BAF[c]	Stage 2 (gastric + intestinal phase)	% BAF[c]	Residual (%)[d]

(*continued on next page*)

Table 1 (*continued*)

(C)

Sample	Soil Texture	pH[e]	% LOI[e]	As						Pb					
				Pseudo-total	Stage 1 (gastric phase)	% BAF[c]	Stage 2 (gastric + intestinal phase)	% BAF[c]	Residual (%)[d]	Pseudo-total	Stage 1 (gastric phase)	% BAF[c]	Stage 2 (gastric + intestinal phase)	% BAF[c]	Residual (%)[d]
#POS1	Sandy clay loam loam	7.2	26.0	49.6 ± 1.5	7.7 ± 0.2	15.5	12.7 ± 1.1	25.6	35.4 ± 0.4 (71.4)	824 ± 2	2.2 ± 0.5	0.3	2.6 ± 0.8	0.3	807 ± 5 (97.9)
#POS2	Sandy clay loam	7.2	35.5	35.7 ± 0.6	3.0 ± 0.3	8.4	4.3 ± 0.5	12.0	29.4 ± 0.3 (82.3)	2746 ± 8	322 ± 8	11.7	213 ± 27	7.8	2433 ± 8 (88.6)
#POS3	Sandy clay loam	7.2	17.0	17.3 ± 0.3	1.7 ± 0.2	9.8	1.5 ± 0.3	8.7	14.5 ± 0.2 (83.8)	274 ± 2	80.0 ± 2.0	29.2	47.7 ± 11.4	17.4	214 ± 2 (78.1)
#POS4	Sandy clay loam	6.9	16.8	13.7 ± 1.4	0.8 ± 0.1	5.8	0.5 ± 0.2	3.6	9.4 ± 0.4 (68.6)	171 ± 1	1.1 ± 0.3	0.6	2.6 ± 0.7	1.5	166 ± 1 (97.1)
#POS5	Sandy clay loam	6.7	27.5	114 ± 1	30.8 ± 2.5	27.0	30.9 ± 3.0	27.1	71.7 ± 1.2 (62.9)	1292 ± 6	255 ± 5	19.7	129 ± 10	10.0	1147 ± 8 (88.8)
#POS6	Sandy clay loam	7.2	17.8	21.3 ± 0.5	5.0 ± 0.1	23.5	5.1 ± 0.6	23.9	17.9 ± 0.2 (84.0)	232 ± 1	78.1 ± 2.0	33.7	39.9 ± 0.3	17.2	187 ± 1 (80.6)
#POS7	Sandy clay loam	7.1	20.1	16.5 ± 0.3	4.9 ± 0.2	29.7	3.5 ± 0.3	21.2	9.4 ± 0.3 (57.0)	360 ± 2	155 ± 1	43.1	51.0 ± 2.8	14.2	298 ± 1 (82.8)
#POS8	Sandy clay loam	5.7	41.4	63.1 ± 2.5	8.6 ± 0.4	13.6	9.1 ± 0.6	14.4	51.6 ± 1.6 (81.8)	667 ± 3	141 ± 1	21.1	99.5 ± 8.3	14.9	564 ± 6 (84.6)
#POS9	Sandy clay loam	7.1	18.9	26.5 ± 0.5	5.7 ± 0.7	21.5	6.9 ± 0.4	26.0	19.2 ± 0.3 (72.5)	446 ± 1	136 ± 1	30.5	64.5 ± 1.1	14.5	372 ± 2 (83.4)
#POS10	Sandy clay loam	5.7	14.2	12.5 ± 0.1	2.7 ± 0.1	21.6	1.7 ± 0.3	13.6	10.5 ± 0.1 (84.0)	184 ± 1	42.2 ± 1.1	22.9	44.0 ± 0.9	23.9	128 ± 1 (69.6)
#POS11	Sandy clay loam	6.9	17.0	14.8 ± 3.3	0.8 ± 0.3	5.4	1.9 ± 0.2	12.8	13.5 ± 0.2 (91.2)	207 ± 1	1.5 ± 0.9	0.7	33.2 ± 1.2	16.0	169 ± 1 (81.6)
#POS12	Sandy clay loam	7	14.9	15.6 ± 0.3	1.6 ± 0.3	10.3	1.9 ± 0.1	12.2	14.1 ± 0.1 (90.4)	193 ± 1	69.0 ± 0.4	35.8	34.5 ± 2.0	17.9	149 ± 1 (77.2)
#POS13	Sandy clay loam	7	14.9	17.4 ± 0.3	4.8 ± 0.2	27.6	1.3 ± 0.5	7.5	16.5 ± 0.8 (94.8)	195 ± 1	74.8 ± 0.9	38.4	30.0 ± 0.3	15.4	159 ± 2 (81.5)
#POS14	Sandy clay loam	6.9	15.0	205 ± 2	35.6 ± 2.0	17.4	37.9 ± 1.8	18.5	155 ± 3 (75.6)	883 ± 4	174 ± 9	19.7	107.0 ± 0.4	12.1	726 ± 3 (82.2)
#POS15	Sandy clay loam	6.7	15.5	16.5 ± 0.4	2.9 ± 0.1	17.6	3.3 ± 0.2	20.0	12.9 ± 0.4 (78.2)	194 ± 1	55.7 ± 1.2	28.7	31.7 ± 10.2	16.3	155 ± 5 (79.9)
#POS16	Sandy clay loam	6.5	18.1	29.8 ± 6.2	6.3 ± 0.3	21.1	6.9 ± 0.9	23.2	22.4 ± 0.4 (75.2)	353 ± 2	126 ± 1	35.7	71.9 ± 0.9	20.4	270 ± 2 (76.5)
#POS17	Sandy clay loam	6.7	15.9	27.6 ± 0.3	4.9 ± 0.4	17.8	3.3 ± 0.8	12.0	19.2 ± 0.3 (69.6)	273 ± 2	80.1 ± 1.3	29.3	54.4 ± 5.0	19.9	203 ± 4 (74.4)
#POS18	Sandy clay loam	6.7	15.9	17.1 ± 0.1	1.1 ± 0.4	6.4	2.2 ± 0.3	12.9	15.5 ± 0.2 (90.6)	293 ± 2	59.3 ± 0.5	20.2	35.6 ± 0.9	12.2	246 ± 2 (84.0)

