Heavy metals and metalloids concentrations across UK urban horticultural soils and the factors influencing their bioavailability to food crops☆

Marta Crispo [a,*], Miriam C. Dobson [a], Roscoe S. Blevins [a], Will Meredith [b], Janice A. Lake [a], Jill L. Edmondson [a]

[a] Department of Animal and Plant Sciences, University of Sheffield, Sheffield, S10 2TN, UK
[b] Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, UK

ABSTRACT

Urban horticulture (UH) has been proposed as a solution to increase urban sustainability, but the potential risks to human health due to potentially elevated soil heavy metals and metalloids (HM) concentrations represent a major constraint for UH expansion. Here we provide the first UK-wide assessment of soil HM concentrations (total and bioavailable) in UH soils and the factors influencing their bioavailability to crops. Soils from 200 allotments across ten cities in the UK were collected and analysed for HM concentrations, black carbon (BC) and organic carbon (OC) concentrations, pH and texture. We found that although HM are widespread across UK UH soils, most concentrations fell below the respective UK soil screening values (C4SLs): 99 % Cr; 98 % As, Cd, Ni; 95 % Cu; 52 % Zn. However, 83 % of Pb concentrations exceeded C4SL, but only 3.5 % were above Pb national background concentration of 820 mg kg^{-1}. The bioavailable HM concentrations represent a small fraction (0.01–1.8 %) of the total concentrations even for those soils that exceeded C4SLs. There was a significant positive relationship between both total and bioavailable HM and soil BC and OC concentrations. This suggest that while contributing to the accumulation of HM concentrations in UH soils, BC and OC may also provide a biding surface for the bioavailable HM concentrations contributing to their immobilisation. These findings have implications for both management of the risk to human health associated with UH growing in urban soils and with management of UH soil. There is a clear need to understand the mechanisms driving soil-to-crop HM transfer in UH to improve potentially restrictive C4SL (e.g. Pb) especially as public demand for UH land is growing. In addition, the UH community would benefit from education programs promoting soil management practices that reduce the risk of HM exposure - particularly in those plots where C4SLs were exceeded.

1. Introduction

More than 50 % of the global population lives in cities and this figure is expected to rise to 70 % by 2050 (UN DESA Population Division, 2012). To date, urban areas account for three quarters of global carbon emissions (Seto et al., 2014) and food consumption by urban dwellers is estimated to represent a major source of these greenhouse gas (GHG) emissions (Goldstein et al., 2017). Urban inhabitants are reliant upon the import of foods from a complex global food system (Olsson et al., 2016) which could threaten urban food security and resilience of supply (Kirwan & Maye, 2013), as seen during the Covid-19 pandemic (Devereux et al., 2020). A key challenge faced within urban areas is the need to feed a growing population, while ensuring sustainable and resilient urban food security (Marin et al., 2016; Vermeulen et al., 2012; Godfray et al., 2010).

Urban horticulture (UH), the primary form of urban agriculture in cities and towns in the global North (Edmondson et al., 2020), is increasingly recognised from local to international levels of governance as an important facet of urban food security and sustainable urban food systems (Jia et al., 2019; Tobarra et al., 2018; Brodt et al., 2013). While delivering fresh and nutritious food, research has also demonstrated that UH supports multiple ecosystem services including habitat for biodiversity (Lin et al., 2015), carbon storage (Dobson et al., 2021; Edmondson et al., 2014) and flood regulation (Zeleňáková et al., 2017). It has also been shown to improve human mental and physical health (Dobson et al., 2020a; Martin et al., 2016) and provide social benefits

(Dobson et al., 2020a; Soga et al., 2017).

In the UK, the largest land area used for UH is urban allotments. Allotments sites are group of allotment plots (each plot is typically 250 m^2) leased to an individual with the purpose of growing fruits and vegetables (The National Allotment Society). However, allotment land provision in the UK is at all-time low, with a 65 % decline in provision (Dobson et al., 2020b). Nevertheless, there is potential to increase the land used for UH in gardens and other greenspaces as allotments or community gardens. A case study in a UK city demonstrated there was enough greenspace land potentially suitable for UH to feed more than the population of the city on the WHO recommended 400 g fresh fruit and vegetables per day (Edmondson et al., 2020).

Despite this, growing food within cities raises major concerns due to the potential risks to human health (Mitchell et al., 2014; Oka et al., 2014) as urban soils often contain elevated concentrations of pollutants including heavy metals and metalloids (HM), derived from atmospheric deposition of industrial, domestic and vehicle emission or natural sources (geogenic) (von Schneidemesser et al., 2019; Krzyzanowski et al., 2014; Wiseman et al., 2013). Application of pesticides, manure, compost, and contaminated irrigation water represent other sources of contamination in UH soils (Szolnoki et al., 2013; Alloway, 2004). Consumption of food produced on contaminated soil can pose severe risks to human health, potentially representing a major constraint for the development of UH at larger scale (Lal, 2020; Ercilla-Montserrat et al., 2018; Hamilton et al., 2014). HM are of particular concern due to their long residence times in soils (Kabata-Pendias, 2010) and their bioavailability to plants, resulting in health risks to growers. The human health risks associated with long-term exposure to HM may lead to reduced growth, cancer, damage to the nervous system, kidneys and lungs, behavioural and cognitive impairment especially in children, and even mortality (Rai et al., 2019).

In the UK, generic assessment criteria known as category four screening levels (C4SLs) were derived as a part of the Part 2A of the Environmental Protection Act 1990 (Defra, 2014) to support regulators and others in deciding whether a land is contaminated and thus unsuitable for UH use. Specifically, C4SLs are associated with a low level of toxicological concern and represent soil screening values that identify sites with low risk to human health. Additionally, Part 2A (Section 3.22) also states that land that presents normal background concentrations (NBCs) of contaminants in excess of C4SLs should not be qualified as contaminated land unless there is a particular reason to consider otherwise (Defra, 2012). To date, a UK-wide picture of UH soil HM concentrations and to what extent these compared to C4SLs and NBCs soils is unknown. Understanding the range and variability of total HM concentrations in UH soils across the UK and their comparison to C4SLs and NBCs could help to determine whether growing food in land currently used for UH poses a risk to human health and could give insight on the potential of expanding UH within cities.

Black carbon (BC) is formed during the incomplete combustion of biomass and fossil fuels and it is often found in association with other anthropogenic pollutants such as HM, which are either co-emitted with BC or adsorbed onto BC once in the atmosphere (Hao et al., 2020; Ramachandran et al., 2020; Peng et al., 2019; Xie et al., 2019; Morillo et al., 2008). Co-deposition of BC-bound HM is therefore inevitable (He & Zhang, 2009). As with HM, urban soils can contain high levels of BC, for example, studies in the UK and USA have reported BC concentrations of more than 20 % of total organic carbon pool (TOC) (Edmondson et al., 2015; Hamilton & Hartnett, 2013; Rawlins et al., 2008). Whilst often being co-deposited with HM, BC could simultaneously act as a strong sorbent of these HM, reducing their mobility and bioavailability and thus reducing the risk of plant uptake (Kim et al., 2015). Given its co-occurrence with HM and its potential to influence the bioavailability of HM in soils it is important to understand BC concentrations in UH soils, however, this is at present unknown. Research focused on the co-occurrence of BC and HM concentrations in UH soils, in combination with understanding HM bioavailability, could provide clear evidence of the role of BC in mitigating the risk to human health of elevated HM concentrations in UH soils.

To expand and scale-up UH within cities it is essential to understand the risks of contaminant exposure in the food chain and identify the major factors that influence variability and bioavailability of HM within UH soils. Through a two-year national sampling campaign, we investigated the bioavailable and total HM soil concentrations, soil BC and TOC concentrations in 200 allotment plots across 10 UK cities. The aims of this study were to:

1. Determine the concentrations of BC across UK UH soils
2. Determine the total HM concentrations across UK UH soils and investigate the soil properties that influence their variability
3. Assess the soil total HM concentrations against C4SLs and NBCs to investigate whether growing food in UH soils could pose a risk to human health
4. Determine the bioavailable concentrations of HM across UK UH soils and investigate the soil properties that influence their bioavailability to assess the risks of HM exposure in the food chain.

2. Material and methods

2.1. Site selection

Ten case study cities across the UK were selected: Bristol (B), Cardiff (CA), Edinburgh (ED), Leeds (LD), Leicester (LE), Liverpool (LV), Milton Keynes (MK), Newcastle (NE), Nottingham (NO) and Southampton (SO) (Fig. 1). These ten urban areas were selected to capture the geographic range across the UK. Within each urban area, four allotment sites were randomly selected using GIS, after dividing each area in four equal quadrants using ArcGIS 10.4.1, which have been presented in more detailed elsewhere (Dobson et al., 2021). In each allotment site, five allotment plots were selected for soil sampling. In total, 200 allotment plots in 40 sites were soil sampled during the 2017 and 2018 growing seasons.

The bedrock geology of each allotment site was derived from the Geology of Britain viewer digital dataset (British Geological Survey). In total, eight bedrock groups were identified on which allotment soils develop from: Sandstone; Mudstone; Argillaceous; Sedimentary; Mudstone, Siltstone and Sandstone (MDSS); Sandstone, Siltstone and Mudstone (SDSM); Dolostone; Clay, Silt and Sand (CLSISA) (Fig. 2).

2.2. Soil sampling strategy and processing

At each allotment plot, three soil samples were taken under one perennial and one annual crop using Eijkelkamp soil auger to 20 cm depth (n = 1200 soil samples). Samples were air-dried and sieved to 2 mm with stainless-steel sieve. Subsamples of each of the three replicates were mixed, composited into one sample, and then homogenised in an agate ball-mill. In total, 400 composite soil samples (200 composite samples under annual crops and 200 composite samples under perennial crops) were processed for chemical and statistical analyses.

2.3. Soil analyses

Soil pH was measured in 0.01 M $CaCl_2$ suspension using a 1:10 soil solution ratio (Houba et al., 2000). Soil texture was determined by Laser Scattering Particle Size Distribution Analyser (Horiba LA 950): prior analyses, TOC was firstly removed by addition of H_2O_2 (9.8 M) to 10 of soil (Mikutta et al., 2005) and then soil samples were mixed with 0.1 % sodium hexametaphosphate. Soil texture was analysed in two allotment plots randomly selected in each allotment site, with a total of 80 soil samples analysed across the 10 cities.

