# Black carbon influence on urban soil ecosystem services: from its contribution to the soil carbon cycle to its role in mitigating the risks of heavy metals exposure into urban horticulture produce

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To my family that taught me

the joy of loving nature.

## Abstract

Urban soils underpin the provision of all ecosystem services delivered by urban greenspaces which are essential in strengthening urban resilience and mitigating many of the environmental and health challenges faced by urban populations. Understanding how to enhance ecosystem service provision by urban soils is crucial to support future greenspace management strategies, such as urban horticulture expansion or the increased multifunctionality of urban greenspaces. Through different experiments and field studies the role of urban soils in carbon sequestration, pollutant bioavailability and mitigation, urban food and nutritional security has been explored, highlighting the crucial contribution of soil black carbon across all these. Black carbon in the form of soot was demonstrated to play an active role in urban soil carbon dynamics by both suppressing the mineralisation of soil labile organic carbon and contributing to soil $CO_2$ effluxes. Field experimental results revealed that soil application of an engineered form of black carbon (biochar) at the rate of 20 t $ha^{-1}$ to a clayey loam urban soil under three different vegetation covers did not influence urban soil ecosystem service provision. The first UK-wide assessment of heavy metals and metalloids concentrations (total and bioavailable) across UK urban horticultural soils demonstrated that growing food across these soils poses a low risk to the urban grower's health and that soil black carbon contributes to mitigating the risk of heavy metals and metalloids uptake into urban horticulture produce. A large-scale field study showed that the long-term exposure to heavy metals and metalloids through consumption of urban horticulture produce is unlikely to pose detrimental human health risks. It also demonstrated that the consumption of urban horticulture produce contributes to the daily intake of all essential minerals, but their concentrations is often lower than those found in equivalent commercial horticultural crops. Future research possibilities are discussed along with the key findings of this research.

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## Declaration

In this thesis format, each data chapter (Chapter 2 to Chapter 5) is presented as a stand-alone research paper. At the time of the of the submission, Chapter 2 has been published in *Science of the Total Environment* (DOI: 10.1016/j.envpol.2021.117960); Chapter 3 has not been submitted for review yet; Chapter 4 has been published in *Environmental Pollution* (DOI: 10.1016/j.scitotenv.2021.149659); Chapter 5 is planned for submission to *Nature Food*. Thus, each chapter has multiple co-authors listed. My contributions to each chapter are as follow:

- Chapter 2

  Conceptualization, methodology, investigation, formal analysis, data curation, visualisation, writing original draft, review, editing and submission.

- Chapter 3

  Conceptualization, methodology, investigation, formal analysis, data curation, visualisation, writing original draft, review and editing.

- Chapter 4

  Conceptualization, methodology, investigation, formal analysis, data curation, visualisation, writing original draft, review, editing and submission.

- Chapter 5

  Conceptualization, methodology, investigation, formal analysis, data curation, visualisation, writing original draft, review and editing.

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# CHAPTER 1

# Introduction

This introductory chapter provides an overview of the challenges posed by urbanisation and the potential of urban soils to mitigate some of these challenges. The ecosystem services provided by urban soils are discussed and the key knowledge-gaps, which are investigated in this thesis, are highlighted.

## 1. URBANISATION

More than half of the world's population live in urban areas, and this figure is expected to grow, with projections that 68% of the global population will be urban by 2050 (UN, 2018). In the UK, the urban population already exceeds this with 84% of the total population, showing a steady increase since 2000 (Statista, 2020). It is estimated that by 2030 the current global urban land areas will nearly triple, with a 185% increase in global urban expansion since 2000 (Seto, Güneralp & Hutyra, 2012). The main underlying drivers of urbanisation are economic, political, social, and demographic changes. Particularly, urbanisation is strongly associated with economic growth: cities are the centres of economic activities, which generate most of the gross domestic product (World Bank, 2008) and where most of the new investments are made (Satterthwaite, Mcgranahan, and Tacoli, 2010). This shift from rural to urban centres has also resulted in a shift in economic activity from agriculture to industry, service, and information activities. Today, around, 65% of the global economically active population works in industries and services (Satterthwaite, Mcgranahan, and Tacoli, 2010).

Despite urbanisation bringing economic growth and increased infrastructure and services, it is also a driver of several negative environmental changes at multiples levels: land-use change and agricultural land loss (Beckers et al. 2020; Pandey and Seto 2015; Jiang et al., 2013; Seto et al. 2011), air pollution (Han et al., 2014; Li et al., 2016; Molina et al., 2012), biodiversity

loss (Sol et al., 2020; Hahs et al., 2009; Grimm et al., 2008) and alteration of biogeochemical cycles (Du and Huang, 2017; Pataki et al., 2006). These have led to a change in the functioning and processing of ecosystems globally (Sol et al., 2020; Wiederkehr et al., 2020; Yule et al., 2015) which can negatively affect the provision of several ecosystem services[1] on which humans vitally depend on (Millennium Ecosystem Assessment, 2005).

Urbanisation has rapidly increased and concentrated industrial, domestic and vehicle emissions in cities transforming them in hotspot of atmospheric pollution (Krzyzanowski et al., 2014; Schneidemesser et al., 2019; Wiseman et al., 2013). Air pollution is a major threat globally, currently causing 4.2 million premature death annually (WHO, 2015) and is associated with increased severe mental illness (Newbury et al., 2021). Particulate matter, which refers to solid or liquid particles suspended in the air derived from wildfires and the combustion of fossil fuels and biomass, is a major component of air pollutants and of particular concern as it is linked to severe health risks (Lee & Greenstone, 2021). It is estimated that globally particulate matter reduces life expectancy by up to five years (Lee & Greenstone, 2021). Particulate matter is often found in association with other anthropogenic-derived pollutants such as black carbon (BC), heavy metals and metalloids (HM) and polycyclic aromatic hydrocarbons (Hao et al., 2020; Peng et al., 2019; Ramachandran, Rupakheti, and Lawrence, 2020; J. Xie et al., 2020). It can remain in the atmosphere for days to weeks, eventually depositing on lands and oceans. For example, it is estimated that annually between 56 and 129 Tg $yr^{-1}$ of BC, a major component of particulate matter, are globally deposited on soil.

[1] Ecosystem services are "the benefits that human obtain from ecosystems. These include provisioning, regulating and cultural services" (Millennium Ecosystem Assessment, 2005).

## 2. URBAN GREENSPACES

Within urban areas, urban greenspaces (UG) play an essential role in strengthening urban resilience and mitigating many of the negative environmental impacts associated with urbanisation. Urban greenspaces refer to a network of areas including parks, forests, roof gardens, living walls, allotments, urban gardens and research has demonstrated that these diverse UG support a multiplicity of ecosystem services (Amorim et al., 2021; Dobson et al., 2021; Edmondson, et al., 2014; Pitman et al., 2015; Tzoulas et al., 2007). These include, provisioning services such as food production (Edmondson et al., 2020a; Mcdougall et al., 2020), regulating services like climate (Larondelle, Haase, and Kabisch, 2014; Roeland et al., 2019; Saaroni et al., 2018) and air quality regulation (Abhijith et al., 2017; Roeland et al., 2019), storm and flood mitigation (Kadaverugu et al., 2021; Liu et al., 2014), carbon sequestration (Roeland et al. 2019; Yildirim, Keshavarzihaghighi, and Aman, 2021), noise reduction (Amorim et al. 2021), support of biodiversity (Lin, Philpott, and Jha, 2015) and pollinators (Baldock et al., 2015; Potter and LeBuhn, 2015) and improve physical and mental health (Amorim et al., 2021; Dobson et al., 2020).

However, the projected growth of the urban population will bring several challenges for UG. These could include competition between UG and other uses of urban land, such as housing or business developments projects (Lee et al., 2015; Tappert et al., 2018), but also conflict between the different uses of UG (e.g. for recreation or horticulture production) (WHO, 2017). However, the Covid-19 pandemic has demonstrated the vital importance of UG for the mental and physical benefits of urban population, with many cities experiencing an increase in the use of UG (Berdejo-Espinola et al., 2021; Kleinschroth and Kowarik, 2020; Venter et al., 2020; NatureScot, 2021). A city-wide case study in the UK, which explored the availability of urban land for urban horticulture (UH) expansion, demonstrated that potentially, if UH was practiced in all existing allotments and domestic gardens and expanded to other UG this could feed more

than the total urban population on their recommended ‘5 a day’ every year (Edmondson et al., 2020b). Other research across ten case study cities in the UK, which investigated the potential of using UG for biofuel production, demonstrated that on average about 4% of city’s administrative UG are potentially suitable for bioenergy production systems, and, on average, these could potentially meet 2% of a city’s residential heating demand (Grafius et al., 2020). It is clear that future urban planning and strategies will need to find win-win management solutions and trade-offs among the different uses of UG and the consequent ecosystem services delivered (Edmondson et al., 2020b; O’Riordan et al., 2021).

## 3. URBAN SOILS

Urban soils are the foundation of UG and underpin the provision of all the ecosystem services delivered by UG (O’Riordan et al., 2021; Morel et al., 2015). Urban soils have been shown to support several regulating ecosystem services such as flood mitigation, especially within urban forest (Phillips et al., 2019); filtering of nutrients and pollutants, preventing them reaching groundwater (Dominati et al., 2010); carbon storage (Dobson et al., 2021; Vasenev & Kuzyakov, 2018; Edmondson et al., 2012); greenhouse gas emissions regulation (Pierre et al., 2016; Livesley et al., 2010) and organic contaminant degradation and recycling (M. Wang et al., 2015). Additionally, although understudied, soils in general have been demonstrated to support provisioning services such as production of food, fibre, and biomass (Adhikari and Hartemink, 2016; Dominati, Patterson, and Mackay, 2010).

However, urban soil are often impacted by human activity resulting is soil chemical, biological and physical changes and consequently compromising their ecosystem services delivery (O’Riordan et al., 2021; Phillips et al., 2019; Morel et al., 2015). Soil pollution is often a driver of urban soil chemical and biological degradation. Urban soils can contain elevated concentrations of organic (e.g. hydrocarbons) and inorganic (e.g. HM) pollutants (Liu et al.,

2010; Mitchell et al., 2014; Morillo et al., 2008; Oka et al., 2014) which can negatively impact soil microbial activities and consequently negatively affect several soil functions such as nutrient cycling, organic matter decomposition and biodiversity regulation (Mónok et al. 2020). Whilst limited in scale and scope, several studies have demonstrated how soil contamination can negatively influence different soil microbial activities. For example, a city-wide case study in Moscow, Russia found low microbial carbon availability and organic matter mineralisation in industrial and residential areas with high concentrations of HM (Ivashchenko et al., 2019). A study across ten urban brownfield areas in the northwest England reported low levels of nitrifying bacteria and lack of fungi in HM contaminated urban soils (Hartley et al., 2008) and another research in the city of Budapest, Hungary found that microbial activity was negatively correlated with urban soil HM concentrations (Mónok et al., 2020).

Urban soil physical degradation as a result of soil compaction can reduce plant growth and water infiltration, increase the risks of erosion and flooding and alter biogeochemical cycling (Scalenghe and Ajmone-Marsan, 2009). Several small-scale studies focussed on urban roadside verges or within urban construction sites have reported high levels of soil compaction (J. H. Gregory et al., 2006; Jim, 1998). For example, within urban construction sites in North Central Florida, compacted soils from heavy construction vehicles have been found to reduce water infiltration rates between 70% and 99% increasing the potential of water runoff (J. H. Gregory et al., 2006). However, city-wide studies have found urban soil bulk densities varying according to urban vegetation cover and time since initial disturbance. For example, a city-wide study in UK, Leicester found that urban soil bulk density was lowest under trees and woody shrubs and highest under herbaceous vegetation. However, across all different urban vegetation covers urban soils were significantly less compacted compared to agricultural ones (Edmondson et al., 2011). Another study across two cities in the USA, Moscow, Idaho and Pullman, Washington found significantly higher soil bulk density within new residential urban

areas (1.73 g $cm^{-3}$) compared to old ones (1.40 g $cm^{-3}$) (Scharenbroch, Lloyd, and Johnson-Maynard, 2005).

Several studies have also investigated urban soil carbon concentration and stock. A review of all these studies have found that urban soils contain 1.5 to 3 times greater carbon than semi-natural soils resulting in 3 to 5 times larger carbon stocks. Additionally, this same review found that across all the climates and city sizes investigated, residential areas showed the largest soil organic carbon[2] (OC) stocks whereas industrial and roadsides areas presented the greatest inorganic[3] and BC stocks (Vasenev and Kuzyakov, 2018).

Urban soil quality is key to ecosystem services delivery, thus understanding how urban soil components and properties support the provision of multiple ecosystems services is crucial for future UG planning and strategies as well as identifying urban soil management practices that maintain and enhance the delivery of these ecosystem services. Additionally, given the great heterogeneity of urban soils and the potential future competition between different UG uses, there is also the need to understand how urban soils function under different UG.

## 4. BLACK CARBON

Black carbon is an important anthropogenic-derived pollutant that characterises urban soils globally (Edmondson et al., 2015; Hamilton & Hartnett, 2013; He & Zhang, 2009; Liu et al., 2011; Schifman et al., 2018). Black carbon is defined as a continuum of particles from slightly charred biomass to highly condensed and refractory soot, derived from the incomplete combustion of fossil fuels from industries, vehicles and home heating or biomass burning (Schifman et al., 2018; Bird et al., 2015; Hedges et al., 2000). Generally, BC presents high

[2] The pool of soil organic carbon comprises ecosystem derived carbon, defined as decaying plant residues, soil biota and exudates and black carbon (Edmondson et al., 2015).

[3] Inorganic carbon in soils in primarily present in the form of calcium and magnesium carbonates and is mainly derived from carbonate minerals such as calcite and dolomite (Guo et al. 2016).

aromaticity, high surface area and porous structure which confer to it high adsorption capacity and high resistance to oxidation and biological decomposition (Koelmans et al., 2006). Research in the UK and USA has demonstrated that BC contributes to the urban soil total OC pool by more than 20% (Edmondson et al., 2015; Hamilton & Hartnett, 2013; Rawlins et al., 2008). In an urban setting, given its properties, BC could potentially enhance and contribute to the multifunctionality of urban soil ecosystem services (Schifman et al., 2018). For instance, in urban soils it can act as a strong sorbents of soil contaminants (Lohmann et al., 2005; Cornelissen et al., 2005) and consequently reduce their leaching into surface and groundwater resources as well as reducing their bioavailability to plant and microorganism uptake. At the same time, because of its high sorption affinity for OC compounds (Kasozi et al. 2010), BC could play an important role in enhancing carbon sequestration in urban soils (Edmondson et al., 2015). However, to date, a large-scale picture of BC concentrations across urban soils as well as its role in the mitigation of pollutant bioavailability to plant crops and its influence on soil OC cycle is still limited.

At the same time, engineered forms of BC like biochar could be applied as amendment in urban soils to improve soil quality and consequently enhance urban soil ecosystem service provision. Indeed, biochar application to urban soils have been found to improve several soil physicochemical and biological properties as well as plant growth. For example, biochar applications on two different urban roadside soils in Korea have been shown to increase the proportion of soil macroaggregates and consequently increase both water infiltration (Yoo, Kim, and Yoo 2020) and water retention (Kim et al., 2021; Yoo, Kim, and Yoo, 2020) while enhancing plant growth (Yoo, Kim, and Yoo 2020). Biochar application to an urban roadside soil in Australia was found to increase microbiological decomposition rates compared to unamended soil and increase a wide range of soil physical properties (Somerville et al. 2020a).

In China, the application of biochar to an urban soil was shown to improve urban soil fertility especially by increasing the concentration of soil total nitrogen, OC, potassium and available phosphorus (Yue et al., 2017). As a soil mix for small-scale urban farming, biochar has been found to increase nutrient soil retention and vegetable (pak choi) nutritional value compared to unamended soil mix (Song et al., 2020). However, knowledge on the effect of biochar on urban soil properties is still limited, especially its potential to enhance urban soil ecosystem services provision under different urban vegetation covers.

## 5. HEAVY METALS AND METALLOIDS

Heavy metals and metalloids are important anthropogenic-derived pollutants that characterise urban soils globally (Clarke et al., 2015; Huang et al., 2018; Mitchell et al., 2014; Szolnoki et al., 2013; Ullah et al., 2018). Urban soils are often exposed to a wide range of anthropogenic activities that increase soil HM concentrations. Anthropogenic sources of HM in urban soils mainly originate from atmospheric deposition of industrial (e.g. ores extraction and smelting), domestic and vehicle emissions (Krzyzanowski et al., 2014; Rawlins et al., 2012; von Schneidemesser et al., 2019; Wiseman et al., 2013). In urban and domestic gardens, applications of pesticides, manure, compost, irrigation water, paint particles, bonfire, runoff from metal surfaces can also represent sources of HM contamination (Alloway, 2004; Mitchell et al., 2014; Szolnoki et al., 2013). Natural sources of HM mainly derive from geochemical processes (e.g. lithogenesis, weathering and erosion) that affected the parent material on which the urban soil has developed (Alloway, 2012; Duffus, 2002; Hu & Cheng, 2013).

Heavy metals and metalloids are of particular concern because of their long residence times in soils (Kabata-Pendias 2010) and their bioavailability to plants, resulting in potential human health risks. The soil bioavailable HM pool consists of free ions, inorganic and organic complexes dissolved in the soil solution phase directly available for plant and microorganism

uptake (Römkens et al. 2009). The bioavailability of HM in soils is governed by several soil and solution properties. Important soil solid phase sorbents with high binding capacities for HM are organic matter, clay minerals and Fe- and Al-(hydr) oxides (Alloway, 2012; Groenenberg et al., 2010; Kalis et al., 2008). Heavy metals can adsorb or precipitate on these soil solid surfaces becoming less available for plant and microorganism uptake. Several mechanisms are responsible for the binding of HM to soil solid phases including soil cation exchange capacity, specific adsorption, occlusion and precipitation. Key soil solution properties that affect HM bioavailability and speciation are soil total HM concentration, soil pH and dissolved OC. In general, there is a positive relationship between soil total HM concentration and the bioavailable HM concentration (Römkens et al., 2009). Bioavailable HM concentrations are usually negatively correlated with pH: lowering the pH leads to a decrease in the HM binding to the soil solid phase, resulting in a higher HM concentration in soil solution. Soil pH is especially important in the desorption of cadmium and zinc (Groenenberg et al., 2010). Dissolved OC is another important factor controlling the speciation of HM in soil solution, which presents a high sorption affinity especially for copper and lead (Aiken, Hsu-Kim, and Ryan, 2011; Araújo et al., 2019).

Currently, an authoritative definition of HM is not present (Duffus, 2002). Some authors based the definition of HM on the mass density, others on the atomic number (Duffus, 2002). “Heavy metals and metalloids” is a common and widely used term in environmental sciences and it has been linked to environmental contamination, potential toxicity and ecotoxicity studies (Pourret and Hursthouse, 2019). In this thesis, the term HM refers to all these potentially toxic elements that are commonly associated with soil contamination, toxicity and ecotoxicity aspects. Arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) are the most common metals found in contaminated sites (Pourret and Hurthhouse, 2019).

## 6. URBAN HORTICULTURE

Urban horticulture, the production of fruits and vegetables (F&V) within urban areas, is increasingly recognised as an important component of transformed urban food systems contributing to food security (Development Initiatives, 2018; Milan Urban Food Policy Pact, 2015; Mbow et al., 2019; Opitz et al., 2016). Globally, it is estimated that about 800 million people are engaged with UH providing 15-20% of the world's food (Lorenz 2015). At city-scale, a city-wide study in Leicester, UK has demonstrated that UH covers about 2% of the total UG feeding about 2.6% of its population on their daily needs of F&V (Edmondson et al., 2020a). Research has demonstrated that there is the potential to expand UH production within existing UG. For instance, a city-wide study in Sheffield, UK, estimated that if UH was practiced in 10% of domestic urban gardens and expanded into 10% suitable urban land, this could potentially feed 12% of the total urban population on their '5 a day' diet per year (Edmondson et al., 2020b). Another research across Sydney, Australia estimated that between 15% and 34% of cities food demand could be met if UH was expanded into vacant urban lot and domestic gardens (Mcdougall, Rader, and Kristiansen 2020).

Increasing the production of fresh F&V within urban areas presents several benefits, for example, this can help in reducing some of the negative impact of the current global food system on the environment - e.g. reduce the greenhouse gases emissions related to long distance transportation by contributing to the development of short supply chains. A case study in Seoul, South Korea demonstrated that if UH was implemented in the city, this could potentially reduce $CO_2$ emissions by 11,668 t $CO_2$ $year^{-1}$ because of the food mileage reduction (Lee et al., 2015). Research has also demonstrated that UH, unlike the current global horticulture system, provides and enhances several ecosystem services including biodiversity (Lin, Philpott, and Jha 2015) and pollinators support (Baldock et al. 2015), carbon storage (Dobson et al., 2021; Edmondson et al., 2014) and flood regulation (Zeleňáková, Diaconu, and Haarstad 2017). In

addition, UH has been demonstrated to improve human mental and physical health (Dobson et al., 2020; Martin et al., 2016; Leake et al., 2009) and provides social benefits (Dobson et al., 2020.; Soga et al., 2017).

Urban horticultural expansion could also play a key role in contributing to the nutritional security of urban population. Globally, it is estimated about 821 million people are undernourished and micronutrient deficiency occurs in one every three people (FAO, 2018). Micronutrient deficiency may arise from limited resources and/or access to healthy food, as diets rich in calories, but low in nutritional values are often less expensive than healthier diets (Darmon et al., 2015); or it can be linked to "food desert" food environments where local retails only provide access to low nutritional quality food (Gamba et al., 2015). Consumption of F&V is crucial for a healthy and nutrition secure population, providing many key nutrients required in the human diet (Public Health England, 2018). Increasing the production of fresh F&V within urban areas could help to improve the access of urban populations to healthier and more nutritious food choices. However, to date, the impact of UH practices on the nutritional characteristics of UH produce and to what extent UH contribute to nutrition security is still unknown.

Coupled to future competition with other UG uses, a potential constraint for the expansion of UH within UG is soil contamination (Jia et al., 2019; Sharma et al., 2014). Indeed, UH soils have been found to contain high concentrations of HM (Alloway, 2004; Entwistle et al., 2018; Mitchell et al., 2014; Oka et al., 2014; Szolnoki et al., 2013) which could pose a risks to human health (Antoniadis, Shaheen, Boersch, Frohne, et al. 2017; Hang et al. 2009; Huang et al. 2018b; Kachenko and Singh 2006; Zheng et al. 2020). Main human exposure pathways to HM are soil ingestion (especially relevant for children), inhalation of soil particles, dermal contact with contaminated soils and consumption of food crops grown in contaminated soils (Ferri et al. 2015; Qu et al. 2012). Exposure to HM may lead to serious human health issues such as

reduced growth (cadmium, lead), cancer (arsenic), damage to the nervous system (mercury, lead), kidneys (copper, cadmium, mercury) and lungs (arsenic), behavioural and cognitive impairment especially in children (lead), and even mortality (Rai et al., 2019; Ali et al., 2013; Alloway, 2012; Sharma et al., 2015).

Although several studies have investigated the concentration of HM in urban soils and the potential human health risks, these are often based on city-wide case studies (Clarke et al., 2015; Entwistle et al., 2018; Huang et al., 2018; Mitchell et al., 2014; Säumel et al., 2012) and only a few studies investigated the bioavailability of these HM (Antoniadis et al., 2017; Ge et al., 2002). To date, a nationwide study investigating the extent of both total and bioavailable HM concentrations across UH soils as well as the concentration of HM in UH produce has not been undertaken. Understanding the potential human health risks associated with UH and its contribution to nutrition security is crucial to provide science-based evidence to support policy making and future expansion of UH.

## 7. THESIS EXPERIMENTS AND FIELD INVESTIGATIONS

Urban soils provide multiple ecosystem services essential in strengthening urban resilience and mitigating many of the environmental challenges posed by urbanisation. However, to date a clear understanding of how major anthropogenic-derived pollutants (HM and BC) influence soil functions and properties and ultimately urban soil ecosystem services is still missing. This is crucial to support future urban soil management strategies such as the expansion of UH, but also to establish multifunctional UG. Through different experiments and field studies these knowledge-gaps are addressed in this research. The influence of BC on urban soil OC dynamics is investigated through two soil microcosm experiments. The potential of using engineered form of BC (biochar) to enhance urban soil ecosystem services provision is investigated through a field experiment simulating different urban vegetation covers. The influence of BC

on soil HM bioavailability and its role in mitigating the risks of HM exposure to urban growers are investigated through a nationwide field study across ten case study cities. The human health risks associated with the consumption of urban grown F&V and their contribution to nutritional security are investigated through a large-scale field study across five case study cities.

# 8. THESIS OBJECTIVES AND OUTLINES

## 8.1. Thesis objectives

The overall aim of this research is to understand the role of anthropogenic-derived pollutant in urban soils and their influence on urban soil ecosystem services provision. The specific objectives of this thesis are:

8.1.1. Investigate the contribution of BC to the soil carbon cycle.

- Does BC, in the form of soot and biochar, influence the mineralisation of the soil ecosystem-derived carbon pool?
- Is BC in the form of soot mineralised in soils over short time scale?

8.1.2. Investigate the influence of BC application, in the form of biochar, and different UG types on urban soil ecosystem services delivery.

- Does BC (biochar) application influence urban soil physical and chemical properties?
- How do different UG types affect urban soil physical and chemical properties?

8.1.3. Determine the concentration of HM across UK UH soils and identify the factors (BC and others) influencing their bioavailability to food crops. Additionally, investigate whether UH soils are suitable for UH production.

- What is the concentration of BC across UK UH soils?
- What is the concentration of total and bioavailable HM across UK UH soils?
- What are the factors that influence the variability and bioavailability of HM concentrations across UK UH soils?

- Are UH soils suitable for UH uses and thus, how HM concentrations in UH soils compared to UK soil screening values?

8.1.4. Investigate the human health risks and benefits associated with the consumption of UK UH produce.

- Does long-term exposure to HM through consumption of UH produce pose a risk to urban growers' health?
- To what extent UH produce contribute to nutrition security?

**8.2. Thesis outline**

Chapter 2 investigates the influence of BC on the soil carbon cycle through two soil microcosm experiments in combination with isotope tracer technology, monitoring $^{13}CO_2$ gases over six-months. In experiment one, $^{13}C$ OC was added to the soil with and without added BC in the form of soot and biochar to investigate the influence of BC on OC mineralisation. In experiment two, $^{13}C$ soot was added to the soil to established whether it is mineralised in soil over a short timescale. This research allowed me to demonstrate for the first time that BC in the form of soot plays an active role in soil carbon dynamics. Particularly, the outcomes of this study have demonstrated that BC in form of soot can suppress the mineralisation of labile OC in soils and, to some extent, soot can be mineralised in soils itself contributing to soil $CO_2$ efflux. [Objective 1]

Chapter 3 examines the influence of BC (biochar) application and on different forms of UG on urban soils ecosystem services delivery. A two-and-a-half-year field manipulation experiment was established in Leicester (UK), where biochar was applied to soil at the rate of 20 t $ha^{-1}$ and 40 t $ha^{-1}$ and three types of urban vegetation cover were used to simulate three different forms

of UG (grassland, UH and bioenergy cropping systems). At the end of the third growing season, soil samples were collected to assess the influence of biochar application and different forms of UG on a range of different urban soil physical and chemical properties linked with the provision of several regulating ecosystem services. This research enabled me to show that, over the experiment period, soil biochar application between 20 t $ha^{-1}$ and 40 t $ha^{-1}$ do not significantly enhance the ecosystem services provided by urban soils and that different UG do not significantly influence urban soil quality. [Objective 2]

Chapter 4 provides the first nationwide assessment of soil HM across UK UH soils and identifies the factors influencing their bioavailability to food crops. Through a two-year national sampling campaign, soil samples were collected in 200 allotments plots across ten cities in the UK and analyses for HM concentrations, BC and OC concentrations, soil pH and texture. This research has found that the majority of HM concentrations are below their respective UK soil guidelines values and that soil bioavailable HM concentrations represent only a minor fraction of the total HM concentrations. Thus, suggesting that growing food across UK UH soils could pose a low risk to the urban grower's health. Additionally, this research has revealed that both soil BC and OC concentrations significantly affect the variability and bioavailability of HM concentrations across UK UH soils. [Objective 3]

Chapter 5 widens the investigation into the potential human health risks associated with the consumption of UK UH produce. Additionally, it examines the contribution of UK UH produce to nutrition security. These were explored through five case study cities in the UK analysing both the HM and nutrient concentrations in UH produce grown across 100 allotment plots. This research allowed me to demonstrate that the consumption of the WHO recommended '5 a day' F&V from UH produce is unlikely to pose a risk to human health in the UK. Additionally, this

research has revealed for the first time that although the consumption of UH produce contributes to the daily intake of all required essential minerals, their concentration is lower than those found in equivalent commercial horticultural crops. [Objective 4]

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# CHAPTER 2

## Opening the black box: Soil microcosm experiments reveal soot black carbon short-term oxidation and influence on soil organic carbon mineralisation

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### ABSTRACT

Soils hold three quarters of the total organic carbon (OC) stock in terrestrial ecosystems and yet we fundamentally lack detailed mechanistic understanding of the turnover of major soil OC pools. Black carbon (BC), the product of the incomplete combustion of fossil fuels and biomass, is ubiquitous in soils globally. Although BC is a major soil carbon pool, its effects on the global carbon cycle have not yet been resolved. Soil BC represents a large stable carbon pool turning over on geological timescales, but research suggests it can alter soil biogeochemical cycling including that of soil OC. Here, we established two soil microcosm experiments: experiment one added $^{13}C$ OC to soil with and without added BC (soot or biochar) to investigate whether it suppresses OC mineralisation; experiment two added $^{13}C$ BC (soot) to soil to establish whether it is mineralised in soil over a short timescale. Gases were sampled over six-months and analysed using isotope ratio mass spectrometry. In experiment one we found that the efflux of $^{13}C$ OC from soil decreased over time, but the addition of soot to soil significantly reduced the mineralisation of OC from 32% of the total supplied without soot to 14% of the total supplied with soot. In contrast, there was not a significant difference after the addition of biochar in the flux of $^{13}C$ from the OC added to the soil. In experiment two, we

found that the efflux $^{13}C$ from soil with added $^{13}C$ soot significantly differed from the control, but this efflux declined over time. There was a cumulative loss of 0.17% $^{13}C$ from soot over the experiment. These experimental results represent a step-change in understanding the influence of BC continuum on carbon dynamics, which has major consequences for the way we monitor and manage soils for carbon sequestration in future.

