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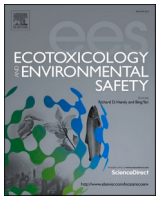

Using oral bioaccessibility measurements to refine risk assessment of potentially toxic elements in topsoils across an urban area

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ABSTRACT

Elevated concentrations of As, Cr, Cu, Ni, Pb, V and Zn in topsoils in Belfast, Northern Ireland have been found to exceed assessment criteria in the city and therefore may pose a risk to human health. Most generic assessment criteria (GAC) for potentially toxic elements (PTEs) in soils assume PTEs are 100% bioavailable to humans. Here we use in-vitro oral bioaccessibility testing using the Unified BARGE method (UBM) to measure what proportion of soil contamination dissolves in the digestive tract and therefore is available for absorption by the body. This study considers how PTE bioaccessibility in soils varies spatially across urban areas and refines human health risk assessment for these PTEs using site specific oral bioaccessibility results to present the first regional assessment of risk that incorporates bioaccessibility testing. A total of 103 urban soil samples were selected for UBM testing. Results showed low bioaccessible fraction (BAF) for the PTEs from geogenic sources: Cr (0.45–5.9%), Ni (1.1–46.3%) and V (2.2–23.9%). Higher BAF values were registered for PTEs from anthropogenic sources: As (8.0–86.9%), Cu (3.4–67.8%), Pb (9.1–106.2%) and Zn (2.4–77.5%). Graphs of bioaccessibility adjusted assessment criteria (BAAC) were derived for each urban land use type and PTE. These provide a visual representation of the significance of oral bioaccessibility when deriving BAAC and how this is affected by 1) dominant exposure pathways for each land use and 2) relative harm posed from exposure to PTEs via each pathway, allowing oral bioaccessibility research to be targeted to contaminants and pathways that most significantly impact risk assessment. Pb was the most widespread contaminant with 16.5% of sites exceeding the Pb GAC. Applying BAAC did not significantly change risk evaluation for these samples as many had Pb BAF>50%. In contrast, all samples that exceeded the As GAC were found to no longer exceed a minimal level of risk when oral bioaccessibility was considered. Oral bioaccessibility testing resulted in a 45% reduction in the number of sites identified as posing a potential risk to human health.

1. Introduction

A legacy of anthropogenic contamination has resulted in widespread pollution of soils in many urban areas with inorganic contaminants including potentially toxic elements (PTEs) (McIlwaine et al., 2017). This widespread contamination arises from a number of airborne sources including traffic (McKinley et al., 2021), industry, historic urbanisation, domestic coal combustion, and waste incineration (Binner et al., 2023). While some organic contaminants decompose with time, PTEs often do not degrade in soil and accumulate over time. Studies of urban

Abbreviations: ABA_{soil}, Absolute oral bioavailability of the chemical in soil; ABA_{tox}, Absolute bioavailability of the chemical in the media that was used in the toxicological studies from which health criteria values were derived; As, Arsenic; BAAC, Bioaccessibility adjusted assessment criteria; BAF, Bioaccessible fraction; C4SL, Category 4 Screening levels; C_b, Bioaccessible concentration; CLEA, Contaminated land exposure Assessment; Cr, Chromium; C_{tot}, Total concentration; Cu, Copper; F_A, Fraction of the solubilised chemical which passes through the gastrointestinal wall and is transported to the liver; F_B, Fraction of a chemical in soil that becomes mobilised into the digestive juices; F_H, Fraction that passes through the liver and enters systemic circulation; G, Gastric phase; GAC, Generic assessment criteria; GI, Gastro-Intestinal phase; Ni, Nickel; Pb, Lead; POS_{park}, Public open space park; POS_{resi}, Public open space near residential; PTE, Potentially toxic element; $RBA_{soil\ tox}$, Relative bioavailability, which is the ratio of ABAsoil and ABAtox; RSD, Relative standard deviation; RwHP, Residential with home-grown produce; RwoHP, Residential without home-grown produce; S4UL, Suitable for use levels; UBM, Unified BARGE method; V, Vanadium; XRF, X-ray fluorescence; Zn, Zinc.

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soils in the UK and Europe have been undertaken for some time (Fordyce et al., 2005; Johnson et al., 2011), however recently attention for urban mapping has increased with numerous studies in the UK (Rothwell and Cooke, 2015; Ferreira et al., 2017; McIlwaine et al., 2017), Europe (Demetriades, Johnson and Birke, 2018; Romzaykina et al., 2020), China (Luo et al., 2012; Cheng et al., 2014) and India (Adimalla, 2020).

Generic assessment criteria (GAC) or threshold values are often used to screen data from urban geochemical surveys to assess long term risks to human health arising from PTEs in soil (Rothwell and Cooke, 2015; McIlwaine et al., 2017). Risk assessment frameworks used internationally to assess human health risks from contaminated land, apply assumptions about the fate and transport of contaminants in the environment to generic land use scenarios to derive GACs. They assume humans are exposed to PTEs in soil via direct ingestion of soils, ingestion of home-grown fruit and vegetables, inhalation of dust and vapours and dermal contact with soil and dust. The contribution each exposure pathway makes to a GAC depends on a number of factors including the physiochemical properties of the contaminant (eg volatility, plant uptake), the difference in toxicity of contaminants via the oral, inhalation and dermal pathways and underlying assumptions relating to the generic land uses (eg housing without home-grown produce has zero exposure via ingestion of home-grown fruit and vegetables).

When assessing the risks PTEs pose to human health, generic risk assessment methodologies for most elements assume 100% of the total concentration of the PTE will be orally bioavailable to humans (ie will enter systemic circulation). The bioavailability of PTEs in soil is difficult to measure, and therefore in-vitro oral bioaccessibility methods are often used to measure the fraction of a PTE that is released during digestion in the gastro–intestinal system (Ruby et al., 1999). Numerous studies have shown that only a proportion of the total concentration of a range PTE's typically encountered on urban sites are orally bioaccessible (Broadway et al., 2010; Okorie, Entwistle and Dean, 2011; Appleton, Cave and Wragg, 2012b; Wragg and Cave, 2021) and therefore oral bioaccessibility is increasingly being considered during human health risk assessment of soils on a site specific basis. However, integration of bioaccessibility testing into assessment of regional geochemical data to date has been limited.

Whilst the direct ingestion pathway is generally considered the most common route of exposure at contaminated sites (Calabrese et al., 1997), oral bioaccessibility testing will have a limited effect on human health risk assessments for a site with a land use where the oral bioaccessibility pathway does not dominate exposure or for contaminants for which inhalation or dermal toxicity dominates oral toxicity. As bioaccessibility testing becomes more widespread, and databases of bioaccessibility results are becoming available at city scale (Appleton, Cave and Wragg, 2012b; Wragg and Cave, 2021), it is essential that oral bioaccessibility's role in human health risk assessment is elucidated to ensure oral bioaccessibility testing is used effectively to refine human health risk assessment (Dean et al., 2020; Billmann et al., 2023).

Conversely, whilst many generic human health risk assessments assume 100% bioaccessibility of contaminants for all exposure pathways, some generic risk assessments do consider bioaccessibility, most often in situations where generic assessment criteria are similar to background levels of PTEs in the soil. For example, GACs for Pb in the UK assume a relative bioavailability ($RBA_{soil\ tox}$) of 60% (Contaminated Land: Applications in Real Environments, 2014b), whilst the USEPA recommends a default relative bioavailability in risk assessments for As of 60% (USEPA, 2012). A recent review of oral bioaccessibility found Pb and As gastric phase bioaccessible fractions of greater that 80% were recorded in more than 10% and approximately 5% of studies respectively (Billmann et al., 2023). Therefore, as oral bioaccessibility testing is often only considered if total concentrations exceed GACs, this approach may underestimate risks, and it may be more appropriate to consider bioaccessibility testing only during detailed site-specific risk assessment.