TOC was measured in a CN elemental analyser (Vario EL Cube; Isoprime, Hanau, Germany): prior analyses, soils were treated with HCl (5.7 M) to remove any inorganic carbon (IC) and consequently dried at
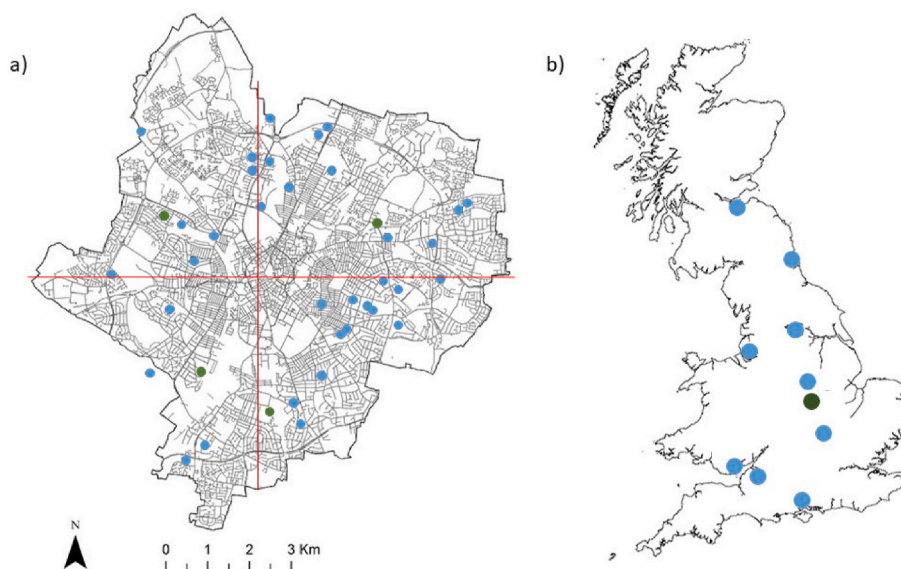
Fig. 1. a) City level allotment sampling strategy for the 10 study cities using Leicester as an example (blue dots: allotment sites, green dots: sampled allotment sites, red lines: north-south, east-west lines dissecting city into four quadrants); b) Geographical distribution of study cities across the UK (blue dots: study cities, green dot: Leicester the city represented in a).
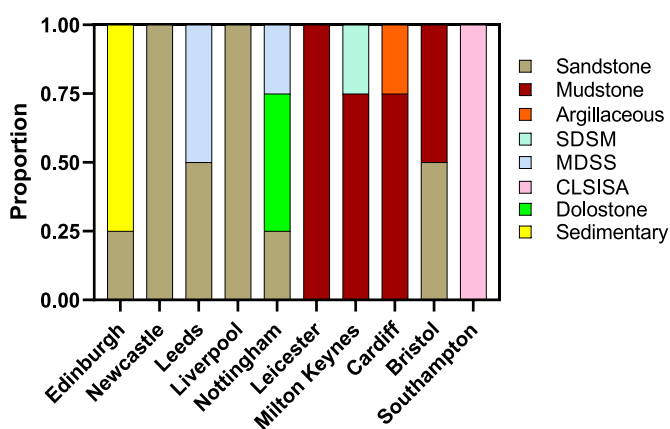

Fig. 2. The bedrock geology of allotments in the ten case study cities.

105 °C for 24 h (Edmondson et al., 2015). The TOC remaining after IC removal comprises of two main components: ecosystem-derived organic carbon (OC) and BC. Hydropyrolysis (hypy), a method which reductively separates labile and refractory TOC fractions in soils through pyrolysis assisted with high hydrogen pressure (150 bar) and dispersed sulphide molybdenum (Mo) catalyst (Meredith et al., 2012; Ascough et al., 2010), was used to determine the relative TOC proportion of OC and BC. BC was quantified by comparing the TOC content before and after the hypy of the soil sample by using Equation (1) as described by Meredith et al. (2012); whereas OC was quantified as OC = TOC - BC$_{hypy}$.

were then digested for 2 h at 120 °C on a heating block. Once cool, the digested samples were filtered using grade 42 Whatman ashless filter and diluted to volume with ultra-pure water. Bioavailable HM concentration in soil was estimated by extraction with 0.01 M CaCl$_2$ (Nabulo et al., 2011; Houba et al., 2000). Samples at a 1: 10 (w: v) ratio were shaken for 2 h at 200 rpm. After extraction, samples were centrifuged at 3000 rpm for 10 min, filtered through 0.45 μm membrane filter and diluted to volume using ultra-pure water. Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the total and bioavailable soil content of Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb) and Zinc (Zn). The CaCl$_2$ extraction method was chosen for the estimation of bioavailable HM concentrations for several reasons. Firstly, the CaCl$_2$-extractable HM are often found to well correlate with their concentrations in plant and thus better predict metal bioavailability compared to other methods, such as EDTA and DTPA, which have been found to poorly predict HM bioavailability (Zhang et al., 2010; Vázquez et al., 2008; Menzies et al., 2007; Rao et al., 2007; Novozamsky et al., 2006). Secondly, research has also reported that this method has a better mobilizing effect for HM in soils compared to other low salt solution, such as NaNO$_3$ (Pueyo et al., 2004). Lastly, this single extraction procedure in combination with ICP-MS allows assessment of the bioavailability of HM simultaneously, which is quite attractive from a laboratory-operational point of view (Milićević et al., 2017; Houba et al., 2000).

2.4. Lead isotopic ratio analysis

A subsample of soil samples (one sample per each allotment site; n = 40) was analysed to identify the Pb sources in UK allotment soils. Lead

$$\text{BC}_{hypy} \left(\frac{\text{BC}}{\text{TOC}} \% \right) = \frac{\text{Residual TOC (mg OC in hypy residues including spent catalyst)}}{\text{Initial TOC (mg OC in soil sample including catalyst)}} \times 100 \quad (1)$$

Soil total HM concentration was determined by digestion with aqua regia in accordance with ISO 11466:1995. Briefly, 0.25 g of soil samples were mixed with 2 ml HNO$_3$ (65–67 %) and 6 ml HCl (37 %) in 50 ml glass tubes and allow to stand for 16 h at room temperature. Samples

isotopic ratios of ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb were measured with quadrupole-based mass spectrometers (ICP-QMS) in the soil digested samples, where the total Pb concentrations were previously quantified. Soil samples were prepared and analysed as describe in Usman et al.

(2018). The isotopic ratios for petrol derived Pb, UK-coal and ore derived Pb were used to identify the sources of Pb in our soil samples. Specifically, the isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) for petrol derived-Pb have been estimated at 1.067 ± 0.0007 and 2.340 ± 0.011, for ore Pb at 1.182 ± 0.0004 and 2.458 ± 0.0002 (Galenas - PbS from Derbyshire and Leicestershire was used as representative of ore Pb) and for Pb in UK coal (Nottinghamshire, Yorkshire, Derbyshire) at 1.184 ± 0.0005 and 2.461 ± 0.012 (Mao et al., 2014).

2.5. Quality assurance

Quality assurance of the HM analyses was ensured through inclusion of reagent blanks, analytical reagent grade, certified soil reference materials (ERM-CC141; ISE 961) and internal reference samples for the ICP-MS. All glassware was soaked in nitric acid solution for 24 h and rinsed with ultra-pure water. The recovery of soil reference material ranged between 93 and 103 % for all the element analysed, apart from Cu which was 86 %. The limits of detection (LOD) for soil bioavailable HM concentrations are presented in Table S1.

2.6. Soil screening values and normal background concentrations

The current land contamination risk assessment in UK involves the comparison of measured total HM concentrations with the soil screening values (SGVs or C4SLs) and the relevant NBCs (Defra, 2014; Environment Agency, 2009). If the total HM concentrations are below the respective screening values and NBCs then a site can be qualified as non-contaminated and suitable for food growing purposes, if the concentrations measured exceed the generic screening values, then a site-specific and detailed quantitative risk assessment may be carried out and further actions assessed (Defra, 2014). Soil total HM concentrations were compared against UK C4SLs for allotment use (Defra, 2014) and NBCs for urban domains (Ander et al., 2013). Some HM (Cu, Ni) did not have a C4SL derived yet and in those cases soil concentration was compared against UK soil guidelines values (SGVs) (Environment Agency, 2009). The SGV for Zn was not available within the current UK guidance, so here concentrations were compared against SGVs set by the Finnish legislation (Ministry of the Environment Finland, 2007) as often applied at European and international level in the context of agricultural soils assessment (Tóth et al., 2016).

NBCs represent the upper 95 % confidence limit of the 95th percentile of HM concentrations found in UK soils resulting from both geogenic and anthropogenic diffuse pollution (Ander et al., 2013). NBCs are categorised into different domains (e.g. mineralisation, urban, principal-non-urban) based on the most important factor controlling the HM concentration in that soil (Ander et al., 2013). In this study, soil total HM concentrations were compared against NBCs for urban domain. Urban NBC was not available for As and Ni, so in these cases soil total concentrations were compared against NBCs for principal domain. To note that NBCs sit above the soil screening values (SGVs and C4SLs) of Cu and Pb, whereas NBCs sit below the soil screening values of As, Cd

and Ni. Table 1 summarises the C4SLs, SGVs and NBCs used for this study.

2.7. Statistical analyses

A linear mixed-effect (LME) model was used to determine the factors influencing total and bioavailable HM soil concentrations across UK allotment soils using the R package *nlme* (Pinheiro et al., 2020). Linear mixed-effect model was chosen as it allows to model hierarchical/nested data structure and account for non-independence when the observations are grouped, as in our case. The need for multilevel models was statistically tested for each model by comparing the Akaike information criterion (AIC), the Bayesian information criterion (BIC) and the log-likelihood of models fit with only the intercept and models fit with the intercept and the random part specified (allotment site was treated as random-effect variable). In total, 14 LME were built, one for each HM investigated (total and bioavailable concentration of As, Cd, Cr, Cu, Ni, Pb and Zn). In all models, the dependent variables were soil total or bioavailable HM concentrations. The fixed-effect variables tested were soil BC concentration; soil OC concentration; soil pH; soil texture (% of clay, sand, and silt particles); bedrock geology (Fig. 2); city (the ten cities investigated, Fig. 1) and crop type (annual or perennial). The categorical variables bedrock geology, city and crop type were entered as factor in R in order to be modelled. Maximum likelihood was used as method of estimation. The AIC was used to compare the performance of the models and identify the best fitting model for each HM. Soil pH and HM, BC and OC concentrations were log transformed prior analysis to meet LME assumptions. Bioavailable HM concentrations below the limits of detection of the ICP-MS were discarded from the statistical analyses.

Spearman's rank correlation coefficients were calculated to assess the association between Pb and the other HM. All statistical analyses were performed using the R software, version 3.5.1 (R Core Team, 2017).