## 1. INTRODUCTION

There is approximately three times more carbon found in soils than is held in the atmosphere as $CO_2$ (Fischlin et al., 2007; Lal, 2004; IPCC, 2019). However, global shifts in land-use from natural and semi-natural ecosystems to agricultural and urban land, along with agricultural intensification have heavily degraded soils, with the resultant loss of an estimated 40 to 90 Pg of soil organic carbon (SOC) (Smith, 2007). As a direct response, signatories of the Kyoto Protocol are required to quantify the amount of carbon stored in soils, in order to monitor the net carbon emissions to the atmosphere by changes in land management or land-use. In spite of the critical role soils play in the global carbon cycle, we fundamentally lack detailed mechanistic understanding of the turnover of major soil organic carbon pools, particularly so-called black carbon (BC). This limits our ability to integrate soils into policies for a net zero future.

Black carbon is the product of the incomplete combustion of biomass and fossil fuels (Masiello, 2004; Hedges et al., 2000; Kuhlbusch & Crutzen, 1995). As such, the term BC describes a continuum of particles from slightly charred biomass to highly condensed and refractory soot and graphite (Bird et al., 2015; Hedges et al., 2000; Kuhlbusch & Crutzen, 1995). Slightly charred particles are generally dominated by small polycyclic aromatic hydrocarbons (PAHs) (2-7 rings) and labile carbon forms and, whereas soot particles are mainly comprised of gas phase re-condensed highly aromatic molecules (PAHs > 7 rings) and stable carbon forms (Bird

et al., 2015; Koelmans et al., 2006; Meredith et al., 2012). Black carbon occurs ubiquitously in the environment, playing an important role in a wide range of biogeochemical processes (Talukdar et al., 2019; Bond et al., 2013; Flanner, 2013; Masiello, 2004), and it has been suggested that it may influence the turnover of more labile ecosystem-derived SOC, defined as decaying plant residues, soil biota and exudates (Liu et al., 2018; Edmondson et al., 2015; Liang et al., 2010; Major et al., 2010). Overall, it is estimated that global BC soil stocks range between 54 and 109 Pg, representing the largest pool in the BC cycle (Bird et al., 2015). BC has been demonstrated to contribute to a significant portion of the total organic carbon (TOC) pool; e.g. in urban soils > 20% (Edmondson et al., 2015; Hamilton & Hartnett, 2013; Liu et al., 2011; Rawlins et al., 2008) and in agricultural soils between 2 and 42% (Lavallee et al., 2019; Hamilton & Hartnett, 2013; Skjemstad et al., 2002). However, the methods used to determine soil carbon stocks do not consistently quantify BC, with the current state-of-the-art deploying CN elemental analysis which does not distinguish between ecosystem-derived carbon and BC (Edmondson et al., 2015). In contrast, alternative approaches such as dichromate oxidation mostly target the more labile ecosystem-derived carbon (Reisser et al., 2016; Knicker et al., 2007). As a direct result, the differential outputs of current analytical methodologies render national carbon inventories incomparable. For example, across Continental Europe and Northern Ireland BC is quantified as part of the TOC pool via elemental analysis (de Brogniez et al., 2015; Xu et al., 2011), while BC is not accounted for in England, Wales (Bradley et al., 2006) and the Republic of Ireland (Cruickshank et al., 1998) where soil carbon measure are derived from dichromate oxidation.

Although BC is ubiquitous in soils globally, our understanding of its contribution to the SOC cycle and the biogeochemical global carbon cycle is poorly resolved (Smith et al., 2015). Understanding of the influence of BC on the SOC cycling and its stability in soils is crucial for climate change mitigation policies due to its potential to offset carbon emission and increase

carbon sequestration and to increase the accuracy of global carbon models simulating carbon cycling under different climate change scenarios (Cotrufo et al., 2016).

Research on the influence of BC on the turnover of more labile, ecosystem-derived SOC, include both suppression and stimulation of SOC mineralisation (Whitman et al., 2015). Liu et al. (2018) reported that addition of biochar (a form of BC) to the soil decreased the cumulative emission of $CO_2$ between 72% to 88% compared to control without biochar. Similarly, Liang et al. (2010) observed that total carbon mineralisation in BC-rich soils was 25.5% lower than in BC-poor adjacent soils. In contrast, Major et al. (2010) observed that 41% and 18% more carbon was respired when biochar was added to the soil compared to control, in two consecutive years. BC represents a largely stable pool of carbon turning over on geological timescales (Lehmann et al., 2015; Singh et al., 2012; Preston & Schmidt, 2006; Masiello, 2004; Goldberg, 1985). However, studies have reported soil BC mineralisation at shorter timescales (Major et al., 2010; Cheng et al., 2006; Hamer et al., 2004), although most of this work is carried out in the context of the more labile biochar, as opposed to soot, which is the more recalcitrant component of the BC continuum, but is a major feature of soils in the industrialised world (Hamilton & Hartnett, 2013; Liu et al., 2011; Sánchez-García et al., 2012; Stanmore et al., 2001). To date, no studies have investigated the stability of soot in soils and its role in the mineralisation of ecosystem-derived organic carbon. To provide a fundamental advance in our understanding of the extent to which BC represents an active component in the soil carbon cycle, we established two microcosm experiments in combination with isotope tracer technology and gas analysis to address two fundamental questions: a) Does BC (soot and biochar) influence the mineralisation of ecosystem-derived carbon pools? and b) Is BC in the form of soot mineralised in soils over short time scale?

## 2. MATERIAL AND METHODS

### 2.1. Experimental microcosm soil

Soil for the microcosm experiment was sampled, in triplicate, from an arable farm in Lincolnshire, UK (53°18' 52.1" N, 0° 26' 17.6" W), in February 2019. The soil samples were subsequently mixed, air-dried and passed through a 2 mm sieve. Prior to analyses, a subsample of this soil was homogenised in an agate ball-mill and sieved to 2 mm to remove any stones. Soil texture was determined by Laser Scattering Particle Size Distribution Analyser (Horiba LA 950): prior analyses, TOC was removed by addition of $H_2O_2$ (9.8 M) to 10 g of soil (Mikutta et al., 2005). Soil pH was measured in a 1:2.5 soil to water solution. Soil TOC concentration was determined in a CN analyser (Vario EL Cube, Elementar, Hanau, Germany) (Edmondson et al., 2012). Before TOC analyses, inorganic carbon was removed by addition of 700 µl of HCl (6 M) to 90 mg of soil (Rawlins et al., 2008). Soil BC concentration was analysed by hydropyrolyses (HyPy), described in detail elsewhere (Meredith et al., 2012). The microcosm soil had a pH of 6.73 and a sandy loamy texture. Soil TOC was 28.72 ± 0.84 mg $g^{-1}$, of which more than 95% was ecosystem-derived organic carbon (26.64 ± 0.91 mg $g^{-1}$), with a BC concentration of 2.08 ± 0.09 mg $g^{-1}$.

### 2.2. Soot and biochar production and characterisation

Samples of soot particulate matter (PM) were generated from methane gas under pyrolysis conditions in an electrically heated flow tube reactor. The equipment and method of particulate generation has been described previously (Eveleigh et al., 2014), and adaptations have been made to the equipment to collect soot PM onto filter papers (Dandajeh et al., 2017). Separate soot PM samples were collected from methane of natural isotopic composition (BOC, UK), and isotopically labelled $^{13}C$ methane (99% $^{13}C$, Sigma Aldrich). The reactor temperature was controlled to 1200 °C gas temperature at the reactor centreline. Flow rates of 20 l $min^{-1}$ nitrogen

and 207 ml $min^{-1}$ of methane were metered by mass flow controllers, resulting in 10,000 ppmv methane concentration. The flow rates resulted in a residence time through the reactor zone of constant heating of ~1 s. Particulate matter was sampled from the reactor centreline and drawn through a stainless-steel sampling tube under vacuum and filtered through glass fibre filters (70 mm filter, 0.7 μm pore size) onto which soot PM was deposited. A total mass of about 0.55 g particulate was collected onto several filters (a total of about 100 mg per filter), for both natural and isotopically labelled methane.

Biochar samples were produced from willow chips using a laboratory pyrolysis unit at the UK Biochar Research Centre at the University of Edinburgh. Approximately 30 g of willow chips were placed in a laboratory batch pyrolysis unit with a vertical quartz tube (inner diameter 50 mm) externally heated by a 12 kW infra-red gold image furnace (P610C; ULVAC RIKO, Yokohama, Japan) described in detail elsewhere (Mašek et al., 2018; Crombie et al., 2013). Before pyrolysis, the reactor was purged with nitrogen to eliminate any residual air within the system. The nitrogen purge was maintained at a rate of 0.3 L $min^{-1}$ for the duration of the experiment. The willow chips were pyrolyzed at a heating rate of 20 °C $min^{-1}$, with the highest treatment temperature (HTT) of 450 °C, and a residence time of 30 min at HTT. After pyrolysis, the system was cooled down under nitrogen flow to prevent oxidation of the biochar.

Soot and biochar samples were analysed using HyPy (Meredith et al., 2012). HyPy tests were performed using the procedure described previously by Ascough et al., (2009). The soot and biochar samples were first loaded with 10% by weight of molybdenum (Mo) catalyst using an aqueous/methanol solution of ammonium dioxydithiomolybdate [$(NH_4)_2MoO_2S_2$] and placed within borosilicate sample holders to allow for the accurate weight loss during pyrolysis of each sample to be determined (Haig et al., 2020). The samples were pyrolyzed with resistive heating from 50 °C to 250 °C at 300 °C $min^{-1}$, and then from 250 °C to 550 °C at 8 °C $min^{-1}$, before being held at the final temperature for 2 min, under a hydrogen pressure of 15 MPa. A

hydrogen sweep gas flow of 5 l $min^{-1}$, measured at ambient temperature and pressure, ensured that the products were quickly removed from the reactor, and subsequently trapped on dry ice cooled silica (Meredith et al., 2004).

The dichloromethane soluble products desorbed from the silica were then analysed on an Agilent GC-MS (7890B GC; 5977A MSD), scanning in the mass range of m/z 40-400 (EI 70 eV, source temperature 200 °C). Product separation was performed on an HP-5MS column (30m×250μm×0.25μm). The GC oven temperature was initially held at 50 °C for 0.5 min, then heated to 300 °C at a rate of 4 °C $min^{-1}$, where it was held for 5 minutes. Individual compounds were identified using a NIST MS library and published data.

The soot appeared to be very similar in composition to the n-hexane soot described in the BC ring trial (Hammes et al., 2007), with a carbon content 93% (compared with 92.9%), and an atomic H/C of 0.21 (compared with 0.19). As expected, the soot was very stable under HyPy conditions ($BC_{HyPy}$ = 69%), although as with the ring trial soot there was a small but significant labile fraction. The biochar carbon concentration was 73% and an atomic H/C of 0.61, similar to atomic H/C of biochars produced at equal pyrolysis temperature (Xiao et al., 2016). Compared to soot, biochar was less stable under HyPy condition ($BC_{HyPy}$ = 52%), however within the range of $BC_{HyPy}$ reported in Meredith et al. (2017) for biochars produced at similar temperature.

GC-MS of this labile non-$BC_{HyPy}$ fraction of the soot was dominated by 4-6 ring parent PAHs structures (Fig 1). This is probably a reflection of the relatively high temperature of formation of the soot, which is known to increase the degree of condensation, and so result in a more restricted distribution of PAHs that are able to be cleaved off by HyPy (McBeath et al., 2015; Meredith et al., 2017). For this soot, the formation temperature of 1200 °C has appeared to suppress 2-4 ring PAHs in preference to 5-6 rings, in addition to the much larger clusters that form the stable $BC_{HyPy}$ fraction.

GC-MS of the labile non-$BC_{HyPy}$ fraction of the biochar show it to be very similar to the soot one, dominated by 4-6 rings PAHs structures (Fig. 2), however soot also presented 7 rings PAHs structures (e.g. Coronene, Fig. 1). The labile biochar fraction contained more alkyl-substituted PAHs resulting in multiple clusters of peaks and an unresolved complex mixture beneath the baseline (Fig. 2). Biochars and charcoals, especially those formed at relatively low temperatures are typically dominated by 2-4 ring structures (Rombolà et al., 2016; Ascough et al., 2010). In this biochar, the 4 rings structures are the most abundant and the 2-3 rings compounds seems to be suppressed at 450 °C.

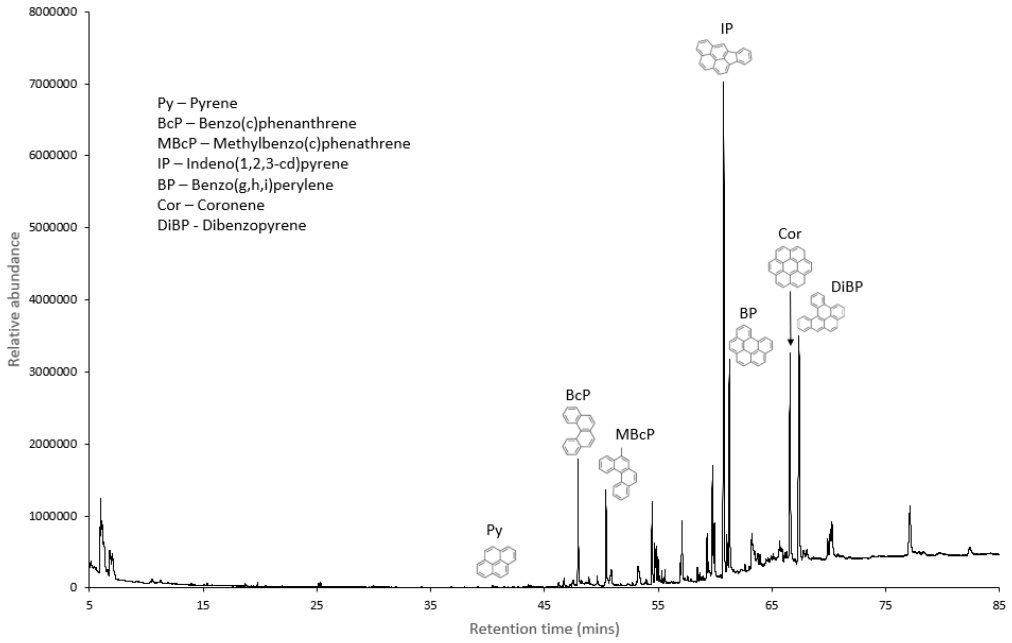


**Figure 1:** Total ion chromatogram of the labile non-$BC_{HyPy}$ of the soot.

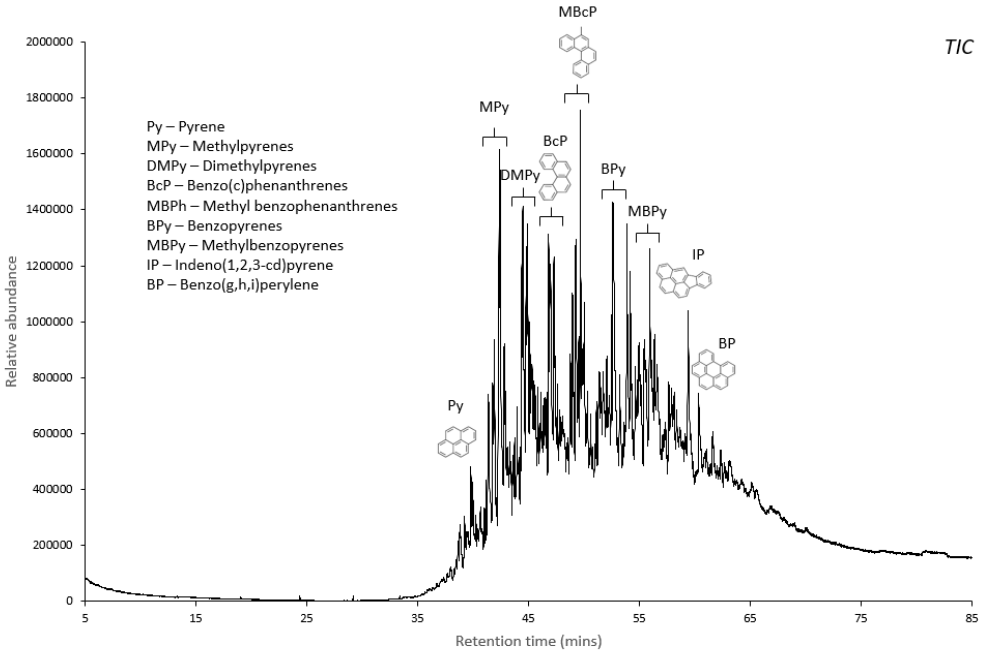


**Figure 2**: Total ion chromatogram of labile non-$BC_{HyPy}$ of the biochar.

### 2.3. Microcosm experiments

Two microcosm chamber experiments were conducted over 168 days: experiment one added $^{13}C$ labelled organic carbon to soil with and without added BC (soot or biochar) to investigate the influence of soot and biochar on organic carbon mineralisation; experiment two added $^{13}C$ soot to soil to investigate the mineralisation rate of soot in soil.

Experiment one treatments were: control (organic carbon) (soil with 19.42 mg $^{13}C$ organic carbon - 99% $^{13}C$ Sucrose, Sigma Aldrich catalogue number 605417); organic carbon and soot (soil with 19.42 mg $^{13}C$ organic carbon and 25 mg of unlabelled soot) and organic carbon and biochar (soil with 19.42 mg $^{13}C$ organic carbon and 25 mg of unlabelled biochar). Soot and biochar were added into the soil at rate of 10 t $ha^{-1}$ which represents a common rate of application in soil-BC research experiments (O'Connor et al., 2018; Jeffery et al., 2011). Sucrose, glucose and fructose are often identified as the most abundant low molecular weight carbon compounds present in root exudates, across all ecosystems (Girkin et al., 2018; Shi et

al., 2011). Thus, sucrose was selected for this experiment as a common photosynthetically derived form of labile organic carbon found in soils across all ecosystems (Canarini et al., 2019; Girkin et al., 2018; Shi et al., 2011). Sucrose was added at the rate of 3.88 mg C $g^{-1}$ dry soil which falls between low and medium root exudates input rates previously reported in literature (Basiliko et al., 2012; Girkin et al., 2018; Shi et al., 2011). Experiment two treatments were: control (soil) and soot (soil with 25 mg of $^{13}C$ soot). All treatments were thoroughly mixed into 5 g dry weight equivalent of soil to homogenise and replicated four times. Each treatment was set up in a 180 ml air-tight plastic container and kept in a controlled environment at constant temperature of 18 °C for the duration of the experiment. Ultra-pure water was added to each experimental unit throughout the duration of the experiment to maintain soil moisture at field capacity. Experiment one ran for 168 days and experiment two ran for 154 days, with measurements at set up and after 1, 7, 14, 21, 28, 35, 42, 49, 56, 70, 84, 98, 112, 126, 140, 154 and 168 days. $^{13}CO_2$ gases were sampled through a one-way stopcock valve with a 10 ml syringe. To avoid anoxic condition, each experimental unit was opened to oxygenate at each sampling point. Gas samples were analysed for $^{13}C$ content by continuous flow isotope ratio mass spectrometry (SERCON ANCA GSL 20-20 IRMS). According to convention, $^{13}C$ enrichment was expressed as $\delta\ ^{13}C$ (relative to the Pee Dee Belemnite international standard) using Equation 1 (Boström et al., 2007).

$$\delta^{13}C\ (‰) = \left( \frac{\left(\frac{^{13}C}{^{12}C}\right)_{Sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{Standard}} \right) x\ 1000$$

*Equation 1*

The cumulative percentage of the $CO_2$ respired from $^{13}C$-labelled soot or organic carbon was calculated by pool dilution using equation 2.

$$C_l = \sum_{n=n^{th}}^{t} \left[ \left( \frac{A_r - A_a}{A_s} \right) x100 \right] \qquad \textit{Equation 2}$$

Where $C_l$ = Cumulative percent $CO_2$ lost; t = sampling time point; n = $n^{th}$ sampling time point; $A_r$ = atom% of the $^{13}C$-$CO_2$ respired (see Table S2 and S4); $A_a$ = atom% of $^{13}C$-$CO_2$ (natural abundance; $A_a$ = 1.09 atom%); $A_s$ = $^{13}C$ atom% of the labelled soot or organic carbon added to the soil.

### 2.4. Statistical analyses

Linear mixed-effect models were used to analyse the differences between $\delta\ ^{13}CO_2$ fluxes in the incubation experiment with or without $^{13}C$ soot and to test for an effect of soot and biochar on $^{13}C$ organic carbon mineralisation over time. The mixed-effect model was applied using the package 'nlme' (Zuur et al., 2009) in R v.3.6.1 (R core Team, 2017), where the random effect variable was replicate, the fixed effect variables were treatments and duration of the experiment (Days) and method of estimation Maximum Likelihood (ML). The Akaike information criterion (AIC) was used to compare the performance of different models and identify the best fitting model. To improve normality, $\delta\ ^{13}CO_2$ modelled data of experiment one were log-transformed prior to statistical analyses. Data below IRMS limit of detection were treated as missing values and thus exclude from the analyses.

## 3. RESULTS

### 3.1. Effect of soot and biochar on the mineralisation of added organic carbon

The addition of soot significantly decreased the flux of $\delta\ ^{13}CO_2$ from the organic carbon added to the soil ($F = 30.152$; d.f. = 1,89; $p < 0.0001$; Fig. 3a). Although the flux of $\delta\ ^{13}CO_2$ from the

organic carbon decreased significantly over time there was a significant interaction between experimental duration (Days) and treatment. The difference between the organic carbon and organic carbon with soot increased over time ($F = 67.372$; d.f. = 2,89; $p < 0.0001$; Fig. 3a). The significant reduction in the flux $\delta\ ^{13}CO_2$ from organic carbon with soot addition resulted in a reduction in cumulative loss of carbon supplied over the duration of the experiment from 32% without soot to 14% with soot (Fig. 3b). In contrast, there was not a significant difference after the addition of biochar in the flux of $\delta\ ^{13}CO_2$ from the organic carbon added to the soil ($F = 2.402$; d.f. = 1,92; $p = 0.1246$; Fig. 3c). However, there was a significant interaction between experimental duration (Days) and treatment. The difference between the organic carbon and organic carbon with biochar slightly increased over time ($F = 23.921$; d.f. = 2,92; $p < 0.0001$; Fig. 3c).

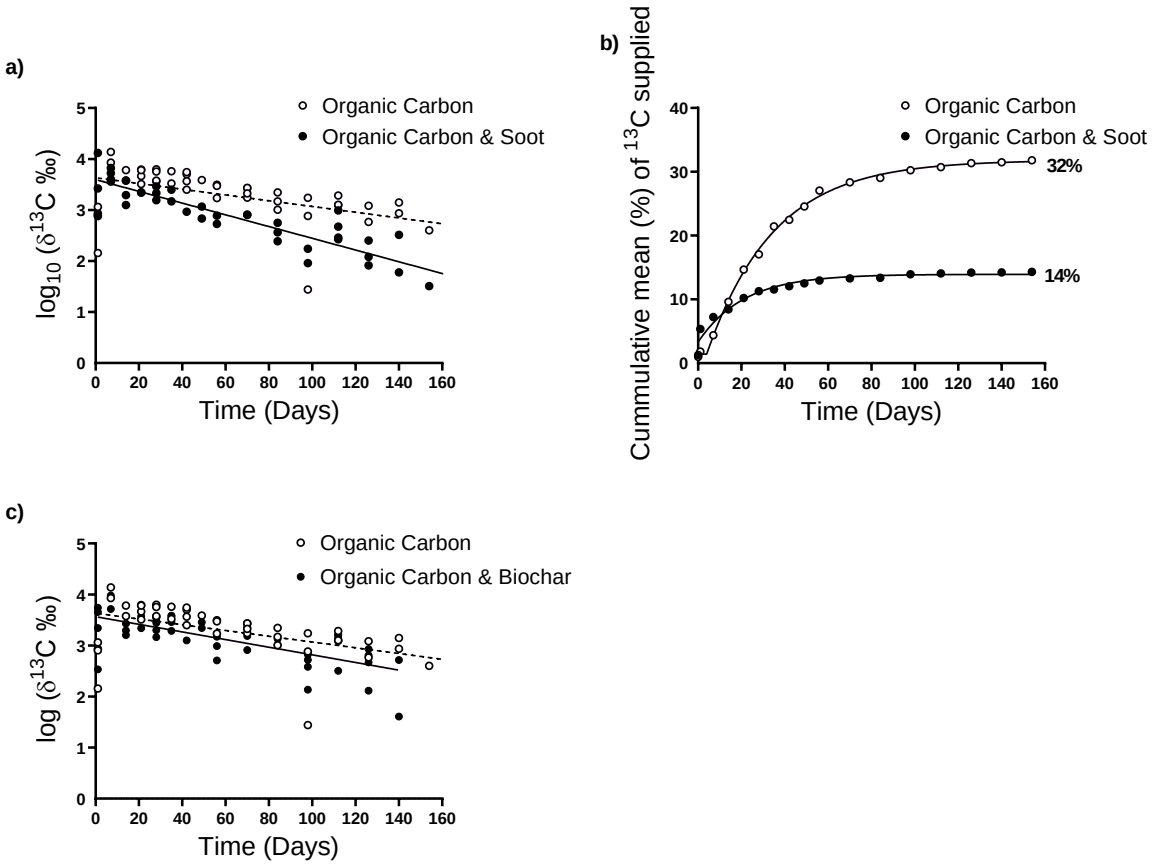


**Figure 3:** The effect of the addition of soot and biochar to soil on the evolution of $CO_2$ from $^{13}C$ labelled organic carbon over time, a) $\log_{10}$ δ $^{13}C$ evolution from soil with added $^{13}C$ labelled organic carbon and $^{13}C$ labelled organic carbon and soot, b) mean cummulative loss of $^{13}C$ supplied as sucrose; standard error bars are too small (see Supporting Information Table S2 for standar error values), c) $\log_{10}$ δ $^{13}C$ evolution from soil with added $^{13}C$ labelled organic carbon and $^{13}C$ labelled organic carbon and biochar and,. Open circles represent soil with $^{13}C$ organic carbon and closed circles represent soil with $^{13}C$ organic carbon and BC added.

### 3.2. Mineralisation of soot in soil

The addition of $^{13}C$ soot significantly increased the flux of δ $^{13}CO_2$ when compared to the control ($F = 234.7715$; d.f. = 1,98; $p < 0.0001$; Fig. 4a), however the δ $^{13}CO_2$ flux $^{13}C$ soot added decreased significantly over the duration of the experiment ($F = 5.9169$; d.f. = 2,98; $p = 0.0037$; Fig. 4a). After 24 h 0.0037 mg of the added $^{13}C$ soot had been mineralised and the cumulative total of mineralised soot increased to 0.039 mg after 168 days (Fig. 4b). The

cumulative loss of carbon added as soot over the duration of the experiment was 0.17% (Fig. 4b).

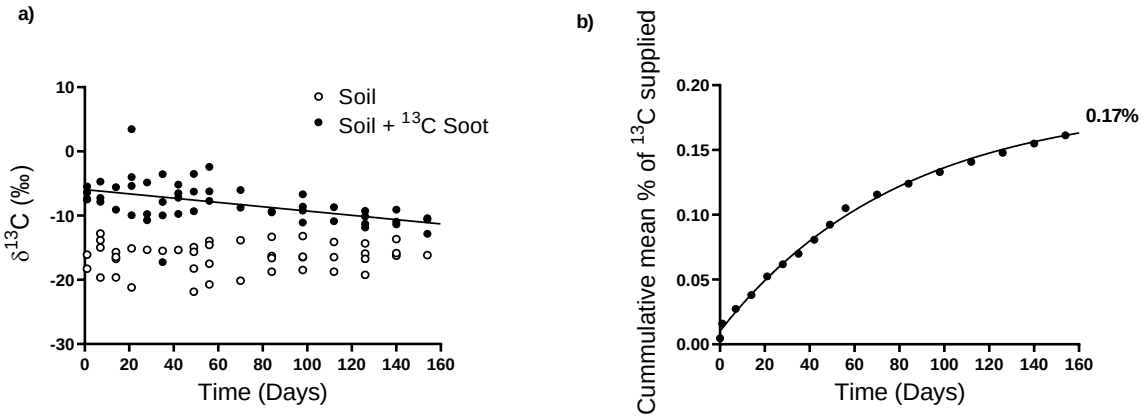


**Figure 4:** a) The δ $^{13}$C flux from soil with added $^{13}$C labelled soot (closed circles) compared to control soil (open circles), and b) mean cumulative loss of $^{13}$C soot supplied from soil for the duration of the experiment; the standard error bars are too small (see Supporting Information Table S4 for standar error values).

## 4. DISCUSSION

It is estimated that the global BC soil pool ranges between 54 and 109 Pg, this is the largest pool in the global BC cycle (Bird et al., 2015) with the soot fraction of this BC pool considered to be the most recalcitrant (Masiello, 2004; Hedges et al., 2000; Kuhlbusch & Crutzen, 1995). Here we show, for the first time, that BC in the form of soot supresses the mineralisation of labile organic carbon in soils, with 18% less $^{13}CO_2$ produced when soot is added to the soil. In addition, we show that BC in the form of soot can be, to some extent, mineralised in soils and contribute to soil $CO_2$ effluxes. Together, these findings cast doubt on the widely held assumption that BC in the form of soot plays a passive role in soil carbon dynamics. Black carbon represents an important component of the carbon cycle that is not accounted for in current models of dynamic carbon fluxes between soils and the atmosphere (Cotrufo et al., 2016). This finding is thus fundamental to our understanding of the soil carbon cycle.