The aims of this paper were therefore to:

measure the oral bioaccessibility of a suite of PTEs (As, Cr, Cu, Ni, Pb, V, and Zn) in 103 shallow urban soil samples.

refine a method for visualising the effect of oral bioaccessibility in human health risk assessment, to allow risk assessors to rapidly determine whether oral bioaccessibility testing will affect the outcomes of their assessment and ensure appropriate utilisation of bioaccessibility testing.

combine bioaccessibility data with existing GACs to develop bioaccessibility adjusted assessment criteria (BBAC) graphs to allow a regional estimation of risks to human health from PTEs in urban soils.

assess whether the relative bioavailability of Pb in these urban soils exceeds the default relative bioavailability included in generic assessment criteria and therefore determine whether risks from Pb contamination are currently under-estimated.

2. Materials and methods

2.1. Study area and sample locations

The Belfast Metropolitan area (UK) has a population of 700,000 and surface area of 300 km^2 (NISRA, 2004). The boundary for the study area used in this research was defined using the Corine land cover seamless vector data (European Environment Agency, 2018) and the spatial distribution of urban Tellus soil samples (Knights, 2006).

The city played an important role during the industrial revolution in the 18th century, and during this time was recognised for linen production, tobacco-processing, and rope works activities. By the beginning of 19th century, it had emerged as one of the world's centres for shipbuilding (Lynch, 2001). Currently, Belfast's economy is focussed mainly on administration, commerce, service provision and cultural amenities (Belfast City Council, 2016).

The geology the city is diverse and is known to have an influence on PTE distribution (McIlwaine et al., 2017). The south eastern portion of the study area is underlain by formations of Silurian greywacke and Silurian shale which are enriched in Pb and As, while Triassic sandstones and mudstones underlie the centre of the city. Cretaceous sandstone and chalks emerge to the west, which are overlain by the Antrim basalts (rich in Cr, Ni and V) in the north-west of the study area (Mitchell, 2004).

2.2. Tellus geochemical data

The Tellus geochemical and geophysical survey was undertaken across Northern Ireland between 2004 and 2007. The Tellus survey was managed by Geological Survey of Northern Ireland (GSNI) and its main purpose was to provide information for geological mapping, environmental management and assessment of natural resources.

Tellus field sampling was carried out in urban areas between May and July 2006. A total of 1166 samples were collected at a density of 4 samples per km^2 following the G-BASE protocol (Johnson, 2005). Soil samples were taken from two depths (shallow (5–20 cm) and deep (35–50 cm)) and analysed for total concentrations of a wide range of major, minor and trace elements. Results reported here are from the shallow horizon, analysed using X-ray fluorescence (XRF) for As, Cu, Cr, Ni, Pb, V and Zn. Analysis by XRF was utilised in this study as this method gave representative values for total concentration in the study area (McIlwaine et al., 2015). The soil samples were stored at the Geological Survey of Northern Ireland archive and are available for scientific research. Research undertaken by McIlwaine et al. (2017) using this database has shown that most contamination within the Belfast area has remained substantially unchanged since each area of the city was first developed. Full details of the urban Tellus geochemical survey are provided in Knights (2006) and detection limits for the XRF analysis are provided in Nice (2010).

2.3. Sample selection

A subset of 103 shallow soil samples was selected from the Tellus

urban dataset for this investigation (Fig. 1). The selection strategy considered underlying bedrock geology, soil type, land use and spatial distribution within the city. Boxplots of total element concentration for the full study data set and the sample subset (Fig. 2) were compared to ensure the subset was representative of the full dataset. Table S3 (in the supplementary information) provides summary data for total concentrations of individual PTEs for the full Tellus data set and the study subset, both measured by XRF analysis. Distributions of total concentrations for As, Cr, Ni, and V indicate a good alignment with a normal distribution, while Cu, Pb and Zn deviate from a normal distribution, suggesting that these PTEs may originate from multiple sources including soil parent material and/or various sources of anthropogenic contamination.

2.4. Bioaccessibility testing

Bioaccessibility extractions were carried out using the Unified BARGE Method (UBM) (BARGE/INERIS, 2011). The Unified BARGE method is ISO accredited in ISO/DIS 17624 and represents a useful *in vitro* extraction method to measure the oral bioaccessibility of contaminants by simulating the human stomach and upper intestine. This method has been calibrated against *in vivo* data and validated for 3 elements As, Cd, and Pb (Denys et al., 2012), and has been used for bioaccessibility studies of Cd, Pb and Zn (Pelfrêne et al., 2012), Sb (Denys et al., 2009), Cr (Broadway et al., 2010), As, Cd, Cr, Cu, Ni, Pb and Zn (Okorie, Entwistle and Dean, 2011) and As, Cd, Co, Cr, Cu, Ni, Pb, U, V and Zn (Barsby et al., 2012). Although both gastric phase (G) bioaccessibility and gastro-intestinal (GI) were measured, results showed that G phase bioaccessibility was higher than GI bioaccessibility in all cases (Figure S1 in the Supplementary Information). Therefore, gastric (G) bioaccessibility consistently provides a conservative estimate of health risks and so, for simplicity, only the G phase methodology and bioaccessibility results are presented here.

Each sample was sieved to <250 μm, as the fine fraction is more likely to stick to the hands and therefore be available for uptake into the body (USEPA, 2000). This was then sub-sampled to obtain 0.4 g for extraction, as the final sample size was restricted by the capacity of the available centrifuge. Quantities of digestive solutions were reduced to maintain the soil-solution ratio contained within the published UBM methodology and the adjustments to the method were validated using BGS102 guidance soils. Reagents used to prepare digestive solutions were purchased from Merck, Sigma, Baker and Carl Roth. Saliva and gastric solutions were prepared one day prior to soil extractions to permit dissolution of reagents and stabilisation. Solution pH was adjusted as required according to UBM specifications using either 37% HCl or 1 M NaOH. Soils not adhering to pH specifications (pH < 1.5) after one hour of gastric extraction were discarded and extractions were repeated. Extracts were analysed for elemental composition by ICP-MS: (Thermo Scientific iCap Q). The instrument was calibrated using multi elemental standards in a range of 0–100 ppb. Rhodium internal standard was added to all samples, blanks and standards at 10 ppb.

Results are expressed in percentages as bioaccessible fraction (BAF) for selected PTEs. BAF is calculated by dividing the bioaccessible concentration (C_b) measured in the UBM test by the total concentration (C_{tot}) in the soil sample, as measured by XRF during the Tellus project, and multiplied by 100 (Eq. 1). In this study C_{tot} was measured on the <2 mm soil fraction as PTE concentrations from soils of this particle size are typically compared with generic assessment criteria by risk assessors, and therefore assessment criteria are often derived for this particle size (Billmann et al., 2023).

$$BAF(\%) = \frac{C_b}{C_{tot}} X100 \quad (1)$$

2.4.1. Bioaccessibility testing - quality control

One blank, two duplicates and one commercially available guidance soil, BGS102, were included with extractions for each sample batch of ten soil samples from the study subset. BGS102 provides consensus UBM values for a range of inorganic elements which have acceptable ranges of