[a] All test samples were determined on <250 μm soil fraction.
[b] Sample identifier.
[c] % BAF: calculated as the stage related bioaccessible (G or G + I) content as fraction of that sample total concentration.
[d] %Residual: calculated from the residual fraction as a fraction of the pseudo-total concentration.
[e] Measured on <2 mm soil fraction.

fitted with XP-1500 reaction vessels or a Start D multiprep 42 microwave digestion system (Analityx Ltd., Milestone Microwave Laboratory Systems, Peterlee, UK) fitted with PFA reaction vessels. An end-over-end rotator (ARHEL, Slovenia or Stuart Rotator SB3, Barloworld Scientific Ltd. Staffordshire, UK)) was used for bioaccessibility testing. Further Experimental details are provided in Supplementary Information along with the analytical data (Table S1).

2.5. Soil analyses

Pseudo-total analyses of soil samples (0.5 g accurately weighed) for As and Pb was done using microwave-assisted acid digestion in pre-cleaned vessels (10% HNO_3 solution). In all cases digestion was done using 13 mL of aqua regia followed by ICP analysis. Test samples, in triplicate, were prepared along with certified reference materials

(CRMs) and blanks to check the quality of the analytical data (see Supplementary Information, Table S2). After cooling, all digests were filtered (Whatman filter paper) and transferred into 50 mL volumetric flask and made up to the mark with deionised water. The filtrate obtained from the digestion was stored in the refrigerator (4 °C) prior to ICP analysis. The ICP instrument was calibrated using the multi-element standard solution for As and Pb. For each instrument a calibration graph was generated with a minimum of 7 data points, alongside analysis of aliquots of the soil extracts, reference material extracts, and blanks with the addition of appropriate internal standard(s).