While the mechanisms underpinning the suppressive effect of soot on the mineralisation of labile organic carbon need further investigation, the high surface area of soot and the high abundance of surface binding sites (surface groups) increase the reactivity and capability of soot to interact with labile organic carbon (Lehmann, 2015), thus potentially explaining this result. Indeed, it has been demonstrated that BC presents a high sorption affinity for organic carbon compounds (Kasozi et al., 2010), making them less accessible for soil microbes. In particular, adsorption and encapsulation have been suggested as potential mechanisms by which BC may suppress the mineralisation of labile organic carbon (Liu et al., 2018; Whitman et al., 2015; Lu et al., 2014; Zimmerman et al., 2011). In the first mechanism, encapsulation, the organic carbon is adsorbed within the pore of black carbon which became physically unavailable for microbes degradation. In the second mechanism, adsorption, the organic carbon is adsorbed on the large surface area of the black carbon which became less accessible to soil microbes. This result corroborates the previously observed correlation between ecosystem-derived soil organic carbon and soil BC concentration, which in the urban context of this study, was most likely soot (Edmondson et al., 2015; Hamilton & Hartnett, 2013; Liu et al., 2011). Additionally, our findings are supported by research demonstrating a supressed mineralisation of ecosystem-derived organic carbon in BC (biochar) amended soils (Wang et al., 2016; Cross & Sohi, 2011; Liang et al., 2010). In contrast, the addition of BC in the form of biochar did not affect the mineralisation of labile organic carbon. Similar results were found by other studies, where no significant effect on the soil organic carbon mineralisation was observed following biochar addition (Wang et al., 2016; Kuzyakov et al., 2009). To understand the mechanisms underpinning the differences between soot and biochar effect on labile organic carbon mineralisation, further research is needed. However, it has been suggested that the decrease in soil organic carbon mineralization due to the sorption properties of BC could be associated with its more recalcitrant fractions (Whitman et al., 2015). This is also what our findings

potentially suggest. The HyPy analyses on soot and biochar showed that soot was more stable under HyPy condition than biochar, with a larger recalcitrant fraction compared to biochar, 69% and 52%, respectively. Potentially suggesting that driving the differences between soot and biochar effect on organic carbon mineralisation might be the presence of a greater recalcitrant fraction in soot compared to biochar. However, further analysis is needed to investigate this hypothesis. Additionally, previous research has demonstrated that the suppression of soil organic carbon increases with increased biochar concentration (Liu et al., 2018). Particularly, in Liu et al. (2018) a significant decrease in soil organic carbon mineralisation was observed only after biochar application rate of about 67 t $ha^{-1}$. Thus, explaining the differences between soot and biochar effect on soil organic carbon mineralisation might also be the rate of biochar applied in this experiment (10 t $ha^{-1}$). However, further research is needed to investigate this. While we show that soot influences the dynamics of labile carbon mineralisation, we have also demonstrated that it is mineralised itself and therefore represents a hitherto overlooked component of the carbon cycle. As suggested by Bird et al. (2015), BC degradation processes in soil can be seen as continuum ranging from more labile lightly charred materials to highly recalcitrant condensed aromatic molecule, although our analyses suggest that even at the recalcitrant end of this continuum a proportion of BC is still mineralizable over short timescales. The chemical analysis of our labelled soot revealed that around 30% of the soot is potentially labile and composed of aromatic hydrocarbons, such as pyrene and phenanthrene, that are known to be readily mineralised by the soil microorganisms (Couling et al., 2010). These PAHs are still likely to represent the minor portion of the soot that was able to be mineralised over the course of the experiment (Couling et al., 2010). Our experimental results also indicated that soot mineralisation declined with time. While the mechanisms behind the decrease in soot mineralisation need further research, microbial toxicity induced by PAHs associated with soot could have played a role in

the slowdown of the soot mineralisation (Patel et al., 2020). Similarly, soot addition could have caused a change in soil pH, unfavourable for soil microbes, thus changing their biomass, composition and activity and consequently reducing soot mineralisation (Thies et al., 2015; Lehmann et al., 2011).

Our research provided the first measure of the turnover of soot in terms of carbon cycling in soils, allowing us to measure mineralisation of soot, even in very small quantities for the first time. We estimated that the amount of carbon mineralised from soot over the course of the experiment is about 0.17%. Since small changes in TOC respiration can have significant impact on atmospheric $CO_2$ concentration (Davidson & Janssens, 2006; Schlesinger & Andrews, 2000), we contextualized this result, estimating both at global and European scale the amount of $CO_2$ related to the mineralization of BC in form of soot. Global BC deposition rate are estimated to be of 17 Tg $yr^{-1}$ (Bird et al., 2015), whereas European BC emission are estimated to be 470 Gg $yr^{-1}$ (Bond et al., 2013). Considering a global land area of 149 $10^8$ ha (excluding ice areas) and a European land area of 10.18 $10^8$ ha we estimated that with mineralisation of 0.17% of BC per ½ year would lead to approximately 27576 ton of $CO_2$ $ha^{-1}$ ½ $yr^{-1}$ and 0.0028 kg of $CO_2$ $ha^{-1}$ ½ $yr^{-1}$ at global and European scale, respectively. To understand the magnitude of the contribution of the soot mineralisation to the global carbon cycle, considering that global emission from land use and land use change are estimated to be about 5.2 ± 2.6 Gt $CO_2$ $yr^{-1}$ (IPCC, 2019), we estimated that BC mineralisation in form of soot contributes to about 0.040% of these emissions.

## 5. CONCLUSION

This research has demonstrated for the first time that BC in the form of soot supresses the mineralisation of labile organic carbon in soils and that BC in the form of soot can be, to some extent, mineralised in soils contributing to soil $CO_2$ effluxes. This research has also shown that

BC in the form of biochar has no effect on the mineralisation of labile organic carbon. These findings represent a step-change in understanding the influence of soot and other compounds on the BC continuum on carbon dynamics, providing compelling evidence that BC in the form of soot plays an active role in soil carbon dynamics. This has major consequences for the way we measure, monitor and manage soils for carbon storage and sequestration in the future. A priority for future research will be understanding which carbon pools in soils are affected by BC, for example, the influence of soot on the mineralisation of labile organic carbon in soils through rhizodeposition from plants (Hütsch et al., 2002), in addition to the microorganisms responsible for the mineralisation of BC itself in soils (Whitman et al., 2016). Further research is also needed to understand the mechanisms driving the differences between soot and biochar influence on the mineralisation of labile organic carbon.

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# CHAPTER 3

## The effect of biochar application and vegetation cover on urban soil quality

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**ABSTRACT**

Urban soils underpin the provision of all the ecosystem services delivered by urban green greenspaces (UG). However, urban soils can often be degraded compromising their ability to deliver ecosystem services. Application of biochar to urban soils has been demonstrated to improve a wide range of soil properties. To support future UG planning and strategies it is crucial to identify urban soil management practices that preserve and enhance the delivery of urban soil ecosystem services and understand the effect of different forms of UG on urban soil properties. In urban areas, biochar production could be integrated with biofuel growing systems, however these may compete with other UG uses (e.g. recreation or urban horticulture (UH)). Through a two and a half year field experiment, we investigated the influence of biochar application and different UG uses (grassland, UH and bioenergy cropping system) on a range of soil quality indicators (pH, bulk density, aggregate stability, water holding capacity, organic carbon and nitrogen concentration) linked with the provision of different regulating ecosystem services. We found that hard-wood biochar applications between 20 t $ha^{-1}$ and 40 t $ha^{-1}$ to a loam to clayey loam urban soil did not significantly influence the soil physicochemical properties investigated, after two and a half years from its addition. Additionally, different UG forms did not have a significant effect on the urban soil properties assessed. The outcomes of this research demonstrated that soil biochar application of 20 t $ha^{-1}$ did not significantly enhance the ecosystem services provided by urban soils, however they suggested the need to investigate the effect of biochar on urban clayey soil at longer-time scales and at higher application rates

(>40 t $ha^{-1}$), that may be more effective in increasing urban soil physicochemical properties and consequently enhance the soil ecosystem services delivered by urban soils.

## 1. INTRODUCTION

More than half of the global population live in cities and towns and by 2070 urban areas are expected to accommodate more than 70% of the global population (UN, 2012). Urban inhabitants vitally depend on the multiplicity of ecosystem services provided by urban greenspaces (UG) (Amorim et al., 2021; European Environment Agency, 2019; Jia et al., 2019; WHO, 2017; Pitman et al., 2015). Urban greenspaces refer to a network of areas including parks, forests, roof gardens, living walls and urban gardens that have been demonstrated to support multiple ecosystem services (Amorim et al., 2021; Dobson et al., 2021; Edmondson et al., 2014; Pitman et al., 2015; Tzoulas et al., 2007). Urban soils are the foundation of UG and underpin the provision of all the ecosystem services provided by UG among others flood mitigation (Phillips et al. 2019); filtering of nutrients and pollutants (Dominati, Patterson, and Mackay 2010); carbon storage (Dobson et al., 2021; Edmondson et al., 2012; Vasenev & Kuzyakov, 2018), greenhouse gas emissions regulation (Livesley et al. 2010; Pierre et al. 2016) and organic contaminant degradation and recycling (Wang et al. 2015). However, urban soils are often impacted by different human activities that can compromise their ecosystem services provision. For instance, urban soils are often exposed to a wide range of anthropogenic activities that increase their heavy metals and metalloids (HM) concentration and negatively affect soil microbial activities and consequently influence several soil functions such as nutrient cycling, organic matter decomposition and biodiversity regulation (Mónok et al., 2020; Ivashchenko et al., 2019; Hartley et al., 2008). Within urban construction sites, compacted soils from heavy construction vehicles have been found to reduce water infiltration rates between 70% and 99% increasing the potential of water runoff and erosion (J. H. Gregory et al. 2006).

As urban populations increase, identification of the urban soil management practices that maintain and enhance the delivery of urban soil ecosystem services is crucial for future UG planning and strategies (O'Riordan et al., 2021). The application of biochar as a soil amendment in urban soils is receiving increasing attention from the scientific community (Kim et al., 2021; Somerville et al., 2020b; Yoo, Kim, and Yoo, 2020; Yue et al., 2017). Biochar is a relatively stable carbon-rich material produced from the pyrolysis of biomass (e.g. plant residues, manures and waste materials) and depending on pyrolysis conditions and feedstock properties it has been shown to increase carbon sequestration, soil fertility, crop production and microbial biomass (Haider et al., 2017; Ding et al., 2016; Lehmann et al., 2011; Sohi et al., 2010; Lehmann et al., 2006). In an urban context, biochar has been found to improve a wide range of soil properties and plant growth. For example, in urban roadside tree systems, biochar application significantly improved soil physical and biological properties and tree responses compared to an unamended system (Somerville et al., 2020b). Biochar application on urban roadside soils suggests that it can mitigate extreme soil water stresses in flooding and drying conditions, while enhancing plant growth (Yoo, Kim, and Yoo, 2020). Indeed, biochar has been found to significantly change urban soil aggregate distribution by either enhancing the proportion of macroaggregate and/or increasing soil pore size which during wet condition increased water drainage and during dry condition might have increased water retention (Yoo, Kim, and Yoo 2020). As a soil mix for small-scale urban farming, biochar was found to increase nutrient soil retention and vegetable (pak choi) nutritional value compared to unamended soil mix (Song et al., 2020). Biochar application to urban soil has been also found to reduce HM accumulation in the aboveground biomass of grass (Yue et al., 2017).

In cities and towns, biochar could be produced from the pyrolysis of biofuel crops such as short rotation coppice (SRC) willow. The use of SRC willow as biofuel crop in UG presents additional benefits. Whilst growing, SRC willow can also deliver several ecosystem services

including flood protection (O'Sullivan et al., 2017), pollution mitigation (Sugiura et al., 2008), soil carbon sequestration (Cunniff et al., 2015) and enhanced biodiversity (Rowe, Street, and Taylor 2009). Research across ten study cities in the UK has demonstrated that on average about 4% of city's administrative UG areas are potentially suitable for biofuel crop production, and, on average, these could potentially meet 2% of a city's residential heating demand (Grafius et al., 2020). In addition, biochar production could be integrated with urban bioenergy generation systems. The gases (e.g. carbon dioxide, hydrogen and methane) and biooil co-produced during the pyrolysis of biofuel crops (e.g. SRC willow) can be captured and used to supply heat and electricity in cities and towns (Trabelsi et al., 2020). At the same time, biochar can be used as a soil amendment in the biofuel growing systems (McCormack et al., 2013).

Biofuel production within UG while increasing cities' sustainability and support the delivery of multiple ecosystem services (Grafius et al., 2020), can also reduce the pressure on high-quality agricultural land to be used for biofuel production (McHugh et al., 2015). However, this may compete with other uses of UG (e.g. recreation, horticultural production, housing or business developments projects) (Lee et al., 2015; Tappert et al., 2018). For example, urban food production, which has also been demonstrated to deliver several ecosystem services and considered an important facet of urban food security (Dobson et al., 2021; Edmondson et al., 2020). Urban greenspaces are also are crucial for human physical and mental well-being, and social benefits (Jabbar et al., 2021; Dobson et al., 2020; WHO, 2017). Increased urbanisation will lead to greater competition between different uses of UG, thus to support future UG planning and strategies, it is crucial to understand the effect of different forms of UG and biochar application on urban soil properties and investigate their influence on urban soils ecosystem services delivery.

Here, through a two and a half year field experiment, we investigated the effect of biochar application and different forms of UG on urban soil physical and chemical properties.

Particularly, we assessed their influence on a range of different soil quality indicators linked with the provision of several regulating ecosystem services: soil pH (important for nutrient cycling and plant nutrition, Neina, 2019), soil total organic carbon (TOC) and nitrogen (N) concentration (important for controlling soil nutrient cycling and climate regulation; Powlson et al., 2011), bulk density (BD), (proxy for soil compaction which gives an indication of flood mitigation; Edmondson et al., 2011), soil wet aggregate stability (as an indicator of soil resistance to erosion; Erktan et al., 2015) and water holding capacity (WHC) (indicator of soil water retention and supply and linked to flood mitigation; Dominati et al., 2010). For this study, we selected three type of urban vegetation cover to simulate three different UG uses: grassland which in a typical UK city covers about 66% of the total UG (Edmondson et al. 2011); UH, which across a typical UK city covers about 2% of the total UG (Edmondson, Cunningham, et al. 2020) and SRC willow to simulate a urban biofuels production system as a potential UG use. The effect of soil biochar application on plant growth is also assessed.

## 2. MATERIAL AND METHODS

### 2.1. Study site

The manipulation experiment was established at Gorse Hill allotments in Leicester (UK) and set up from April 2018 till October 2020. The mean annual temperature is 9.9 °C and the mean annual rainfall is 620 mm (Climate-Data.org, 2021). The initial soil properties in the top 20 cm of the experimental plot were: loam to clayey loam soil texture, bulk density of 1.07 ± 0.02 g $cm^{-3}$ (± standard error), TOC concentration of 51.62 ± 2.11 mg $g^{-1}$, C:N ratio of 13.04 ± 0.24, black carbon concentration of 3.25 ± 0.31 mg $g^{-1}$ and pH of 6.69 ± 0.06.

## 2.2. Experimental design

The experimental plot was arranged in a randomized block design with four replicates for each treatment. The size of each individual plot was 1.55 m x 3.50 m and all plots were separated with a buffer unplanted strip of 2.5 m. The experimental design included the following seven treatments: control grassland (Grassland), grassland with biochar applied at the rate of 20 t $ha^{-1}$ (Grassland + Biochar 20), control SRC willow (SRC Willow), SRC willow with biochar applied at the rate of 20 t $ha^{-1}$ (SRC Willow + Biochar 20), control vegetables (cabbages) (Vegetable), vegetables with biochar applied at the rate of 20 t $ha^{-1}$ (Vegetable + Biochar 20), and vegetables with biochar applied at the rate of 40 t $ha^{-1}$ (Vegetable + Biochar 40) (Table 1). Because of space constraint biochar was applied at the rate of 40 t $ha^{-1}$ only in the vegetable plots.

Commercially available hard-wood (mainly *Acacia*) derived biochar, pyrolyzed between 400 °C and 600 °C was purchased from Carbon Gold, Bristol (UK). The biochar had a pH of 9.2, bulk density of 0.44 g $cm^{-3}$, 64.6 mg $g^{-1}$ TOC concentration, 10.2 mg $g^{-1}$ total N concentration and a C:N ratio of 63:1. More information on the chemical and physical properties of the biochar are available in Annex A, Table S1. Biochar was uniformly incorporated into the soil to 20 cm depth using a rotavator at the beginning of the experiment in April 2018.

In grassland plot, amenity grass seeds of *Lolium perenne* provided by Leicester City Council were sown in April 2018. In SRC willow plot, willow cuttings were planted following SRC plantation guidelines recommended by Defra (2004): cuttings were laid out in twin rows 0.75 m apart and spaced 0.60 m along each raw. In total, ten willow cuttings were planted per plot in April 2018. Willow cuttings of SRC *Salix* spp. hybrid "Terra Nova" (LA940140 [*S. viminalis* × *Salix triandra*]) were purchased from Crops for Energy, Bristol (UK). Seeds of cabbage tundra F1 (*Brassica oleracea* var. *capitata)* were germinated in a greenhouse under a day/night regime of 8/16 h at 15/20 °C. Cabbage seedlings (~0.20 m height) were then transplanted in

vegetable plots under protective nettings. Cabbages were sown in June and transplanted in vegetable plots in July every year.

**Table 1** Experimental design treatments

| Treatments | | |
|---|---|---|
| **Control** | **Biochar (20 t ha$^{-1}$)** | **Biochar (40 t ha$^{-1}$)** |
| Grassland | Grassland + Biochar 20 | |
| SRC Willow | SRC Willow + Biochar 20 | |
| Vegetables | Vegetables + Biochar 20 | Vegetables + Biochar 40 |

### 2.3. Soil sampling and analysis

In each plot, three soil samples were collected using Eijkelkamp soil auger to 20 cm depth and two soil samples at three depths (0-7 cm; 7-14 and 14-21 cm) were sampled using a bulk density soil corer (Eijkelkamp Ring Kit C). All plots were soil sampled at the end of the third growing season in October 2020.

#### 2.3.1. Soil pH, water holding capacity and aggregate stability analyses

Auger soil samples were air-dried, and the three replicates mixed and composited into one sample and analysed for pH, water holding capacity (WHC) and soil aggregate stability. Soil pH was measured in 0.01 M $CaCl_2$ suspension using a 1:10 soil solution ratio: 10 g of air-dried soil were extracted with 30 ml of 0.01 $CaCl_2$ solution at room temperature. After two hours of shaking, the solution was left to settle and then the pH was measured using a pH meter (Houba et al. 2000). The WHC was determined as field capacity: 10 g of air-dried soil were place in a 50 ml tube and distilled water was added to completely submerged the soil for 24 h. After 24 h, the tube was placed on a fine mesh and allowed to drain for another 24 h. The soil was removed from the tubes and weighed (wet weight), then dried at 105 °C for 48 h and weighed

again (dry weight). The WHC was determined as the weight of water held in the soil compared to the 105 °C oven-dried soils weight ([wet weight - dry weight]/dry weight) (Werner, Sanderman, and Melillo 2020). Soil aggregate stability was assessed using a wet automatic sieving following the method described by Sheng et al., 2020. Prior to analyses, air-dried soil samples were sieved to 9 mm to homogenise the large aggregate size and dried at 40 °C for 24 h. Aliquots of 100 g were then sequentially sieved through 2 mm, 0.25 mm and 0.053 mm sieves. The sieves were immersed in deionised water and vertically agitated at 50 cycles over 2 minutes. All aggregate fractions on the sieves were washed into a pre-weighted aluminium tray and oven dried at 105 °C for 24 hours. The aggregates were then weighed to determine to mass distribution among four aggregate size classes: large macroaggregate (>2 mm), small macroaggregate (0.25-2 mm), large microaggregate (0.053-0.25 mm) and small microaggregate (mineral fraction) (<0.053 mm). The mean weight diameter (MWD) which is used as an index to evaluate soil aggregate stability was calculated as follow (Song et al., 2019):

$$MWD(\text{mm}) = \frac{\sum_{i=1}^{n}(X_i W_i)}{\sum_{i=1}^{n}(W_i)}$$

where $n$ is the number of aggregate size classes ($n$ = 4), $X_i$ is the mean diameter of each aggregate size class and $W_i$ is the weight percentage of each aggregate size class respect to the total sample weight.

### 2.3.2. Soil bulk density, total organic carbon and nitrogen concentration

Soil core samples were analysed for soil BD and TOC and N concentration. Soil samples were dried at 105 °C for 24 h and sieved to 1 mm (Edmondson et al., 2014). Any material greater than 1 mm was then weight and removed from soil total weight. The volume of this material (> 1 mm) was then volumetrically measured and removed from the total volume to calculate soil BD (g $cm^{-3}$). Soil TOC and N were analysed in a CN elemental analyser (Vario EL Cube;

Isoprime, Germany): prior to analyses, the soil samples were homogenised in agate ball-mill and sieved to 1 mm and inorganic carbon was removed by addition of 5.7 M HCl (Edmondson et al., 2014).

### 2.4. Plant sampling and analysis

All plant samples were collected at the end of the third growing season in October 2020. In each vegetable plot, five cabbage heads were sampled, and the total head weight recorded. Cabbage heads were then clean with ultra-pure water to remove any soil particles and a subsample of about 100 g was frozen at -20 °C and consequently freeze-dried. The cabbage samples were then powdered and homogenised using a grinder mill. In grassland plot, grass samples were collected from a 30 x 30 cm quadrat. The biomass in each quadrat was then used to calculate the total grass biomass in each plot. Grass samples were weighed, oven dried at 70 °C till constant weight and homogenised using a grinder mill. In each SRC willow plot, five willow trees were cut at the base using a chainsaw and each tree was shredded into chips using a woodchipper. The wood chips were then collected in a bag, weighed and a subsample of about 100 g was taken for analyses. These subsamples were oven dried at 70 °C till constant weight and homogenised using a grinder mill. Two subsamples per each plant sample were analysed for TOC and N concentration in a CN elemental analyser (Vario EL Cube; Isoprime, Germany).

### 2.5. Statistical analyses

The effect of biochar and vegetation cover (UG use) on soil pH, WHC and aggregate stability were tested by two-way ANOVA, while the effect of biochar and vegetation cover on soil BD and TOC and N concentrations across different soil depths were tested by three-way ANOVA. The Tukey HSD post-hoc test was used to compare the significant differences (F-test; $p < 0.05$)

in soil physiochemical properties between vegetation cover or biochar. One-way ANOVA followed by the Tukey HSD post-hoc ($p < 0.05$) and unpaired t-test was performed to assess the effect of biochar on TOC and N concentration in plant samples and total plant biomass. All statistical analysis were conducted in GraphPad Prism version 9.0.0 and R version 4.0.0.

## 3. RESULTS

### 3.1. Effect of biochar and vegetation cover on soil pH

Biochar addition and vegetation cover did not have a significant effect on soil pH, after three growing seasons (Figure 1; $F(1, 18) = 0.07$; $p = 0.79$ and $F(2,18) = 0.31$; $p = 0.74$). Mean soil pH ranged from $6.43 \pm 0.01$ (± SE) to $6.39 \pm 0.05$ and $6.47 \pm 0.01$ under grassland, SRC willow and vegetable plot, respectively (Figure 1). There was not a significant difference in soil pH in vegetables plots after addition of 20 and 40 t $ha^{-1}$ of biochar compared to control (Figure 2; $F(5, 16) = 0.83$; $p = 0.54$).

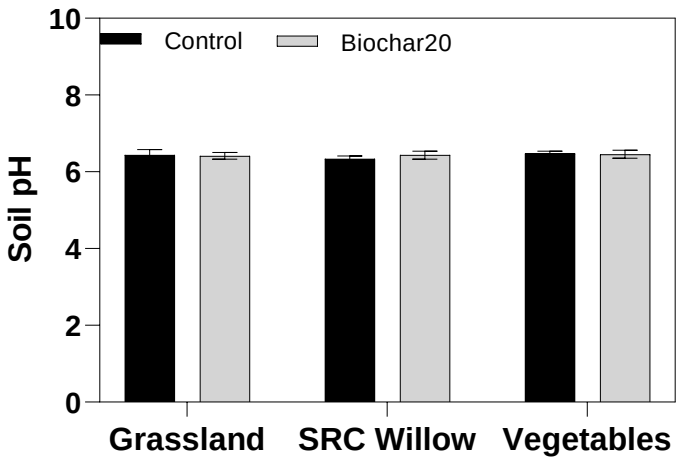


**Figure 1** Effect of biochar application at 20 t $ha^{-1}$ (Biochar 20) and vegetation cover on soil pH after three growing seasons. Bars are means from four replicates ± standard errors of means.

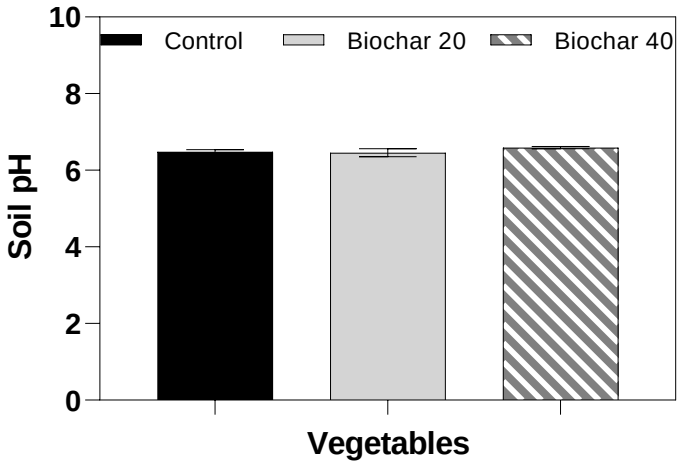


**Figure 2** Effect of biochar application at 20 t $ha^{-1}$ (Biochar 20) and 40 t $ha^{-1}$ (Biochar 40) on soil pH in vegetables plots after three growing seasons. Bars are means from four replicates ± standard errors of means.

### 3.2. Effect of biochar and vegetation cover on soil TOC and N concentrations and C:N ratio

Biochar application did not have a significant effect on soil TOC and N concentration at the three soil depths investigated (Figure 3 a-f; Table S2). Additionally, no significant difference in soil TOC and N concentration was detected across the different vegetation covers at the three soil depths investigated (Figure 3 a-f; Table S2). There was not a significant difference in soil TOC and N concentration in vegetables plots after addition of 20 and 40 t $ha^{-1}$ of biochar compared to control (Figure 4; $p > 0.05$).

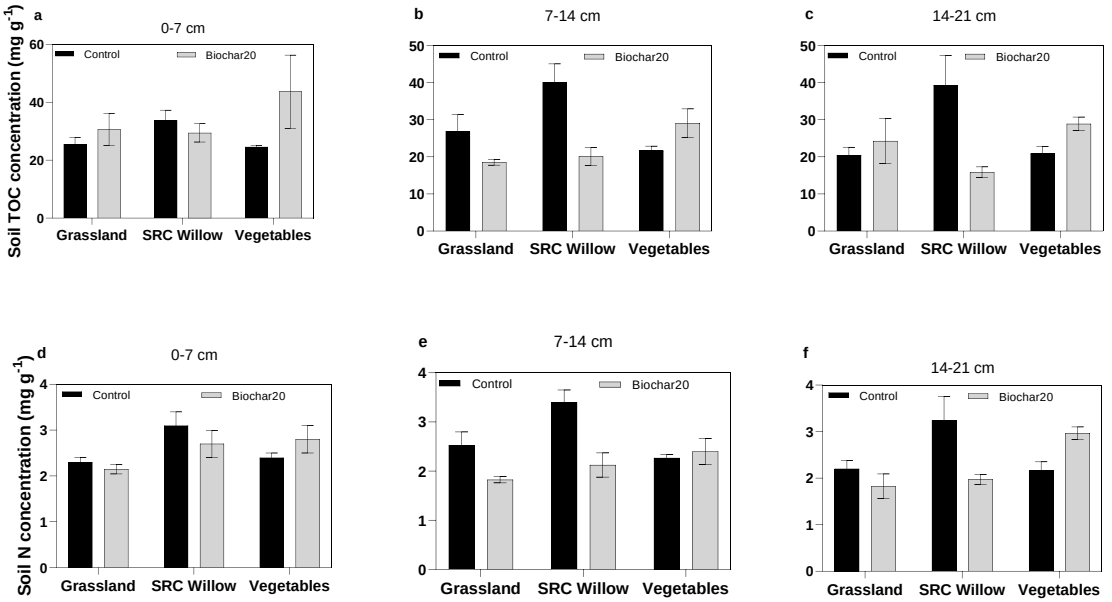


**Figure 3** Effect of biochar application at 20 t ha$^{-1}$ (Biochar 20) and 40 t ha$^{-1}$ (Biochar 40) and vegetation cover on soil total organic carbon (TOC) (a-c) and nitrogen (N) (d-f) concentration (mg g$^{-1}$) at three soil depths (0-7; 7-14; 14-21 cm) after three growing seasons. Bars represent means from four replicates ± standard errors of means.