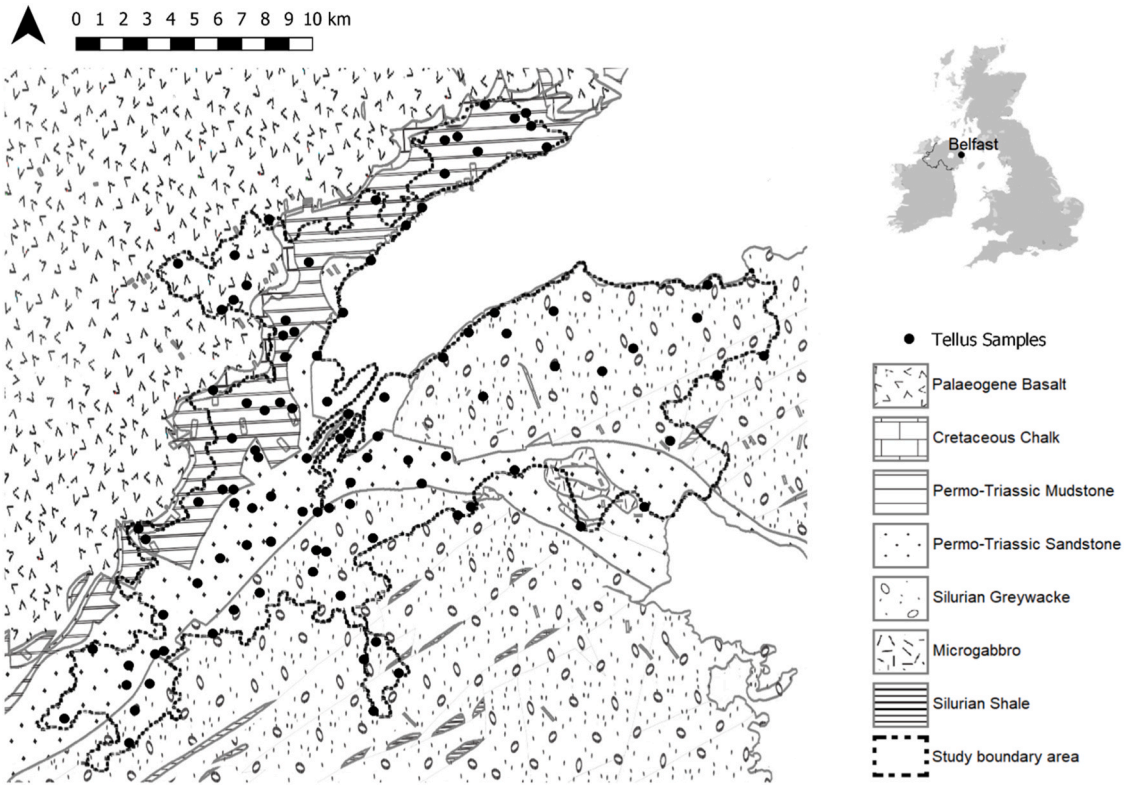


Fig. 1. Map showing Tellus sample locations, bedrock geology (GSNI, Crown Copyright) and the boundary of the study area.

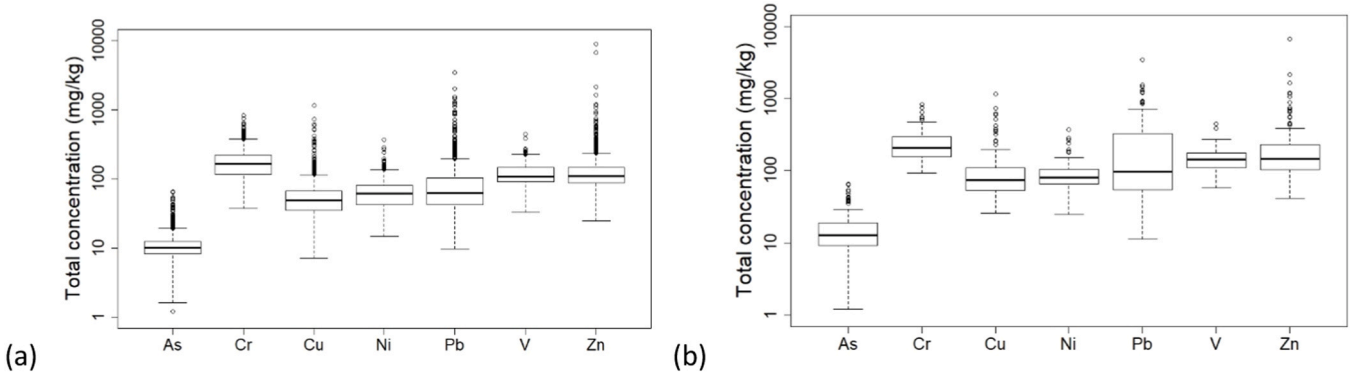


Fig. 2. Boxplots of total element concentration by XRF in shallow soils in (a) the full Tellus urban data set (n=1166) and (b) the study subset (n=103).

concentrations (Wragg et al., 2011; Hamilton et al., 2015). Reproducibility of As, Cr, Cu, Ni, Pb, V and Zn bioaccessible concentrations for a selection of 28 samples performed in duplicate was calculated as relative standard deviation (RSD) across all batches. RSD ranged from 3% to 5% for gastric phase extractions. Analysis of BGS102 for the gastric extractions, displayed an RSD of < 30% for all investigated elements, which is in good agreement with RSD values reported for BGS102 (Wragg et al., 2011; Hamilton et al., 2015).

2.5. Risk assessment

2.5.1. Generic risk assessment

The Contaminated Land Exposure Assessment (CLEA) model (Environment Agency, 2009) has been used to undertake risk assessment in this study as it integrates a number of exposure pathways, and also allows modification of the oral bioavailability of contaminants, therefore allowing bioaccessibility to be considered in the regional risk assessment.

6 generic land use scenarios were considered. Full details of these land uses are contained in Environment Agency (2009) and Contaminated Land: Applications in Real Environments (CL:AIRE), (2014a):

1) residential with home-grown produce (RwHP),
2) residential without home-grown produce (RwoHP),
3) allotments,
4) commercial,
5) public open space near residential (POSresi), and
6) public open space park (POSpark).

For the purposes of this risk assessment, each sampling location was assigned one of these land use categories using the Corine land cover data (European Environment Agency, 2012), satellite images and current Ordnance Survey of Northern Ireland (OSNI) mapping. If assessment suggested a variety of land uses, a conservative approach was followed, with the land use that is most susceptible to human health risks from PTEs being assigned.

Once a land use had been assigned for each site, total concentrations of each PTE was compared with the relevant generic assessment criteria (GAC), set out in Table 1. Where available, Suitable for Use Levels (S4ULs) have been used in this study. Pb does not however have a S4UL and therefore Pb total concentrations were compared with the relevant Pb Category 4 Screening Level (C4SL). S4ULs are intended for use identifying land that is suitable for redevelopment, whereas C4SLs are used in the identification of contaminated land. Therefore, S4ULs are more protective of human health than C4SLs.

Sites that exceeded the GAC were flagged for further assessment. Sampling locations that had a Pb Relative Bioavailability ($RBA_{soil\ tox}$) of >60% were also flagged for further assessment even if the GAC was not exceeded as the C4SL for Pb assumes a $RBA_{soil\ tox}$ of 60%. The BAF of lead in soil that would correspond to a $RBA_{soil\ tox}$ of 60% has not been conclusively measured (Contaminated Land: Applications in Real Environments, 2014b). However using the assumptions set out in Contaminated Land: Applications in Real Environments (2014b), a Pb $RBA_{soil\ tox}$ of 60% would equate to a Pb BAF of 75% (Eq. 2).

$$RBA_{soil\ tox\ Pb} = 0.8\ x\ BAF_{Pb} \quad (2)$$

For those samples identified for further assessment, BAAC were derived for each PTE that exceeded the GAC (or had a Pb BAF of greater than 75%) using the land use information for the site, the site specific BAF for that contaminant and the BAAC graphs (described below). Total concentration (measured on the <2 mm soil fraction) was compared to the BAAC to identify any sites where a potential risk to human health was posed.

As recent versions of the CLEA have been developed using a deterministic model, it is not possible to quantify uncertainty. However, "adopting conservative values for all input parameter values decreases the probability of the model under-predicting exposure for an individual within the critical receptor group. The current configuration of CLEA uses a mixture of "central tendency" and "reasonable worst case" values

Table 1
Generic assessment criteria for residential with home-grown produce (RwHP), residential without home-grown produce (RwoHP), allotment, commercial, public open space residential (POS_{resi}) and public open space park (POS_{park}) land uses. Unless otherwise specified all criteria are S4ULs (Nathanail et al., 2015).