In addition, soil pH, loss on ignition (LOI) and soil texture were determined on the 2 mm soil fraction for all samples using standard procedures i.e. pH using a 1:2.5 w/v suspension of soil/deionised water (Rowell, 1994); LOI using a furnace temperature of 500 °C for 4 h (Ball, 1964); and, soil texture using the Munsell Soil Chart (https://munsell.com/).

2.6. Oral bioaccessibility extraction

The Unified Bioaccessibility Method (UBM) for *in vitro* bioaccessibility testing was applied to all soil samples (<250 μm fraction) from the three urban environments. Four simulated body fluids i.e. saliva, gastric fluid, duodenal fluid and bile were prepared to mimic the gastrointestinal environment according to the UBM protocol (Wragg et al., 2011; BSI, 2018). The stage-related extraction protocol consisted of two parallel sequential extractions: the gastric extraction phase simulating the mouth and stomach compartments; and, the gastric-intestinal extraction phase simulating the mouth, stomach and intestinal compartments. Prior to extraction of the samples, the fluids were prepared on the previous day and stored in a refrigerator at <4 °C. A guidance material for the UBM (BGS 102), and three certified reference materials NIST 2710a, GBW07401 and CRM059-50 were prepared along with a blank within each batch of soil sample analyses for quality control purposes. Finally, each soil sample residue was dried (e.g. <40 °C for a minimum of 4 days) and microwave-digested, as per pseudo-total analyses, prior to ICP analysis. All samples and reference materials were prepared, and analysed, in triplicate.

3. Results and discussion

3.1. Pseudo-total concentration and oral bioaccessibility testing across the sites

The robustness of the analytical methodology relating to the pseudo-total analysis and oral bioaccessibility of As and Pb in certified reference materials was investigated (see Supplementary Information, Table S1 and S2). The pseudo-total concentrations of As and Pb measured in the <250 μm fraction of forty test soils from two urban environments and one public space were determined. The pseudo-total concentrations of As and Pb from the different sampling locations across the investigated sites are presented in Table 1. The range of total elemental concentrations observed across the 3 sites for As and Pb varied from 12.5 to 24,900, and 149–5930 mg/kg, respectively. The mean total concentrations for As and Pb were as follows: site 1 As 429 mg/kg, site 2 As 3743 mg/kg, site 3 As 40 mg/kg; and, site 1 Pb 422 mg/kg, site 2 for Pb 1398 mg/kg, site 3 Pb 544 mg/kg. Furthermore, the maximum concentrations for As (24,900 mg/kg), and Pb (5930 mg/kg) were found in site 2.

Previous studies in the UK, have also identified that total As and Pb concentrations can vary quite widely in urban topsoils (Appleton et al., 2012A). Whilst the mean total As in three distinct geographical areas in the UK (Glasgow, London and Northampton) was reported to be fairly consistent at 32, 25 and 36 mg/kg, the ranges were broad at 8–130, 7–88 and 17–70 mg/kg, respectively. Similarly, the mean total Pb in four distinct geographical areas varied considerably (836, 1736, 85 and 821 mg/kg Pb) with wide ranges of 133–1709, 99–13,557, 27–335 and 90–6766 mg/kg Pb, respectively. The commonly elevated Pb levels in urban topsoils reflects the anthropogenic nature of human activities including the burning of fossil fuels (Flight and Scheib, 2011; Appleton and Adlam, 2012), while elevated As levels can be indicative of past industrial activity including non-ferrous smelters (Marchant et al., 2011).

The UBM method was undertaken to measure As and Pb contents in 22 urban soils and 18 public open space soils to assess the risks of these contaminants to human health. The bioaccessible fraction (%) of As and Pb in the gastric and gastric-intestinal phases are shown in Fig. 1. Fig. 1 shows the 3 studied sites and the variation in the bioaccessible data that exists across the sites. In terms of the bioaccessible fraction (%), for site 1, a residential urban garden site, the bioaccessible As fraction in the gastric and gastric-intestinal phases ranged from 14.1 to 50.2% and 9.5–44.6%, respectively. While, the bioaccessibe Pb fraction in the gastric and gastric-intestinal phases ranged from 12.0 to 64.8% and 0.5–35.6%, respectively. For site 2, a residential urban garden site, the bioaccessible As fraction in the gastric and gastric-intestinal phases ranged from 10.3 to 38.7% and 9.4–54.0%, respectively. While, the bioaccessibe Pb fraction in the gastric and gastric-intestinal phases ranged from 0.2 to 66.0% and 0.4–49.2%, respectively. While for the public open space site (Site 3) the bioaccessible As fraction in the gastric and gastric-intestinal phases ranged from 5.4 to 29.7% and 3.6–27.1%, respectively. While, the bioaccessibe Pb fraction in the gastric and gastric-intestinal phases ranged from 0.3 to 38.4% and 0.3–23.9%, respectively.