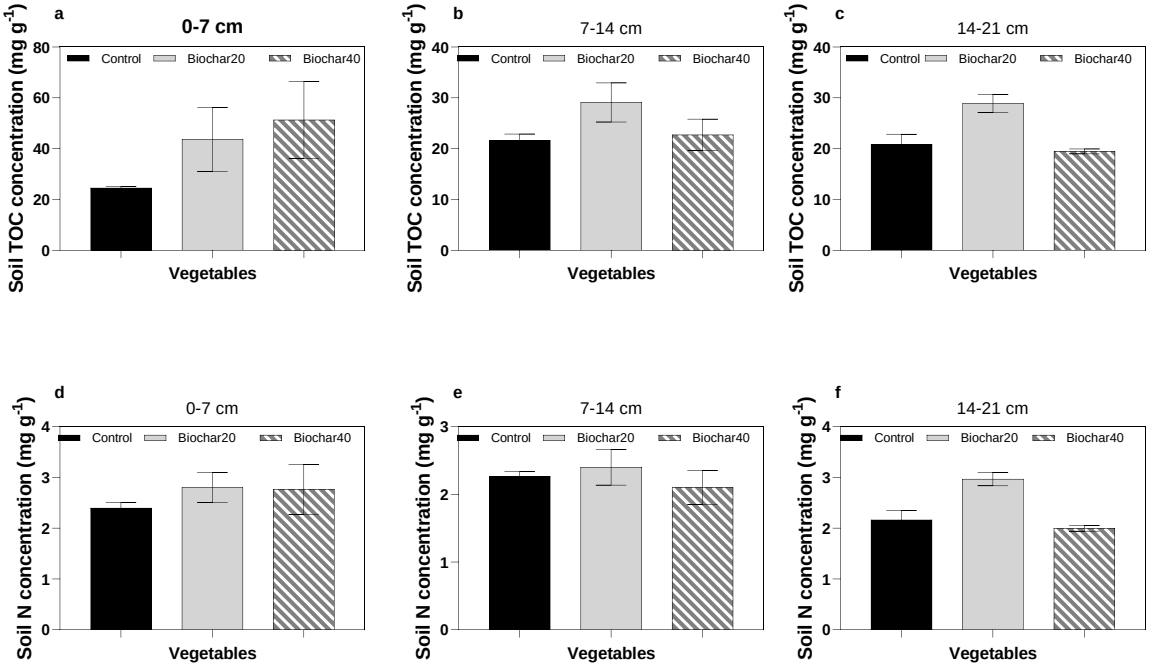


**Figure 4** Effect of biochar application at 20 t ha$^{-1}$ (Biochar 20) and 40 t ha$^{-1}$ (Biochar 40) on soil total organic carbon (TOC) (a-c) and nitrogen (N) (d-f) concentration (mg g$^{-1}$) at three soil depths (0-7; 7-14; 14-21 cm) in vegetables plot after three growing seasons. Bars represent means from four replicates ± standard errors of means.

**Table 2** Descriptive statistics of soil total organic carbon and nitrogen concentration under different treatments: mean and standard error (SE).

| | | Control | | Biochar 20 | | Biochar 40 | |
|---|---|---|---|---|---|---|---|
| | | **Mean** | **SE** | **Mean** | **SE** | **Mean** | **SE** |
| **TOC (mg $g^{-1}$) at 0-7 cm** | Grassland | 25.45 | 2.38 | 30.60 | 5.58 | | |
| | SRC willow | 33.68 | 3.61 | 24.42 | 3.13 | | |
| | Vegetables | 24.57 | 0.61 | 43.68 | 12.62 | 51.33 | 15.15 |
| **TOC (mg $g^{-1}$) at 7-14 cm** | Grassland | 26.85 | 4.52 | 18.52 | 0.74 | | |
| | SRC willow | 40.03 | 5.05 | 20.10 | 2.37 | | |
| | Vegetables | 21.63 | 1.25 | 29.10 | 3.84 | 22.73 | 3.09 |
| **TOC (mg $g^{-1}$) at 14-21 cm** | Grassland | 20.48 | 2.14 | 24.27 | 6.08 | | |
| | SRC willow | 39.30 | 8.07 | 15.85 | 1.45 | | |
| | Vegetables | 20.87 | 1.99 | 28.9 | 1.83 | 19.46 | 0.49 |
| **N (mg $g^{-1}$) at 0-7 cm** | Grassland | 2.30 | 0.11 | 2.15 | 0.10 | | |
| | SRC willow | 3.10 | 0.29 | 2.70 | 0.29 | | |
| | Vegetables | 2.40 | 0.10 | 2.80 | 0.30 | 2.77 | 0.49 |
| **N (mg $g^{-1}$) at 7-14 cm** | Grassland | 2.53 | 0.27 | 1.83 | 0.06 | | |
| | SRC willow | 3.40 | 0.25 | 2.13 | 0.25 | | |
| | Vegetables | 2.26 | 0.07 | 2.40 | 0.26 | 2.10 | 0.25 |
| **N (mg $g^{-1}$) at 14-21 cm** | Grassland | 2.2 | 0.18 | 1.82 | 0.27 | | |
| | SRC willow | 3.25 | 0.51 | 1.98 | 0.11 | | |
| | Vegetables | 2.16 | 0.19 | 2.97 | 0.13 | 2.00 | 0.06 |

### 3.3. Effect of biochar and vegetation cover on soil BD

Biochar application and vegetation cover did not have a significant effect on soil BD at the three soil depths investigated (Figure 5 a-c; Table S3). There was not a significant difference in soil TOC and N concentration in vegetables plots after addition of 20 and 40 t $ha^{-1}$ of biochar compared to control (Figure 6; $p > 0.05$).

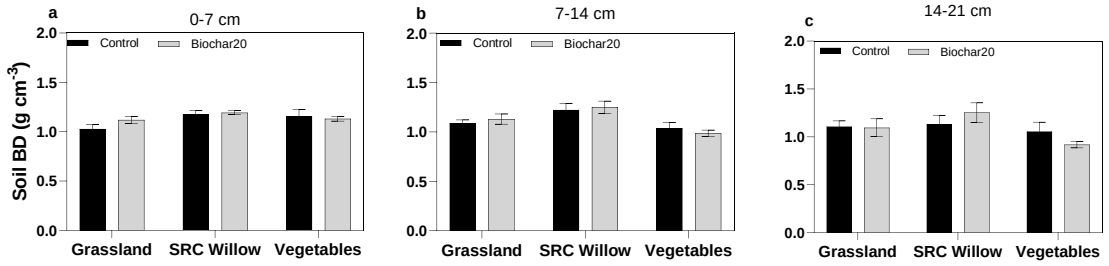


**Figure 5** Effect of biochar application at 20 t ha$^{-1}$ (Biochar 20) and vegetation cover on soil bulk density (BD) (g cm$^{-3}$) at three soil depths (0-7, 7-14, 14-21 cm). Bars represents means of four replicates ± standard errors of means.

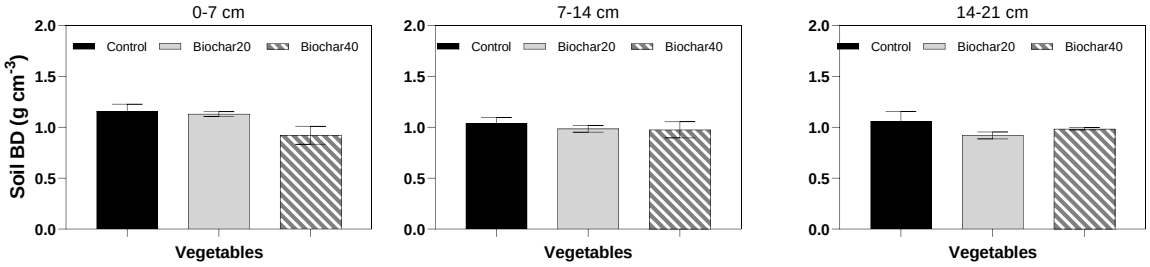


**Figure 6** Effect of biochar application at 20 t ha$^{-1}$ (Biochar 20) and 40 t ha$^{-1}$ (Biochar 40) on bulk density (BD) (g cm$^{-3}$) at three soil depths (0-7; 7-14; 14-21 cm) in vegetables plot after three growing seasons. Bars represent means from four replicates ± standard errors of means.

**Table 3** Descriptive statistics (mean and standard error (SE)) of soil bulk density (g cm$^{-3}$) at three soil depths (0-7, 7-14, 14-21 cm) under different treatments.

| | | **Control** | | **Biochar 20** | | **Biochar 40** | |
|---|---|---|---|---|---|---|---|
| | | **Mean** | **SE** | **Mean** | **SE** | **Mean** | **SE** |
| **0-7 cm** | Grassland | 1.03 | 0.04 | 1.11 | 0.03 | | |
| | SRC willow | 1.17 | 0.03 | 1.19 | 0.01 | | |
| | Vegetables | 1.15 | 0.06 | 1.13 | 0.02 | 0.92 | 0.08 |
| **7-14 cm** | Grassland | 1.09 | 0.03 | 1.13 | 0.05 | | |
| | SRC willow | 1.22 | 0.07 | 1.25 | 0.06 | | |
| | Vegetables | 1.04 | 0.06 | 0.99 | 0.03 | 0.98 | 0.08 |
| **14-21 cm** | Grassland | 1.11 | 0.06 | 1.09 | 0.09 | | |
| | SRC willow | 1.32 | 0.09 | 1.25 | 0.10 | | |
| | Vegetables | 1.06 | 0.09 | 0.92 | 0.35 | 0.99 | 0.01 |

### 3.4. Effect of biochar and vegetation cover on soil aggregate distribution and stability

The proportion of different aggregate fractions under different urban vegetation cover showed similar distribution patterns with small macroaggregate (0.25-2.0 mm) representing the largest percentage of the total soil aggregate follow by the large macroaggregate (> 2.0 mm), microaggregate (0.053-0.25 mm) and the mineral fraction (<0.053 mm) (Figure 7 a-d).

The effect of biochar and vegetation cover on soil aggregate stability was investigated by calculating the MWD: the higher the MWD the stronger the soil aggregation and thus soil aggregate stability. Grassland plot had the largest MWD of 2.52 ± 0.012 mm, SRC willow plot had the lowest MWD of 1.84 ± 0.199 and vegetables plot MWD was of 2.36 ± 0.153 mm (Figure 8). However, no significant difference in the soil aggregate stability after biochar application and under the different vegetation covers was observed (Figure 8; $F(2,20) = 4.73$, $p = 0.33$; $F(2,20) = 1.61$, $p = 0.05$). There was not a significant difference in soil aggregate stability in vegetables plots after addition of 20 and 40 t $ha^{-1}$ of biochar compared to control (Figure 9; $p > 0.05$).

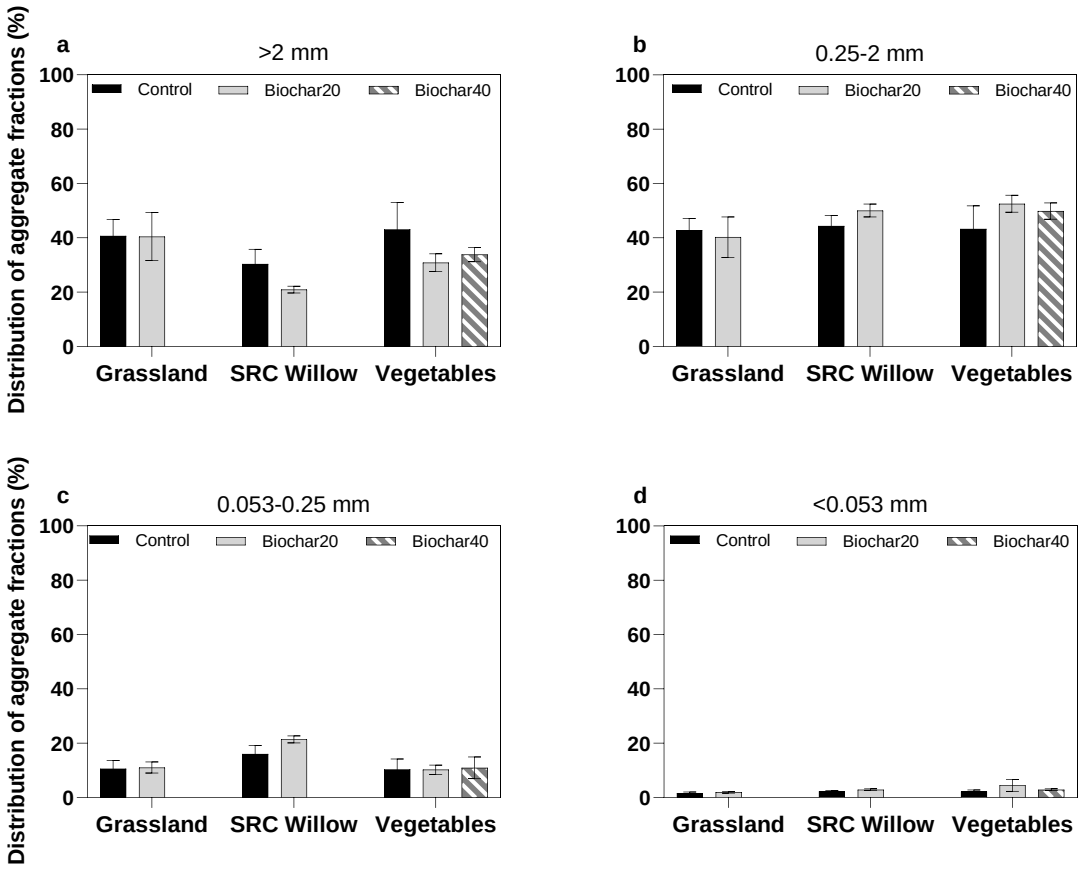


**Figure 7** Distribution of soil aggregate fractions (%) across treatments. Bars are means from four replicates ± standard errors of means.

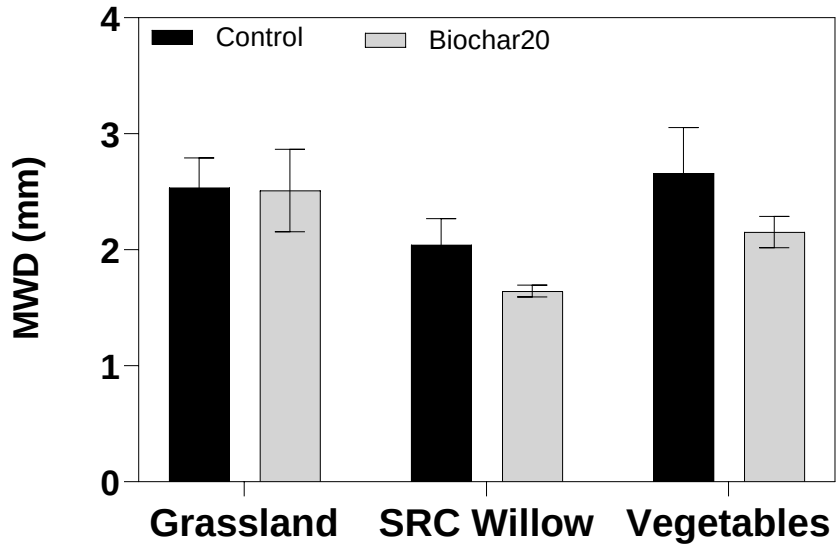


**Figure 8** Effect of biochar application at 20 t $ha^{-1}$ (Biochar 20) and UG on soil aggregate stability. MWD is the mean weight diameter (mm). Bars are means from four replicates ± standard errors of means.

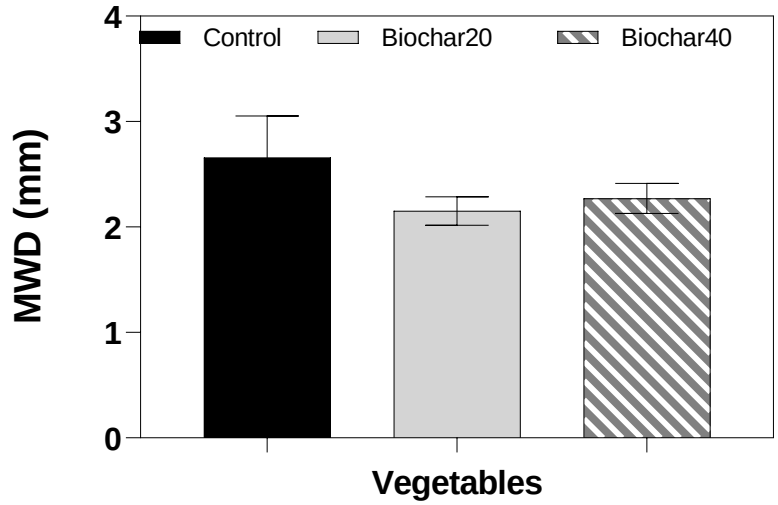


**Figure 9** Effect of biochar application at 20 t $ha^{-1}$ (Biochar 20) and 40 t $ha^{-1}$ (Biochar 40) on soil aggregate stability in vegetables plots. MWD is the mean weight diameter (mm). Bars are means from four replicates ± standard errors of means.

### 3.5. Effect of biochar and vegetation cover on soil WHC

There was an increasing trend in WHC following biochar addition across all vegetation covers, however, this was not statistically significant (Figure 10; $F(2,20) = 4.93$, $p > 0.05$). Additionally, there was not a significant effect of vegetation cover in soil WHC (Figure 10; F

(2,20) = 1.97, p = 0.17). The median water holding capacities were of 85.15% ± 1.68 in grassland, 82.31% ± 2.03 in SRC willow and 82.57% ± 3.78 in vegetable plots (Table 4).

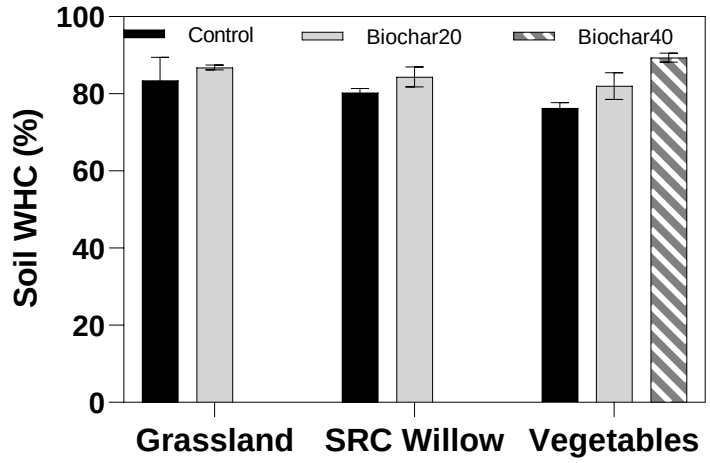


**Figure 10** Effect of biochar application at 20 t ha$^{-1}$ (Biochar 20) and 40 t ha$^{-1}$ (Biochar40) and vegetation cover on soil water holding capacity (WHC) (%). Bars are means from four replicates ± standard errors of means.

**Table 4** Descriptive statistics of soil water holding capacity (%) under different treatments: mean and standard error (SE).

| | **Control** | | **Biochar 20** | | **Biochar 40** | |
|---|---|---|---|---|---|---|
| | **Mean** | **SE** | **Mean** | **SE** | **Mean** | **SE** |
| **Grassland** | 83.46 | 5.97 | 86.83 | 0.66 | | |
| **SRC willow** | 80.28 | 1.11 | 84.34 | 2.58 | | |
| **Vegetables** | 76.31 | 1.43 | 82.02 | 3.45 | 89.37 | 1.17 |

### 3.6. Biochar effect on plant biomass

The total biomass of grass and SRC willow with biochar application of 20 t ha$^{-1}$ was slightly lower compared to control, however it was not statistically significant (Figure 11 a-b; t (6) = 1.04, p = 0.35; t (38) = 1.57, p = 0.12). Whereas mean cabbage head biomass was significantly higher in vegetable plots with 20 t ha$^{-1}$ biochar compared to control and vegetable plots at 40 t ha$^{-1}$ biochar (Figure 11 c; F (2,22) = 4.79, p = 0.02, Tukey's HSD p-value = 0.04 and 0.04).

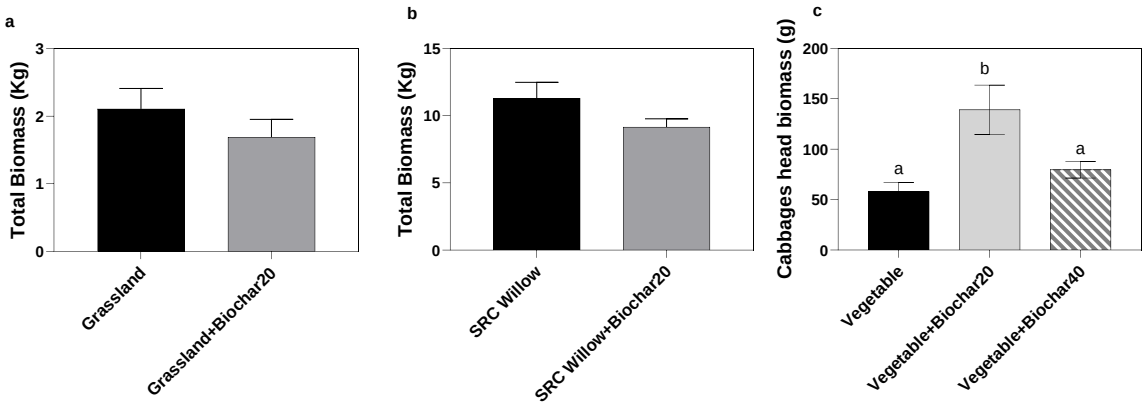


**Figure 11** Effect of biochar application at 20 t $ha^{-1}$ (Biochar 20) and 40 t $ha^{-1}$ (Biochar40) on plant biomass. a) Mean total grass biomass (kg), b) mean SRC willow biomass (kg) and c) mean biomass of five cabbage heads. Bars are means from four replicates ± standard errors of means. Different letters indicate significant differences in biomass.

### 3.7. Biochar effect on plant TOC and N concentrations

There was no significant effect of biochar addition in plant TOC and N concentrations (Figure 12 a-b; Table S4 and Table S5). Mean TOC concentrations were of 429.11 ± 25.30 mg $g^{-1}$ in grass samples, 553.03 ± 10.09 mg $g^{-1}$ in SRC willow samples and 392.75 ± 4.16 mg $g^{-1}$ in vegetable samples. Mean N concentrations varied from 13.70 ± 1.05 mg $g^{-1}$ to 24.64 ± 0.61 mg $g^{-1}$ and 39.93 ± 0.53 mg $g^{-1}$ in grass, SRC willow and vegetable samples, respectively.

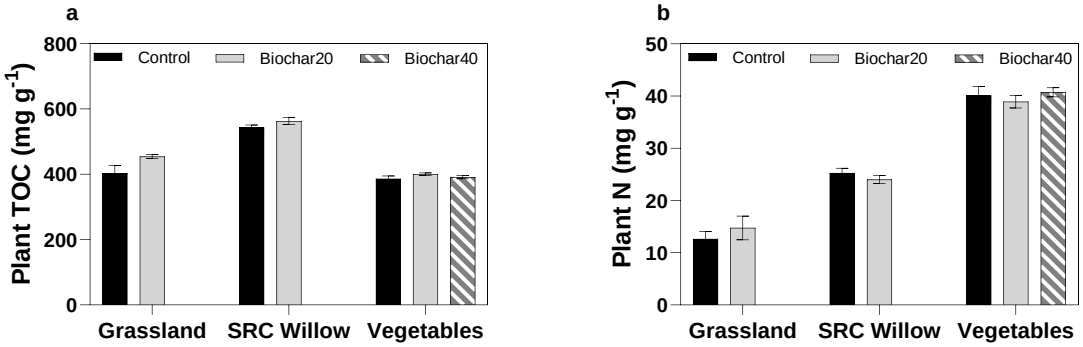


**Figure 12** Effect of biochar application at 20 t $ha^{-1}$ (Biochar 20) and 40 t $ha^{-1}$ (Biochar 40) on plant total organic carbon (TOC) and nitrogen (N) concentration (mg $g^{-1}$). Bars are means from eight replicates ± standard errors of means.

## 4. DISCUSSION

Several studies have shown a significant positive effect of biochar application on soil physicochemical properties depending on soil type, biochar characteristic and application rate (Purakayastha et al., 2019; Agegnehu et al., 2017; Sun & Lu, 2014). In this study, we demonstrated that hard-wood biochar applications between 20 t $ha^{-1}$ and 40 t $ha^{-1}$ to a loam to clayey loam urban soil under different vegetation covers did not significantly influence the soil physicochemical properties investigated, after two and a half years from its addition. At the same time, different vegetation covers did not have a significant effect on the urban soil properties assessed.

An increase in soil pH following biochar addition is often reported in both short and long term studies (Ghosh et al., 2015; Jeffery, 2011). Here, we did not observe a change in soil pH after biochar application (Figure 1-2). This is in line with a previous study where biochar application to urban clay soil did not significantly affect soil pH at similar application rates (25 t $ha^{-1}$) (Scharenbroch et al.,, 2013). This is probably because of the buffering capacities of clayey loam soil (Scharenbroch et al., 2013). Soil pH play a major role in several soil processes such as nutrient bioavailability, HM bioavailability and microbial activity. Soil pH values around 6-7 are usually recommended for optimal plant growth and nutrient availability (Royal Horticultural Society, 2021). The fact that biochar application did not change soil pH and instead a neutral soil pH was maintained across all urban vegetation covers after three growing seasons from its application, could suggest that long-term biochar application may not negatively impact soil processes and thus plant growth.

Although the change in soil bulk density is often larger in course-textured soils than in fine-textured soils (Blanco-Canqui, 2017), research has reported a decrease in soil bulk density of 9.2% following biochar addition of 20 t $ha^{-1}$ in fine-texture soils after two years from

application (Xiao et al., 2016). In this research, soil BD was not significantly influenced by biochar addition. Soil BD is a direct measure of soil compaction, with higher soil BD negatively impacting plant growth and flood mitigation (Edmondson et al., 2011). The outcomes of this research suggest that biochar application rates of 20 t $ha^{-1}$ are not effective in significantly decreasing fine-texture soil BD and thus enhancing the ecosystem services derived from it. However, our results also indicate that higher biochar application rates (40 t $ha^{-1}$) might be more efficient in decreasing the BD of the fine-texture soil investigated. Indeed, soil BD has been found to linearly decrease with the amount of biochar applied to soil (Obia et al., 2018; Głąb et al., 2016).

Biochar macropores have been found to positively correlate with biochar WHC and once applied to soil it can consequently increase soil WHC (Werdin et al., 2020; Karhu et al., 2010). In this study, biochar application did not significantly increase soil WHC, however there was a consistently higher trend in those plots where biochar was applied compared to control (Figure 11). As with soil BD, higher biochar application rate may result in more significant change in soil WHC over time. Further research is needed to investigate this, especially in this soil type.

Soil aggregate stability is an important indicator of soil structural stability, and it influences many soil processes like macropore development, water infiltration and water erosion (Blanco-Canqui, 2017). Soil biochar application has been reported to increase wet aggregate stability across several textural classes (Blanco-Canqui, 2017) by increasing the amount of macroaggregates (Lu, Sun and Zong, 2014) and short-term incubation studies have found a significant increase in clayey soil wet aggregate stability, with a larger increase after addition of approximately 80 t $ha^{-1}$ (Lu Sun, and Zong, 2014; Sun and Lu, 2014). However, other studies

have indicated that biochar influence on soil aggregate stability is larger in sandy soils than in clayey soils (Burrell et al., 2016; Ouyang et al., 2013). At the same time, short-term incubation studies have found a significant increase in clayey soil wet aggregate stability, with a larger increase after addition of about 80 t $ha^{-1}$ (Lu, Sun and Zong, 2014; Sun and Lu, 2014). In this research, soil aggregate stability was not significantly affected by biochar application (Figure 8-9), however a small, but not significant, trend for an increase in the distribution of small macroaggregate (0.25-2 mm) under SRC willow and vegetables plots was observed after biochar addition (Figure 7 b). This increase in small macroaggregates may have been promoted by biochar addition which may have provided the organic binding agents needed for the formation of soil aggregates (Blanco-Canqui, 2017). As for soil BD and WHC, research has demonstrated that soil aggregate stability improves with the increase of biochar amount (Blanco-Canqui, 2017), thus further research is needed to investigate the effect of biochar on soil aggregate stability in urban soils at higher application rates and over longer timescales.

A recent meta-analysis found that soil biochar application can increase crop yield by up to 78%, decrease the yield by up to 16% or have no effect (Purakayastha et al., 2019). In this research, we have found that biochar did not have a significant influence on plant biomass (Figure 8). Whilst further research is needed to investigate the mechanisms underlying this, several reasons may explain this result. Firstly, biochar applications did not significantly affect soil and plant carbon and nitrogen concentrations, indeed no difference between biochar amended and control plots was observed (Figure 3 and Figure 13). Although biochar is enriched with carbon and contains a range of macro and micronutrients, their availability for plant uptake can be variable (Liu et al., 2012). Particularly, in biochar amended soils it has been reported a decrease in nutrient availability with the increase of pyrolysis temperature (Uchimiya et al., 2012). In our study, hard-wood derived biochar generated between 400 °C and 600 °C with a C: N ratio of 63:1 was applied to the soil. Whilst the high temperature of formation increased

biochar total carbon concentration and that of other nutrients, at the same time it may also have decreased their availability with nutrients present mainly in non-labile forms (e.g. lock in heterocyclic aromatic structures), thus less accessible for plant uptake and microbial degradation (Purakayastha et al., 2019; Spokas et al., 2012), potentially explaining the lack of a beneficial effect of biochar application in plant nutrient content and plant growth. Secondly, biochar addition did not increase the overall urban soil quality which may explain why no change in plant growth was observed.

In addition to biochar application rate, climatic conditions and experimental duration may also potentially explain the overall limited effect of biochar observed on soil properties as well as on plant biomass. Although there are limited studies looking at the effect of biochar under different climatic conditions, a recent meta-analysis found that soil biochar application promotes a larger positive crops response in tropical and subtropical climate than in continental and temperate climate (Ye et al., 2020). This difference in crop response may be partly explained by the difference in microbial activity at different temperatures. In general, soil microbial activity increases with temperature (Zaidi and Imam, 2008). Biochar has been shown to stimulate soil microbial activity and promote shift in microbial community and diversity (Jones et al., 2012; Dai et al., 2021), at higher temperature, as in tropical and subtropical climates, this effect may be accentuated resulting in a more accelerated biochar degradation. An increase in biochar degradation could result in an increase in plant available nutrients and a higher crop response.

In this experiment, biochar particles were still clearly visible in soil, almost intact, at the end of the third growing season, suggesting that biochar underwent only a minimal microbial degradation, thus potentially also explaining the limited soil and plant effects observed. Factors

that may have contributed to the minimal degradation of biochar could be the mean annual temperature experienced by our site (9.9 °C) or the short duration of the experiment. Further experiments at longer-time scales are needed to investigate biochar influence on soil properties as well as investigating the factor contributing to its minimal degradation.