Potentially toxic element	RwHP (mg kg^{-1})	RwoHP (mg kg^{-1})	Allotments (mg kg^{-1})	Commercial (mg kg^{-1})	POS_{resi} (mg kg^{-1})	POS_{park} (mg kg^{-1})	Relative oral bioavailability ($RBA_{soil,\ tox}$) assumed in GAC
As	37	40	43	640	79	170	1.0 (100%)
Cu	2400	7100	520	68,000	12,000	44,000	1.0 (100%)
Cr(III)	910^{T}	910^{T}	$18{,}000^{T}$	8600^{T}	1500^{T}	$33{,}000^{T}$	1.0 (100%)
Ni	130	180^{T}	53	980^{T}	230^{T}	800	1.0 (100%)
Pb *	200	310	80	2300	630	1300	0.6 (60%)
V	410	1200	91	9000^{T}	2000^{T}	5000	1.0 (100%)
Zn	3700	40,000	620	730,000	81,000	170,000	1.0 (100%)

* C4SLs used as generic assessment criteria for Pb, as no S4UL is available for Pb (Contaminated Land: Applications in Real Environments, 2014b)
^{T}GAC derived using only inhalation health criteria values as inhalation of dust provides a conservative estimate of potential risks

and, as a result, is likely to over-predict exposure for the majority of individuals within each critical receptor group" (CL:AIRE and DEFRA, 2014).

2.5.2. Development of bioaccessibility adjusted risk assessment (BAAC) graphs

Bioaccessibility adjusted assessment criteria were derived using the CLEA tool (version 1.071) (Environment Agency, 2015) by changing the chemical, soil, building or land use datasets. Full details of the assumptions used in the CLEA model are reported in Environment Agency (Environment Agency, 2009) and (Contaminated Land: Applications in Real Environments, 2014a).

For elements where concentrations in samples exceeded the GAC, the generic assessment criteria were modified using the CLEA model to develop BAAC graphs that accounted for the bioaccessibility of the element in the soil. Within the CLEA model, bioavailability of contaminants is considered using relative bioavailability ($RBA_{soil,\ tox}$). $RBA_{soil,\ tox}$ is the ratio of the absolute oral bioavailability of the chemical in soil (ABA_{soil}) and the absolute bioavailability of the chemical in the media that was used in the toxicological studies from which health criteria values were derived (ABA_{tox}) (Eq. 3) (Environment Agency, 2009). In their extensive review of the use of oral bioaccessibility testing in soils and its use in human health risk assessment, Billmann et al. (2023) found that some articles did not provide sufficient detail of how bioaccessibility results were integrated into risk assessment. Therefore, full details of the methods used to establish ABA_{soil} and ABA_{tox} values used in this study are included in the Supplementary Information for this article.

$$RBA_{soil,tox} = \frac{ABA_{soil}}{ABA_{tox}} \tag{3}$$

The CLEA tool was then run, with a range of $RBA_{soil,\ tox}$ values to obtain BAAC graphs for each land use and PTE with total concentrations that exceeded the relevant GAC, using the approach developed by Scott and Nathanail (2011).

2.5.3. Regional risk assessment

BAAC graphs were used to identify BAAC corresponding to the oral bioaccessibility measured for each PTE in samples that exceeded the relevant generic assessment criteria (GAC) and for Pb in samples with Pb BAF $>$ 75%. Samples that did not exceed these BAAC criteria were identified as not posing a risk to human health. This assessment of risk was confirmed by calculating the Hazard Quotient (HQ) (Eq. 4) and Cancer Risk (CR) (Eq. 5), using the Average Daily Exposure (ADE) that was calculated by the CLEA model and the relevant Health Criteria Value (HCV) used in the CLEA model and Slope Factor (SF) found in literature (Table S2 in the supplementary information).

$$HQ = \frac{ADE}{HCV} \tag{4}$$

$$\mathrm{CR} = \mathrm{ADE} \times \mathrm{SF} \tag{5}$$

2.6. Data processing and spatial analysis

Statistical analysis, including boxplots of individual element concentrations and correlations, were produced using R software version 22.07.2+576 (RStudio Team, 2022). Maps of BAF for individual PTEs have been produced using QGIS software, version 3.28.1-Firenze (QGIS Development Team, 2022).

3. Results

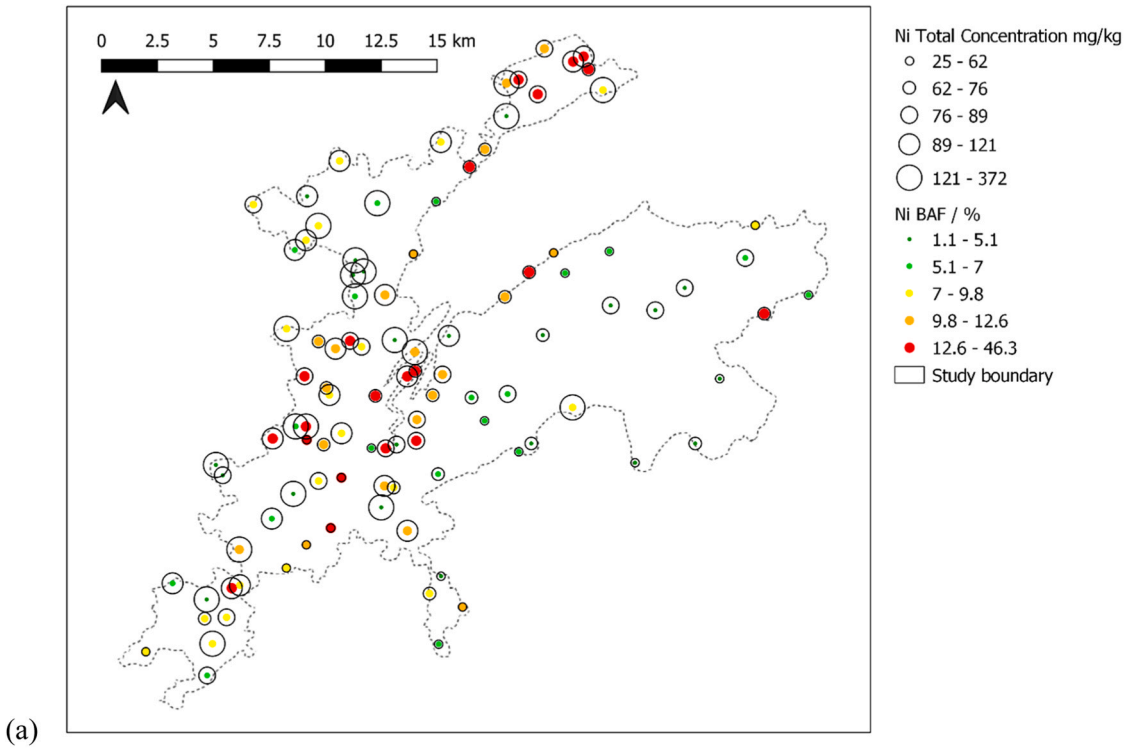
3.1. Bioaccessibility results

The lowest BAF values (G) were registered for the geogenic contaminants: Cr (0.45–5.9%), Ni (1.1–46.3%) and V (2.2–23.9%). These values are similar to BAF values obtained for Ni and V (Barsby et al., 2012; Palmer et al., 2013, 2014) and Cr (Barsby et al., 2012; Palmer et al., 2014) in a rural context within Northern Ireland. Higher G phase BAF values were registered for As (8.0–86.9%), Cu (3.4 – 67.8%), Pb (9.1–106.2%) and Zn (2.4% - 77.5%). A similar tendency for contamination from anthropogenic sources to have higher BAFs was noted by Appleton, Cave and Wragg (2012a). Indeed Pb and As BAFs in this study are significantly higher than BAFs in soils from rural areas of Northern Ireland (Barsby et al., 2012).