In this study, the bioaccessible element contents in the gastric phase have been considered as more conservative (highest) estimate of the contaminant released in the human gut. This is in line with previously reported studies, where the higher bioaccessibility values occur in the gastric phase (Elom et al., 2014; Lu et al., 2011; Du et al., 2020). The bioaccessibility of the studied elements observed in the gastric phase is higher than in the gastric-intestinal phase (Fig. 1). This is mainly caused by the low pH (1.2) in the gastric phase that gradually changes to a higher pH (6.3) in the gastric-intestinal phase.

Previous studies reported have identified typical gastric (stomach) bioaccessibilities, in topsoil from an urban recreational site in the UK, 42–64% for As and 25–58% for Pb.

(Okorie et al., 2011). Similarly, mean gastric bioaccessibilites across sites in the UK i.e. Glasgow, London, Northampton and Swansea, have ranged from 6 to 30% As (Appleton et al., 2012A) and from 39 to 70% for Pb (Appleton et al., 2012B). Elsewhere bioaccessibility values for As in urban community gardens, in Puerto Rico, ranged from 19 to 42% for As and 61–100% for Pb (Misenheimer et al., 2018). Lead bioaccessibility in the gastric phase has been identified to vary depending on soil type. For example, Li et al., (2015), identified lead bioaccessibility in the gastric phase to be generally lower in mining soils (0.5–29%) than smelting (19–92%) and farming soils (13–99%). Soil depth in urban soil has also led to differences in Pb bioaccessibities; for example, Yang and Cattle (2015) reported %Pb bioaccessibilites of 24–89% in top soil and 16–100% in sub soil. It is concluded therefore, that the observed variation in bioaccessibility at sites 1 to 3 maybe the result of the site-specific parameters such as former industrial activity, soil pH, organic content and the geological parent material (Palmer et al., 2015; Yang and Cattle, 2015; Li et al., 2015; Appleton et al., 2013; Juhasz et al., 2014)).

3.2. Generic Quantitative Risk Assessment as a driver for bioaccessibility testing

A staged or tiered approach to risk assessment is common in many countries, in part to improve the cost and efficiency in managing contaminated sites, (e.g. UK; Australia; the Netherlands). The regulatory guidance for identifying potentially contaminated sites in the UK is under the Part 2 A of Environmental Protection Act (1990). In keeping with many other countries, a risk-based approach is taken in the UK to establish the likelihood of a pollutant linkage in which soil contaminants