Whilst biofuels growing in cities can increase the sustainability and resilience of urban systems by supporting the delivery of several ecosystem services and reducing greenhouse gases emission linked with energy production systems, the use of biochar as a soil amendment in biofuel growing systems needs careful consideration. This research has shown that soil application of biochar to SRC willow neither improves urban soil ecosystem services nor increases SRC willow biomass production. In addition, it has been demonstrated that SRC willow bioenergy system generating electricity and heat are more energy efficient when the biofuel crop is directly combusted compared to when is pyrolyzed and biochar is applied to soils (Ericsson et al.,

2017). Both these findings suggest that the integration of biochar into urban SRC willow bioenergy system may not represent a win-win scenario, however further research is needed to understand impact of biochar application on biofuels growing systems on a wider range of ecosystem services.

## 5. CONCLUSION

In conclusion, this research has demonstrated that soil biochar application of 20 t $ha^{-1}$ did not significantly enhance the ecosystem services provided by urban soils and vegetation cover did not influence urban soil quality over the experimental period. However, the outcomes of this research suggest the need to investigate the effect of biochar on urban clayey soil at longer time-scale and higher application rates (>40 t $ha^{-1}$), that may be more effective in increasing

urban soil physicochemical properties and consequently enhance the soil ecosystem services delivered by urban soils.

To support future UG planning strategies, further research is needed to investigate soil biochar application and different UG uses on urban soil quality. Further studies should include investigating the effect of different types of biochar on a wider range on urban soil properties and processes associated with the provision of different soil ecosystem services such as its impact on soil water dynamics, biological activity, and nutrients availability.

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# CHAPTER 4

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

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### 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, 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 systems (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) (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) (Figure 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.


**Figure 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).

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) (Figure 2).

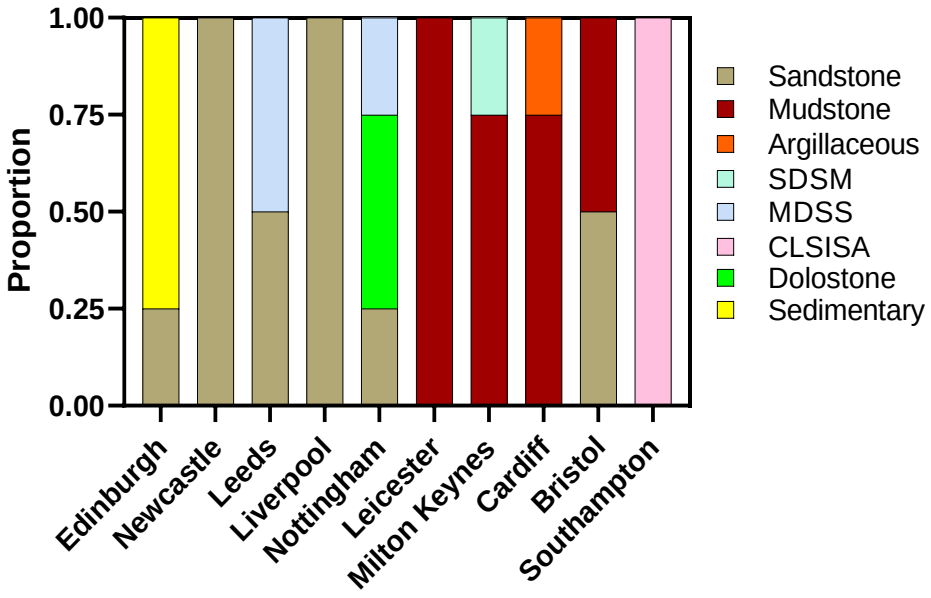


**Figure 2** The bedrock geology of allotments in the ten case study cities.

### 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 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 - $BC_{hypy}$.

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

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 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 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 95$^{th}$ 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.

**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

### 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 (Figure 2); city (the ten cities investigated, Figure 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 2020).

## 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 ($p < 0.0001$; Figure 3 a-c). Milton Keynes had the lowest OC and BC concentrations, whereas Newcastle had the highest OC and BC concentrations (Figure 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, Figure 3d). The 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%) (Figure 3d).

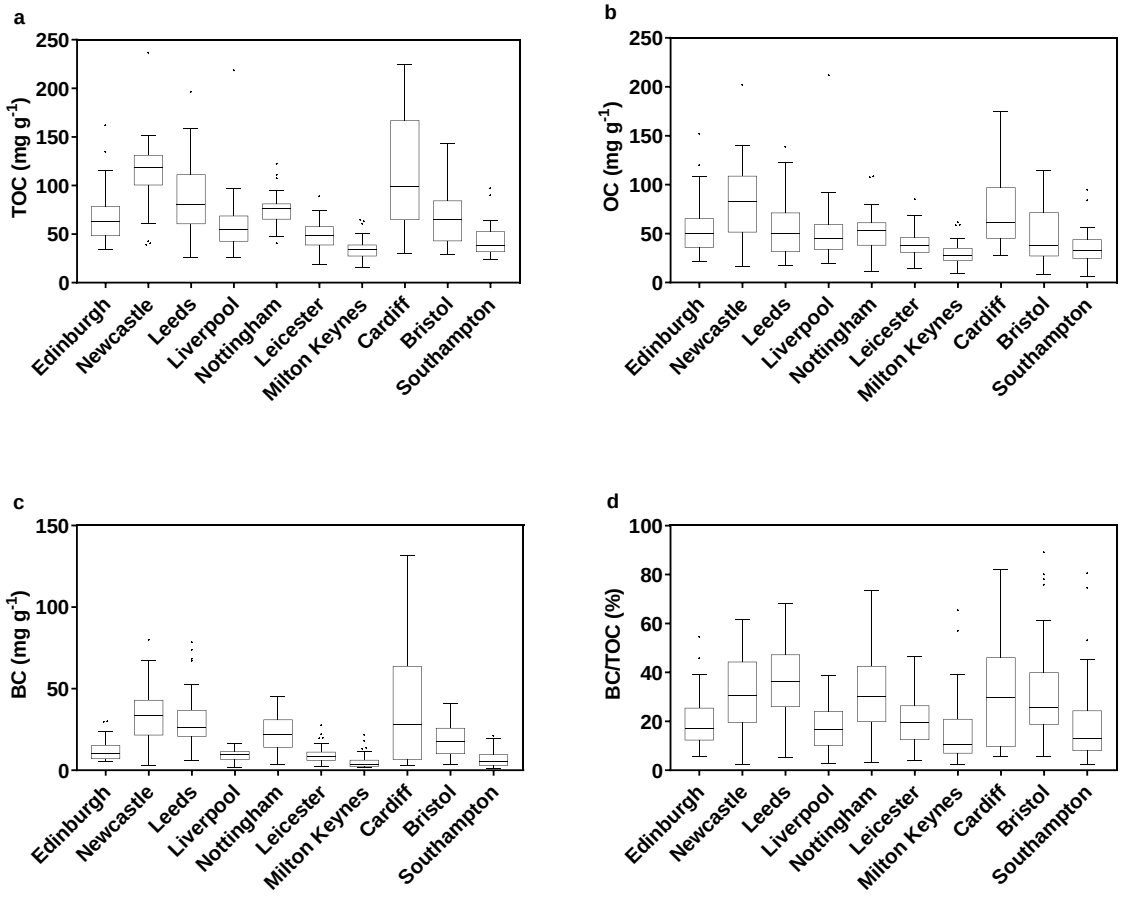


**Figure 3** Soil TOC, OC and BC concentrations in mg $g^{-1}$ (a, b and c) and soil BC contribution to TOC in % (d) across ten urban areas in the UK (n=357). Boxes represent 25$^{th}$, 50$^{th}$ and 75$^{th}$ percentiles; black dots represent outliers.

### 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, Figure 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.

**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 |

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 (Figure 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 (Figure 4 d-f). Of these total concentrations exceeding Cu and Pb soil screening values, 4% (representing 16 allotment plots) and 3.5% (representing 14 allotment plots) were also above the NBCs of Cu and Pb respectively (Figure 4 d-e).

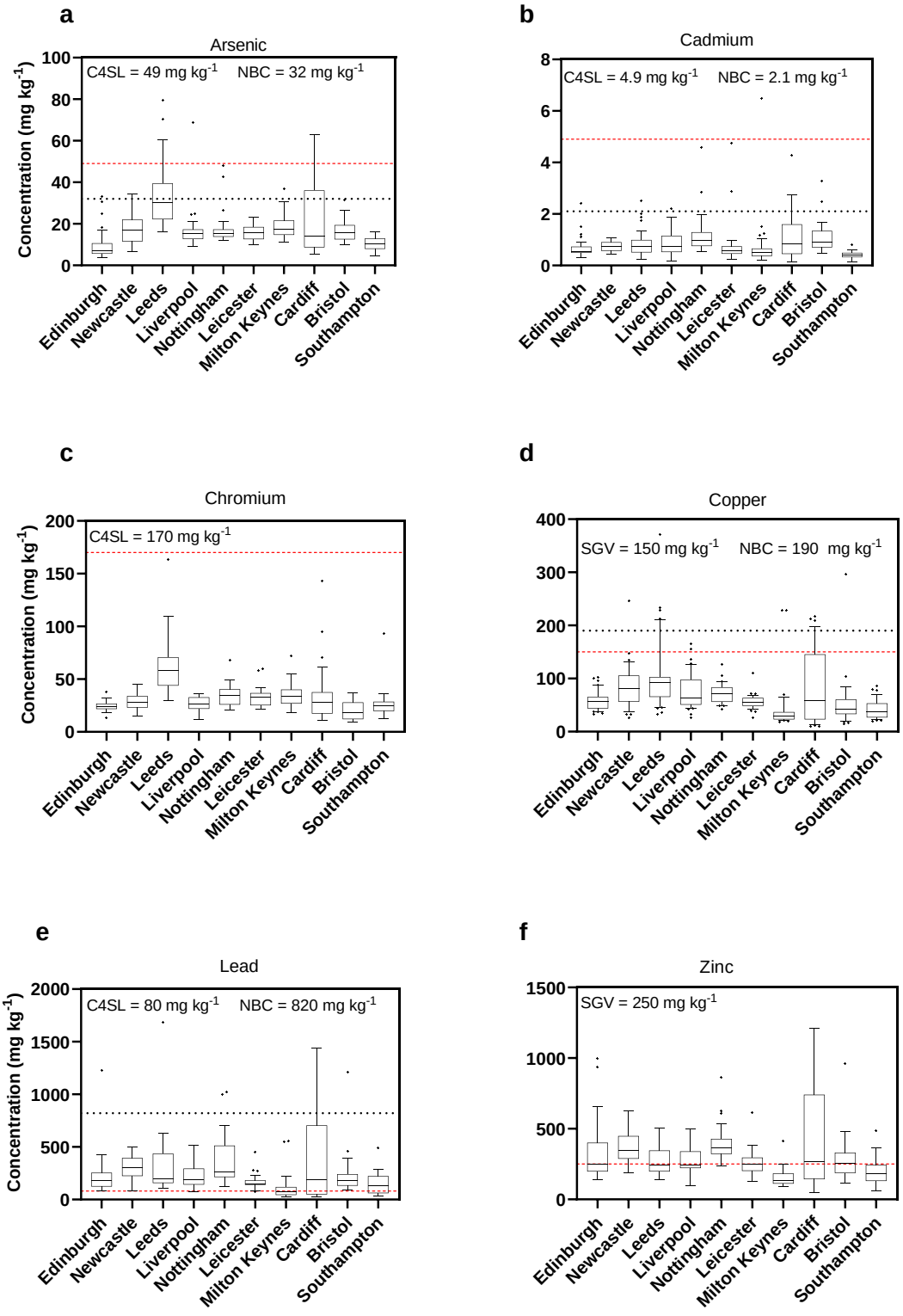


**Figure 4** Soil total HM concentrations (mg kg $^{-1}$) across ten cities in the UK (n=391 composite soil samples). The concentration of As, Cd, Cr, Cu, Pb, Zn is presented in **a-f**, respectively. Boxes represent 25$^{th}$, 50$^{th}$ and 75$^{th}$ percentiles; black dots represent outliers. The red dashed line indicates the C4SLs and SGVs, whereas the black dotted line indicates the NBCs.

### 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 (Figure 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.

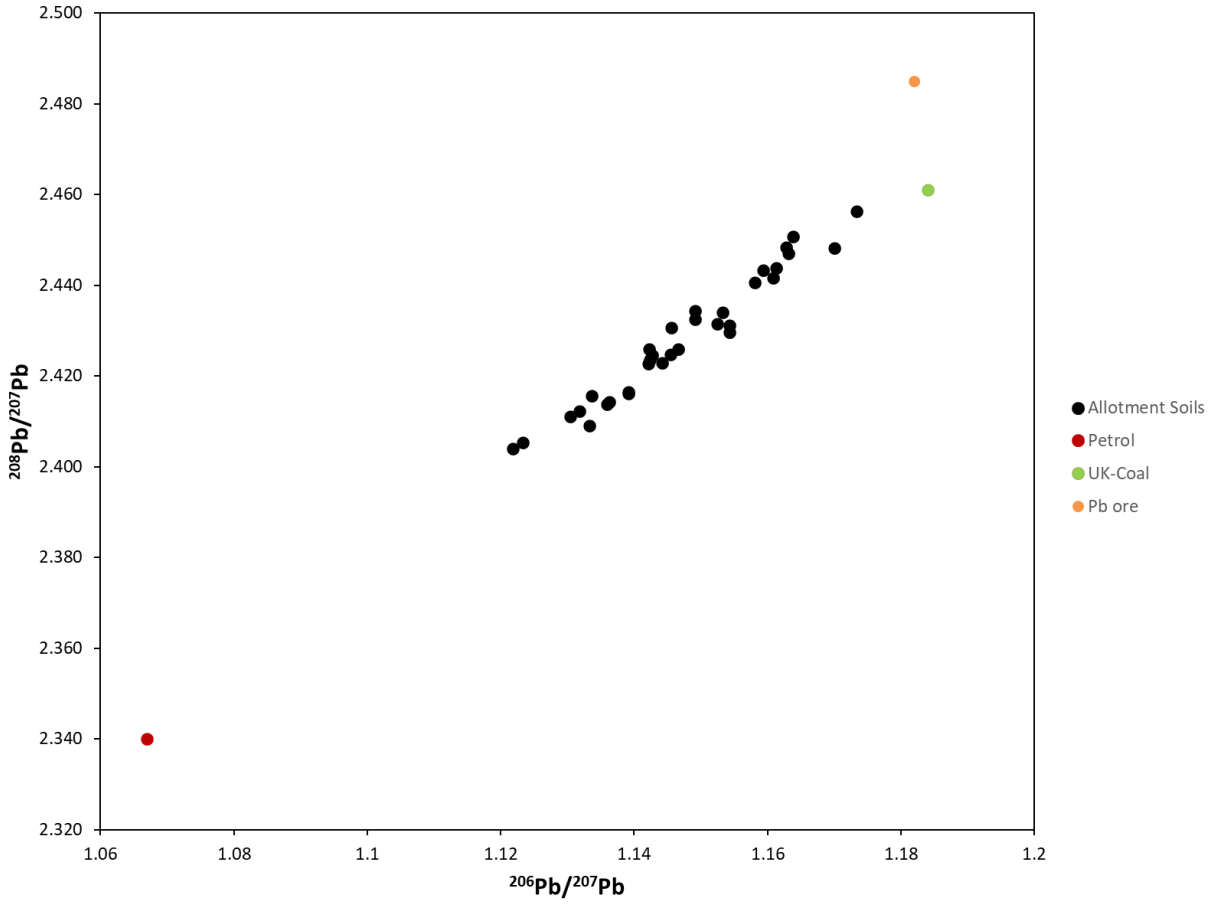


**Figure 5** Lead isotopic ratios in allotment soils across ten cities in the UK (n=40). Mixing line of Pb isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) with median values for UK coal (Nottinghamshire, Yorkshire, Derbyshire), Pb ore (Galenas in Derbyshire and Leicestershire) and source of Pb in petrol.

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.

**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 |

### 3.4. 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) (Figure 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.

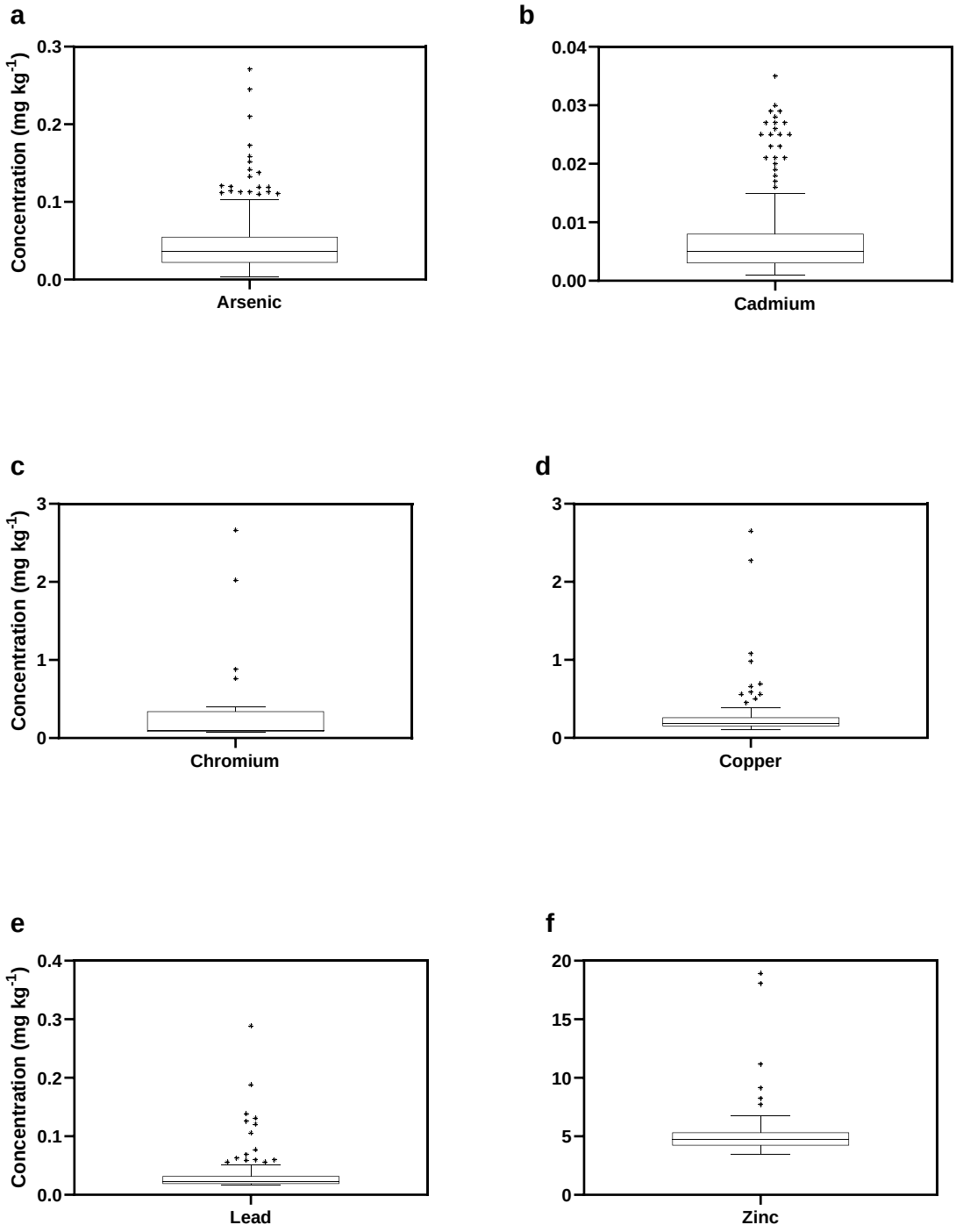


**Figure 6** Soil bioavailable HM concentrations (mg kg $^{-1}$) across ten cities in the UK. The concentration of As (n=370), Cd (n=370), Cr (n=65), Cu (n=147), Pb (n=210), Zn (n=92) is presented in **a-f**, respectively. Boxes represent 25$^{th}$, 50$^{th}$ and 75$^{th}$ percentiles and black dots represent outliers.

**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 | | | | |

## 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% (Figure 3d). In general, the BC/TOC ranges found across UK UH soils were similar to those reported 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 (Figure 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 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; Figure 4 a-f) and BC (Figure 3 c). Similarly,

some of the highest median total concentrations of Cd, Cu, Pb and Zn (Figure 4 a-f) are found in Leeds, Nottingham, Newcastle and Cardiff where some of the greatest median BC concentrations are also observed (Figure 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.

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# CHAPTER 5

## The concentration of potentially toxic elements and essential minerals in UK urban horticulture produce: a case study from five UK cities

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**ABSTRACT**

Urban horticulture (UH) is increasingly recognised as an important component of sustainable urban food systems but poses potential risks from widespread soil contamination of potentially toxic elements (PTE). To fully understand the risks and benefits of UH expansion both the potential risks of consumption of PTE from UH produce and the potential benefits to human nutrition from essential minerals that may be enriched in these environments needs to be investigated. We explore this through five case-study cities in the UK, where we demonstrated that the consumption of the recommended World Health Organisation five fruits and vegetables a day from soil-grown UH produce is unlikely to pose a risk to human health through consumption of PTE. Additionally, we found that the consumption of UH produce contributes to the daily intake of essential minerals: calcium, copper, iron, magnesium, phosphorus, potassium, selenium and zinc. With the exception of calcium, median concentrations of essential minerals were typically 27% (17-41 range) lower than reported values for commercial horticulture, when expressed as daily dietary intakes based on 5-a-day and 10-a-day fruit and vegetable portions.

## 1. INTRODUCTION

Urban horticulture (UH), the production of fruit and vegetables (F&V) within urban areas, is increasingly recognised as a potentially important component of a transformed sustainable food system, bringing the production of fresh F&V close to urban centres (Artmann & Sartison, 2018.; Langemeyer et al., 2021; Morgan, 2015). This is particularly important as the global population becomes increasingly urban. Indeed, it is estimated that 68% of the population by 2050 will live in cities and towns (UN, 2018) and in many countries of the Global North most of the population is already urban, for example, in the UK more than 80% of people live in cities and towns (UK Government Office for Science,2021). Increased production of F&V in close proximity to the majority of the population could enhance the nutritional security of urban dwellers (Development Initiatives, 2018; Milan Urban Food Policy Pact, 2015.) many of whom are disconnected from food production systems (Martin et al., 2016), and reduce the environmental impacts by shorter supply chains. Consumption of F&V is crucial for a healthy and food secure population, providing essential vitamins and minerals including calcium, chloride, chromium, copper, fluoride, iron, iodine, manganese, magnesium, molybdenum, phosphorus, sodium, selenium and zinc, required in the human diet (Public Health England, 2018).

There is growing recognition of the potentially important role for UH in a sustainable food system amongst both policy-makers and the public (Morgan, 2015), particularly in response to the food supply shocks like those experienced during Covid-19 pandemic (Lal, 2020). Coupled to this, recent research has demonstrated the potential contribution of food growing by individual households in allotments, gardens and community gardens (Edmondson et al., 2019, 2020), showing that, if just 10% of urban greenspaces identified as potentially suitable for UH production in the UK were utilized, they could feed up to 15% of a city's residents on the recommended minimum '5 a day' portions of fruit and vegetables (Edmondson et al., 2020).

However, these studies have not considered the nutritional quality of the produce and its potential contamination by potentially toxic elements (PTE) including arsenic, cadmium, copper, lead and zinc, which tend to be enriched in urban soils, especially in areas where there was formerly heavy industries, widespread burning of coal and motor vehicle emissions (Alloway, 2004).

Crop production in UH systems is small-scale with relatively low inputs of synthetic fertilisers contrasting with commercial horticultural production (Dobson et al., 2021). These different crop production practices may impact upon the mineral composition of F&V crops – which could impact upon the nutritional value of UH crops compared to commercial horticultural crops.

Globally, about 800 million of people are already engaged with UH (Lorenz, 2015), thus understanding the contribution of UH to the nutritional security of urban dwellers is crucial, however at the present this is unknown. Studies focussed on investigating both the potential risks of consumption of PTE from UH produce, and the potential benefits to human nutrition could provide clear evidence to support future expansion of UH.

In addition, there have been historical concerns over the scale-up of UH due to contamination of urban soils with pollutants, especially PTE (Entwistle et al., 2018; Leake et al., 2009; Sharma et al., 2014). Indeed, recent studies have found that PTE are ubiquitous across UK UH soils and, in some cases, PTE concentrations are above the UK soil guidelines values (especially lead) (Crispo et al., 2021). Despite this, their bioavailability is minimal suggesting low risks of PTE uptake by food crops (Crispo et al., 2021). This is supported by reported lead concentrations of UH produce in one UK city found to be within the safety regulation limits, despite 98% of the soils samples exceeded the guidelines values (Entwistle et al., 2018). However, widespread testing of PTE concentrations in UH F&V crops would further support these findings.

Here, we use a large-scale study of UH F&V crops from five UK cities to determine both the potential risk to human health from PTE consumption and the mineral concentrations found in UH F&V crops. The PTE concentrations in UH produce were compared against the food safety standard maximum levels and the potential human health risks from the long-term exposures to PTE through consumption of UH produce were assessed by estimating the target hazard quotient (THQ), developed by the United States Environmental Protection Agency (US EPA, 2000). Additionally, the mineral intake derived from the consumption of UH produce was compared to that derived from the consumption of equivalent commercial horticultural crops sold across European supermarkets and retailers.

## 2. METHODS

### 2.1 Study area

Five case study cities across the UK were selected for this research: Edinburgh, Leeds, Liverpool, Milton Keynes, and Cardiff. These five urban areas have different pollution legacy and capture a range of population sizes, demographics, climatic condition across UK (Table S1), with a population size ranging from 249,000 to 752,000 (Office for National Statistics (ONS), 2011), average annual rainfall varying from 58.7 mm to 97.8 mm, and average annual minimum and maximum daily temperature varying from 5.9 °C to 7.8 °C and 12.6 °C to 14.7 °C (Climate-Data.org, 2021). Urban allotments have been selected as UH sites as they cover a large proportion of the areas for UH ubiquitously across UK and European cities (Speak et al., 2015; Ward, 1997). Each urban area was divided in four equal quadrants using ArcGIS 10.4.1 and four allotment sites were randomly selected from each quadrant (Dobson et al., 2021). Within each allotment site, five allotment plots were selected for food crop sampling. In total, 100 allotment plots in 20 sites were sampled during the 2018 growing season. In addition, for each allotment plot, the area assigned to individual food crop was recorded.

## 2.2. Food crop sampling and processing

A total of 116 food crop samples were collected across 100 allotment plots. At each allotment plot, 100 g of the edible part of one perennial and one annual food crop were collected, if available. The food crops sampled comprised seven categories: root/bulb (5 beetroots, 4 onions); potato (10 potatoes); leafy vegetables (4 chards, 6 lettuces, 3 spinaches); legume (3 French beans, 8 runner beans); cucurbit fruiting (11 courgettes, 3 cucumbers); solanaceous fruiting (10 tomatoes) and fruit (11 apples, 14 raspberries, 24 rhubarbs). Rhubarb samples were included into the fruit category as often have culinary uses as fruits. The samples were stored in polythene bags and kept at 4 °C for transport. The food crop samples were thoroughly cleaned using ultra-pure water to remove any soil particles, frozen at -20 °C and freeze-dried. Lastly, the food crop samples were powdered and homogenised using a stainless-steel grinding mill.

## 2.3. Food crop chemical analyses

The PTE and minerals concentration in food crop samples was determined by digestion with aqua regia and addition of $H_2O_2$ based on EPA Method 3052 (US EPA, 1996), however instead of using a microwave digestion system, samples were digested on a heating block. Briefly, 0.25 g of food crop sample 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 hours at room temperature. $H_2O_2$ (30%) was then added until the solution became transparent. Samples were then digested for 2 hours at 120 °C on a heating block. Once cool, the digested food crop samples were filtered using grade 42 Whatman ashless filter paper and diluted to volume with ultra-pure water. Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the food crop concentration of Arsenic (As), Calcium (Ca), Cadmium (Cd), Copper (Cu), Iron (Fe), Potassium (K), Magnesium (Mg), Manganese (Mn), Nickel (Ni), Phosphorus (P), Lead (Pb), Selenium (Se)

and Zinc (Zn). Quality assurance of the analyses was ensured through inclusion of reagent blanks, analytical reagent grade, certified reference materials (IPE 899) 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 prior to use.

### 2.4. Food safety standard maximum levels of contaminants in food crops

The PTE concentration in food crop samples were compared against the food safety standard maximum levels of contaminants set in China (National Standard for food safety GB2762-2012) and the EU (European Commission Regulation No 1881/2006) regulations. The maximum levels represent toxicologically acceptable levels at which the public health is protected. The maximum levels of As, Cd and Pb for six food crop categories are summarised in Table S2. For this study we used the average between China and EU food standard maximum level expressed in mg $kg^{-1}$ fresh weight (FW): As = 0.5, Cd = 0.1, Pb = 0.15 for root/tuber/bulb; As = 0.5, Cd = 0.2, Pb = 0.3 for leafy vegetables; As = 0.5; Cd = 0.1; Pb = 0.2 for legume; As = 0.5; Cd = 0.05; Pb = 0.1 for cucurbit fruiting/solanaceous fruiting/fruit.

### 2.5. Health risk assessment

The potential human health risk associated with long-term exposure to PTE through consumption of food crops was assessed using the target hazard quotient (THQ) method, developed by the United States Environmental Protection Agency (US EPA, 2021). The THQ for each PTE from food crops was calculated using Equation (1).

$$\mathrm{THQ} = \frac{\mathrm{EF\ x\ ED\ x\ IR\ x\ C}}{\mathrm{RfD\ x\ AT\ x\ BWa}} \quad (1)$$

Where EF is the exposure frequency (365 days $year^{-1}$); ED is the exposure duration (81.25 year, average between male and female adult life expectancy in UK ((ONS), 2020)); IR is the food

ingestion rate (80 g $day^{-1}$ representing one portion of fruit and vegetable of 'five a day' diet recommended by WHO (WHO, 2004); for potatoes we used 95.2 g $day^{-1}$ which is the average between the ingestion rate for potatoes across UK allotment growers and the estimate of how much potatoes are eaten daily by the UK population based on their annual potatoes spending (Edmondson et al., 2019; Entwistle et al., 2018); C is the PTE (As, Cd, Cu, Ni, Pb, Zn) concentration in the edible parts of the food crop (mg $kg^{-1}$ FW) (Table S3); RfD is the oral reference dose (g $kg^{-1}$ $day^{-1}$) (As, Cd, Cu, Ni, Pb and Zn values are 0.0003, 0.001, 0.04, 0.02, 0.0035, 0.3 mg $kg^{-1}$ $day^{-1}$) (US EPA, 2021); AT is the average exposure time for non-carcinogens (EF x ED = 29656 days ); BWa is the average body weight (76.9 kg, average between male and female adult body weight in UK; ONS, 2018). The target hazard index (THI) was used to estimate the overall risks posed by multiple PTE and corresponds to the sum of the individual THQ of each PTE assessed for each food crop category. The THI was calculated by using Equation (2):

$$THI = \sum_{i=1}^{n} THQ_i \quad (2)$$

THQ and THI values smaller than 1 indicate that the intake of a crop by a population is assumed safe; THQ and THI values greater than 1 indicate that the exposure is likely to pose a human health risk.