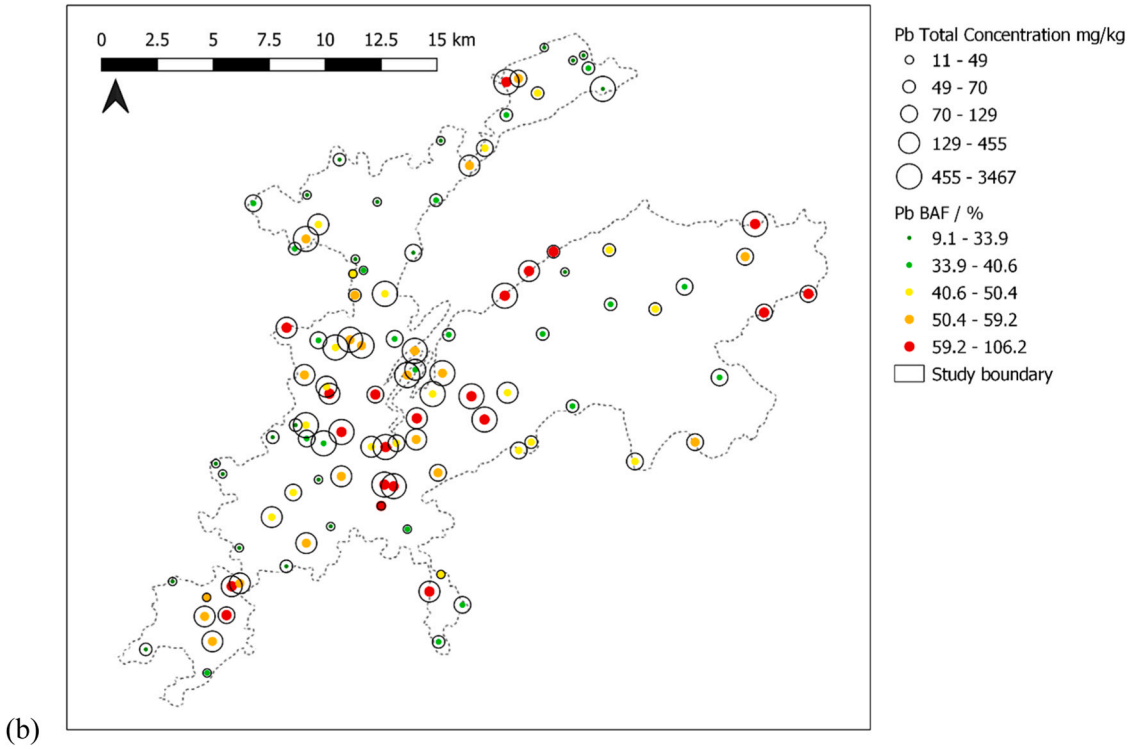
The Pb BAF values exceed 75% (the value used in UK generic risk assessments) in 7 samples. In one sample a Pb BAF of 106.2% was recorded. A bioaccessibility of greater than 100% is possible, because bioaccessibility is measured on the $<$250 μm fraction, which can contain more elevated levels of contamination that the $<$2 mm fraction, on which total concentration is measured. As noted above, C_{tot} was measured on the $<$2 mm soil fraction as PTE concentrations from soils of this particle size are typically compared with generic assessment criteria by risk assessors, and therefore assessment criteria are derived for this particle size.

Fig. 3 and Figures S4 to S8 illustrate the spatial distribution of the total concentration of individual PTEs (open circle) and their BAFs (coloured dots) across the metropolitan area of Belfast. Lower BAF values were registered for Cr, Ni and V in the north-west of Belfast, where total concentrations of these PTEs are elevated due to their presence in the underlying Antrim Basalts (Palmer et al., 2014), suggesting that although the Basalts supply significant amounts of these PTEs to soils, it is in a form that is less accessible to humans via oral ingestion than other sources of these PTEs in the Belfast area. This supports previous research conducted that found low BAF for Cr, Ni, and V in soils originating from Antrim Basalts (Barsby et al., 2012; Palmer et al., 2014), where the Cr was found to be in the form of chrome spinel, whilst Ni was more widely dispersed within the soils including within carbonates and weathering products, including secondary iron oxides and precursor clay minerals (Cox, Rollinson and McKinley, 2017). Studies of the form of V in soils overlying the Antrim basalts have not been carried out, however De Vos and Tarvainen (2006) report that vanadium can be present as a trace element in apatite, pyroxene and amphibole and that V in soils is present in iron oxides. Both Ni and Cr^{3+} are more mobile under acidic conditions, explaining their higher bioaccessibility in the gastric phase, and geogenic V and Ni are reported as being typically more mobile than Cr (De Vos and Tarvainen, 2006) which explains their higher bioaccessibility compared to Cr.

Higher BAF values were registered for As, Cu, Pb and Zn in areas where soil has been affected by industrial activities (areas of Belfast developed prior to 1965, which tend to be towards the centre of the city (McIlwaine et al., 2017)). Similar findings were reported for As (Ljung et al., 2007; Appleton, Cave and Wragg, 2012a; Han et al., 2020; Wragg and Cave, 2021), Pb (Ljung et al., 2007; Poggio et al., 2009; Appleton, Cave and Wragg, 2012b; Han et al., 2020; Wragg and Cave, 2021) and Cu and Zn (Poggio et al., 2009; Gu and Gao, 2018; Han et al., 2020) in studies in other industrialised cities in the UK, Europe and China. This correlates with findings from literature that typically higher BAFs are found for elements from anthropogenic sources (Appleton, Cave and Wragg, 2012a; Billmann et al., 2023) and findings from Han et al. (2020) and Gu and Gao (2018) of anthropogenic influences on Cr bioaccessibility in Guangzhou and Jiaozuo, China. In contrast, Cave et al. (2013) found a strong geogenic control on As bioaccessibility in Northampton, UK.



(a)



(b)

Fig. 3. Maps showing the total concentration by XRF (mg kg^{-1}) (black circles) and BAF (%) (coloured dots) of (a) Ni and (b) Pb across Belfast.

3.2. Generic risk assessment

Of the 103 locations assessed, 38 land uses were residential, of which the majority (32) were residential with home-grown produce (RwHP). 39 locations were designated as Public Open Space (POS), 25 sites were identified as commercial and only 1 site was found to be an allotment (see Table S4 in the Supplementary Information).

Speciation of Cr in the soil samples was not undertaken during the Tellus survey and therefore, total Cr concentrations could be compared with either the S4UL for Cr(III) or the more conservative S4UL for Cr (VI). However, McIlwaine at al. (2017) identified the Tertiary Basalts underlying Belfast to be a dominant control on Cr concentrations, and Cr in soils overlying similar basalts in a rural part of Northern Ireland was found to be predominantly in the form of chrome spinel (Cox, Rollinson

and McKinley, 2017), which is in the form Cr(III) (De Vos and Tarvainen, 2006). Therefore, for this assessment, the Cr(III) S4UL has been used. Total Cr in all samples was below the S4UL for Cr(III).

6 samples had concentrations of As that exceeded the relevant S4UL (all were in areas designated RwHP). 7 samples had Ni concentrations that exceeded the Ni S4UL (2 in RwHP, 1 in RwoHP, 1 in allotments and 3 in POSresi). In total 17 samples (16.5%) had Pb concentrations that exceeded the Pb C4SL, with 10 of these being in a RwHP land use, 4 in a RwoHP land use, 1 in a commercial area and 2 in POSresi areas. No samples exceeded the relevant S4ULs for Cu and Zn and only 1 sample (an allotment land use) exceeded the relevant S4UL for V.