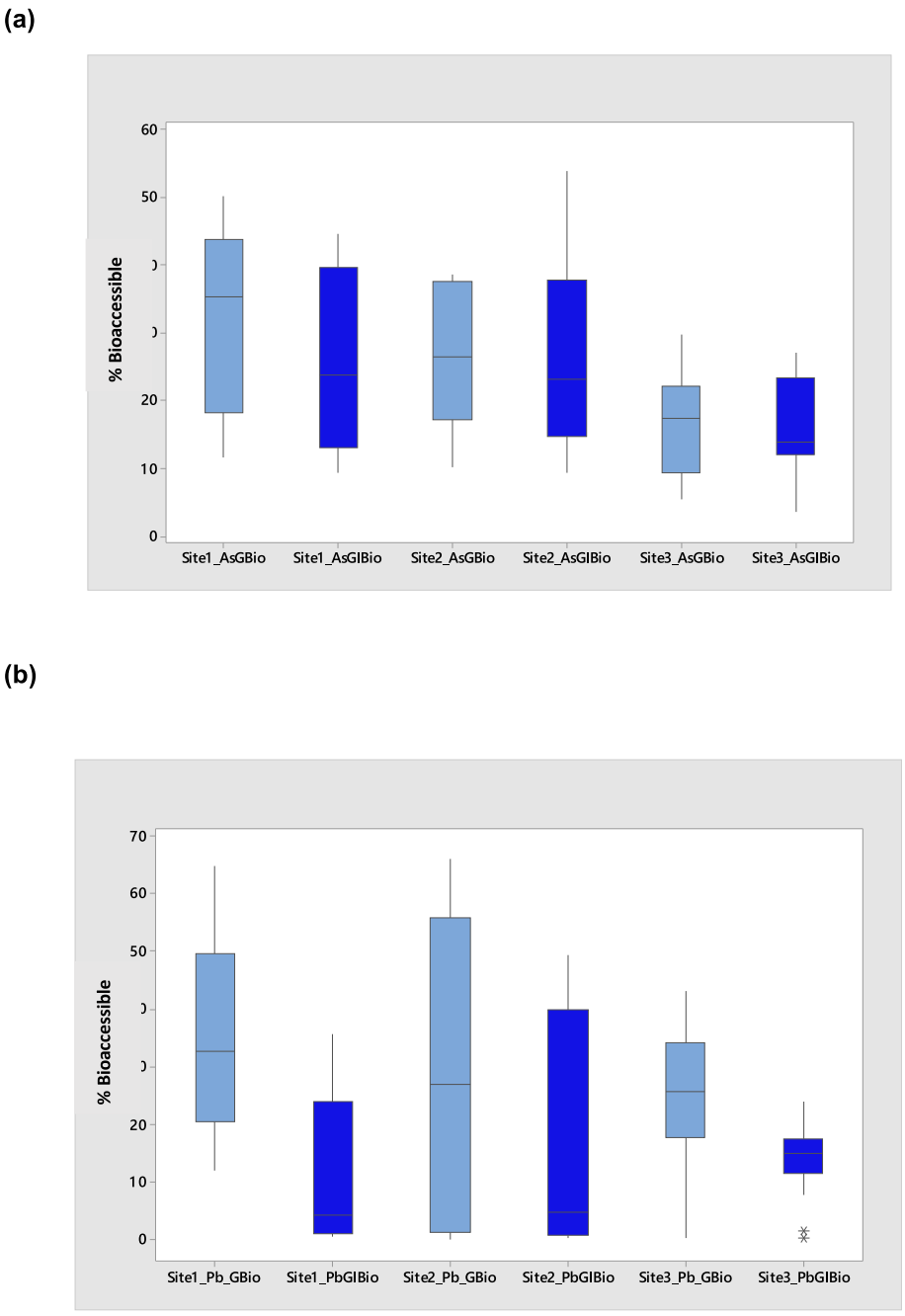

Fig. 1. Box-plot showing the variation of % bioaccessible (gastric and gastric-intestinal) of (a) As and (b) Pb from residential urban gardens (sites 1–2) and public open space (site 3).

through various exposure routes (i.e. oral, inhalation and dermal) can reach the receptors. If a significant contaminant linkage is established as part of the site conceptual model, then a Generic Quantitative Risk Assessment (GQRA) is undertaken. This is done by comparing the concentration of the pollutant in a set of preliminary onsite samples against established guideline or screening values. In the case of the latter, category 4 screening levels (C4SLs) have recently been introduced in the UK (DEFRA, 2014) to screen out low risk sites. Each specific C4SL provides a set of generic screening levels which while more pragmatic in nature (but still strongly precautionary), are based on human health toxicology, exposure assessment and normal ambient levels of contaminants in the environment.