3. Results

3.1. Urban horticultural soil properties across UK

The median properties of UH soils were pH of 6.48 (4.84–7.21 range); percentage of sand particles of 38.61 % (17.12–54.08 range); percentage of silt particles of 50.40 % (35.45–68.82 range); percentage of clay particles of 9.99 % (4.37–19.49 range); TOC concentration of 60.50 mg g^{-1} (15.10–221.7 range); OC concentration of 45 mg g^{-1} (6.05–211.9 range) and BC concentration of 12.35 mg g^{-1} (1.34–132.4 range) (Table S2). Soil TOC, OC and BC concentrations varied significantly by city (p < 0.0001; Fig. 3 a-c). Milton Keynes had the lowest OC and BC concentrations, whereas Newcastle had the highest OC and BC concentrations (Fig. 3 b-c). Black carbon comprised a significant portion of the TOC across all allotment soils with a median proportional contribution of BC to TOC of 21.6 % (2.27–89.73 range, Fig. 3d). The

Table 1

Soil screening values (C4SLs and SGVs) and NBCs for the total heavy metal and metalloids investigated. Values are expressed in mg kg^{-1} soil dry weight.

	As	Cd	Cr	Cu	Ni	Pb	Zn
NBCs [a]	32 [b]	2.1 [c]		190 [c]	42 [b]	820 [c]	
C4SLs for allotment [d]	49	4.9	170			80	
SGVs for allotment [e]				150	230		
SVGs for agricultural soils [f]							250

[a] NBCs for English soils, Ander et al. (2013).
[b] NBCs for principal domain, Ander et al. (2013).
[c] NBCs for urban domain, Ander et al. (2013).
[d] C4SLs for allotments, Defra, 2014.
[e] SGVs for allotment, Environment Agency, 2009.
[f] Standard set in the Finnish legislation for contaminated agricultural soil, Ministry of Environment Finland (2007).
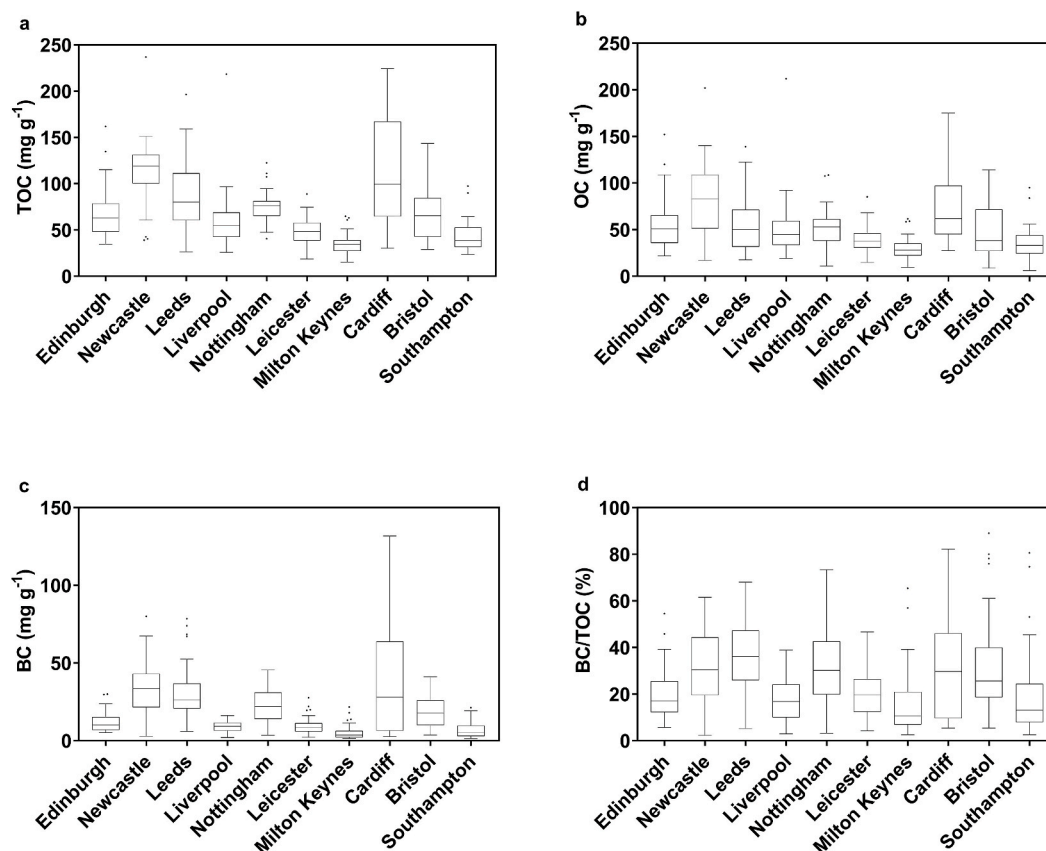
Fig. 3. Soil TOC, OC and BC concentrations in mg g^{-1} (a, b and c) and soil BC contribution to TOC in % (d) across ten urban areas in the UK (n = 357). Boxes represent 25th, 50th and 75th percentiles; black dots represent outliers.

Table 2
Outcomes of the linear mixed effect models explaining the variability of soil total HM concentrations across UK UH soils. Results included model terms (fixed and random effect) and the results of type III analyses of variance of each of the fixed effect variables included in each model. Abbreviations stand for: soil black carbon concentration (BC) and soil organic carbon concentration (OC).

Outcome variables	Random effect	Model results	Fixed effect variables					
			City	Bedrock geology	BC	OC	BC:OC	Crop type
Arsenic	Site	F (d.f.)		10.92 (7,37.68)				
		p <		0.001				
Cadmium	Site	F (d.f.)	2.36 (8,39.61)	4.61 (7,40.09)	17.12 (1,331.15)	7.87 (1,329.47)		
		p <	0.05	0.001	0.001	0.01		
Chromium	Site	F (d.f.)	14.98 (8,34.36)	9.21 (7,36.26)				
		p <	0.001	0.001				
Copper	Site	F (d.f.)	2.21 (8,38.19)	3.30 (7,38.46)	18.81 (1,327.47)	17.09 (1,325.37)		
		p <	0.05	0.01	0.001	0.001		
Lead	Site	F (d.f.)	3.11 (8,38.13)	5.47 (7,38.33)	21.85 (1,325.73)	5.89 (1,323.60)		
		p <	0.01	0.001	0.05	0.001		
Nickel	Site	F (d.f.)	9.60 (8,36.35)	10.85 (7,37.51)	6.93 (1,332.35)			
		p <	0.001	0.001	0.05			
Zinc	Site	F (d.f.)	2.61 (8,37.35)	5.10 (7,38.02)	11.07 (1,326.19)	13.21 (1,322.39)	4.73 (1,327)	4.90 (1,297.02)
		p <	0.05	0.001	0.001	0.001	0.05	0.05

greatest BC to TOC ratios (BC/TOC) were found in Leeds (36 %) followed by Newcastle, Nottingham and Cardiff (30 %); the lowest in Milton Keynes (10 %) and Southampton (13 %) (Fig. 3d).

3.2. Total HM concentrations across UK urban horticultural soils and factors influencing their concentrations

The national median total concentrations of the HM investigated were: As 15.14 mg kg^{-1} (3.68–79.49 range); Cd 0.67 mg kg^{-1} (0.14–6.5 range); Cr 28.33 mg kg^{-1} (9.36–580.1 range); Cu 56.85 mg kg^{-1} (9.66–751.5 range); Ni 25.23 mg kg^{-1} (4.5–1020 range); Pb 182.6 mg

kg^{-1} (28.78–3943 range) and Zn 251 mg kg^{-1} (46.16–1213 range) (Table S4). For soil total concentration of Cd, Cu, Ni, Pb and Zn the best fitting model explaining their variability included bedrock geology, city, and soil BC concentration (Table 2, Fig. 4). For Cd, Cu, Pb and Zn total concentrations the addition of soil OC concentration to the model significantly improved the fit (Table 2). The model for Zn total concentrations was also improved by the addition of crop type and the interaction between OC and BC (Table 2). The most parsimonious model for As total concentration only included bedrock geology as a fixed effect and for Cr included bedrock geology and city (Table 2). Soil pH and soil texture did not influence the variability of total HM concentrations.
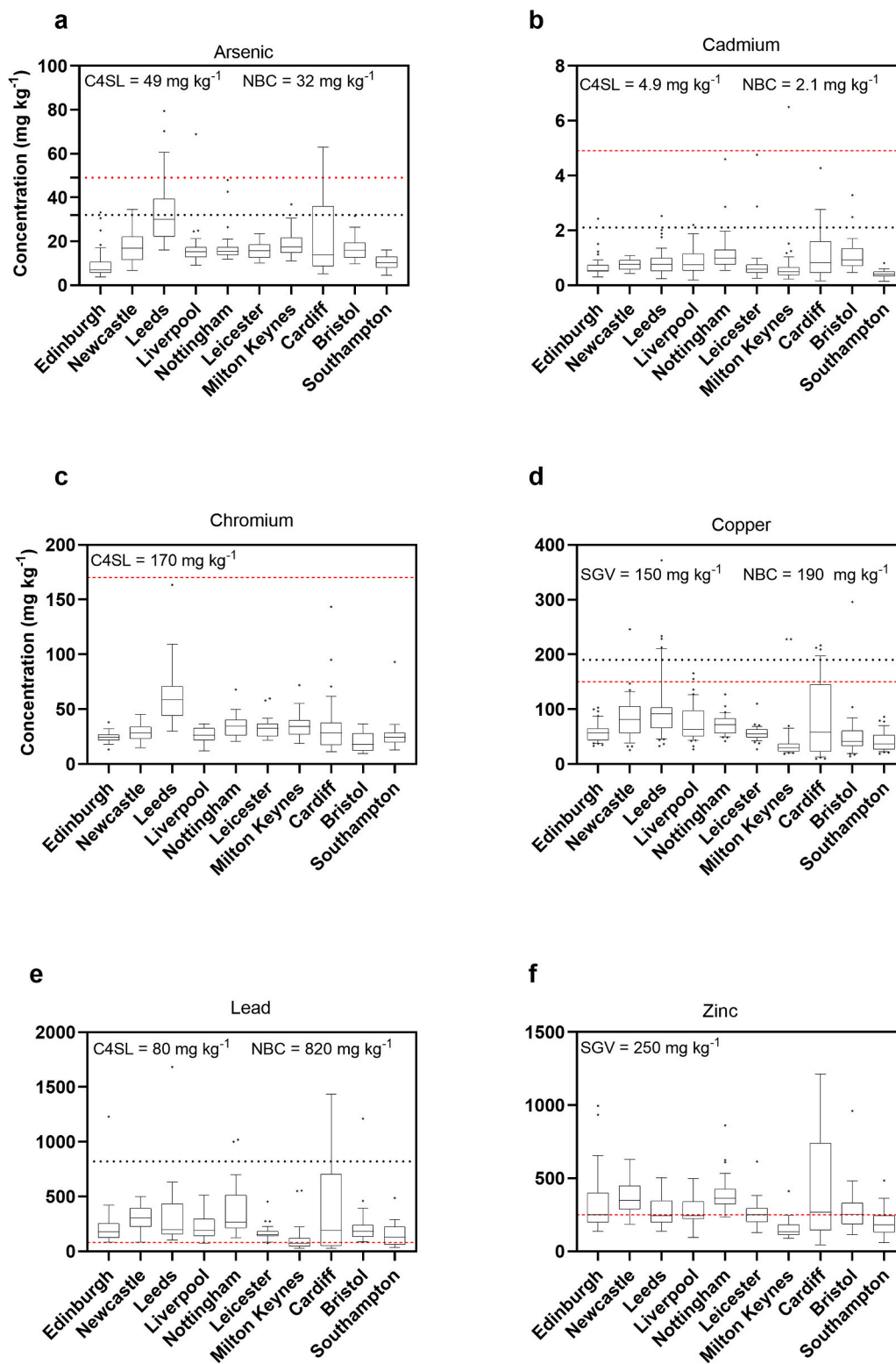
Fig. 4. Soil total HM concentrations (mg kg^{-1}) across ten cities in the UK (n = 391 composite soil samples). The concentration of As, Cd, Cr, Cu, Pb, Zn is presented in **a-f**, respectively. Boxes represent 25th, 50th and 75th percentiles; black dots represent outliers. The red dashed line indicates the C4SLs and SGVs, whereas the black dotted line indicates the NBCs.