In total 79 samples locations did not have total concentrations that exceeded the GACs for any of the elements under consideration. 19 locations had exceedances for just 1 element. 5 locations had exceedances for 2 elements (4 of which were for As and Pb in a RwHP area and 1 was for an allotment land use with exceedances of Ni and V). Only 1 location had exceedances for 3 elements (As, Pb and Ni in a RwHP land use).

3.3. Bioaccessibility adjusted assesment criteria (BAAC) graphs

BAAC graphs with varying BAF for As are shown in Fig. 4. This shows that for both residential land uses, the BAAC for As increases with reducing bioaccessibility until a threshold is reached. This threshold is the limit at which exposure to As in soil via the inhalation route would cause local damage to the lungs. This threshold is the same for both residential land uses as the only difference when modelling these land uses is the inclusion of consumption of home-grown produce and soil attached to the produce. As the inhalation pathway in the CLEA tool is not affected, once this threshold is reached (121 mg kg^{-1} (Nathanail et al., 2015)), the BAAC remains constant at this level in spite of further decreases in BAF. The commercial land use shows similar behaviour, however the inhalation threshold is closer to the S4UL in this case

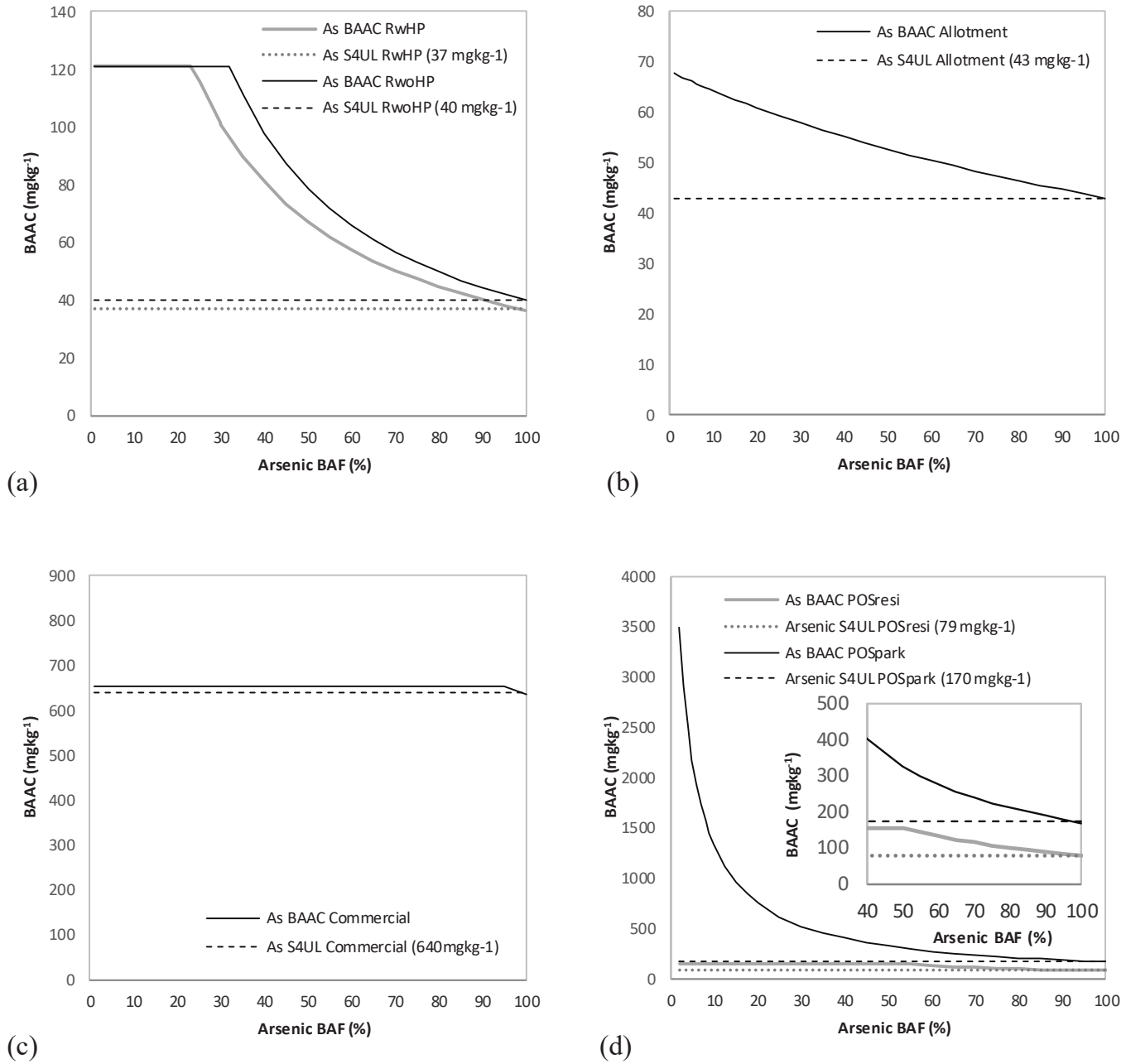


Fig. 4. Bioaccessibility Adjusted Assessment Criteria (BAAC) for As for (a) Residential, (b) Allotment, (c) Commercial and (d) Public Open Space (POS) land uses.

(665 mg kg^{-1} (Nathanail et al., 2015)).

Both the POSresi and POSpark land uses have a similar cap on the BAAC as BAF reduces. However, the POSresi cap is much lower than in the POSpark land use, as inhalation of indoor dust dominates the inhalation route in this land use (Nathanail et al., 2015). In contrast, the BAAC for As in an allotment land use does not change as substantially with variation of oral BAF as in the other land uses. This is due to the fact that the consumption of home-grown produce and attached soil pathway contributes 67% of receptors' exposure to As in this land use.

Similar BAAC graphs were developed for Ni (see Figure S2 in the Supplementary Information). As the inhalation HCV is much lower than the oral HCV for Ni, the inhalation route dominates the RwoHP, Commercial and POSresi land uses at all BAFs and dominates the ReswHP land use when BAF falls below 60% and the POSpark land use at BAFs of less than 13%.

For Pb, the HCV for inhalation is similar to the HCV for ingestion and health effects for Pb are most often associated with Pb in systemic circulation. Therefore, it is not necessary to model inhalation separately as for As and Ni. As a result, none of the BAAC graphs for Pb (see Figure S3 in the Supplementary Information) are cut off horizontally in the same way as Ni and As (Contaminated Land: Applications in Real Environments, 2014b). However, as the C4SL assumes a $RBA_{soil\ tox}$ of 60% for Pb, and $RBA_{soil\ tox}$ = 0.8 x BAF (Eq. 2) all graphs show the C4SL intersecting the BAAC curve at 75% BAF.

As noted above, it was not possible to determine an ABA_{tox} value for V. However only 1 sample exceeded the GAC for V in an allotment land use. As shown above, the inclusion of the consumption of home-grown produce pathway in the allotment land use means that oral bioaccessibility has limited effect on the allotment BAAC. Therefore, although the V BAF for this sample was just 10.3%, as the total V concentration is almost 2 times the S4UL, it is considered unlikely that, if BAF was considered, the V concentration would be below the BAAC. In addition, Ni concentrations in this sample exceed the BAAC, and therefore the location requires further assessment on the basis of the Ni concentration alone.

3.4. Regional risk assessment incorporating bioaccessibility results

When samples that had exceeded GAC were compared with BAACs (Table 2), all samples with As concentrations that had exceeded GACs were below the relevant BAAC and had a HQ<1 when oral bioaccessibility was taken into consideration. This indicated that none of the samples exceeded a minimal or tolerable level of risk from As in soil. However, this was not the case with nickel, as often the BAAC was

Table 2
Total soil concentration (by XRF), Generic Assessment Criteria (GAC), Bioaccessible fraction (BAF), Bioaccessibility Adjusted Assessment Criteria (BAAC), Hazard Quotient (HQ) and Cancer Risk (CR) for samples that exceed the GAC.