The GQRA can only be valid if the assumptions used to derive the soil screening value (i.e. C4SL) are applicable to the specific site under investigation. A residential scenario, with home-grown produce, has a different C4SL than public open space (POS). For example, the C4SL concentrations for residential (with home grown produce) are 37 mg/kg for As and 200 mg/kg for Pb. Differences in exposure duration (length of visit) and frequency (how often a site visit is made), and the likelihood for backtracking of soil and dusts into the home, drive the lower recommended C4SL in the residential scenario compared to POS (DEFRA, 2014, Table 2). The UK guidelines identify two types of POS: POS_{resi}, grassed areas sufficiently close to housing for tracking back of soil to be of concern, and POS_{park}, park-type open space where no tracking back is included in the exposure model (DEFRA, 2014). The C4SL concentrations for POS_{park} are 170 mg/kg for As and 1300 mg/kg Pb while for POS_{resi} they are 79 mg/kg for As and 630 mg/kg for Pb. In the case of residential soil contamination, it is possible for residents to

Table 2
Summary of data for generic and site-specific assessment criteria (SSAC).

Contaminant of interest	C4SL[c] for Residential (with home grown produce)[a] (mg/kg)	Site 1		Site 2		C4SL[c] for Public Open Space (park)[b] (mg/kg)	Site 3[b]	
		Concentration (mg/kg)	% mean bioaccessibility[d](n = 12)	Concentration (mg/kg)	% mean bioaccessibility[d](n = 10)		Concentration (mg/kg)	% mean bioaccessibility[d](n = 16)
As	37	X = 429 UCL_{95} = 995 X > C4SL[a]	32.3 ± 13.6	X = 3743 UCL_{95} = 14,252 X ≫ C4SL[a]	25.8 ± 10.5	170	X = 40 UCL_{95} = 89 X < C4SL[b]	17.2 ± 7.8
Pb	200	X = 422 UCL_{95} = 682 UCL_{95} and X > C4SL[a]	36.5 ± 17.8	X = 1398 UCL_{95} = 3775 UCL_{95} and X ≫ C4SL[a]	29.2 ± 26.2	1300	X = 544 UCL_{95} = 1191 X ≪ C4SL[b] but UCL_{95} ≈ C4SL[b]	23.2 ± 13.8

[#]The scenario of green space close to housing that includes tracking back of soil (POSresi).
X = sample mean concentration.
UCL_{95} = 95th upper confidence limit.
[a] The scenario of a residential home with the possibility of the family growing home-grown produce, within their garden, for consumption.
[b] A park-type scenario where the park is at a sufficient distance that there is negligible tracking back of soil (POSpark).
[c] C4SL data from DEFRA (2014)
[d] % mean bioaccessibility based on the gastric phase only.

unintentionally consume PHEs through the produce from their gardens, although, the uptake of contaminants through produce consumption is relatively small compared with direct soil and dust ingestion (Intawongse and Dean, 2006). In our case study examples (sites 1 and 2), the use of the C4SL residential (with home grown produce) scenario is a cautious approach, given the small-scale gardens available to each household, however the presence of some fruit trees (in at least one of the gardens) makes this approach precautionary. Various statistical tests can be employed to objectively evaluate the soil contamination data compared to a screening level (C4SL), or critical concentration (Cc). In the UK, recommended statistical guidance involves establishing that there is a 95% probability that the true population mean (μ) is less than or equal to the Cc (EA, 2015; CL:AIRE/CIEH, 2008). In practical terms, this involves comparing the 95th Upper Confidence Limit (as might be used by the land developer as part of an initial planning stage scenario; UCL_{95}) or Lower Confidence Limit (as might be used by the local, regional or national land regulator; LCL_{95}) of the soil contamination data to the Cc and establishing if we reject or accept the null hypothesis. Taking the planning stage scenario as our example, where not only the UCL_{95}, but also the sample soil mean concentration (X) exceed the Cc then it is clear that the true mean population will also exceed the Cc and, unless further data collection is warranted, the action will be remedial treatment or an intervention of some form. In such situations, bioaccessibility testing is simply not warranted or necessary. At sites 1 and 2, both the UCL_{95} and the sample soil mean concentration (X), greatly exceed the Cc for both contaminants (Table 2). Such elevated concentrations of As across sites 1 and 2 are clearly an issue of concern to human health considering the present use of these sites as residential housing estates. The concentrations of As are sufficiently high for intervention to be required, even in a situation where bioaccessibility was less than 10% rather than the actual determined bioaccessibility of up to 50% at site 1 and 40% at Site 2. SPOSH exists regardless of the As bioaccessibility and bioaccessibility testing is an extra unwarranted cost and in a worst-case-scenario may even slow down decisions about remedial actions.