All soil total concentrations fell below the C4SL for Cr, with 99 % and 98 % of soils below the C4SL for As and Cd respectively and 98 % of soils below the SGV for Ni (Fig. 4 a-c; Table S4). However, 83 % of soil total concentrations exceeded the C4SL for Pb and 48 % and 5 % exceeded the SGVs for Zn and Cu respectively (Fig. 4 d-f). Of these total

concentrations exceeding Cu and Pb soil screening values, 4 % (repre-senting 16 allotment plots) and 3.5 % (representing 14 allotment plots) were also above the NBCs of Cu and Pb respectively (Fig. 4 d-e).
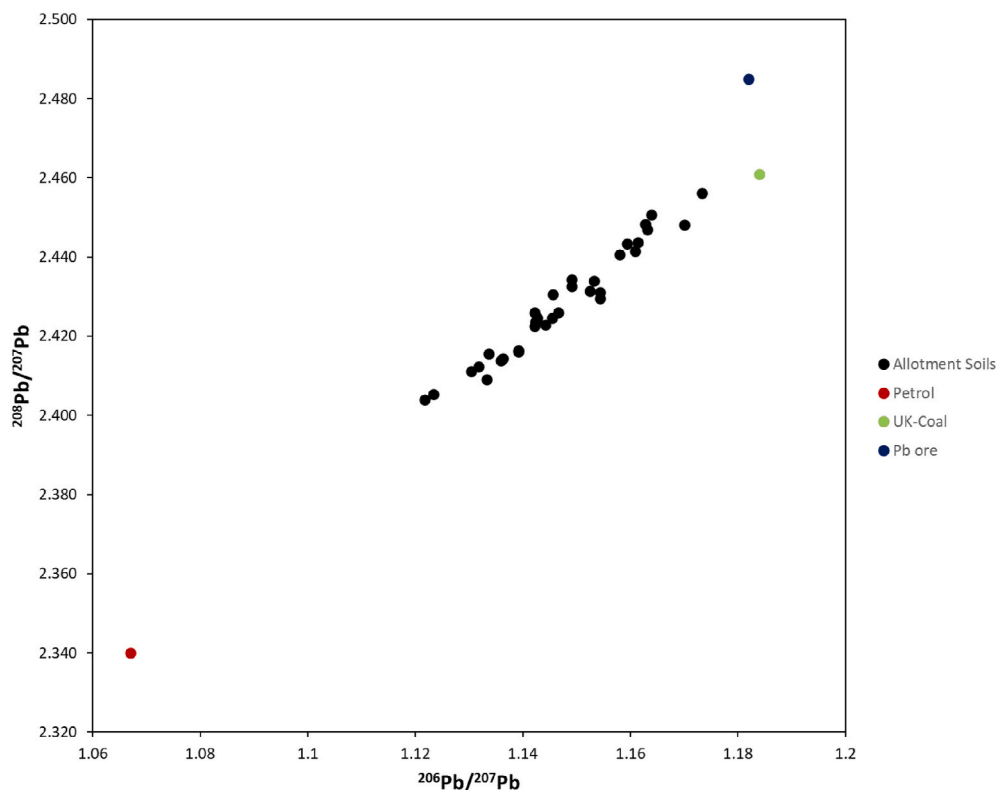
Fig. 5. Lead isotopic ratios in allotment soils across ten cities in the UK (n = 40). Mixing line of Pb isotopic ratios (^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb) with median values for UK coal (Nottinghamshire, Yorkshire, Derbyshire), Pb ore (Galenas in Derbyshire and Leicestershire) and source of Pb in petrol.

Table 3
Spearman's r coefficient for the correlations between Pb and other HM (As, Cd, Cr, Cu, Ni and Zn).

	Pb vs. As	Pb vs. Cd	Pb vs. Cr	Pb vs. Cu	Pb vs. Ni	Pb vs. Zn
Spearman's r	0.36	0.50	0.18	0.64	0.42	0.86
p	0.022	0.0009	0.28	<0.0001	0.0071	<0.0001

3.3. Lead source in UK urban horticultural soils and correlations with other HM

The isotopic ratios (^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb) of the total soil Pb concentrations fell on the mixing line between the isotopic ratio from petrol and UK coal/Pb ore (Fig. 5) indicating that Pb in UK allotment soils resulted from a combination between petrol and UK coal/ore Pb derived. The contribution of coal and ore derived Pb was ubiquitous across UK UH soils ranging between 47 % and 91 % with a mean of 68 % ± 1.93 (±standard error; Table S5). The greatest mean concentrations of coal and ore Pb derived were found in Bristol (77 %), Nottingham (73 %) and Leeds (74 %) soils. The contribution of petrol derived Pb in allotment soils was also ubiquitous across UK allotment soils, ranging between 9 % and 53 %, but lower compared to coal and ore Pb derived with a mean of 31 % ± 1.93 (±standard error; Table S5). The greatest mean concentrations of petrol derived Pb were found in Cardiff (41 %) and Liverpool (37 %) soils.

There was a significant positive correlation between Pb and all the other HM, except for Cr (Table 3). A strong correlation was particularly observed between Pb and Cu and Zn (Table 3, Spearman's r = 0.64–0.86, p < 0.0001). These significant associations provide indirect information on the sources of these other HM, which may share some common sources with Pb in UK UH soils.

3.4. Bioavailable HM concentrations across UK urban horticultural soils and factors influencing their concentrations

The bioavailable median concentrations of HM across all cities were: As 0.037 mg kg^{-1} (0.004–0.2710 range); Cd 0.005 mg kg^{-1} (0.001–0.035 range); Cr 0.1 mg kg^{-1} (0.07–2.66 range); Cu 0.18 mg kg^{-1} (0.1–2.65 range); Ni 0.068 mg kg^{-1} (0.03–1.56 range); Pb 0.023 mg kg^{-1} (0.017–0.29 range) and Zn 4.73 mg kg^{-1} (3.45–5.33 range) (Fig. 6 a-f) (Table S6). There were 78 %, 63 %, 62 % 46 % and 76 % of the bioavailable concentrations of Cr, Cu, Ni, Pb and Zn respectively below the LOD of the ICP-MS (Table S1). The remaining soil samples had median bioavailable concentrations which represented only a minor fraction (0.01–1.8 %) of the total soil concentrations of Cr, Cu, Ni, Pb and Zn. The bioavailable concentration of As and Cd below the LOD account for only 5 % of the total soil samples but as with the other HM the median bioavailable concentrations represented a minor fraction (0.2 % and 0.6 % respectively) of the total soil concentration of As and Cd. For the bioavailable concentration of Pb and Ni the best fitting model explaining their bioavailability included only soil BC concentration (Table 4). For Cd and Cr, the model best fitting the data included soil OC concentration, and the interaction between OC and pH (Table 4). In addition, for bioavailable Cr concentration the model estimation was improved by including the total Cr soil concentration and soil pH (Table 4). No fixed-effect variable was found to explain the bioavailability of As and Zn.