Additionally, the average THI across all food crop categories (except potato) was used to estimate the overall risks posed by multiple PTE derived from a '5 a day' or '10 a day' diet (Aune et al., 2017; WHO, 2004); which recommend eating 5 or 10 portions of fruit and vegetables of 80 g each, respectively.

### 2.6. Mineral concentration in food crop and nutrient intake

The concentrations (mg 100 $g^{-1}$ FW) of Ca, Cu, Fe, K, Mg, P, Se and Zn in food crops grown across UH soils were compared against the mineral concentrations of equivalent commercial horticultural crops sold across European supermarkets and retailers, specifically in seven countries Finland, France, Germany, Italy, Netherlands, Sweden, and United Kingdom, as it is estimated that about 26% of food consumed in the UK is supplied within the European Union (DEFRA, 2020). The nutrient concentrations in commercial horticultural crops were derived from the EFSA food composition database (EFSA, 2021), where the amount of minerals contained in different food crops is provided.

The nutrient intakes of Ca, Cu, Fe, K, Mg, P, Se and Zn were investigated across two types of diet: '5 a day' and '10 a day', which recommend the daily intake of five portions (400 g) and ten portions (800 g) of F&V, respectively, where a portion of fruit or vegetables is 80 g (Aune et al., 2017; WHO, 2004). For this purpose, the concentration (mg 100 $g^{-1}$ FW) of Ca, Cu, Fe, K, Mg, P, Se and Zn in food crops grown across UH soils and equivalent commercial horticultural crops were expressed as mg 80 $g^{-1}$ FW. A resampling methodology was used to generate 100 random diet combinations of five or ten different food crops. The mean and standard error of each mineral across the 100 diets was then derived and used to express the concentration of Ca, Cu, Fe, K, Mg, P, Se and Zn as a percentage of adult's (19+ years; females and males) daily reference nutrient intakes (RNI) for minerals recommended by the UK government agency Public Health England (2016). The RNI for the minerals investigated are as follow: Ca = 800 mg $day^{-1}$ male and female; Cu = 1.2 mg $day^{-1}$ female and male; Fe = 14.8 mg $day^{-1}$ female (19-50 years) and 8.7 mg $day^{-1}$ male and female (50+ years); K = 3500 mg $day^{-1}$ male and female; Mg = 270 mg $day^{-1}$ female and 300 mg $day^{-1}$ male; P = 550 mg $day^{-1}$ female and male; Se = 60 µg $day^{-1}$ female and 75 µg $day^{-1}$ male; Zn = 7 mg $day^{-1}$ female and 9.5 mg $day^{-1}$ male.

### 2.7. Statistical Analysis

The resampling methodology was performed in R v 3.5.1. Independent t-test was used to compare the differences in the daily intake of essential minerals from UH produce and commercial horticultural crops. Mann-Whitney U test was used to test for differences between non-normally distributed data. All descriptive statistics were performed using GraphPad Prism version 9.0.0, California USA.

## 3. RESULTS

### 3.1. PTE concentrations in UH produce are below food safety maximum levels

The concentrations of As, Cd and Pb in UH produce are below the respective safety maximum levels for contaminant in food, set by the European and China regulations, in 99% of the samples, across all six food crop categories (Figure 1 a-c). The median concentration of As, Cd and Pb in UH produce varies across the six food crop categories from 0.001 to 0.0023 mg $kg^{-1}$, from 0.0025 to 0.0066 mg $kg^{-1}$ and from 0.0081 to 0.039 mg $kg^{-1}$ respectively. The median concentration of Cu and Zn in UH produce varies across the six food crop categories between 0.19 and 0.35 mg $kg^{-1}$ and between 1.8 and 3.6 mg $kg^{-1}$, respectively (Figure 1 d-e).

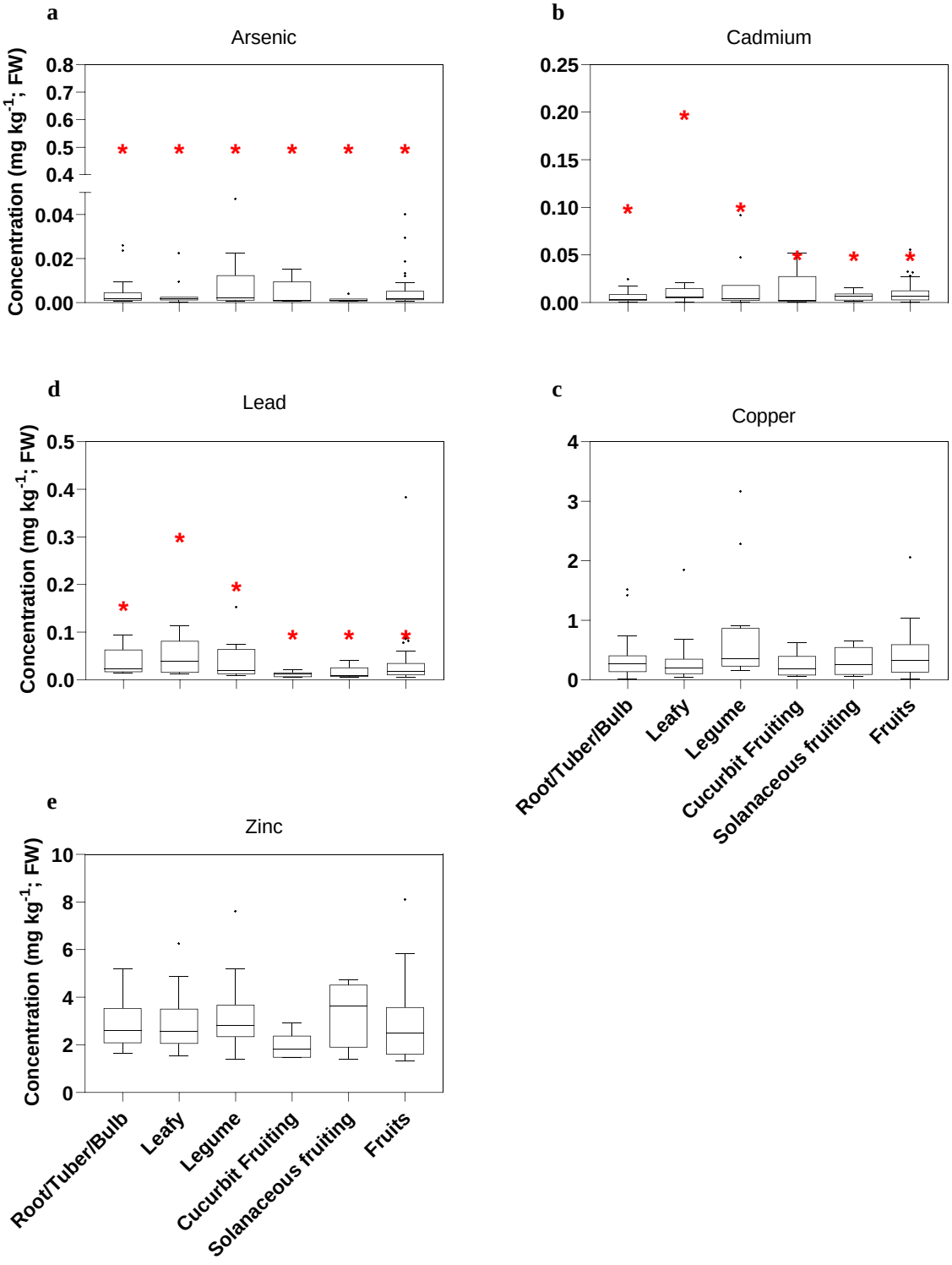


**Figure 1** Potentially toxic element concentration (mg $kg^{-1}$ FW) in the edible parts of food crops grown on urban horticultural soils across five cities in the UK. Concentrations are presented according to six food crop categories. The concentration of As, Cd, Pb, Cu and Zn is presented in **a-e**, respectively. Boxes represent 25$^{th}$, 50$^{th}$ and 75$^{th}$ percentiles and black dots represent outliers. The red star dots

correspond to the food safety standard maximum levels of contaminants in food crops, which are only available for As, Cd and Pb.

### 3.2. Consumption of UH produce is unlikely to pose a risk to human health

Consumption of a food crop is likely to cause detrimental human health effects when target hazard values (THQ) are greater than one. The assessment of the potential human health risks through the consumption of UH produce has shown that the target hazard quotients (THQ) values of As, Cd, Cu, Pb and Zn are all far below the limit (one), across all seven food crops categories (Figure 2 a-e). The median THQ values for As, Cd, Cu, Pb and Zn varied across the seven food crops categories from 0.0034 to 0.0091, from 0.0025 to 0.0075, from 0.0049 to 0.0093, from 0.0024 to 0.01 and from 0.0063 to 0.013, respectively. The median THQ of Cd from solanaceous fruiting vegetables and Pb from cucurbit fruiting vegetables are the lowest with values of 0.0024 and 0.0025, respectively. The median THQ of Pb from leafy vegetables and root/bulb crops and the median THQ of Zn from solanaceous fruiting vegetable and root/bulb crops are the highest with value of 0.01. The results on the overall risks posed by the exposure of multiple PTE through the consumption of UH produce also reveal that the target hazard index (THI) values are far below one, across all seven food crops categories. Particularly, legumes present the highest median THI value (0.05) and solanaceous fruiting vegetables present the lowest median THI (0.024) (Table 1). Additionally, our analysis has found that the THI derived from the consumption of the WHO recommended 5 a day portions of fruits and vegetable from UH produce is below one, with a value of 0.17 ± 0.04 (SD; Table 1). Similarly, considering a 10 a day portion of fruits and vegetables, the THI is far below one, with a value of 0.34 ± 0.83 (SD; Table 1).

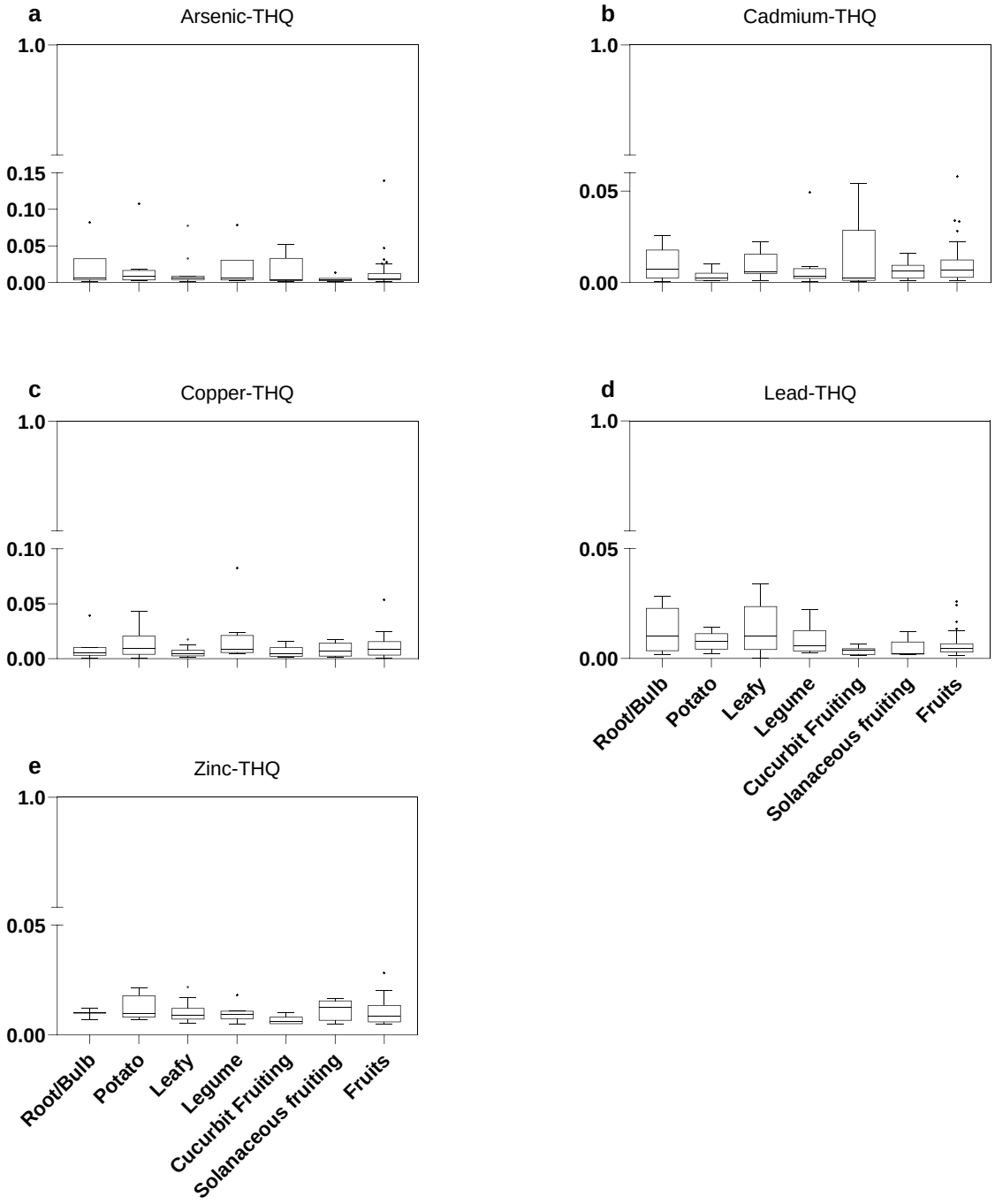


**Figure 2** Target hazard quotient (THQ) associated with the consumption of different food crops grown on urban horticultural soils across five cities in the UK. The THQ values are presented for five PTE (As, Cd, Cu, Pb and Zn) according to seven food crop categories in **a-e**, respectively. Boxes represent 25$^{th}$, 50$^{th}$ and 75$^{th}$ percentiles and black dots represent outliers. THQ ≥ 1 indicates that the intake of a food crop is likely to cause detrimental human health effects.

**Table 1** The median target hazard index (THI) and ranges of all PTE combined (As, Cd, Cu, Ni, Pb, Zn) according to seven food crop categories and the THI across all food crop categories (except potato) ± standard deviation (SD) for two diet types. THI ≥ 1 indicates that the exposure is likely to pose detrimental human health risk.

| Food crop category | THI (ranges) |
|---|---|
| Root/Bulb | 0.034 (0.005-0.21) |
| Leafy | 0.034 (0.017-0.14) |
| Legume | 0.050 (0.010-0.23) |
| Cucurbit fruiting | 0.027 (0.004-0.12) |
| Solanaceous fruiting | 0.024 (0.007-0.058) |
| Potato | 0.032 (0.002-0.15) |
| Fruit | 0.036 (0.002-0.24) |
| Total '5 a day' diet | 0.17 ± 0.04 (SD) |
| Total '10 a day' diet | 0.34 ± 0.83 (SD) |

### 3.3. Comparison between UH and commercial F&V crops

Our analysis has revealed that the median mineral concentrations in all classes of UH grown F&V crops for Ca, Cu, Fe, K, Mg, P and Zn are generally lower than those found in equivalent commercial horticultural crops, but within the same order of magnitude (Figure 3 a-f). Apple crops are the only exception, where the median mineral concentrations in UH apple crops are constantly higher compared to commercial ones (Figure 3 a-f). Similarly, onion UH crops present higher concentration of Ca, Fe, K, Mg and Zn compared to commercial ones. We found that there was a statistically significant difference ($p < 0.0001$, Table S6) between the daily intake of essential minerals from the consumption of UH produce and commercial horticultural crops. Although the consumption of the WHO recommended 400 g of F&V from UH produce makes an important contribution to the daily intake of essential minerals, the median intake of Cu, Fe, K, Mg, P and Zn from the consumption of UH produce would be 27% (17-41 range;

99% for Se) lower than those from commercial horticultural crops (Figure 4 and Table S4). This is also valid when a ‘10 a day’ diet is considered (Figure 4). In contrast, median Ca intake from consumption of UH produce is 47% higher than the commercial one (Figure 4).

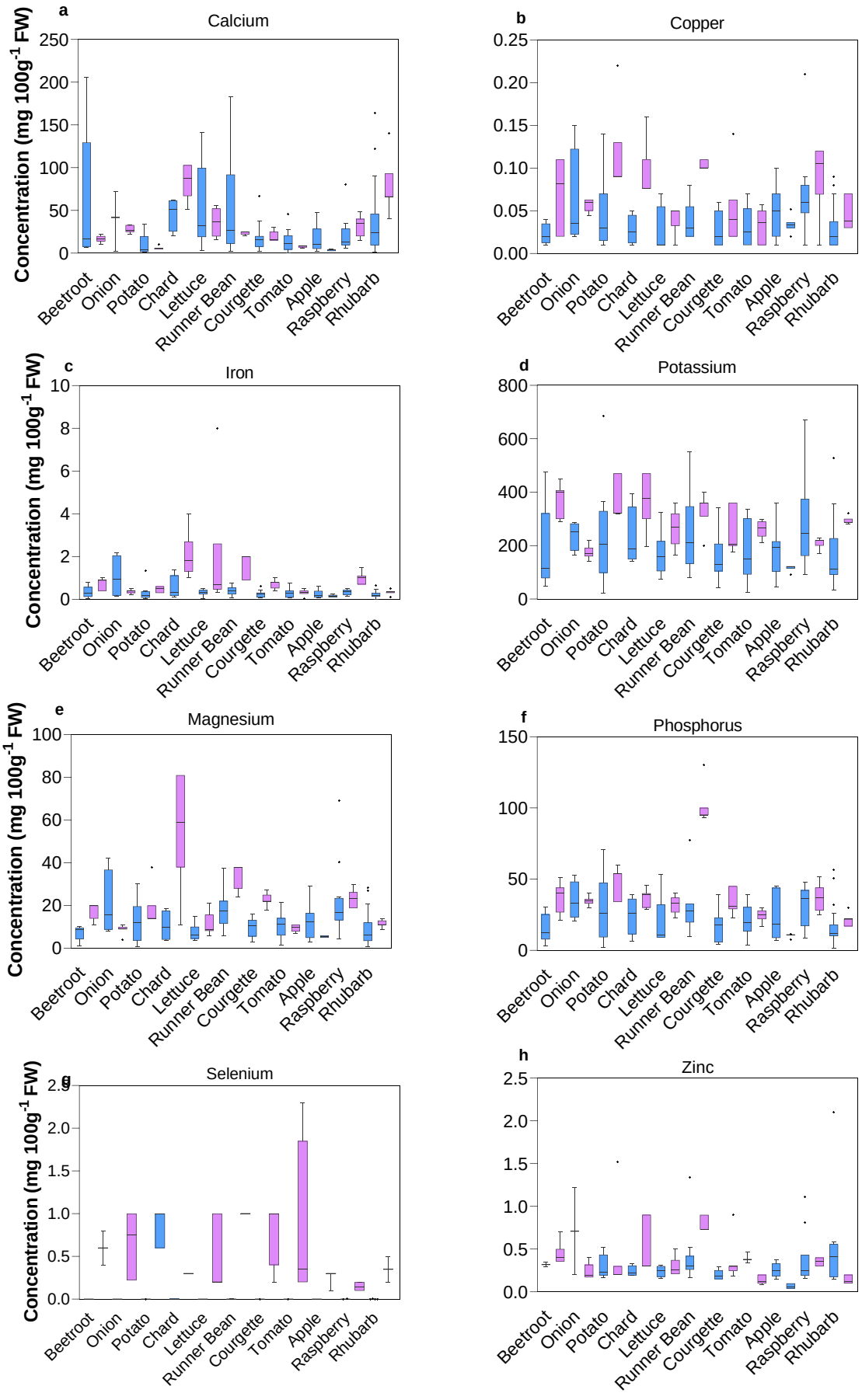
a
Calcium
Concentration (mg 100g-1 FW)
250
200
150
100
50
0
b
Copper
0.25
0.20
0.15
0.10
0.05
0.00
c
Iron
10
8
6
4
2
0
d
Potassium
800
600
400
200
0
e
Magnesium
100
80
60
40
20
0
f
Phosphorus
150
100
50
0
g
Selenium
2.5
2.0
1.5
1.0
0.5
0.0
h
Zinc
2.5
2.0
1.5
1.0
0.5
0.0
Beetroot
Onion
Potato
Chard
Lettuce
Runner Bean
Courgette
Tomato
Apple
Raspberry
Rhubarb

**Figure 3** Mineral concentration in food crop edible parts grown on urban horticultural soils (blue boxes) across five cities in the UK compared to food crops commonly consumed across EU (pink boxes). The concentration of Ca, Cu, Fe, K, Mg, P, Zn (mg $100g^{-1}$ FW) and Se (µg $100g^{-1}$ FW) is presented in **a-h**, respectively. Boxes represent $25^{th}$, $50^{th}$ and $75^{th}$ percentiles and black dots represent outliers. Selenium bars are too small (see Supporting Information Table S4).

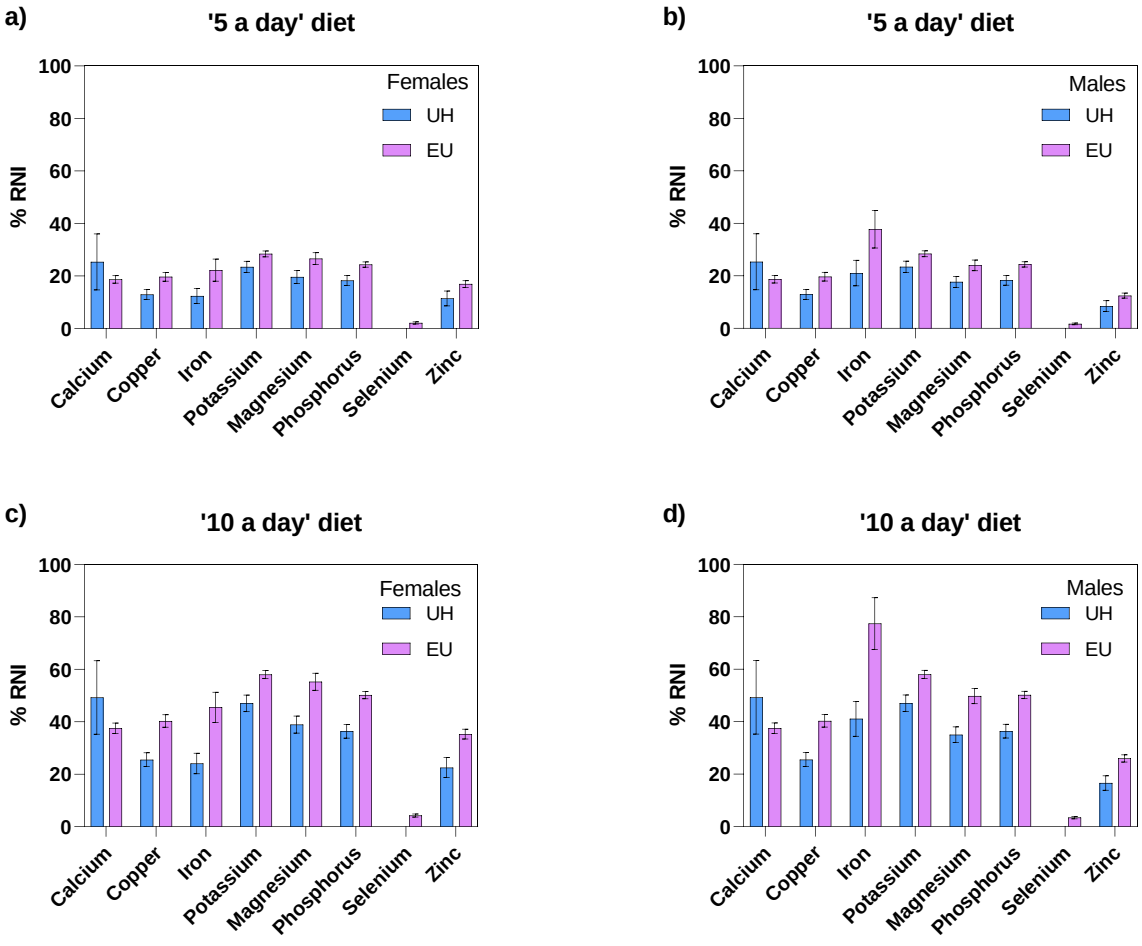


**Figure 4** Nutrient content expressed as percentage of the reference nutrient intake (% RNI for adults) derived from the consumption of UH produce grown on urban horticultural soils across five cities in UK (blue bars) and commercial horticultural crops commonly consumed across EU (pink bars). The % RNI for adult females and males are presented for Ca, Cu, Fe, K, Mg, P, Se and Zn across two types of diet in **a-d**. The graphs present the mean ± standard error of Ca, Cu, Fe, K, Mg, P, Se and Zn derived

from 100 random generated ‘5 a day’ (400g F&V) and ’10 a day’ diets (800g F&V). Selenium bars are too small (see Supporting Information Table S5).

## 4. DISCUSSION

Production of fresh and healthy F&V is one of the primary drivers for participation in UH (Säumel et al., 2012; Smith & Jehlička, 2013), however, a major internationally recognised barrier for UH expansion is the potential risk to human health from growing crops in soils contaminated with PTE (Jia et al., 2019). Here we demonstrated that the consumption of UH produce is unlikely to pose a risk to human health, despite previous research reporting that PTE are ubiquitous across UK UH soils and in some cases above UK soil guidelines values (Crispo et al., 2021; Entwistle et al., 2018),. The outcome of our analysis have shown that a diet based on the intake of the WHO recommended 5 a day portions of F&V (400g) solely from UK UH produce is unlikely to pose potential human health risks (Table 1). Even the consumption of a ‘10 a day’ (800 g) diet from UH F&V crops recommended for public health benefits linked to reducing cardiovascular disease and premature mortality risks (Aune et al., 2017), is unlikely to pose an overall risk to human health (Table 1). These findings provide compelling evidence to support the expansion of UH. These results are supported by reported blood Pb levels in UK UH growers, which in a UK city study were found to not significantly differ from the blood Pb levels in non-grower neighbours (Entwistle et al., 2018). Interestingly, there have been incidents where PTE concentrations in commercial horticultural produce were found to exceed maximum levels both in UK (Norton et al., 2015) and other countries (Ashraf et al., 2021; Liu et al., 2013a; Rusin et al., 2021; Zheng et al., 2020), and the consumption of these produce have been reported to pose a potential risks to human health (Ashraf et al., 2021; Liu et al., 2013b; Zheng et al., 2020; Zhou et al., 2016).

Although the expansion of UH supported by policy-makers from local to national levels is in part to ensure nutrition security to urban dwellers, to date no studies have investigated to what extent UH contributes to nutrition security (Opitz et al., 2016). Here, we demonstrated for the first time that whilst the consumption of UH produce makes an important contribution to the daily intake of several essential minerals, their concentration is often significantly lower than those found in equivalent commercial horticultural crops, but within the same order of magnitude (Figure 3).

Research has found that UH growers consume more fruits and vegetables per day than non-growers, suggesting 1.4 times more vegetable and fruits per day are consumed by UH growers (Alaimo et al., 2008). When applying this 1.4 factor to our results (corresponding to 6.4 portions of fruits and vegetables a day), the mineral intake derived from the consumption of UK UH produce is still lower than that of equivalent commercial horticultural crops (Table S4).

Although further research is needed to understand the mechanism driving the different minerals concentrations in UH and commercial horticultural crops, the difference in the management practices adopted by the two cropping systems may be an explanatory factor. In commercial horticulture nutrients are mainly applied by means of mineral fertilisers, often at excessive rate (Li et al., 2018), in forms that are readily available for plant uptake (Bhatt et al., 2019; Fess & Benedito, 2018; Harkes et al., 2019). Whereas UH growers often rely on different form of organic amendments for crop nutrition management: a recent study across UK UH growers found that 92% and 82% of the respondents apply garden waste compost and manure to their plots, respectively, and only 27% of the respondents add non-organic fertiliser to their plot (Dobson et al., 2021). Although organic amendments are a source of minerals, their concentrations vary from the feedstock materials (Towett et al., 2020) and their availability depends on the type of amendment, for example, composts release nutrients in soils more

slowly than manure (Thomas et al., 2019). Additionally, mineral bioavailability in soils is governed by several other factors (e.g. soil pH, cation exchange capacity, etc.) (Dhaliwal et al., 2019; Moharana et al., 2017) and nutrient management practices (e.g. application rate and applications rate over years). A survey conducted across 180 UK UH growers found that 76% of respondents have no previous growing experience (Dobson et al., 2021). As nutrient management depend on several factors, the minimal growing experience of the majority of UK UH growers may have led to an imbalance soil nutrient system and in part explain the lower mineral concentration found in UH produce compared to the equivalent horticultural commercial one.

However, research comparing commercial organic and conventional farming systems, have reported higher mineral concentrations in the edible parts of vegetables grown in cropping systems relaying solely on organic amendments compared to those receiving mineral fertiliser applications (Hattab et al., 2019) and higher soil mineral bioavailability in soil treated with organic amendments compared to inorganic fertilised soils (Moharana et al., 2017). Thus, further research is needed to understand the mechanisms underlying the lower mineral concentrations in UH F&V as well as investigate how UH soil management influences the concentrations of many other essential nutrients (e.g. vitamins) in UH produce. This will be important for a holistic understanding of UH contribution to the nutrient intake of urban populations.