In contrast to sites 1 and 2, in situations where the UCL_{95}, is close to the Cc bioaccessibility testing is a pragmatic option to provide an additional line of evidence to support site determinations. Site 3 is a good example of a 'grey-area' site where determining the bioaccessibility is warranted so as to provide additional information on which to base the site risk assessment. Furthermore, the presence of 'hotspots' of contamination, and illegal bottle digging activity at the site are increasing the direct exposure of receptors to soil and dust, and therefore justify a more detailed quantitative risk assessment (DQRA) to be undertaken at the site, including determination of both As and Pb bioaccessibility, as detailed below.

3.3. *In vitro* bioaccessibility and the derivation of site-specific assessment criteria

The CLEA input parameters used in deriving site-specific assessment criteria (SSAC) for site 3, along with the justification for selection, are presented in Table 3. A vast array of approaches are used in the literature for assessing dose and exposure. In the context of environmental risk assessment from soil, *in-vitro* bioaccessibility refers to that portion of the contaminant that can be extracted and released from the soil during passage through the human GI system and is thus available for absorption. Absolute bioavailability (ABA) is the amount of a contaminant which crosses biological membranes and is absorbed into the systemic circulation (enHealth, 2012). Relative Bioavailability (RBA) is the ratio of the oral bioavailability of the contaminant in soil (i.e. the absolute bioavailability) to the oral bioavailability of the contaminant from the medium used in the critical toxicity study (enHealth, 2012). In relation to As, we can assume that the fraction absorbed from the soil is similar to that fraction absorbed into the systemic circulation however, with respect to Pb, the situation is less clear (Ng et al., 2010). The health criteria data for Pb are based on dietary intakes modelled to produce the adopted blood Pb action value (DEFRA, 2014). In the US, the IEUBK model assumes default oral bioavailability figures of 30% for ingestion of soil and dust and 50% for dietary intake and thus a relative bioavailability of 60% is recommended (based on the ratio of soil to dietary exposure), (USEPA, 2011). The Dutch soil Pb intervention values are modelled following a more complex methodology and use a default relative bioavailability of 0.74 for Pb (SoBRA, 2012), whilst Ng et al. (2010), in their draft National Environmental Protection Measure, suggest defaults of 50% for Pb and 70% for As from soil/dust for use in derivation of health investigation levels. The current UK CLEA model default RBA value for As still assumes 100% bioavailability, whilst for Pb is has been reduced to (60%), although it is acknowledged that there is some uncertainty in how the Pb UBM *in-vitro* results relate to the RBA for use in the CLEA model (DEFRA, 2014). Clearly of critical importance in the utilisation of bioaccessibility data is how we relate the fraction released during *in vitro* bioaccessibility protocols to the RBA used in the exposure assessment models. Despite the often complex dissolution kinetics, a number of studies have indicated *in vitro* bioaccessibility may be used as an indicator of *in vivo* bioavailability (USEPA, 2011; Juhasz

Table 3
Range of CLEA parameter values used for calculating Pb and As site specific assessment criteria (SSAC) for Site 3.