4. Discussion

Previous studies have found that UK UH soils contain a high concentration of TOC (Dobson et al., 2021; Edmondson et al., 2014), this research has demonstrated that BC represent a significant fraction of this TOC pool across all UH soils, with a national median value of 21.6 % and a range between 2.27 % and 2.27–89.73 % (Fig. 3d). In general, the BC/TOC ranges found across UK UH soils were similar to those reported
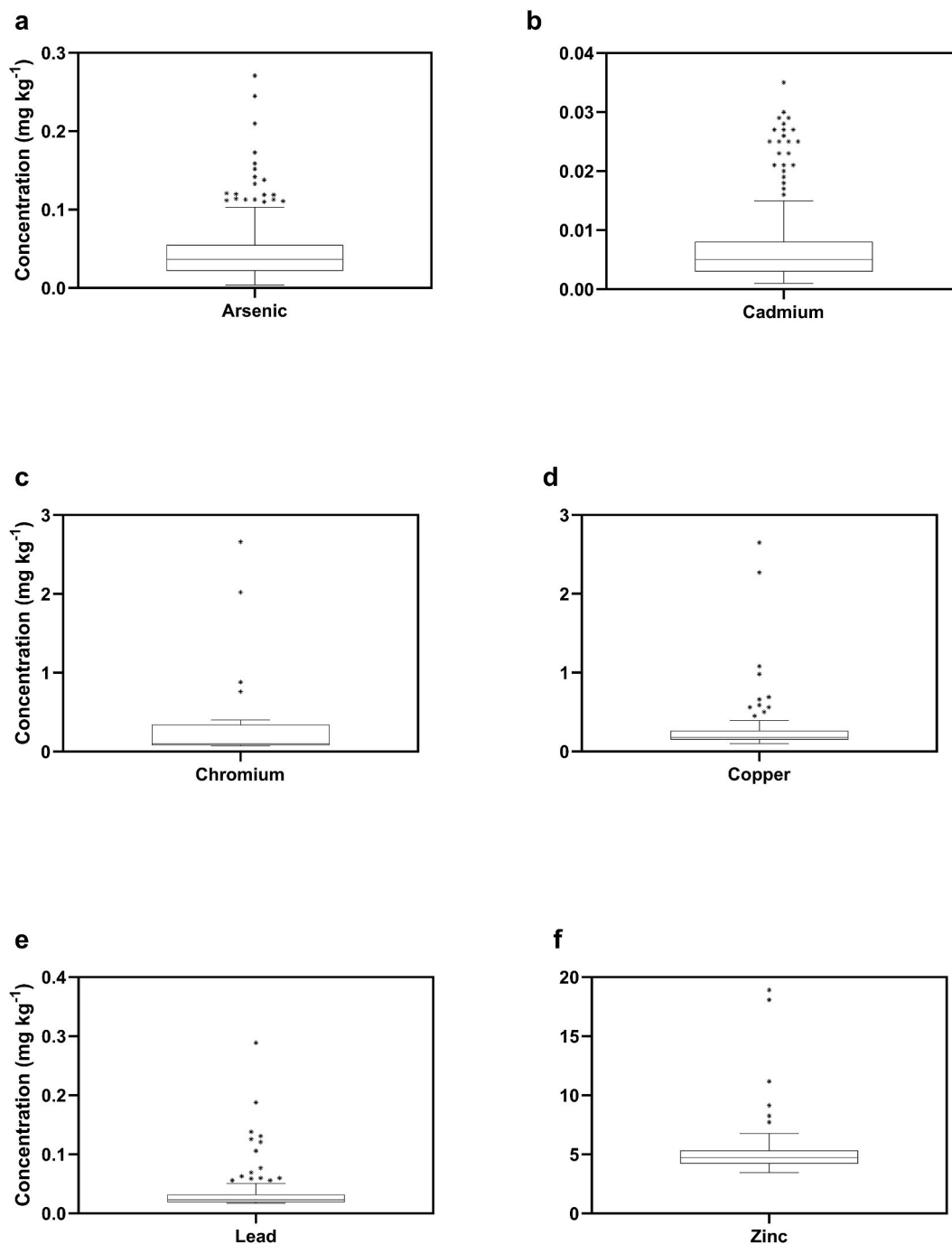
Fig. 6. Soil bioavailable HM concentrations (mg kg $^{-1}$) across ten cities in the UK. The concentration of As (n = 370), Cd (n = 370), Cr (n = 65), Cu (n = 147), Pb (n = 210), Zn (n = 92) is presented in **a-f**, respectively. Boxes represent 25th, 50th and 75th percentiles and black dots represent outliers.

in several research studies across different urban areas (Edmondson et al., 2015; Wang et al., 2014; Mitchell et al., 2014; Liu et al., 2011).

This research also provided the first nationwide assessment of the variability of total HM concentrations across UK UH soils and the factors influencing these concentrations. The median total HM concentrations observed across UK UH soils (Fig. 4 a-f) were comparable to those previously reported in 33 allotment plots across the city of Bristol (Giusti, 2011) and those observed across 12 urban allotment sites sampled across North and South UK in 2004 (Weeks et al., 2007). However, the total concentrations of Cd and Pb were lower compared to those reported in Weeks et al. (2007). Similarly, the mean total concentrations of Cr, Cu and Pb were lower compare to the those found across four allotment sites in the city of Glasgow (Hursthouse et al., 2004) and the

median total concentrations of Cd, Pb and Zn found across 4000 urban gardens in UK (Alloway, 2004). In contrast, the median total concentrations of Pb and Cd found Nottingham and Leeds allotment plots were higher compared to those found in 10 allotment plots in Nottingham and Leeds in 1988 (Moir & Thornton, 1989).

An important factor explaining the variability of total HM concentration across UK UH soils is bedrock geology (Table 2). Indeed, the geochemical processes that affect the bedrock geology are one of the key factors influencing the natural concentrations of HM in soils (Alloway, 2012; Duffus, 2002). However, our research also revealed that BC is another significant factor determining the variability of total HM concentrations (Cd, Cu, Ni, Pb and Zn) across UK UH soils (Table 2). We could ascribe this to the coexistence of BC and HM in soils as a result of

Table 4

Outcomes of the linear mixed effect models explaining soil HM bioavailability across UK UH soils. Results included model terms (fixed and random effect) and the results of type III analyses of variance of each of the fixed effect variables included in each model. Abbreviations stand for: soil black carbon concentration (BC), soil organic carbon concentration (OC), soil pH (pH) and soil total HM concentration (Total [Me]).

Outcome variables	Random effect	Model results	Fixed effect variables				
			BC	OC	pH	OC:pH	Total [HM]
Cadmium	Site	F (d.f.)		3.90 (1,318.22)		4.06 (1,318.40)	
		p <		0.05		0.05	
Chromium	Site	F (d.f.)		11.84 (1,36.98)	8.01 (1,37.031)	10.05 (1,37)	6.46 (1,38.90)
		p <		0.01	0.01	0.01	0.05
Lead	Site	F (d.f.)	8.03 (1,66.44)				
		p <	0.01				
Nickel	Site	F (d.f.)	11.04 (1,113.65)				
		p <	0.01				

their co-deposition, as also suggested in He & Zhang (2009) where a significant correlation between HM and BC was observed. Extensive past and current industrial activities in the UK represent a source of HM in urban soils. Biomass burning and fossil fuel combustion during operations like mining, smelting, plating and metal working are all major sources of BC-bound Cu, Cd, Ni, Pb and Zn emissions (Rawlins et al., 2012). This might potentially explain why BC is a significant factor contributing to HM variability. Providing further evidence of this are the differences in total HM and BC concentrations across the soils investigated. For instance, Milton Keynes and Southampton had the lowest median concentrations of both total HM (Cd, Cu, Pb, Zn; Fig. 4 a-f) and BC (Fig. 3 c). Similarly, some of the highest median total concentrations of Cd, Cu, Pb and Zn (Fig. 4 a-f) are found in Leeds, Nottingham, Newcastle and Cardiff where some of the greatest median BC concentrations are also observed (Fig. 3c). Petrol, ore and coal derived Pb are other major sources of total Pb in urban soils (Clarke et al., 2015; Szolnoki et al., 2013: Morillo et al., 2008).

In the UK, the Clean Air Act of 1956 led to a decrease of BC emissions (Novakov & Hansen, 2004), leading to a reduction in BC-bound Pb emissions. In addition, the introduction of lead-free petrol in the 1990s has further reduced the UK atmospheric co-depositions of BC-bound Pb. However, UK UH soils have retained high level of Pb, thus potentially explaining the strong modelled contribution of BC in the variability of total Pb concentrations (Table 2). This was confirmed by the analyses on the Pb isotopic ratios of soil total Pb concentrations, which indicate that Pb sources in UK UH soils are a combination of petrol and coal and ore Pb derived; in line with findings from previous research across UK urban soils (Mao et al., 2014). The important role of BC in the variability of total HM concentrations in UK UH soils could also be attributed to the large specific surface area and cation exchange capacity of BC, resulting in high sorption capacity for HM (Uchimiya et al., 2011; Park et al., 2011; Beesley et al., 2011). Indeed, we found that BC is a significant factor in determining the bioavailability of Ni and Pb (Table 4). This suggests that while contributing to the accumulation of HM concentrations in UH soils, BC may provide a biding surface for the bioavailable HM concentrations or forming soluble stable complexes and thus contribute to their immobilisation (Koelmans et al., 2006). Further research is needed to understand the specific mechanisms that governed HM immobilisation on BC in UH soils and the conditions at which HM may became available for plant uptake.

Soil OC is another significant factor explaining the variability of Cd, Cu, Pb and Zn total concentrations across UK UH soils (Table 2). Soil organic application of compost and manure can be an important source of metals in UH soils (Alloway, 2004). A recent study of more than 180 allotment holders found that the addition organic amendments to allotment soils was almost ubiquitous, with 92 % of respondents adding purchased compost and 82 % adding manure (Dobson et al., 2021). This potentially explains the significant association between OC and HM variability. However, as with BC, the relationship between HM and OC could also be linked to the adsorption of HM onto OC, which represents an important solid phase sorbent with high biding affinity for these HM

(Zeng et al., 2011). Indeed, soil OC is also a significant factor in determining the bioavailability of Cr and Cd (Table 4). This suggests that the management practices (e.g. addition of organic amendment) adopted by allotment growers across UK UH soils while increasing the total concentrations of HM in soils may also influence their bioavailability contributing to its immobilisation.

None of the soil properties tested have a significant impact on the bioavailability of As, Cu, and Zn. For Cu and Zn, this is probably because of the high number of bioavailable concentrations are below LOD. The bioavailability of As is mostly governed by the content of Iron oxy/hydroxide in soils (Williams et al., 2011; Wenzel et al., 2001), which was not measured in this research, but perhaps explaining why the soil properties tested here did not have a significant influence on As bioavailability.

The outcomes of this research have demonstrated that although HM are widespread across UK UH soils, most of the HM concentrations fall below the respective soil screening level (99 % Cr; 98 % As, Cd, Ni; 95 % Cu; 52 % Zn). However, 83 % of the total Pb concentration were above C4SL, but only 3.5 % of these exceeded Pb NBC. This suggest that growing food across UK UH soils pose low risk to the allotment growers health. However, further site-specific risk assessment may be needed in those allotment plots where the total HM concentrations were found above the soil screening level. Localised sources of pollution could be important in explaining the elevated concentrations of HM for the small number of soil samples that exceeded the current screening values for As, Cd, Cr and Cu. The application of organic and inorganic fertiliser, manure, compost, but also application of pesticides, paint particles, bonfires, rubber tires, runoff from metal surfaces (gutter and metal roof) can be all sources of high HM concentration such as As, Cd, Cr, Pb and Zn (Mitchell et al., 2014; Szolnoki et al., 2013; Alloway, 2004) and could have potentially influenced the HM concentrations in these specific plots.