Educational programmes focused on sustainable nutrient management practices may benefit the UH grower community. These could include those practices adopted by organic farming systems such as time/seasonal management of different organic amendments, including application rates, crop rotation and cover crop (Fess & Benedito, 2018). However, the selection of F&V varieties by UH practitioners may also in part explain the differences in the mineral

concentrations in UH F&V compared to commercial horticulture ones. Indeed, mineral concentrations have been found to vary by cultivar for instance in lettuce, pea and carrot (Alexander et al., 2006; K et al., 2013).

These results have important implications for future urban food strategies, particularly for the sustainable management of UH that ensure nutritionally adequate UH produce, whilst maintaining public safety. In addition, future urban food strategies should consider the establishment of frameworks where both nutrient and contaminant concentrations of UH produce is monitored to maintain a healthy and food secure urban population. For instance, urban horticultural produce could be integrated into existing governmental monitoring systems of contaminants and nutrients in food.

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# CHAPTER 6

## General discussion and conclusions

Urban populations face major environmental and health risks, thus understanding ways to enhance the quality of urban systems is a priority for policy-makers and civil society organisations locally and internationally. Throughout this thesis the role of urban soils in carbon sequestration, pollutant bioavailability mitigation, and urban food and nutritional security has been explored, highlighting the crucial contribution of soil black carbon (BC) across all these. In particular, this thesis demonstrated the ability of BC to potentially increase soil carbon sequestration, reduce heavy metal and metalloids (HM) bioavailability and thus contribute to urban food security. In addition, it demonstrated the crucial role urban soils play in urban nutrition security.

Black carbon is a major component of airborne particulate matter negatively influencing several atmospheric processes and causing severe human health effects. However, this research has demonstrated that once deposited in soils BC can positively influence a multiplicity of soil regulating ecosystem services. Chapter 2 demonstrated that BC in the form of soot can suppress the mineralisation of soil labile organic carbon (OC), with 18% less $^{13}CO_2$ produced when soot is added to the soil and thus potentially contribute to urban soil carbon storage and enhance soil carbon sequestration. Chapter 4 demonstrated that BC, which in urban soils is mostly present in the form of soot, is significantly correlated with both total and bioavailable HM concentrations, and thus contributing to HM immobilisation and consequently contributing to mitigate the risk of HM exposure into own-grown food crops across UH soils. Chapter 3 findings suggest that large application of engineered BC in the form of biochar could also potentially positively influence several urban soil physicochemical properties supporting soil-

water cycling and regulating ecosystem service like flood mitigation, however this needs more research.

In addition, this research has provided strong evidence crucial to support future UK urban food strategies aiming to develop UH at larger scales. Chapter 4 demonstrated that although HM are ubiquitous 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 $kg^{-1}$. Chapter 4 also showed that the bioavailable HM pool across these soils represents only a small fraction (0.01-1.8%) of the total pool even for those HM that exceed UK soil screening values, suggesting that the risks of HM crop uptake are low. These findings are further supported by the results presented in Chapter 5. This demonstrated that HM concentrations in fruits and vegetables (F&V) cultivated across UK UH soils are within the respective safety levels for contaminants in food and a diet based on the intake of the recommended 400g a day of these F&V is unlikely to pose detrimental human health risks. Overall, Chapter 4 and Chapter 5 demonstrated for the first time that although HM are ubiquitous across UK UH soils, growing and consuming F&V grown across these soils pose low risk to the urban grower health providing combinatorial evidence much needed to support future expansion of UH across urban areas. In addition, Chapter 5 provided the first experimental results on the potential contribution of UK UH to food and nutrition security demonstrating that the consumption of F&V grown across UK UH soils contribute to the daily intake of all essential minerals required to maintain a healthy lifestyle. These findings provide additional evidence in support of future urban food strategies aiming to expand UH production. This research has also demonstrated the crucial role urban soils and especially the soil management practices adopted by urban growers play in urban food and nutrition security by mitigating the risks of pollutant bioavailability and influencing the nutritional values of urban

grown F&V. Chapter 4 showed that soil OC significantly affects the bioavailability of HM across UK UH soils suggesting that soil management practice adopted by urban growers like organic application of compost and manure can contribute to HM immobilisation. Chapter 5 found that the minerals concentration in F&V grown across UK UH soils is generally lower than those found in equivalent commercial horticultural crops suggesting that the soil management practices adopted by urban growers may, in part, negatively influence plant minerals availability. Overall, these results imply that the risks and benefits associated with UH can be further regulated by improving the soil management practices adopted by urban growers.

Overall, these findings provided a series of evidence suggesting that BC, especially in the form of soot plays an important role in enhancing and supporting the multifunctionality of urban soil ecosystem services. In addition, these outcomes have demonstrated how urban soils, which often contain elevated concentration of soil BC can contribute to enhance the multifunctionality of urban greenspaces (UG) and thus contribute to the mitigation of some of the environmental and health challenges faced by urban populations. These outcomes will be informative for future urban soils and UG strategies aiming, for instance, to expand urban horticulture (UH) or increase soil carbon sequestration. Although further research is needed, these results have provided a suite of new evidence from which future studies can build on to understand how BC could be integrated in future urban soil management strategies to improve urban soils ecosystem services provision.

**Directions for future research**

The results of this research project suggest several possible directions for future research.

Whilst Chapter 2 demonstrated how BC can significantly influence soil carbon dynamics, this research has focused only on one soil labile carbon pool. Further research is needed to

investigate the effect of soot on all soil carbon pools which will allow better understanding the role of soot in urban soil carbon sequestration as well as quantify its effect. Chapter 2 findings also highlighted the need to understand the mechanisms underlying the suppressive effect of soot on soil OC mineralisation which will be invaluable for future soil management strategies aiming to increase carbon storage and sequestration. Further research is also needed to investigate soot mineralisation over longer time-scales, but also understand the mechanisms underpinning the decrease of soot mineralisation over short-time scale which will allow to better understand the role of soot in soil $CO_2$ effluxes and thus its contribution to the global carbon cycle.

Chapter 3 highlighted the need of further research on the long-term effect of higher biochar application rate on a wider-range of urban soil properties under different vegetation covers. An integrated understanding of how biochar application across different UG support multiple ecosystem services will be invaluable for future UG strategies and planning. With climate change increasing the risks of severe natural disasters (e.g. floods and droughts) globally, understanding how soil biochar application could help to mitigate the negative impact of climate change within cities will be another important aspect to address in future research. This could include for instance understanding the role of biochar to urban soils water dynamics.

The outcomes presented in Chapter 4 has shown that HM and BC are ubiquitous across UK UH soils. Whilst this research has shown that BC can contribute to mitigate the risk of HM exposure into UH produce, questions remain on the long-term effect of BC on HM immobilisation and the mechanisms governing this. Being a possible source of energy for soil microorganisms, it will be important to understand the interaction between soil microorganisms and BC. This will enable an understanding of whether soil microorganisms have a potential role in the long-term effect of BC on HM immobilisation.

Both Chapter 4 and Chapter 5 demonstrated the need to develop soil screening values that are more reflective of UH characteristics to better assess the human health risks associated with UH.

Whilst Chapter 5 demonstrated that the consumption of UH produce is unlikely to pose a risk to human health, this research has focussed only on the non-carcinogenic risks linked with the consumption of HM. Further research is needed to look at the whole range of pollutants potentially present in UH soils and estimate the human health risks associated with these. Finally, Chapter 5 results highlighted the need to further investigate how UH practices influence the concentration of other nutrients essential for the human diet such as vitamins in UH produce. This will be important for a holistic understanding of UH contribution to the nutritional security of urban populations.

# SUPPLEMENTARY INFORMATION TO CHAPTERS

# CHAPTER 2

## CONTENT

**Table S1** Evolution of δ $^{13}C$ and $log_{10}$ δ $^{13}C$ from soil with added $^{13}C$ labelled organic carbon; soil with added $^{13}C$ labelled organic carbon and soot and soil with added $^{13}C$ labelled organic carbon and biochar

| TREATMENTS | REPLICATE | DAYS | Δ $^{13}C$ | $LOG_{10}$(Δ $^{13}C$) |
|---|---|---|---|---|
| SOIL+$^{13}C$ SUCROSE | 1 | 0 | 618.95 | 2.82 |
| SOIL+$^{13}C$ SUCROSE | 2 | 0 | 957.07 | 3.00 |
| SOIL+$^{13}C$ SUCROSE | 3 | 0 | 980.58 | 3.01 |
| SOIL+$^{13}C$ SUCROSE | 4 | 0 | 1041.64 | 3.03 |
| SOIL+ SOOT+$^{13}C$ SUCROSE | 1 | 0 | * | * |
| SOIL+ SOOT+$^{13}C$ SUCROSE | 2 | 0 | 2307.32 | 3.37 |
| SOIL+ SOOT+$^{13}C$ SUCROSE | 3 | 0 | * | * |
| SOIL+ SOOT+$^{13}C$ SUCROSE | 4 | 0 | 2464.08 | 3.40 |
| SOIL+ BIOCHAR+$^{13}C$ SUCROSE | 1 | 0 | 2128.78 | 3.328131 |
| SOIL+ BIOCHAR+$^{13}C$ SUCROSE | 2 | 0 | 2119.88 | 3.326311 |
| SOIL+ BIOCHAR+$^{13}C$ SUCROSE | 3 | 0 | 2222.6 | 3.346861 |
| SOIL+ BIOCHAR+$^{13}C$ SUCROSE | 4 | 0 | * | * |
| SOIL+$^{13}C$ SUCROSE | 1 | 1 | 143.66 | 2.26 |
| SOIL+$^{13}C$ SUCROSE | 2 | 1 | 854.45 | 2.95 |
| SOIL+$^{13}C$ SUCROSE | 3 | 1 | 805.94 | 2.93 |
| SOIL+$^{13}C$ SUCROSE | 4 | 1 | 1153.63 | 3.08 |
| SOIL+ SOOT+$^{13}C$ SUCROSE | 1 | 1 | 760.61 | 2.90 |
| SOIL+ SOOT+$^{13}C$ SUCROSE | 2 | 1 | 13107.22 | 4.12 |
| SOIL+ SOOT+$^{13}C$ SUCROSE | 3 | 1 | * | * |
| SOIL+ SOOT+$^{13}C$ SUCROSE | 4 | 1 | 2649.15 | 3.43 |
| SOIL+ BIOCHAR+$^{13}C$ SUCROSE | 1 | 1 | 340.31 | 2.531875 |
| SOIL+ BIOCHAR+$^{13}C$ SUCROSE | 2 | 1 | 5508.15 | 3.741006 |

| | | | | |
|---|---|---|---|---|
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 1 | 2201.68 | 3.342754 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 1 | 4530.09 | 3.656107 |
| SOIL+$^{13}$C SUCROSE | 1 | 7 | 13793.28 | 4.14 |
| SOIL+$^{13}$C SUCROSE | 2 | 7 | 8506.36 | 3.93 |
| SOIL+$^{13}$C SUCROSE | 3 | 7 | * | * |
| SOIL+$^{13}$C SUCROSE | 4 | 7 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 7 | 6649.82 | 3.83 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 7 | 3612.61 | 3.56 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 7 | 4012.28 | 3.61 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 7 | 5292.8 | 3.73 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 7 | 9528.86 | 3.98 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 7 | 5183.37 | 3.71 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 7 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 7 | * | * |
| SOIL+$^{13}$C SUCROSE | 1 | 14 | * | * |
| SOIL+$^{13}$C SUCROSE | 2 | 14 | * | * |
| SOIL+$^{13}$C SUCROSE | 3 | 14 | 6066.536 | 3.78 |
| SOIL+$^{13}$C SUCROSE | 4 | 14 | 3756.31 | 3.57 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 14 | 3801.09 | 3.58 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 14 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 14 | 1250.83 | 3.11 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 14 | 1959.88 | 3.30 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 14 | 2679.02 | 3.43 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 14 | 1973.88 | 3.30 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 14 | * | * |

| | | | | |
|---|---|---|---|---|
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 14 | 1598.85 | 3.20 |
| SOIL+$^{13}$C SUCROSE | 1 | 21 | 6200.52 | 3.80 |
| SOIL+$^{13}$C SUCROSE | 2 | 21 | 4627.39 | 3.67 |
| SOIL+$^{13}$C SUCROSE | 3 | 21 | 6056.26 | 3.79 |
| SOIL+$^{13}$C SUCROSE | 4 | 21 | 3231.71 | 3.51 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 21 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 21 | 2230.96 | 3.36 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 21 | 2187.71 | 3.35 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 21 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 21 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 21 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 21 | 3719.02 | 3.57 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 21 | 2179.82 | 3.34 |
| SOIL+$^{13}$C SUCROSE | 1 | 28 | 6306.27 | 3.80 |
| SOIL+$^{13}$C SUCROSE | 2 | 28 | 3651.92 | 3.57 |
| SOIL+$^{13}$C SUCROSE | 3 | 28 | 5670.25 | 3.76 |
| SOIL+$^{13}$C SUCROSE | 4 | 28 | 3764.52 | 3.58 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 28 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 28 | 2900.22 | 3.47 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 28 | 1558.98 | 3.20 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 28 | 2136.40 | 3.34 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 28 | 2762.07 | 3.44 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 28 | 1992.61 | 3.30 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 28 | 3031.16 | 3.48 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 28 | 1456.36 | 3.16 |

| | | | | |
|---|---|---|---|---|
| SOIL+$^{13}$C SUCROSE | 1 | 35 | * | * |
| SOIL+$^{13}$C SUCROSE | 2 | 35 | * | * |
| SOIL+$^{13}$C SUCROSE | 3 | 35 | 5735.89 | 3.76 |
| SOIL+$^{13}$C SUCROSE | 4 | 35 | 3320.95 | 3.53 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 35 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 35 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 35 | 1473.72 | 3.18 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 35 | 2499.69 | 3.40 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 35 | 3836.00 | 3.58 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 35 | 2871.44 | 3.46 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 35 | 3799.47 | 3.58 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 35 | 1939.93 | 3.29 |
| SOIL+$^{13}$C SUCROSE | 1 | 42 | 5020.82 | 3.70 |
| SOIL+$^{13}$C SUCROSE | 2 | 42 | 3666.20 | 3.57 |
| SOIL+$^{13}$C SUCROSE | 3 | 42 | 5532.82 | 3.75 |
| SOIL+$^{13}$C SUCROSE | 4 | 42 | 2497.65 | 3.40 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 42 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 42 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 42 | 923.59 | 2.98 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 42 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 42 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 42 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 42 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 42 | 1256.16 | 3.10 |
| SOIL+$^{13}$C SUCROSE | 1 | 49 | 3877.21 | 3.59 |

| | | | | |
|---|---|---|---|---|
| SOIL+$^{13}$C SUCROSE | 2 | 49 | * | * |
| SOIL+$^{13}$C SUCROSE | 3 | 49 | * | * |
| SOIL+$^{13}$C SUCROSE | 4 | 49 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 49 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 49 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 49 | 681.23 | 2.86 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 49 | 1162.91 | 3.08 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 49 | 2195.32 | 3.34 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 49 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 49 | 2858.39 | 3.46 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 49 | * | * |
| SOIL+$^{13}$C SUCROSE | 1 | 56 | 3130.10 | 3.50 |
| SOIL+$^{13}$C SUCROSE | 2 | 56 | * | * |
| SOIL+$^{13}$C SUCROSE | 3 | 56 | 2969.35 | 3.48 |
| SOIL+$^{13}$C SUCROSE | 4 | 56 | 1709.66 | 3.24 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 56 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 56 | 533.98 | 2.76 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 56 | 773.40 | 2.91 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 56 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 56 | 1484.00 | 3.17 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 56 | 976.99 | 2.99 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 56 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 56 | 509.83 | 2.71 |
| SOIL+$^{13}$C SUCROSE | 1 | 70 | 2681.96 | 3.43 |
| SOIL+$^{13}$C SUCROSE | 2 | 70 | 1743.08 | 3.25 |

| | | | | |
|---|---|---|---|---|
| SOIL+$^{13}$C SUCROSE | 3 | 70 | 2712.99 | 3.44 |
| SOIL+$^{13}$C SUCROSE | 4 | 70 | 2112.07 | 3.33 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 70 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 70 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 70 | 799.82 | 2.92 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 70 | 815.49 | 2.93 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 70 | 2251.21 | 3.35 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 70 | 1531.26 | 3.19 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 70 | 2224.69 | 3.35 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 70 | 813.84 | 2.91 |
| SOIL+$^{13}$C SUCROSE | 1 | 84 | * | * |
| SOIL+$^{13}$C SUCROSE | 2 | 84 | 1011.10 | 3.02 |
| SOIL+$^{13}$C SUCROSE | 3 | 84 | 2217.65 | 3.35 |
| SOIL+$^{13}$C SUCROSE | 4 | 84 | 1473.74 | 3.18 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 84 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 84 | 560.55 | 2.78 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 84 | 243.32 | 2.45 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 84 | 365.32 | 2.61 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 84 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 84 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 84 | 1338.20 | 3.13 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 84 | * | * |
| SOIL+$^{13}$C SUCROSE | 1 | 98 | 27.66 | 1.83 |
| SOIL+$^{13}$C SUCROSE | 2 | 98 | * | * |
| SOIL+$^{13}$C SUCROSE | 3 | 98 | 1730.63 | 3.25 |

| | | | | |
|---|---|---|---|---|
| SOIL+$^{13}$C SUCROSE | 4 | 98 | 762.30 | 2.90 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 98 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 98 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 98 | 90.98 | 2.12 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 98 | 173.43 | 2.33 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 98 | 523.47 | 2.72 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 98 | 382.10 | 2.58 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 98 | 668.72 | 2.83 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 98 | 136.42 | 2.13 |
| SOIL+$^{13}$C SUCROSE | 1 | 112 | * | * |
| SOIL+$^{13}$C SUCROSE | 2 | 112 | 1239.02 | 3.11 |
| SOIL+$^{13}$C SUCROSE | 3 | 112 | 1924.74 | 3.29 |
| SOIL+$^{13}$C SUCROSE | 4 | 112 | 1270.21 | 3.12 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 112 | 982.79 | 3.01 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 112 | 266.45 | 2.49 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 112 | 287.64 | 2.52 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 112 | 471.19 | 2.71 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 112 | 1573.26 | 3.20 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 112 | 1412.95 | 3.15 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 112 | 1651.21 | 3.22 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 112 | 320.18 | 2.51 |
| SOIL+$^{13}$C SUCROSE | 1 | 126 | 581.63 | 2.79 |
| SOIL+$^{13}$C SUCROSE | 2 | 126 | * | * |
| SOIL+$^{13}$C SUCROSE | 3 | 126 | * | * |
| SOIL+$^{13}$C SUCROSE | 4 | 126 | 1210.26 | 3.10 |

| | | | | |
|---|---|---|---|---|
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 126 | 120.30 | 2.20 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 126 | 81.88 | 2.09 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 126 | 251.97 | 2.47 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 126 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 126 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 126 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 126 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 126 | 130.24 | 2.11 |
| SOIL+$^{13}$C SUCROSE | 1 | 140 | * | * |
| SOIL+$^{13}$C SUCROSE | 2 | 140 | * | * |
| SOIL+$^{13}$C SUCROSE | 3 | 140 | 863.05 | 2.96 |
| SOIL+$^{13}$C SUCROSE | 4 | 140 | 1400.75 | 3.16 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 140 | 325.83 | 2.56 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 140 | 60.03 | 2.00 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 140 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 140 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 140 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 140 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 140 | 518.18 | 2.71 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 140 | 40.53 | 1.61 |
| SOIL+$^{13}$C SUCROSE | 1 | 154 | * | * |
| SOIL+$^{13}$C SUCROSE | 2 | 154 | * | * |
| SOIL+$^{13}$C SUCROSE | 3 | 154 | * | * |
| SOIL+$^{13}$C SUCROSE | 4 | 154 | 400.51 | 2.64 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 154 | 32.20 | 1.86 |

| | | | | |
|---|---|---|---|---|
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 154 | 32.25 | 1.86 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 154 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 154 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 154 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 154 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 154 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 154 | * | * |
| SOIL+$^{13}$C SUCROSE | 1 | 168 | * | * |
| SOIL+$^{13}$C SUCROSE | 2 | 168 | 282.41 | 2.51 |
| SOIL+$^{13}$C SUCROSE | 3 | 168 | 566.23 | 2.78 |
| SOIL+$^{13}$C SUCROSE | 4 | 168 | 256.21 | 2.47 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 1 | 168 | 214.08 | 2.40 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 2 | 168 | 30.26 | 1.85 |
| SOIL+ SOOT+$^{13}$C SUCROSE | 3 | 168 | * | * |
| SOIL+ SOOT+$^{13}$C SUCROSE | 4 | 168 | 15.49 | 1.74 |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 1 | 168 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 2 | 168 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 3 | 168 | * | * |
| SOIL+ BIOCHAR+$^{13}$C SUCROSE | 4 | 168 | * | * |

**Table S2** Mean cumulative loss of $^{13}C$ organic carbon ± standard error of the mean (SE)

| TREATMENTS | DAYS | $A_R$ (AVERAGE ATOM % OF THE $^{13}CO_2$ RESPIRED) | C*L* (CUMULATIVE PERCENT $CO_2$ LOST) | SE |
|---|---|---|---|---|
| SOIL+ $^{13}C$ SUCROSE | 0 | 2.09 | 1.00 | 0.02 |
| SOIL+ $^{13}C$ SUCROSE | 1 | 1.92 | 1.82 | 0.05 |
| SOIL+ $^{13}C$ SUCROSE | 7 | 6.22 | 4.38 | 0.22 |
| SOIL+ $^{13}C$ SUCROSE | 14 | 6.33 | 9.62 | 0.26 |
| SOIL+ $^{13}C$ SUCROSE | 21 | 6.15 | 14.67 | 0.18 |
| SOIL+ $^{13}C$ SUCROSE | 28 | 5.83 | 17.04 | 0.26 |
| SOIL+ $^{13}C$ SUCROSE | 35 | 5.48 | 21.44 | 0.27 |
| SOIL+ $^{13}C$ SUCROSE | 42 | 5.20 | 22.46 | 0.17 |
| SOIL+ $^{13}C$ SUCROSE | 49 | 3.89 | 24.56 | 0.14 |
| SOIL+ $^{13}C$ SUCROSE | 56 | 3.59 | 27.05 | 0.10 |
| SOIL+ $^{13}C$ SUCROSE | 70 | 2.80 | 28.33 | 0.09 |
| SOIL+ $^{13}C$ SUCROSE | 84 | 2.02 | 29.03 | 0.12 |
| SOIL+ $^{13}C$ SUCROSE | 98 | 2.71 | 30.24 | 0.11 |
| SOIL+ $^{13}C$ SUCROSE | 112 | 2.08 | 30.73 | 0.08 |
| SOIL+ $^{13}C$ SUCROSE | 126 | 2.34 | 31.36 | 0.09 |
| SOIL+ $^{13}C$ SUCROSE | 140 | 1.55 | 31.47 | 0.06 |
| SOIL+ $^{13}C$ SUCROSE | 154 | 1.51 | **31.79** | 0.03 |
| SOIL+SOOT+ $^{13}C$ SUCROSE | 0 | 3.67 | 1.29 | 0.02 |
| SOIL+SOOT+ $^{13}C$ SUCROSE | 1 | 6.52 | 5.36 | 0.70 |
| SOIL+SOOT+ $^{13}C$ SUCROSE | 7 | 3.60 | 7.24 | 0.71 |
| SOIL+SOOT+ $^{13}C$ SUCROSE | 14 | 3.48 | 8.43 | 0.15 |

| | | | | |
|---|---|---|---|---|
| SOIL+SOOT+ $^{13}$C SUCROSE | 21 | 3.47 | 10.21 | 0.08 |
| SOIL+SOOT+ $^{13}$C SUCROSE | 28 | 3.24 | 11.29 | 0.13 |
| SOIL+SOOT+ $^{13}$C SUCROSE | 35 | 2.12 | 11.54 | 0.13 |
| SOIL+SOOT+ $^{13}$C SUCROSE | 42 | 2.11 | 12.05 | 0.10 |
| SOIL+SOOT+ $^{13}$C SUCROSE | 49 | 1.70 | 12.50 | 0.06 |
| SOIL+SOOT+ $^{13}$C SUCROSE | 56 | 1.99 | 12.95 | 0.03 |
| SOIL+SOOT+ $^{13}$C SUCROSE | 70 | 1.54 | 13.29 | 0.02 |
| SOIL+SOOT+ $^{13}$C SUCROSE | 84 | 1.26 | 13.37 | 0.02 |
| SOIL+SOOT+ $^{13}$C SUCROSE | 98 | 1.66 | 13.94 | 0.04 |
| SOIL+SOOT+ $^{13}$C SUCROSE | 112 | 1.23 | 14.07 | 0.04 |
| SOIL+SOOT+ $^{13}$C SUCROSE | 126 | 1.32 | 14.19 | 0.03 |
| SOIL+SOOT+ $^{13}$C SUCROSE | 140 | 1.15 | 14.22 | 0.03 |
| SOIL+SOOT+ $^{13}$C SUCROSE | 154 | 1.21 | **14.30** | 0.01 |

**Table S3** Evolution of δ $^{13}$C from soil and soil with added $^{13}$C labelled soot

| **TREATMENTS** | **REPLICATE** | **DAYS** | **Δ $^{13}$C** |
|---|---|---|---|
| SOIL | 1 | 0 | * |
| SOIL | 2 | 0 | -6.55 |
| SOIL | 3 | 0 | -15.34 |
| SOIL | 4 | 0 | -13.62 |
| SOIL + $^{13}$C SOOT | 1 | 0 | * |
| SOIL + $^{13}$C SOOT | 2 | 0 | -13.06 |
| SOIL + $^{13}$C SOOT | 3 | 0 | -12.61 |
| SOIL + $^{13}$C SOOT | 4 | 0 | -12.87 |

| | | | |
|---|---|---|---|
| SOIL | 1 | 1 | * |
| SOIL | 2 | 1 | -18.28 |
| SOIL | 3 | 1 | * |
| SOIL | 4 | 1 | -16.09 |
| SOIL + $^{13}$C SOOT | 1 | 1 | -5.46 |
| SOIL + $^{13}$C SOOT | 2 | 1 | -7.50 |
| SOIL + $^{13}$C SOOT | 3 | 1 | -7.40 |
| SOIL + $^{13}$C SOOT | 4 | 1 | -6.41 |
| SOIL | 1 | 7 | -12.80 |
| SOIL | 2 | 7 | -19.66 |
| SOIL | 3 | 7 | -14.98 |
| SOIL | 4 | 7 | -13.84 |
| SOIL + $^{13}$C SOOT | 1 | 7 | -4.72 |
| SOIL + $^{13}$C SOOT | 2 | 7 | -7.24 |
| SOIL + $^{13}$C SOOT | 3 | 7 | -7.86 |
| SOIL + $^{13}$C SOOT | 4 | 7 | * |
| SOIL | 1 | 14 | -15.69 |
| SOIL | 2 | 14 | -19.64 |
| SOIL | 3 | 14 | -16.73 |
| SOIL | 4 | 14 | -16.45 |
| SOIL + $^{13}$C SOOT | 1 | 14 | * |
| SOIL + $^{13}$C SOOT | 2 | 14 | * |
| SOIL + $^{13}$C SOOT | 3 | 14 | -9.07 |
| SOIL + $^{13}$C SOOT | 4 | 14 | -5.57 |
| SOIL | 1 | 21 | -15.10 |

| | | | |
|---|---|---|---|
| SOIL | 2 | 21 | -21.20 |
| SOIL | 3 | 21 | * |
| SOIL | 4 | 21 | * |
| SOIL + $^{13}$C SOOT | 1 | 21 | -4.00 |
| SOIL + $^{13}$C SOOT | 2 | 21 | -5.39 |
| SOIL + $^{13}$C SOOT | 3 | 21 | -9.94 |
| SOIL + $^{13}$C SOOT | 4 | 21 | 3.47 |
| SOIL | 1 | 28 | -15.34 |
| SOIL | 2 | 28 | * |
| SOIL | 3 | 28 | * |
| SOIL | 4 | 28 | * |
| SOIL + $^{13}$C SOOT | 1 | 28 | -4.84 |
| SOIL + $^{13}$C SOOT | 2 | 28 | -9.76 |
| SOIL + $^{13}$C SOOT | 3 | 28 | -10.73 |
| SOIL + $^{13}$C SOOT | 4 | 28 | * |
| SOIL | 1 | 35 | -15.48 |
| SOIL | 2 | 35 | * |
| SOIL | 3 | 35 | * |
| SOIL | 4 | 35 | * |
| SOIL + $^{13}$C SOOT | 1 | 35 | -3.55 |
| SOIL + $^{13}$C SOOT | 2 | 35 | -17.26 |
| SOIL + $^{13}$C SOOT | 3 | 35 | -9.97 |
| SOIL + $^{13}$C SOOT | 4 | 35 | -7.87 |
| SOIL | 1 | 42 | -15.35 |
| SOIL | 2 | 42 | * |

| | | | |
|---|---|---|---|
| SOIL | 3 | 42 | * |
| SOIL | 4 | 42 | * |
| SOIL + $^{13}C$ SOOT | 1 | 42 | -5.19 |
| SOIL + $^{13}C$ SOOT | 2 | 42 | -7.23 |
| SOIL + $^{13}C$ SOOT | 3 | 42 | -9.75 |
| SOIL + $^{13}C$ SOOT | 4 | 42 | -6.51 |
| SOIL | 1 | 49 | -14.91 |
| SOIL | 2 | 49 | -21.85 |
| SOIL | 3 | 49 | -18.26 |
| SOIL | 4 | 49 | -15.66 |
| SOIL + $^{13}C$ SOOT | 1 | 49 | * |
| SOIL + $^{13}C$ SOOT | 2 | 49 | -6.27 |
| SOIL + $^{13}C$ SOOT | 3 | 49 | -9.32 |
| SOIL + $^{13}C$ SOOT | 4 | 49 | -3.51 |
| SOIL | 1 | 56 | -13.96 |
| SOIL | 2 | 56 | -20.73 |
| SOIL | 3 | 56 | -17.50 |
| SOIL | 4 | 56 | -14.58 |
| SOIL + $^{13}C$ SOOT | 1 | 56 | * |
| SOIL + $^{13}C$ SOOT | 2 | 56 | -6.23 |
| SOIL + $^{13}C$ SOOT | 3 | 56 | -2.42 |
| SOIL + $^{13}C$ SOOT | 4 | 56 | -7.72 |
| SOIL | 1 | 70 | -13.85 |
| SOIL | 2 | 70 | -20.14 |
| SOIL | 3 | 70 | * |

| | | | |
|---|---|---|---|
| SOIL | 4 | 70 | * |
| SOIL + $^{13}C$ SOOT | 1 | 70 | -6.03 |
| SOIL + $^{13}C$ SOOT | 2 | 70 | * |
| SOIL + $^{13}C$ SOOT | 3 | 70 | * |
| SOIL + $^{13}C$ SOOT | 4 | 70 | -8.76 |
| SOIL | 1 | 84 | -18.75 |
| SOIL | 2 | 84 | -13.30 |
| SOIL | 3 | 84 | -16.29 |
| SOIL | 4 | 84 | -16.62 |
| SOIL + $^{13}C$ SOOT | 1 | 84 | * |
| SOIL + $^{13}C$ SOOT | 2 | 84 | * |
| SOIL + $^{13}C$ SOOT | 3 | 84 | -9.51 |
| SOIL + $^{13}C$ SOOT | 4 | 84 | -9.32 |
| SOIL | 1 | 98 | -13.20 |
| SOIL | 2 | 98 | -18.47 |
| SOIL | 3 | 98 | -16.50 |
| SOIL | 4 | 98 | -16.39 |
| SOIL + $^{13}C$ SOOT | 1 | 98 | -9.23 |
| SOIL + $^{13}C$ SOOT | 2 | 98 | -8.61 |
| SOIL + $^{13}C$ SOOT | 3 | 98 | -11.09 |
| SOIL + $^{13}C$ SOOT | 4 | 98 | -6.70 |
| SOIL | 1 | 112 | -14.11 |
| SOIL | 2 | 112 | -18.74 |
| SOIL | 3 | 112 | -16.46 |
| SOIL | 4 | 112 | * |

| | | | |
|---|---|---|---|
| SOIL + $^{13}C$ SOOT | 1 | 112 | * |
| SOIL + $^{13}C$ SOOT | 2 | 112 | * |
| SOIL + $^{13}C$ SOOT | 3 | 112 | -10.87 |
| SOIL + $^{13}C$ SOOT | 4 | 112 | -8.69 |
| SOIL | 1 | 126 | -14.33 |
| SOIL | 2 | 126 | -19.23 |
| SOIL | 3 | 126 | -15.92 |
| SOIL | 4 | 126 | -16.75 |
| SOIL + $^{13}C$ SOOT | 1 | 126 | -10.14 |
| SOIL + $^{13}C$ SOOT | 2 | 126 | -11.29 |
| SOIL + $^{13}C$ SOOT | 3 | 126 | -11.86 |
| SOIL + $^{13}C$ SOOT | 4 | 126 | -9.28 |
| SOIL | 1 | 140 | -13.66 |
| SOIL | 2 | 140 | * |
| SOIL | 3 | 140 | -16.24 |
| SOIL | 4 | 140 | -15.85 |
| SOIL + $^{13}C$ SOOT | 1 | 140 | * |
| SOIL + $^{13}C$ SOOT | 2 | 140 | -10.95 |
| SOIL + $^{13}C$ SOOT | 3 | 140 | -11.37 |
| SOIL + $^{13}C$ SOOT | 4 | 140 | -9.07 |
| SOIL | 1 | 154 | * |
| SOIL | 2 | 154 | * |
| SOIL | 3 | 154 | * |
| SOIL | 4 | 154 | -16.15 |

| | | | |
|---|---|---|---|
| SOIL + $^{13}C$ SOOT | 1 | 154 | -10.62 |
| SOIL + $^{13}C$ SOOT | 2 | 154 | -10.41 |
| SOIL + $^{13}C$ SOOT | 3 | 154 | -12.83 |
| SOIL + $^{13}C$ SOOT | 4 | 154 | * |
| SOIL | 1 | 168 | -13.01 |
| SOIL | 2 | 168 | -17.34 |
| SOIL | 3 | 168 | * |
| SOIL | 4 | 168 | -15.33 |
| SOIL + $^{13}C$ SOOT | 1 | 168 | * |
| SOIL + $^{13}C$ SOOT | 2 | 168 | -11.66 |
| SOIL + $^{13}C$ SOOT | 3 | 168 | -12.44 |
| SOIL + $^{13}C$ SOOT | 4 | 168 | * |