Parameter	CLEA defaults for C4SL for Public Open Space (parkland)	Adopted parameters to generate the SSAC	Justification
Exposure pathways	*Oral* (direct soil and dust ingestion), *Dermal* (outdoor), *Inhalation* (outdoor dust; outdoor vapour)	Default exposure pathways adopted	Exposure outdoor only but with homegrown produce consumption possible.
pH; soil organic matter (SOM); soil type	7; 6%; sandy loam	Default parameters adopted.	Default parameter not changed as there is no influence on metal(oid) assessment criteria of these parameters in the CLEA model.
Receptor	Female child, age classes (0–6 yrs)	Default parameters adopted.	Default parameters not changed.
Outdoor exposure frequency (days/year)	Age class 0–1 yr: 85 Age classes 1–6 yrs: 170	Age class 0–1 yr: 0 Age classes 1–6 yrs: 250	During site survey only school aged children and adults visited the site, principally to access school. (200 school days and 50 additional visits)
Occupancy period (outdoor hr/day)	2.0	0.5 (30 min)	None of the site users crossing the site were observed to remain within the site for more than 10 min, which is approximately the time taken to walk from one end of the site to the other. In addition, allowance is included in the exposure scenario for additional more intensive use during summer evenings and periods of good weather.
Relative bioavailability via soil ingestion	1.0 for As 0.6 for Pb	0.3 for As 0.4 for Pb	Highest recorded % bioaccessible fraction converted to relative bioavailability.
C4SL for $POS_{parkland}$ (mg/kg)	As: 170 Pb: 1300	As SSAC: 443 Pb SSAC: 1718	

et al., 2007), and, the risk assessor needs to be cognisant of which bioaccessibility protocols have been validated and for which types of contaminated source material. Denys et al. (2012) undertook *in vitro* – *in vivo* comparisons of the UBM and indicated the protocol to be a reliable predictor of *in vivo* RBA for Pb and As in soils contaminated by mining slags and by particles emitted from a smelting plant (fly-ash) across a range of concentrations and bioaccessibilities (Denys et al., 2012). Our site 3 was a landfill from at least 1856, receiving commercial and household waste, and whilst the source of the As and Pb would be of mixed origin, the ashy nature of the soil and subsurface suggests ash as a likely source of the contaminants. Using the maximum UBM determined % bioaccessibility for each of the elements of concern, in keeping with a conservative/protective application of bioaccessibility data, we adjusted the relative bioavailability parameter in the CLEA model to As 0.3 (actual maximum 29.7%) and Pb 0.4 (actual maximum 38.4%).

The soil ingestion rate and exposure factors (e.g. frequency, duration, bioavailability of the contaminant) contribute to chronic exposure risks. During our site survey we noted mainly school aged children accessing site #3 to attend school, a potential exposure duration of 10 min. To allow for additional exposure both on their return journey from school, and during the summer period, when daylight is longer, we have used 30 min (0.5 h) as our occupancy period per day. We have calculated the SSAC using the age class 1–6 (and an exposure duration of 250 days days/year, largely based on the school year plus some additional time in summer), in accordance with the CLEA v.1.071 software. The SSAC was calculated to be 443 mg/kg As and 1718 mg/kg Pb (Table 3). On that basis, and in accordance with the assumptions used, site 3 would be deemed to provide minimal risk to the main site users. Risk posed by the site to illegal site users is difficult to quantify. Here the far lower oral bioaccessiblty of As than that on which the C4SL is based does provide some additional level of re-assurance that infrequent (illegal) exposure does not provide a significant possibility of significant harm.

4. Conclusion

We report on the role that oral bioaccessibility testing can contribute at contaminated land sites, with a specific focus on As and Pb contamination given both of these elements have been validated by *in vivo* to *in vitro* studies. Using our data from two residential sites we highlight that oral bioaccessibility testing can be of limited, to no value, in supporting a sites determination as contaminated. Whereas for a less contaminated 'grey-area' site we highlight the importance of oral bioaccessibility testing as emphasized as part of a 'lines of evidence approach' that supports the site-specific risk assessment. Furthermore, we highlight the importance of giving due consideration to how we relate the fraction released during *in vitro* bioaccessibility protocols to the RBA used in many of the exposure assessment models. The appropriate use (rather than an uncritical or 'mis-use') of oral bioaccessibility testing is paramount if it is to add to the risk-assessors tool kit.

Credit author statement

John R Dean was the principal doctoral supervisor of both Patrick M. Amaibi and Alexander Okorie. He was responsible for the direction of the research and its focus. Patrick M. Amaibi was a doctoral student undertaking part of this research. Alexander Okorie was a doctoral student undertaking part of this research. Jane A. Entwistle was the other doctoral supervisor of both Patrick M. Amaibi and Alexander Okorie.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix B. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envres.2020.109915.

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