The current risk assessment model known as Contaminated Land Exposure Assessment (CLEA), used to derived UK C4SLs, predicts HM crops uptake using soil to plant concentration factor which relates the total concentration of HM in soils to its concentration in the crops (Cruz et al., 2014; Hough et al., 2004). However, studies suggest that metal bioavailability is a better indicator of HM crop availability than the total HM concentration in soils as plants take up most of the nutrients from the soil solution (Ge et al., 2000). Studies have indeed found that the CLEA model significantly overestimates the HM uptake when using soil to plant concentration factor based on total HM concentrations (Entwistle et al., 2018). Here, we found that HM bioavailability across UK UH soils is very low indicating a low risk of crop uptake. However, further investigation on the HM concentrations in the crops produced on these soils is needed to verify that the levels of HM are within the regulation limits. Bioavailable concentrations represented only a minor fraction (0.1 %–1.8 %) of the total concentrations. This was also true for those soils where total Pb and Zn concentrations were 83 % and 48 % above the respective soil screening values. The low HM bioavailability across the 10 cities may be explained by the neutral pH values found

across the allotment soils (mean soil pH = 6.4 ± 0.02; Table S2), level at which metal availability is decreased as most of the cationic metals are expected to be adsorbed to the negatively charged soil solid surfaces.

These findings have implications for both management of the risk to human health associated with UH growing in urban soils and with management of UH soil. In a study conducted across Newcastle (UK) UH soils, the authors found that, despite 98 % of the UH soils were above the C4SL for Pb and Pb was highly bioaccessible in soils, the crop Pb concentrations below the regulation limits and no significant difference between blood Pb levels in allotment growers and non-gardening neighbours (Entwistle et al., 2018). Based on site-specific data, the author then estimated that soil assessment criteria of 722–1642 mg kg ^{1} for Pb may be more appropriate. The outcome of both these studies seems to indicate that growing food crops across UK UH soils may pose low risk to human health, although the elevated soil total Pb concentrations. Thus suggesting the need to define new site-specific C4SLs based on model parameters that are reflective of UH characteristics, as the current C4SLs may be overly conservative for UH scenario, especially for Pb (Entwistle et al., 2018; Leake et al., 2009).

In addition, allotment growers and urban growers in general would benefits from education programs promoting UH soil management practices that reduce the risk of HM exposure, especially in those plots where the soil screening values were exceeded. These practices could include the use of raised beds, addition of clean compost, cover cropping and sustainable pest management (Laidlaw et al., 2018; Gregory et al., 2016; Mitchell et al., 2014). In those plots with elevated Pb concentrations, additional practices to reduce the risk of exposure could include avoiding the growing of food crops that are known to accumulate high concentration of Pb such as leafy vegetables (lettuce) and root vegetables (carrots, onions, turnips, and radishes) (Laidlaw et al., 2018; Alexander et al., 2006). Finally, it is recommended to thoroughly washed all food crops before consumption to remove any contaminated soil particles deposited on the crops surface (Attanayake et al., 2014). This could potentially reduce the need for investment in expensive remediation treatments or prevent the unnecessary closure of a particular allotment plot.

5. Conclusion

Our research suggests that growing food across UK UH soils pose low risk to the allotment growers health. However, further site-specific risk assessment may be needed in those allotment plots where the total HM concentrations were found above the soil screening level. At the same time, soil bioavailable HM concentrations represented only a minor fraction of the soil total concentration, also for those soils that exceeded HM screening values, suggesting a low risk of crop uptake. Our results also demonstrated that UK UH soils contain high concentrations of BC which play a significant role in the variability and bioavailability of HM concentrations. While contributing to build up HM concentrations, BC may also provide a biding surface for the bioavailable HM concentrations and contribute to their immobilisation. Consequently, BC contributes to mitigate the risk of HM exposure into own-grown food crops across UH soils. Soil OC also significantly affect both variability and bioavailability of HM across UK UH soils, suggesting that soil management practices adopted in UK UH soils, like manure and compost addition, while increasing the HM concentration in soils, they could also contribute to HM immobilisation.

We suggest that the derivation of C4SLs that are more suitable for UH scenario and the development of education programs to promote soil management practices that reduce the risk of HM exposure among allotment growers could be a more appropriate approach in the assessment and management of the risks especially in these soils where the HM concentrations were found above the soil screening values for As, Cu, Pb and Zn.

Further research should investigate the specific mechanisms that governed HM immobilisation on BC and the conditions at which HM can

become bioavailable such as the effect of soil microorganisms and environmental conditions crucial in the degradation of BC in soil. In addition, further assessment of the HM concentrations in the food crops grown across UH soils and the associated risks are also needed.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117960.

Author statement

Marta Crispo: Conceptualisation; Methodology; Data curation; Formal analysis; Investigation; Project administration; Visualization; Writing – original draft. **Miriam C. Dobson:** Investigation; Formal analysis. **Roscoe S. Blevins**: Investigation. **Will Meredith:** Investigation; Formal analysis. **Janice A. Lake:** Conceptualisation; Methodology; Writing – review & editing. **Jill L. Edmondson:** Conceptualisation; Methodology; Validation; Resources, Funding acquisition; Supervision; Writing – review & editing.

References

Alexander, P.D., Alloway, B.J., Dourado, A.M., 2006. Genotypic variations in the accumulation of Cd, Cu, Pb and Zn exhibited by six commonly grown vegetables. Environ. Pollut. 144 (3), 736–745. https://doi.org/10.1016/J.ENVPOL.2006.03.001.

Alloway, B., 2012. Heavy Metals in Soils Trace Metals and Metalloids in Soils and Their Bioavailability. In: Heavy Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability. https://doi.org/10.1007/9789400744707.

Alloway, B.J., 2004. Contamination of domestic gardens and allotments. Land Contam. Reclamat. 12 (3), 179–187. https://doi.org/10.2462/09670513.658.

Ander, E.L., Johnson, C.C., Cave, M.R., Palumbo-Roe, B., Nathanail, C.P., Lark, R.M., 2013. Methodology for the determination of normal background concentrations of contaminants in English soil. Sci. Total Environ. 454 (455), 604–618. https://doi.org/10.1016/J.SCITOTENV.2013.03.005.

Ascough, P.L., Bird, M.I., Meredith, W., Wood, R.E., Snape, C.E., Brock, F., Higham, T.F.G., Large, D.J., Apperley, D.C., 2010. Hydropyrolysis: implications for radiocarbon pretreatment and characterization of black carbon. Radiocarbon 52 (3), 1336–1350. https://doi.org/10.1017/S0033822200046427.

Attanayake, C.P., Hettiarachchi, G.M., Harms, A., Presley, D., Martin, S., Pierzynski, G.M., 2014. Field evaluations on soil plant transfer of lead from an urban garden soil. J. Environ. Qual. 43 (2), 475–487. https://doi.org/10.2134/JEQ2013.07.0273.

Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J.L., Harris, E., Robinson, B., Sizmur, T., 2011. A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. In: Environmental Pollution, vol. 159. Elsevier, pp. 3269–3282. https://doi.org/10.1016/j.envpol.2011.07.023. Issue 12.

British Geological Survey materials © UKRI, 2021. https://www.bgs.ac.uk/map-viewers/geology-of-britain-viewer/.

Brodt, S., Kramer, K.J., Kendall, A., Feenstra, G., 2013. Comparing environmental impacts of regional and national-scale food supply chains: a case study of processed tomatoes. Food Pol. 42, 106–114. https://doi.org/10.1016/j.foodpol.2013.07.004.

Clarke, L.W., Jenerette, G.D., Bain, D.J., 2015. Urban legacies and soil management affect the concentration and speciation of trace metals in Los Angeles community garden soils. Environ. Pollut. 197, 1–12. https://doi.org/10.1016/j.envpol.2014.11.015.

Cruz, N., Rodrigues, S.M., Coelho, C., Carvalho, L., Duarte, A.C., Pereira, E., Römkens, P.F.A.M., 2014. Urban agriculture in Portugal: availability of potentially toxic

elements for plant uptake. Appl. Geochem. 44, 27–37. https://doi.org/10.1016/j.apgeochem.2013.07.003.

Department for Environment Food & Rural Affairs (Defra), 2012. Environmental Protection Act 1990: Part 2A Contaminated Land Statutory Guidance www.official-documents.gov.uk.

Department for Environment Food & Rural Affairs (Defra), 2014. Development of Category 4 Screening Levels for Assessment of Land Affected by Contamination – Policy Companion Document www.official-documents.gov.uk.

Devereux, S., Béné, C., Hoddinott, J., 2020. Conceptualising COVID-19's impacts on household food security. Food Security 12 (4), 769–772. https://doi.org/10.1007/s12571-020-01085-0.

Dobson, Miriam C., Crispo, M., Blevins, R.S., Warren, P.H., Edmondson, J.L., 2021. An assessment of urban horticultural soil quality in the United Kingdom and its contribution to carbon storage. Sci. Total Environ. 777, 146199. https://doi.org/10.1016/j.scitotenv.2021.146199.

Dobson, Miriam Clare, Reynolds, C., Warren, P.H., Edmondson, J.L., 2020a. "My little piece of the planet": the multiplicity of well-being benefits from allotment gardening. Br. Food J. 123 (3), 1012–1023. https://doi.org/10.1108/BFJ-07-2020-0593.

Dobson, Miriam C., Edmondson, J.L., Warren, P.H., 2020b. Urban food cultivation in the United Kingdom: quantifying loss of allotment land and identifying potential for restoration. Landsc. Urban Plann. 199, 103803. https://doi.org/10.1016/j.landurbplan.2020.103803.

Duffus, J.H., 2002. Heavy metals —a meaningless term? Pure Appl. Chem. 74 (5), 793–807. https://doi.org/10.1351/pac200274050793.

Edmondson, J.L., Cunningham, H., Densley Tingley, D.O., Dobson, M.C., Grafius, D.R., Leake, J.R., McHugh, N., Nickles, J., Phoenix, G.K., Ryan, A.J., Stovin, V., Taylor Buck, N., Warren, P.H., Cameron, D.D., 2020. The hidden potential of urban horticulture. Nature Food 1 (3), 155–159. https://doi.org/10.1038/s43016-020-0045-6.

Edmondson, J.L., Davies, Z.G., Gaston, K.J., Leake, J.R., 2014. Urban cultivation in allotments maintains soil qualities adversely affected by conventional agriculture. J. Appl. Ecol. 51 (4), 880–889. https://doi.org/10.1111/1365-2664.12254.

Edmondson, J.L., Stott, I., Potter, J., Lopez-Capel, E., Manning, D.A.C., Gaston, K.J., Leake, J.R., 2015. Black carbon contribution to organic carbon stocks in urban soil. Environ. Sci. Technol. https://doi.org/10.1021/acs.est.5b00313.

Environment Agency, 2009. Using soil guideline values. Science report: SC050021/SGV introduction www.environment-agency.gov.uk.

Entwistle, J.A., Amaibi, P.M., Dean, J.R., Deary, M.E., Medock, D., Morton, J., Rodushkin, I., Bramwell, L., 2018. An apple a day? Assessing Gardeners' Lead Exposure in Urban Agriculture Sites to Improve the Derivation of Soil Assessment Criteria. Environment International. https://doi.org/10.1016/j.envint.2018.10.054.