Sample ID	Total Concentration(mg kg-1)	GAC (mg kg-1)	HQ (excl BA)	CR oral (excl BA)	BAF (%)	BAAC (mg kg-1)	HQ (incl BA)	CR oral (excl BA)
As								
RwHP								
369274	38.1	37	1.00	4.50E-04	17.3	121 *	0.31	1.40E-04
384989	39.4	37	1.04	4.68E-04	18.3	121 *	0.33	1.49E-04
372755	43.4	37	1.14	5.13E-04	28.8	105	0.37	1.67E-04
364811	51.7	37	1.36	6.12E-04	29.6	102	0.45	2.03E-04
388880	65.9	37	1.73	7.79E-04	32	97	0.62	2.79E-04
382356	41.3	37	1.09	4.91E-04	60.1	57	0.68	3.06E-04
Ni								
RwHP								
382356	137	130	1.09	2.78E-03	9.6	181 *	0.75	1.91E-03
367893	152.8	130	1.21	3.08E-03	10	181 *	0.84	2.14E-03
RwoHP								
380316	243.3	180 *	1.34	3.41E-03	3	181 *	1.34	3.41E-03
Allotments								
389343	73.3	53	1.38	3.52E-03	13.6	58 *	1.27	3.24E-03
POSresi								
380155	266.7	230 *	1.15	2.93E-03	1.1	231 *	1.15	2.93E-03
371673	265.1	230 *	1.15	2.93E-03	5.1	231 *	1.15	2.93E-03
383367	287.1	230 *	1.24	3.16E-03	5.4	231 *	1.24	3.16E-03
Pb								
RwHP								
369274	364.6	200	1.81	9.69E-06	40.7	285	1.29	6.91E-06
382356	216.7	200	1.08	5.78E-06	47.8	262	0.82	4.39E-06
364811	208.1	200	1.04	5.57E-06	52.4	249	0.84	4.50E-06
372755	231.8	200	1.15	6.16E-06	53.3	247	0.94	5.03E-06
381711	1454.8	200	7.24	3.88E-05	56.6	239	6.08	3.26E-05
384989	303.3	200	1.51	8.09E-06	58.5	234	1.30	6.96E-06
388728	656.5	200	3.27	1.75E-05	64.8	220	2.99	1.60E-05
373646	504.8	200	2.51	1.34E-05	65.6	219	2.30	1.23E-05
380284	424.7	200	2.11	1.13E-05	73.9	203	2.09	1.12E-05
382378	1229.9	200	6.12	3.28E-05	77.1	197	6.25	3.35E-05
RwoHP								
366299	409.6	310	1.31	7.02E-06	54.3	434	0.94	5.03E-06
374801	359.6	310	1.15	6.16E-06	60.4	390	0.92	4.93E-06
370662	475.3	310	1.51	8.09E-06	64.4	366	1.31	7.02E-06
373700	370.5	310	1.18	6.32E-06	94.4	250	1.49	7.98E-06
Commercial								
374685	3466.9	2300	1.50	8.03E-06	86.8	2005	1.72	9.21E-06
POSresi								
374789	908.6	630	1.45	7.76E-06	46.6	1007	0.90	4.82E-06
370737	849.6	630	1.36	7.28E-06	60.4	776	1.09	5.84E-06
V								
Allotments								
389343	163.8	91	NA	NA	10.3	NA	NA	NA

*Inhalation exposure dominates derivation of GAC/BAAC

limited by Ni exposure via the inhalation route. Therefore, even though low oral BAFs were reported (1–10%), except for the RwHP land use, these did not affect the BAAC or reduce the HQ to less than 1.0.

Lifetime oral cancer risks ranged from 4.50 $\times10^{-4}$ to 7.79 $\times10^{-4}$ for soils that exceeded the GAC for As before bioaccessibility was taken into consideration (Table 2). This reduced to between 1.4 $\times10^{-4}$ to 3.06 $\times10^{-4}$ when bioaccessibility was considered. Likewise oral cancer risks from Ni exposure in soils that exceed this Ni GAC, reduced from between 2.78 $\times10^{-3}$ and 3.52 $\times10^{-3}$ to between 1.91 $\times10^{-3}$ to 3.41 $\times10^{-4}$ when bioaccessibility was considered. Understandably, when inhalation dominated the derivation of the Ni GAC (in the residential without homegrown produce and public open space residential land uses), adjusting for bioaccessibility did not affect the oral cancer risk.

In both cases (As and Ni), the inhalation cancer risk was calculated for samples where inhalation exposure dominated derivation of either GAC or BAAC. In all cases, inhalation CR was found to be less than 1 $\times10^{-5}$. This difference in lifetime oral and inhalation cancer risks is due to the fact that the oral HCV in the S4UL guidance for both Ni and As have been set to not disproportionately affect contamination sources in soil compared to other PTEs sources (see Table S2 in supplementary information). However a similar level of risk was not applied for the inhalation pathway. Therefore, despite the exposure pathways being deemed equivalent at these concentrations, in reality a significant difference in cancer risk is evident. If a similar level of risk was applied to the inhalation pathway as the oral pathway, oral bioaccessibility testing would most likely refine the risk assessment further in these samples.

In contrast the lowest Pb BAF was 40.7% and a significant number of the samples that exceeded the Pb GAC had Pb BAFs over 50%. Therefore, applying the BAAC did not significantly change the evaluation of risk for these samples. Indeed, in 3 of these samples (where the GAC was exceeded and the BAF was greater than 75%), the BAAC was lower than the GAC and the HQ increased after inclusion of bioaccessibility data. Therefore, in these samples, a higher level of risk was found to be present than the generic assessment had suggested. Lifetime oral cancer risks from Pb in soils that exceeded the Pb GAC reduced from between 5.57 $\times10^{-6}$ and 3.88 $\times10^{-5}$ before bioaccessibility was taken into consideration, to between 4.39 $\times10^{-6}$ and 3.55 $\times10^{-5}$ when oral bioaccessibility was considered (Table 2).

However, reassuringly, in the samples where Pb BAFs were greater than 75% but total Pb concentration was less than the GAC (Table 3), applying the higher BAFs to derive BAAC did not significantly change the assessment of risk for any samples.

4. Discussion

BAAC graphs clearly show that the exposure pathways that dominate for a particular land use and the relative harm posed to humans from exposure to PTEs via each pathway affect how significant changes in oral bioaccessibility will be for human health risk assessment. Although this assessment has been undertaken using UK guidance, this finding will apply in any international context where a number of exposure pathways are combined to provide an overall understanding of risk. As the dominant pathway is affected by a range of parameters it is not possible to have a rule of thumb that fits all contaminants and all land uses. Of the PTEs for which BAAC graphs were derived, assessment criteria for As and Pb were most influenced by oral bioaccessibility. For each contaminant the influence of oral bioaccessibility on assessment criteria was as follows:

As: POS_{park} >> RwHP & RwoHP > Allotment >> Commercial & POS_{resi}

Ni: POS_{park} > RwHP > Allotment > Commercial, POS_{resi} & RwoHP

Pb: RwoHP, Commercial, POS_{resi} & POS_{park} >> RwHP >> Allotment

For Pb, inhalation risk does not limit the effect of oral bioaccessibility on the assessment criteria and therefore bioaccessibility has a significant effect for all land uses where the oral pathway controls exposure (RwoHP, commercial, POS_{resi}, POS_{park}). The RwHP and allotment land uses are less significantly affected by changes in oral bioaccessibility as consumption of home-grown produce contributes to risk in these land uses.