Ercilla-Montserrat, M., Muñoz, P., Montero, J.I., Gabarrell, X., Rieradevall, J., 2018. A study on air quality and heavy metals content of urban food produced in a Mediterranean city (Barcelona). J. Clean. Prod. 195, 385–395. https://doi.org/10.1016/j.jclepro.2018.05.183.

Ge, Y., Murray, P., Hendershot, W.H., 2000. Trace metal speciation and bioavailability in urban soils. Environ. Pollut. 107 (1), 137–144. https://doi.org/10.1016/S0269-7491(99)00119-0.

Giusti, L., 2011. Heavy metals in urban soils of Bristol (UK). Initial screening for contaminated land. J. Soils Sediments 11 (8), 1385–1398. https://doi.org/10.1007/s11368-011-0434-4.

Godfray, H.C.J., Crute, I.R., Haddad, L., Muir, J.F., Nisbett, N., Lawrence, D., Pretty, J., Robinson, S., Toulmin, C., Whiteley, R., 2010. The future of the global food system. In: Philosophical Transactions of the Royal Society B: Biological Sciences, vol. 365. Royal Society, pp. 2769–2777. https://doi.org/10.1098/rstb.2010.0180. Issue 1554.

Goldstein, B., Birkved, M., Fernández, J., Hauschild, M., 2017. Surveying the environmental footprint of urban food consumption. J. Ind. Ecol. 21 (1), 151–165. https://doi.org/10.1111/jiec.12384.

Gregory, M.M., Leslie, T.W., Drinkwater, L.E., 2016. Agroecological and social characteristics of New York city community gardens: contributions to urban food security, ecosystem services, and environmental education. In: Urban Ecosystems, vol. 19. Urban Ecosystems. https://doi.org/10.1007/s11252-015-0505-1. Issue 2.

Hamilton, A.J., Burry, K., Mok, H.F., Barker, S.F., Grove, J.R., Williamson, V.G., 2014. Give peas a chance? Urban agriculture in developing countries. A review. In: Agronomy for Sustainable Development, vol. 34. EDP Sciences, pp. 45–73. https://doi.org/10.1007/s13593-013-0155-8. Issue 1.

Hamilton, G.A., Hartnett, H.E., 2013. Soot black carbon concentration and isotopic composition in soils from an arid urban ecosystem. Org. Geochem. 59, 87–94. https://doi.org/10.1016/J.ORGGEOCHEM.2013.04.003.

Hao, Y., Luo, B., Simayi, M., Zhang, W., Jiang, Y., He, J., Xie, S., 2020. Spatiotemporal patterns of PM 2.5 elemental composition over China and associated health risks. Environ. Pollut. https://doi.org/10.1016/j.envpol.2020.114910.

He, Y., Zhang, G.L., 2009. Historical record of black carbon in urban soils and its environmental implications. Environ. Pollut. 157 (10), 2684–2688. https://doi.org/10.1016/j.envpol.2009.05.019.

Houba, V.J.G., Temminghoff, E.J.M., Gaikhorst, G.A., van Vark, W., 2000. Soil analysis procedures using 0.01 M calcium chloride as extraction reagent. Commun. Soil Sci. Plant Anal. 31 (9–10), 1299–1396. https://doi.org/10.1080/00103620009370514.

Hough, R.L., Breward, N., Young, S.D., Crout, N.M.J., Tye, A.M., Moir, A.M., Thornton, I., 2004. Assessing potential risk of heavy metal exposure from consumption of home-produced vegetables by urban populations. Environ. Health Perspect. 112 (2), 215–221. https://doi.org/10.1289/ehp.5589.

Hursthouse, A., Tognarelli, D., Tucker, P., Marsan, F.A., Martini, C., Madrid, L., Madrid, F., Diaz-Barrientos, E., 2004. Metal content of surface soils in parks and allotments from three European cities: initial pilot study results. Land Contam. Reclamat. 12 (3), 189–196. https://doi.org/10.2462/09670513.644.

Jia, G., Shevliakova, E., Artaxo, P., De Noblet-Ducoudré, N., Houghton, R., House, J., Kitajima, K., Lennard, C., Popp, A., Sirin, A., Sukumar, R., Verchot, L., 2019. Land–climate interactions. In: Shukla, P.R., Skea, J., Calvo Buendia, E., Masson-Delmotte, V., Pörtner, H.-O., Roberts, D.C., Zhai, P., Slade, R., Connors, S., van Diemen, R., Ferrat, M., Haughey, E., Luz, S., Neogi, S., Pathak, M., Petzold, J., Portugal Pereira, J., Vyas, P., Huntley, E., Kissick, K., Belkacemi, M., Malley, J. (Eds.), Climate Change and Land: an IPCC Special Report on Climate Change, Desertification, Land Degradation, Sustainable Land Management, Food Security, and Greenhouse Gas Fluxes in Terrestrial Ecosystems (in press).

Kabata-Pendias, A., 2010. Chapter 8 elements of group 13 (previously group IIIa). In: Trace Elements in Soils and Plants. CRC Press, pp. 343–360. https://doi.org/10.1201/b10158-25.

Kim, H.-S., Kim, K.-R., Kim, H.-J., Yoon, J.-H., Yang, J.E., Ok, Y.S., Owens, G., Kim, K.-H., 2015. Effect of biochar on heavy metal immobilization and uptake by lettuce (Lactuca sativa L.) in agricultural soil. Environmental Earth Sciences 74 (2), 1249–1259. https://doi.org/10.1007/s12665-015-4116-1.

Kirwan, J., Maye, D., 2013. Food security framings within the UK and the integration of local food systems. J. Rural Stud. 29, 91–100. https://doi.org/10.1016/j.jrurstud.2012.03.002.

Koelmans, A.A., Jonker, M.T.O., Cornelissen, G., Bucheli, T.D., Van Noort, P.C.M., Gustafsson, Ö., 2006. Black carbon: the reverse of its dark side. Chemosphere 63 (3), 365–377. https://doi.org/10.1016/J.CHEMOSPHERE.2005.08.034.

Krzyzanowski, Michal, Apte, Joshua, Bonjour, Sophie, Brauer, Michael, Cohen, Aaron, Prüss-Ustün, Annette, 2014. Air Pollution in the Mega-cities. Current Environmental Health Reports 1, 185–191. https://doi.org/10.1007/s40572-014-0019-7.

Laidlaw, M.A.S., Alankarage, D.H., Reichman, S.M., Taylor, M.P., Ball, A.S., 2018. Assessment of soil metal concentrations in residential and community vegetable gardens in Melbourne, Australia. Chemosphere 199, 303–311. https://doi.org/10.1016/J.CHEMOSPHERE.2018.02.044.

Lal, R., 2020. Home gardening and urban agriculture for advancing food and nutritional security in response to the COVID-19 pandemic. Food Security 12 (4), 871–876. https://doi.org/10.1007/s12571-020-01058-3.

Leake, J.R., Adam-Bradford, A., Rigby, J.E., 2009. Health benefits of "grow your own" food in urban areas: implications for contaminated land risk assessment and risk management? Environ. Health. https://doi.org/10.1186/1476-069X-8-S1-S6.

Lin, B.B., Philpott, S.M., Jha, S., 2015. The future of urban agriculture and biodiversity-ecosystem services: challenges and next steps. In: Basic and Applied Ecology, vol. 16. Elsevier GmbH, pp. 189–201. https://doi.org/10.1016/j.baae.2015.01.005. Issue 3.

Liu, S., Xia, X., Zhai, Y., Wang, R., Liu, T., Zhang, S., 2011. Black carbon (BC) in urban and surrounding rural soils of Beijing, China: spatial distribution and relationship with polycyclic aromatic hydrocarbons (PAHs). Chemosphere 82 (2), 223–228. https://doi.org/10.1016/J.CHEMOSPHERE.2010.10.017.

Mao, L., Bailey, E.H., Chester, J., Dean, J., Ander, E.L., Chenery, S.R., Young, S.D., 2014. Lability of Pb in soil: effects of soil properties and contaminant source. Environ. Chem. 11 (6), 690. https://doi.org/10.1071/EN14100.

Marin, A., Ely, A., van Zwanenberg, P., 2016. Co-design with aligned and non-aligned knowledge partners: implications for research and coproduction of sustainable food systems. In: Current Opinion in Environmental Sustainability, vol. 20. Elsevier B.V, pp. 93–98. https://doi.org/10.1016/j.cosust.2016.09.003.

Martin, G., Clift, R., Christie, I., 2016. Urban cultivation and its contributions to sustainability: nibbles of food but oodles of social capital. Sustainability 8 (5). https://doi.org/10.3390/su8050409.

Menzies, N.W., Donn, M.J., Kopittke, P.M., 2007. Evaluation of extractants for estimation of the phytoavailable trace metals in soils. Environ. Pollut. 145 (1), 121–130. https://doi.org/10.1016/j.envpol.2006.03.021.

Meredith, W., Ascough, P.L., Bird, M.I., Large, D.J., Snape, C.E., Sun, Y., Tilston, E.L., 2012. Assessment of hydropyrolysis as a method for the quantification of black carbon using standard reference materials. Geochem. Cosmochim. Acta 97, 131–147. https://doi.org/10.1016/j.gca.2012.08.037.

Mikutta, R., Kleber, M., Kaiser, K., Jahn, R., 2005. Review: organic matter removal from soils using hydrogen peroxide, sodium hypochlorite, and disodium peroxodisulfate. Soil Sci. Soc. Am. J. 69 (1), 120. https://doi.org/10.2136/sssaj2005.0120.

Milićević, T., Relić, D., Škrivanj, S., Tešić, Ž., Popović, A., 2017. Assessment of major and trace element bioavailability in vineyard soil applying different single extraction procedures and pseudo-total digestion. Chemosphere. https://doi.org/10.1016/j.chemosphere.2016.12.090.

Ministry of the Environment Finland, 2007. Government Decree on the Assessment of Soil Contamination and Remediation Needs, 214/2007.

Mitchell, R.G., Spliethoff, H.M., Ribaudo, L.N., Lopp, D.M., Shayler, H.A., Marquez-Bravo, L.G., Lambert, V.T., Ferenz, G.S., Russell-Anelli, J.M., Stone, E.B., McBride, M.B., 2014. Lead (Pb) and other metals in New York City community garden soils: factors influencing contaminant distributions. Environ. Pollut. 187, 162–169. https://doi.org/10.1016/j.envpol.2014.01.007.

Moir, A.M., Thornton, I., 1989. Lead and cadmium in urban allotment and garden soils and vegetables in the United Kingdom. Environ. Geochem. Health 11 (3–4), 113–119. https://doi.org/10.1007/BF01758660.

Morillo, E., Romero, A.S., Madrid, L., Villaverde, J., Maqueda, C., 2008. Characterization and sources of PAHs and potentially toxic metals in urban environments of Sevilla (southern Spain). Water Air Soil Pollut. 187 (1–4), 41–51. https://doi.org/10.1007/s11270-007-9495-9.

Nabulo, G., Black, C.R., Young, S.D., 2011. Trace metal uptake by tropical vegetables grown on soil amended with urban sewage sludge. Environ. Pollut. https://doi.org/10.1016/j.envpol.2010.11.007.

Novakov, T., Hansen, J.E., 2004. Black Carbon Emissions in the United Kingdom during the past four decades: an empirical analysis. In: Atmospheric Environmenta, vol. 38. Issue 25. https://escholarship.org/uc/item/1726b5k2.

Novozamsky, I., Lexmond, T.M., Houba, V.J.G., 2006. A single extraction procedure of soil for evaluation of uptake of some heavy metals by plants. In*t. J. Environ. Anal. Chem.* 51 (1–4), 47–58. https://doi.org/10.1080/03067319308027610.

Oka, G., Thomas, L., Lavkulich, L., 2014. Soil assessment for urban agriculture: a Vancouver case study. J. Soil Sci. Plant Nutr. https://doi.org/10.4067/S0718-95162014005000052.

Olsson, E., Kerselaers, E., Søderkvist Kristensen, L., Primdahl, J., Rogge, E., Wästfelt, A., 2016. Peri-urban food production and its relation to urban resilience. Sustainability 8 (12), 1340. https://doi.org/10.3390/su8121340.

Park, J.H., Choppala, G.K., Bolan, N.S., Chung, J.W., Chuasavathi, T., 2011. Biochar reduces the bioavailability and phytotoxicity of heavy metals. Plant Soil 348 (1–2), 439–451. https://doi.org/10.1007/s11104-011-0948-y.

Peng, Fen, Tsuji, Gaku, Zhang, Jian-Zhong, Chen, Zhou, Furue, Masutaka, 2019. Potential role of PM2.5 in melanogenesis. Environ. Int. 132, 105063. https://doi.org/10.1016/j.envint.2019.105063.

Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., R Core Team, 2020. Nlme: Linear and Nonlinear Mixed Effects Models. R Package Version 3.1, p. 147. https://CRAN.Rproject.org/package=nlme.

Pueyo, M., López-Sánchez, J.F., Rauret, G., 2004. Assessment of CaCl2, NaNO3 and NH4NO3 extraction procedures for the study of Cd, Cu, Pb and Zn extractability in contaminated soils. Anal. Chim. Acta 504 (2), 217–226. https://doi.org/10.1016/J.ACA.2003.10.047.

R Core Team, 2017. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/.

Rai, P.K., Lee, S.S., Zhang, M., Tsang, Y.F., Kim, K.H., 2019. Heavy metals in food crops: health risks, fate, mechanisms, and management. In: Environment International, vol. 125. Elsevier Ltd, pp. 365–385. https://doi.org/10.1016/j.envint.2019.01.067.

Ramachandran, S., Rupakheti, M., Lawrence, M.G., 2020. Black carbon dominates the aerosol absorption over the Indo-Gangetic Plain and the Himalayan foothills. Environ. Int. 142 https://doi.org/10.1016/j.envint.2020.105814.

Rao, C.R.M., Sahuquillo, A., Sanchez, J.F.L., 2007. A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. Water Air Soil Pollut. 291–333. https://doi.org/10.1007/S11270-007-9564-0, 2007 189:1, 189(1).

Rawlins, B.G., McGrath, S., Breward, N., Cave, M., Lister, T.R., Ingham, M., Gowing, C., Carter, S., 2012. The advanced soil geochemical atlas of England and Wales. British Geological Survey. www.bgs.ac.uk/gbase/advsoilatlasEW.html.

Rawlins, B.G., Vane, C.H., Kim, A.W., Tye, A.M., Kemp, S.J., Bellamy, P.H., 2008. Methods for estimating types of soil organic carbon and their application to surveys of UK urban areas. Soil Use Manag. 24 (1), 47–59. https://doi.org/10.1111/j.1475-2743.2007.00132.x.

Seto, K.C., Dhakal, S., Bigio, A., Blanco, H., Delgado, G.C., Dewar, D., Huang, L., Inaba, A., Kansal, A., Lwasa, S., McMahon, J.E., Müller, D.B., Murakami, J., Nagendra, H., Ramaswami, A., 2014. Human settlements, infrastructure and spatial planning. In: Edenhofer, O., Pichs-Madruga, R., Sokona, Y., Farahani, E., Kadner, S., Seyboth, K., Adler, A., Baum, I., Brunner, S., Eickemeier, P., Kriemann, B., Savolainen, J., Schlömer, S., von Stechow, C., Zwickel, T., Minx, J.C. (Eds.), Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, pp. 923–1000.

Soga, M., Cox, D.T.C., Yamaura, Y., Gaston, K.J., Kurisu, K., Hanaki, K., 2017. Health benefits of urban allotment gardening: improved physical and psychological well-being and social integration. Int. J. Environ. Res. Publ. Health 14 (1). https://doi.org/10.3390/ijerph14010071.

Szolnoki, Z., Farsang, A., Puskás, I., 2013. Cumulative impacts of human activities on urban garden soils: origin and accumulation of metals. Environ. Pollut. 177, 106–115. https://doi.org/10.1016/j.envpol.2013.02.007.

The National Allotment Society – National Society of Allotment and Leisure Gardeners https://www.nsalg.org.uk/.

Tobarra, M.A., López, L.A., Cadarso, M.A., Gómez, N., Cazcarro, I., 2018. Is seasonal households' consumption good for the nexus carbon/water footprint? The Spanish fruits and vegetables case. Environ. Sci. Technol. 52 (21), 12066–12077. https://doi.org/10.1021/acs.est.8b00221.

Tóth, G., Hermann, T., Da Silva, M.R., Montanarella, L., 2016. Heavy metals in agricultural soils of the European Union with implications for food safety. Environ. Int. 88, 299–309. https://doi.org/10.1016/j.envint.2015.12.017.

Uchimiya, M., Wartelle, L.H., Klasson, K.T., Fortier, C.A., Lima, I.M., 2011. Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. J. Agric. Food Chem. 59 (6), 2501–2510. https://doi.org/10.1021/jf104206c.

UN DESA Population Division, 2012. World Urbanization Prospects: the 2011 Revision. United Nations Department of Economic and SocialAffairs, New York, USA esa.un.org/unpd/wup/index.htm.

Usman, A., Ander, E.L., Bailey, E.H., Nelms, S., Pashley, V., Young, S.D., Chenery, S.R., 2018. Optimisation of a current generation ICP-QMS and benchmarking against MC-ICP-MS spectrometry for the determination of lead isotope ratios in environmental samples. J. Anal. Atomic Spectrom. 33 (12), 2184–2194. https://doi.org/10.1039/C8JA00290H.

Vázquez, S., Moreno, E., Carpena, R.O., 2008. Bioavailability of metals and as from acidified multicontaminated soils: use of white lupin to validate several extraction methods. Environ. Geochem. Health 30, 193–198. https://doi.org/10.1007/s10653-008-9143-3.

Vermeulen, S.J., Campbell, B.M., Ingram, J.S.I., 2012. Climate change and food systems. In: Annual Reviews, vol. 37, pp. 195–222. https://doi.org/10.1146/annurev-environ-020411-130608. Annual Review of Environment and Resources.

von Schneidemesser, E., Steinmar, K., Weatherhead, E.C., Bonn, B., Gerwig, H., Quedenau, J., 2019. Air pollution at human scales in an urban environment: impact of local environment and vehicles on particle number concentrations. Sci. Total Environ. 688, 691–700. https://doi.org/10.1016/j.scitotenv.2019.06.309.

Wang, Q., Liu, M., Yu, Y., Du, F., Wang, X., 2014. Black carbon in soils from different land use areas of Shanghai, China: level, sources and relationship with polycyclic aromatic hydrocarbons. Appl. Geochem. 47, 36–43. https://doi.org/10.1016/j.apgeochem.2014.04.011.

Weeks, C.A., Brown, S.N., Vazquez, I., Thomas, K., Baxter, M., Warriss, P.D., Knowles, T. G., 2007. Multi-element survey of allotment produce and soil in the UK. Food Addit. Contam. 24 (8), 877–885. https://doi.org/10.1080/02652030701305462.

Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. Anal. Chim. Acta 436 (2), 309–323. https://doi.org/10.1016/S0003-2670(01)00924-2.

Williams, P.N., Zhang, H., Davison, W., Meharg, A.A., Hossain, M., Norton, G.J., Brammer, H., Rafiqul, M., 2011. Organic matter-solid phase interactions are critical for predicting arsenic release and plant uptake in Bangladesh paddy soils. Environ. Sci. Technol. 45, 6080–6087. https://doi.org/10.1021/es2003765.

Wiseman, C.L.S., Zereini, F., Püttmann, W., 2013. Traffic-related trace element fate and uptake by plants cultivated in roadside soils in Toronto, Canada. Sci. Total Environ. 442, 86–95. https://doi.org/10.1016/j.scitotenv.2012.10.051.

Xie, Y., Lin, T., Yang, M., Zhang, Z., Deng, N., Tang, M., Xiao, Y., Guo, H., Deng, Q., 2019. Co-exposure to polycyclic aromatic hydrocarbons and metals, four common polymorphisms in microRNA genes, and their gene-environment interactions: influences on oxidative damage levels in Chinese coke oven workers. Environ. Int. 132 https://doi.org/10.1016/j.envint.2019.105055.

Zeleňáková, M., Diaconu, D.C., Haarstad, K., 2017. Urban water retention measures. Procedia Engineering 190, 419–426. https://doi.org/10.1016/j.proeng.2017.05.358.

Zeng, F., Ali, S., Zhang, H., Ouyang, Y., Qiu, B., Wu, F., Zhang, G., 2011. The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. Environ. Pollut. 159 (1), 84–91. https://doi.org/10.1016/j.envpol.2010.09.019.

Zhang, M.-K., Liu, Z.-Y., Wang, H., 2010. Use of single extraction methods to predict bioavailability of heavy metals in polluted soils to rice. Commun. Soil Sci. Plant Anal. 41 (7), 820–831. https://doi.org/10.1080/00103621003592341.