The geogenic elements (Cr, Ni, and V) had consistently low BAFs throughout the city. For this group, areas of elevated total concentration in the north east of the city, where Cr, Ni and V contamination is derived from the Antrim Basalts, were associated with low BAF values and therefore, for Cr and V, suggest minimal risk. However, Cr was compared to the S4UL level for Cr(III) in this assessment on the assumption that Cr contamination is geogenic in origin. Further investigation of Cr speciation, especially in hotspot areas is highly recommended, as Cr of anthropogenic origin or Cr released from basalts during intense weathering (i.e. no longer in spinel form) could be in the form Cr (VI). Levels of total Ni were also elevated in the north east of the city (exceeding the GAC at 7 sites), and again BAFs were generally low.

Boxplots (Figure S1 in the Supplementary information) for As, Cu, Pb and Zn showed substantial numbers of outliers with the highest BAF values for As, Cu and Zn registered in central Belfast, suggesting that these PTEs may act as a fingerprint of former industrial activity. Pb was widespread throughout the study area, with 17% of samples exceeding the GAC, potentially suggesting an atmospheric deposition source from industrial activities, leaded fuel burn, tyre wear and brake pads (McIlwaine et al., 2017). This suggests, that rather than focusing on potentially contaminated sites for risk assessment associated with contamination, we should instead assess urban areas or domains as potentially contaminated zones, especially as climate change impacts such as heat island effects, increased dust generation and increased urban flooding potentially mobilising contaminated soils are considered in contaminated land risk assessments.

After considering bioaccessibility, the risks assessed from Pb were significantly refined, with over 35% of sites that were initially assessed as presenting a potential risk to human health being reassessed as being below the relevant Pb BAAC. This was more marked for As, with 100% of samples that were initially found to exceed the As GAC, being below BAAC after bioaccessibility was considered. In contrast, as the inhalation pathway provides a conservative estimate of health risks for Ni (except for a RwHP land use), applying BAAC did not significantly refine Ni risks in the other land uses, with potentially elevated risks from Ni contamination still reported after more detailed risk assessment for 5 locations. In order to refine risks posed by the inhalation pathway, it is

Table 3
Total soil concentration (by XRF), Generic Assessment Criteria (GAC), Bioaccessible fraction (BAF), Bioaccessibility Adjusted Assessment Criteria (BAAC), Hazard Quotient (HQ) and Cancer Risk (CR) for samples that had a Pb BAF of greater than 75%.

Sample ID	Total Concentration (mg kg-1)	GAC (mg kg-1)	HQ (excl BA)	CR oral (excl BA)	BAF (%)	BAAC (mg kg-1)	HQ (incl BA)	CR oral (excl BA)
RwHP								
364869	76.9	200	0.38	2.03E-06	91.5	176	0.44	2.36E-06
379264	99.3	200	0.49	2.62E-06	106.2	158	0.63	3.37E-06
Commercial								
373089	504.8	2300	0.22	1.18E-06	75.7	2296	0.22	1.18E-06
379180	585.2	2300	0.25	1.34E-06	90.8	1916	0.31	1.66E-06

recommended that inhalation bioaccessibility is undertaken for Ni in future studies (Boisa et al., 2014).

The research also shows that the RBA that is selected for derivation of GAC is significant in risk assessment for Pb. In the UK a RBA of 0.6 was used to develop Pb GAC. This is protective of human health only if the underlying assumptions relating to the bioaccessibility of dietary exposure are correct. If for example the bioaccessibility of Pb in dietary exposure tested via the UBM is less than 100% (as is discussed in Oomen et al., 2006), the conversion factor in Eq. 1 will increase, meaning that the BAF of Pb equivalent to an RBA of 0.6 will reduce from 75% to potentially as little as 30% (Oomen et al., 2006). This could significantly increase the number of soils that are more bioaccessible than is assumed by current GAC. Therefore, studies investigating the bioaccessibility of dietary lead (by the UBM) are required to increase confidence in current assessment criteria.

5. Conclusions

Assessment of total As, Cr, Cu, Ni, Pb, V, and Zn concentrations against land use appropriate GAC showed that 77% of samples locations (79 out of 103) did not exceed GAC for any PTE. Pb was the most widespread contaminant with 16.5% of sites exceeding the Pb GAC, mostly for a RwHP land use, following by Ni (7%), As (6%) and V (1%). The anthropogenic contaminants As, Cu, Pb and Zn were found to be most elevated within the central area of the city developed prior to 1965, whilst the geogenic contaminants Cr, Ni and V were most elevated in the northern portion of the city underlain by the Antrim Basalts.

The way that BAAC change with changes in oral bioaccessibility is affected by both the dominant exposure pathways for each land use and the relative harm posed to humans from exposure to PTEs via each pathway. As this is affected by a range of land use and contaminant specific parameters it is not possible to have a rule of thumb that fits all contaminants and all land uses. However, deriving BAAC graphs for each land use and PTE provides risk assessors with a valuable visual representation of the relative changes to BAAC with oral bioaccessibility. A review undertaken by Billmann et al. (2023) found that some articles did not provide sufficient detail of how bioaccessibility results were integrated into risk assessment. Also Dean et al. (2020) concluded that "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". Therefore, in addition to advancing the science of the factors controlling exposure and risk, developing an intuitive understanding of how the oral exposure pathway interacts with other pathways in human health risk assessment is valuable. This paper addresses this need by providing a visual representation on how the oral pathway interacts with other pathways to inform use of oral bioaccessibility testing and ensures research is targeted to contaminants and pathways that most significantly impact risk assessment.

A total of 103 samples were selected for bioaccessibility testing using the UBM. This showed that gastric phase (G) bioaccessibility was higher than gastro-intestinal (GI) bioaccessibility in all cases and therefore gastric bioaccessibility consistently provides a conservative estimate of potential health risks arising from the soils. The lowest BAF values (G) were registered for the geogenic contaminants Cr, Ni and V while higher G phase BAF values were registered for As, Cu, Pb and Zn. Pb BAF values exceed 75% (the value used in UK generic risk assessments) in 4 samples. In one sample a Pb BAF of greater than 100% was recorded.

A significant number of the samples that exceeded the Pb GAC had Pb BAFs over 50%. Therefore, applying BAAC did not significantly change the evaluation of risk for these samples. In particular, 7% of samples had a BAF greater than 75% (the BAF assumed in the derivation of GAC for Pb in the UK). There is some uncertainty surrounding the selection of a RBA for use in Pb GAC. Therefore, studies investigating the bioaccessibility of dietary lead (by the UBM) are required to increase confidence in current assessment criteria. In addition, including RBA in generic assessment criteria is not recommended, and instead it is proposed that bioaccessibility should not be considered under later stages of risk assessment. This is similar to what is currently recommended in the Netherlands (Oomen et al., 2006).

Bioaccessibility data was presented spatially and related to the distribution of underlying geogenic sources and historical urban development. Integration with BAAC graphs allowed a regional assessment of risk, which showed that none of the samples that exceeded the GAC when considering total As concentration exceeded a minimal or tolerable level of risk from As in soil when oral bioaccessibility was considered. However, this was not the case with nickel, as the BAAC for Ni was limited by exposure via the inhalation route. Application of oral bioaccessibility testing resulted in a 45% reduction in the number of sites identified as posing a potential risk to human health.

CRediT authorship contribution statement

Manus Carey: Writing – review & editing, Resources. **Ulrich Ofterdinger:** Writing – review & editing, Supervision. **Jennifer Newell:** Writing – review & editing, Visualization, Data curation. **Rory Doherty:** Writing – review & editing, Supervision. **Siobhan Fiona Cox:** Writing – original draft, Supervision, Methodology, Conceptualization. **Mark Cave:** Writing – review & editing, Methodology. **Ada Wong:** Investigation. **Matthew Robb:** Investigation. **Tatiana Cocerva:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Conceptualization.

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.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2024.116293.

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