**Table S4** Cumulative loss of $^{13}C$ soot supplied from soil for the duration of the experiment ± standard error of the mean (SE)

| TREATMENTS | DAYS | $A_R$ (AVERAGE ATOM % OF THE $^{13}CO_2$ RESPIRED) | C*L* (CUMULATIVE PERCENT $CO_2$ LOST) | SE |
|---|---|---|---|---|
| SOIL+ $^{13}C$ SOOT | 0 | 1.0971 | 0.005 | 2.93E-05 |
| SOIL+ $^{13}C$ SOOT | 1 | 1.1039 | 0.016 | 1.24E-04 |
| SOIL+ $^{13}C$ SOOT | 7 | 1.1040 | 0.027 | 2.41E-04 |
| SOIL+ $^{13}C$ SOOT | 14 | 1.1032 | 0.038 | 3.79E-04 |
| SOIL+ $^{13}C$ SOOT | 21 | 1.1069 | 0.052 | 7.78E-04 |
| SOIL+ $^{13}C$ SOOT | 28 | 1.1020 | 0.062 | 8.18E-04 |
| SOIL+ $^{13}C$ SOOT | 35 | 1.1006 | 0.070 | 8.36E-04 |
| SOIL+ $^{13}C$ SOOT | 42 | 1.1034 | 0.081 | 7.72E-04 |
| SOIL+ $^{13}C$ SOOT | 49 | 1.1042 | 0.092 | 4.45E-04 |
| SOIL+ $^{13}C$ SOOT | 56 | 1.1052 | 0.105 | 5.10E-04 |
| SOIL+ $^{13}C$ SOOT | 70 | 1.1031 | 0.116 | 4.28E-04 |
| SOIL+ $^{13}C$ SOOT | 84 | 1.1009 | 0.124 | 2.47E-04 |
| SOIL+ $^{13}C$ SOOT | 98 | 1.1014 | 0.133 | 2.32E-04 |
| SOIL+ $^{13}C$ SOOT | 112 | 1.1005 | 0.141 | 3.04E-04 |
| SOIL+ $^{13}C$ SOOT | 126 | 1.0995 | 0.148 | 2.46E-04 |
| SOIL+ $^{13}C$ SOOT | 140 | 1.0997 | 0.155 | 2.15E-04 |
| SOIL+ $^{13}C$ SOOT | 154 | 1.0988 | 0.161 | 2.32E-04 |
| SOIL+ $^{13}C$ SOOT | 168 | 1.0980 | **0.167** | 1.85E-04 |

# CHAPTER 3

**Table S1** Biochar properties

| | IN THE DRY MATTER | IN FRESH SAMPLE |
|---|---|---|
| **BULK DENSITY (G/L)** | | 440 |
| **OVEN DRY MATTER (%)** | | 91.1 |
| **MOISTURE (%)** | | 8.1 |
| **ORGANIC MATTER (% W/W)** | 86.6 | |
| **ORGANIC CARBON (50.3 %W/W)** | 50.3 | |
| **PH** | | 9.2 |
| **ELECTRICAL CONDUCTIVITY (MS/M)** | | 42 |
| **TOTAL NITROGEN (N) (MG/KG)** | 10200 | |
| **TOTAL CARBON (C) (MG/KG)** | 646000 | |
| **C:N RATIO** | 63:1 | |
| **TOTAL PHOSPHORUS (MG/KG)** | 281 | |

**Table S2** Results of three-way ANOVA on the influence of biochar application, vegetation cover and soil depth on soil total organic carbon and nitrogen concentration.

| | **Factor** | **F (d.f.)** | **p value** |
|---|---|---|---|
| Soil TOC (mg $g^{-1}$) | Vegetation cover | F (2, 63) = 0.90 | p = 0.91 |
| | Biochar | F (1, 20) = 0.21 | p = 0.88 |
| | Depth | F (1, 63) = 0.50 | p = 0.48 |
| | Depth: Vegetation cover | F (2, 63) = 0.63 | p = 0.54 |
| | Depth: Biochar | F (1, 63) = 0.02 | p = 0.89 |
| | Biochar: Vegetation cover | F (2, 63) = 1.34 | p = 0.27 |
| Soil N (mg $g^{-1}$) | Vegetation cover | F (2, 63) = 1.01 | p = 0.37 |
| | Biochar | F (1, 20) = 0.12 | p = 0.73 |
| | Depth | F (1, 63) = 0.08 | p = 0.77 |
| | Depth: Vegetation cover | F (2, 63) = 0.13 | p = 0.88 |
| | Depth: Biochar | F (1, 63) = 0.21 | p = 0.65 |
| | Biochar: Vegetation cover | F (2, 63) = 0.37 | p = 0.69 |

**Table S3** Results of three-way ANOVA on the influence of biochar application, vegetation cover and soil depth on soil bulk density.

| | **Factor** | **F (d.f.)** | **p value** |
|---|---|---|---|
| **Soil BD (g $cm^{-3}$)** | Vegetation cover | F (2, 92) = 2.99 | p = 0.06 |
| | Biochar | F (1, 92) = 1.76 | p = 0.18 |
| | Depth | F (1,92) = 1.34 | p = 0.25 |
| | Depth: Vegetation cover | F (2, 92) = 2.08 | p = 0.13 |
| | Depth: Biochar | F (1, 92) = 0.87 | p = 0.35 |
| | Biochar: Vegetation cover | F (2, 92) = 2.31 | p = 0.10 |

**Table S4** Results of unpaired t-test on the influence of biochar application on grass and SRC willow TOC and N concentrations.

| | |
|---|---|
| **Grassland TOC (mg $g^{-1}$)** | t (14) = 2.14; p = 0.05 |
| **SRC willow TOC (mg $g^{-1}$)** | t (14) = 1.51; p = 0.15 |
| **Grassland N (mg $g^{-1}$)** | t (14) = 0.78; p = 0.45 |
| **SRC willow N (mg $g^{-1}$)** | t (14) = 1.01; p = 0.33 |

**Table S5** Results of one-way ANOVA on the influence of biochar application on vegetables TOC and N concentrations.

| | |
|---|---|
| **Vegetables TOC (mg $g^{-1}$)** | F (2, 22) = 1.23; p = 0.31 |
| **Vegetables N (mg $g^{-1}$)** | F (2, 22) = 0.12; p = 0.89 |

# CHAPTER 4

## CONTENT



**Table S1** Limits of detection (LOD) for ICP-MS of the bioavailable heavy metal and metalloid concentrations investigated. Values are expressed in mg kg-1 soil dry weight.

| Element | As | Cd | Cr | Cu | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|
| **LOD** | 0.00076 | 0.000943 | 0.075292 | 0.144926 | 0.045747 | 0.017267 | 4.064027 |

**Table S2** Descriptive statistics for the soil properties investigated across UK urban horticultural soils in ten British cities. Median, mean, standard deviation (SD) and range of soil pH; % of sand, silt, and clay particles; soil total organic carbon concentration (TOC); soil organic concentration (OC); soil black carbon concentration (BC) and BC/TOC ratio

| | n | Median | Mean | SD | Range |
|---|---|---|---|---|---|
| **pH** | 367 | 6.48 | 6.4 | 0.39 | 4.84-7.21 |
| **Sand (%)** | 80 | 38.61 | 38.13 | 8.85 | 17.12-54.08 |
| **Silt (%)** | 80 | 50.40 | 51.96 | 7.79 | 35.45-68.82 |
| **Clay (%)** | 80 | 9.99 | 9.09 | 3.39 | 4.37-19.49 |
| **TOC (mg $g^{-1}$)** | 357 | 60.50 | 71.22 | 39.86 | 15.10-221.7 |
| **OC (mg $g^{-1}$)** | 357 | 45 | 52.01 | 30.78 | 6.05-211.9 |
| **BC (mg $g^{-1}$)** | 357 | 12.35 | 19.30 | 20.11 | 1.34-131.1 |
| **BC/TOC (%)** | 357 | 21.6 | 25.68 | 17.28 | 2.27-89.73 |

**Table S3** Samples number for soil total organic carbon concentration (TOC); soil organic concentration (OC); soil black carbon concentration (BC) and BC/TOC ratio across UK urban horticultural soils in ten British cities.

| | TOC | OC | BC | BC/TOC |
|---|---|---|---|---|
| **Edinburgh** | 37 | 38 | 37 | 37 |
| **Newcastle** | 34 | 33 | 34 | 34 |
| **Leeds** | 40 | 40 | 40 | 40 |
| **Liverpool** | 40 | 40 | 40 | 40 |
| **Nottingham** | 29 | 29 | 28 | 28 |
| **Leicester** | 37 | 37 | 37 | 37 |
| **Milton Keynes** | 37 | 37 | 37 | 37 |
| **Cardiff** | 34 | 34 | 32 | 32 |
| **Bristol** | 36 | 36 | 32 | 32 |
| **Southampton** | 33 | 33 | 31 | 31 |

**Table S4** Descriptive statistics for soil total heavy metal and metalloid concentrations across UK urban horticultural soils in ten British cities. Values are expressed in mg $kg^{-1}$ soil dry weight.

| | n | As | | Cd | | Cr | | Cu | | Ni | | Pb | | Zn | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Median | Range | Median | Range | Median | Range | Median | Range | Median | Range | Median | Range | Median | Range |
| Edinburgh | 40 | 6.93 | 3.66-33.21 | 0.54 | 0.30-2.4 | 24.13 | 13.24-38.13 | 56.65 | 33.30-102.9 | 29.70 | 16.10-42.58 | 179 | 83.44-1229 | 249.6 | 138.3-996.0 |
| Newcastle | 34 | 16.86 | 6.68-27.85 | 0 .76 | 0.43-1.1 | 28.04 | 14.94-45.31 | 81.33 | 25.40-245.9 | 26.49 | 15.94-40.62 | 303.4 | 82.00-500.9 | 349.3 | 185.20-629.3 |
| Leeds | 40 | 30.00 | 16.00 - 79.49 | 0.76 | 0.24-2.5 | 58.42 | 29.90-163.4 | 91.82 | 32.69-371.8 | 28.03 | 18.40-39.79 | 197.4 | 103.9-1682 | 245.2 | 138.6-502.8 |
| Liverpool | 40 | 15.25 | 9.14-68.88 | 0.75 | 0.19-2.2 | 26.25 | 11.90-36.51 | 62.87 | 26.74-165.6 | 20.88 | 10.08-1020 | 192.1 | 75.60-514.20 | 245.2 | 93.87-497.1 |
| Nottingham | 30 | 15.39 | 11.90 - 48.00 | 0.98 | 0.54-4.6 | 34.71 | 20.56-67.90 | 71.79 | 41.85-127.1 | 33.71 | 21.17-57.77 | 266.1 | 124.4-1019 | 363.3 | 234.9-861.9 |
| Leicester | 36 | 15.65 | 10.11-23.35 | 0.58 | 0.25-4.8 | 32.71 | 21.34-59.81 | 54.68 | 26.94-110.2 | 25.91 | 17.26-49.65 | 150.9 | 75.87-453.5 | 249.9 | 127.4-614.0 |
| Milton Keynes | 37 | 17.41 | 11.01-36.84 | 0.49 | 0.21-6.5 | 34.10 | 18.58-71.89 | 29.80 | 18.55-227.8 | 25.73 | 17.85-39.61 | 75.98 | 28.78-3943 | 132.9 | 88.60-412.5 |
| Cardiff | 38 | 14.00 | 5.23-63.00 | 0.83 | 0.15-4.3 | 28.18 | 11.22-143.4 | 58.63 | 9.66-216.4 | 24.10 | 7.27-70.68 | 193.3 | 29.95-2149 | 268.1 | 46.16-1213.0 |
| Bristol | 36 | 15.88 | 9.75-31.54 | 0.91 | 0.46-3.3 | 17.93 | 9.36-36.73 | 41.90 | 14.05-751.5 | 16.05 | 5.88-40.48 | 185.0 | 87.76-1211 | 253.4 | 114.5-960.0 |
| Southampton | 37 | 10.39 | 4.62-16.04 | 0.40 | 0.14-0.80 | 24.44 | 12.85-93.14 | 36.78 | 18.78-86.13 | 10.93 | 4.50-21.60 | 132.3 | 34.34-488.0 | 181.1 | 59.71-484.5 |
| | | | | | | | | | | | | | | | |
| National | 391 | 15.14 | 3.67-79.49 | 6.495 | 0.13-6.49 | 28.33 | 9.36-143.4 | 56.85 | 9.66-751.5 | 25.00 | 4.50-1020 | 182.6 | 28.78-3943 | 251.0 | 46.16-1213.0 |

**Table S5** Isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) of the total soil Pb concentrations across UK urban horticultural soils in ten British cities.

| | **Isotope ratio ($^{206}Pb/^{207}Pb$** | **Isotope ratio ($^{208}Pb/^{207}Pb$)** | **% Petrol-derived Pb** | **% Coal/Ore-derived Pb** |
|---|---|---|---|---|
| **Bristol 1** | 1.15805655 | 2.441 | 22.17 | 77.83 |
| **Bristol 2** | 1.16318697 | 2.447 | 17.79 | 82.21 |
| **Bristol 3** | 1.170008316 | 2.448 | 11.96 | 88.04 |
| **Bristol 4** | 1.135899704 | 2.414 | 41.11 | 58.89 |
| **Cardiff 1** | 1.142180987 | 2.423 | 35.74 | 64.26 |
| **Cardiff 2** | 1.159504801 | | | |
| **Cardiff 3** | 1.137477008 | | | |
| **Cardiff 4** | 1.130426656 | 2.411 | 45.79 | 54.21 |
| **Edinburgh 1** | 1.142236785 | 2.426 | 35.70 | 64.30 |
| **Edinburgh 2** | 1.145403851 | 2.425 | 32.99 | 67.01 |
| **Edinburgh 3** | 1.140037498 | | | |
| **Edinburgh 4** | 1.159335846 | 2.443 | 21.08 | 78.92 |
| **Leeds 1** | 1.153296401 | 2.434 | 26.24 | 73.76 |
| **Leeds 2** | 1.163868411 | 2.451 | 17.21 | 82.79 |
| **Leeds 3** | 1.162796474 | 2.448 | 18.12 | 81.88 |
| **Leeds 4** | 1.133691176 | 2.416 | 43.00 | 57.00 |
| **Leicester 1** | 1.161332897 | 2.444 | 19.37 | 80.63 |
| **Leicester 2** | 1.131756911 | 2.412 | 44.65 | 55.35 |
| **Leicester 3** | 1.133246592 | 2.409 | 43.38 | 56.62 |
| **Leicester 4** | 1.145558011 | 2.431 | 32.86 | 67.14 |
| **Liverpool 1** | 1.12178793 | 2.404 | 53.17 | 46.83 |
| **Liverpool 2** | 1.144181299 | | | |
| **Liverpool 3** | 1.152433899 | 2.431 | 26.98 | 73.02 |
| **Liverpool 4** | 1.146629221 | 2.426 | 31.94 | 68.06 |
| **Milton Keynes 1** | 1.173312965 | 2.456 | 9.13 | 90.87 |
| **Milton Keynes 2** | 1.144179407 | 2.423 | 34.03 | 65.97 |
| **Milton Keynes 3** | 1.123306499 | 2.405 | 51.87 | 48.13 |
| **Milton Keynes 4** | 1.139122538 | 2.416 | 38.36 | 61.64 |
| **Nottingham 1** | 1.160873666 | 2.442 | 19.77 | 80.23 |
| **Nottingham 2** | 1.154341566 | 2.430 | 25.35 | 74.65 |
| **Nottingham 3** | 1.142645051 | 2.425 | 35.35 | 64.65 |
| **Newcastle 1** | 1.136295933 | 2.414 | 40.77 | 59.23 |
| **Newcastle 2** | 1.154339442 | 2.431 | 25.35 | 74.65 |
| **Newcastle 3** | 1.142315614 | 2.424 | 35.63 | 64.37 |
| **Newcastle 4** | 1.149078947 | 2.433 | 29.85 | 70.15 |
| **Southampton 1** | 1.139192903 | 2.416 | 38.30 | 61.70 |
| **Southampton 2** | 1.150017616 | | | |
| **Southampton 3** | 1.149109909 | 2.434 | 29.82 | 70.18 |
| **Petrol** | 1.067 | 2.340 | | |
| **Pennine Ore** | 1.182 | 2.485 | | |
| **England/Wales coal** | 1.184 | 2.461 | | |

**Table S6** Descriptive statistics for the soil bioavailable heavy metal and metalloid concentrations across UK urban horticultural soils in ten British cities. Values are expressed in mg $kg^{-1}$ soil dry weight.

| | As | | Cd | | Cr | | Cu | | Ni | | Pb | | Zn | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Median | Range | Median | Range | Median | Range | Median | Range | Median | Range | Median | Range | Median | Range |
| Edinburgh | 0.018 | 0.008-0.099 | 0.007 | 0.001-0.029 | | | 0.18 | 0.14-0.24 | 0.062 | 0.045-0.14 | 0.026 | 0.018-0.046 | 5.29 | 4.41-6.77 |
| Newcastle | 0.058 | 0.014-0.11 | 0.003 | 0.002-0.013 | 0.08 | 0.08-0.40 | 0.19 | 0.14-0.59 | 0.055 | 0.042-0.23 | 0.021 | 0.017-0.051 | 4.30 | 4.06-4.99 |
| Leeds | 0.047 | 0.005-0.14 | 0.003 | 0.001-0.025 | | | 0.17 | 0.14-0.66 | 0.051 | 0.046-0.073 | 0.022 | 0.017-0.063 | 5.37 | 4.95-7.73 |
| Liverpool | 0.041 | 0.012-0.093 | 0.004 | 0.001-0.030 | | | 0.18 | 0.10-0.98 | 0.061 | 0.061-0.061 | 0.020 | 0.017-0.13 | 4.09 | 4.08-18.9 |
| Nottingham | 0.048 | 0.022-0.16 | 0.006 | 0.001-0.027 | 0.15 | 0.15-0.15 | 0.20 | 0.14-2.7 | 0.084 | 0.061-0.11 | 0.025 | 0.017-0.19 | 4.50 | 3.45-18.1 |
| Leicester | 0.039 | 0.015-0.21 | 0.004 | 0.001-0.035 | 0.34 | 0.30-2.7 | 0.15 | 0.12-0.19 | 0.022 | 0.056-1.60 | 0.023 | 0.017-0.60 | 4.51 | 4.00-11.2 |
| Milton Keynes | 0.022 | 0.004-0.078 | 0.004 | 0.001-0.027 | 0.34 | 0.31-2.0 | 0.26 | 0.14-0.56 | 0.23 | 0.29-1.10 | 0.020 | 0.017-0.29 | 4.30 | 4.05-9.15 |
| Cardiff | 0.056 | 0.018-0.27 | 0.006 | 0.003-0.027 | | | 0.21 | 0.14-0.36 | 0.064 | 0.044-0.10 | 0.032 | 0.019-0.14 | 7.01 | 7.01-7.01 |
| Bristol | 0.032 | 0.005-0.11 | 0.006 | 0.001-0.028 | 0.08 | 0.07-0.10 | 0.17 | 0.14-0.30 | 0.060 | 0.046-0.18 | 0.036 | 0.018-0.11 | 4.89 | 4.16-6.19 |
| Southampton | 0.021 | 0.007-0.045 | 0.004 | 0.001-0.015 | 0.08 | 0.07-0.88 | 0.15 | 0.14-0.26 | 0.057 | 0.042-0.56 | 0.019 | 0.018-0.037 | 5.18 | 4.69-5.68 |
| | | | | | | | | | | | | | | |
| National | 0.036 | 0.004-0.27 | 0.005 | 0.001-0.035 | 0.10 | 0.07-2.7 | 0.18 | 0.10-2.7 | 0.068 | 0.029-1.60 | 0.023 | 0.017-0.29 | 4.73 | 3.45-18.9 |

**Table S7** Samples number for the soil bioavailable heavy metal and metalloid concentrations across UK urban horticultural soils in ten British cities.

| | As | Cd | Cr | Cu | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|
| **Edinburgh** | 40 | 40 | | 2 | 20 | 14 | 7 |
| **Newcastle** | 40 | 40 | 3 | 22 | 13 | 17 | 8 |
| **Leeds** | 40 | 38 | | 12 | 3 | 36 | 19 |
| **Liverpool** | 40 | 40 | | 16 | 1 | 17 | 5 |
| **Nottingham** | 30 | 29 | 1 | 22 | 2 | 24 | 12 |
| **Leicester** | 40 | 40 | 6 | 18 | 24 | 29 | 22 |
| **Milton Keynes** | 40 | 40 | 20 | 8 | 28 | 24 | 13 |
| **Cardiff** | 40 | 40 | | 29 | 16 | 25 | 1 |
| **Bristol** | 40 | 39 | 15 | 3 | 24 | 14 | 3 |
| **Southampton** | 20 | 20 | 20 | 15 | 20 | 4 | 2 |
| | | | | | | | |
| **National** | 370 | 366 | 65 | 147 | 151 | 190 | 85 |

# CHAPTER 5

## CONTENT

**Table S1** Population size and climatic conditions of the UK cities investigated

| Case study urban areas | 2011 UK population census | Average annual rainfall (mm) [a] | Average minimum temperature (°C) [a] | Average maximum Temperature (°C) [a] |
|---|---|---|---|---|
| Edinburgh | 476,626 | 72.3 | 5.6 | 10.8 |
| Leeds | 751,485 | 67.4 | 6.2 | 12.6 |
| Liverpool | 466,400 | 97.8 | 7.8 | 12.6 |
| Milton Keynes | 248,800 | 59 | 6.8 | 13.5 |
| Cardiff | 346,100 | 89.3 | 7.7 | 12.9 |

a Climate-Data.org, 2021

**Table S2** Food safety standard maximum levels of As, Cd and Pb (mg kg-1 FW) for six different food crop categories 5

| Food crop group | Maximum Levels | As | Cd | Pb |
|---|---|---|---|---|
| **Root/Tuber/Bulb** | EU[a] | | 0.1 | 0.1 |
| | CHN[b] | 0.5 | 0.1 | 0.2 |
| | Average | 0.5 | 0.1 | 0.15 |
| **Leafy** | EU[a] | | 0.2 | 0.3 |
| | CHN[b] | 0.5 | 0.2 | 0.3 |
| | Average | 0.5 | 0.2 | 0.3 |
| **Legume** | EU[a] | | 0.1 | 0.2 |
| | CHN[b] | 0.5 | 0.1 | 0.2 |
| | Average | 0.5 | 0.1 | 0.2 |
| **Cucurbit Fruiting** | EU[a] | | 0.05 | 0.1 |
| | CHN[b] | 0.5 | 0.05 | 0.1 |
| | Average | 0.5 | 0.05 | 0.1 |
| **Solanaceous Fruiting** | EU[a] | | 0.05 | 0.1 |
| | CHN[b] | 0.5 | 0.05 | 0.1 |
| | Average | 0.5 | 0.05 | 0.1 |
| **Fruits** | EU[a] | | 0.05 | 0.1 |
| | CHN[b] | 0.5 | 0.05 | 0.1 |
| | Average | 0.5 | 0.05 | 0.1 |

a China National Standards (GB2762-2012; GB1511999-1994; GB13106-1991)

b EU Commission Regulation (EC) No 1881/2006, 2006

**Table S3** Descriptive statistics (mg $kg^{-1}$; FW) of potentially toxic elements (As, Cd, Cu, Pb and Zn) in food crop edible parts grown on urban horticultural soils across five cities in the UK.

| Food crop groups | Food crop | | As | Cd | Cu | Pb | Zn |
|---|---|---|---|---|---|---|---|
| Root/Tuber/Bulb | Beetroot (n=5) | Median | 0.0028 | 0.0079 | 0.019 | 0.055 | 1 |
| | | Ranges | 0.0006-0.0094 | 0.002-0.017 | 0.0032-0.038 | 0.015-0.071 | 0.25-3.5 |
| | | Mean±SE | 0.0039±0.0021 | 0.0086±0.003 | 0.017±0.062 | 0.047±0.17 | 1.6±0.67 |
| | Onion (n=4) | Median | 0.0019 | 0.011 | 0.35 | 0.054 | 1.4 |
| | | Ranges | 0.0017-0.024 | 0.0026-0.025 | 0.17-1.5 | 0.014-0.095 | 0.38-12 |
| | | Mean±SE | 0.009±0.007 | 0.012±0.0054 | 0.59±0.31 | 0.054±0.041 | 3.9±2.8 |
| Leafy | Potato (n=10) | Median | 0.0022 | 0.0021 | 0.3 | 0.023 | 2.2 |
| | | Ranges | 0.0007-0.026 | 0.0008-0.0084 | 0.016-1.4 | 0.018-0.041 | 0.27-5.2 |
| | | Mean±SE | 0.0051±0.003 | 0.003±0.001 | 0.42±0.13 | 0.026±0.005 | 2.3±0.62 |
| | Cavolo Nero (n=2) | Median | 0.002 | 0.015 | 1.00 | 0.016 | 4.9 |
| | | Ranges | 0.0014-0.0026 | 0.015 | 0.19-1.9 | 0.013-0.019 | 4.9 |
| | | Mean±SE | 0.002±0.0006 | 0.015 | 1±0.83 | 0.016±0.003 | 4.9 |
| | Chard (n=4) | Median | 0.0015 | 0.011 | 0.25 | 0.073 | 2.3 |
| | | Ranges | 0.0005-0.023 | 0.0066-0.015 | 0.055-0.49 | 0.039-0.075 | 1.9-3.3 |
| | | Mean±SE | 0.0065±0.0053 | 0.0011±0.0025 | 0.026±0.092 | 0.062±0.012 | 2.4±0.3 |
| | Lettuce (n=6) | Median | 0.0024 | 0.005 | 0.12 | 0.056 | 1.9 |
| | | Ranges | 0.0005-0.0096 | 0.001-0.015 | 0.048-0.68 | 0.012-0.11 | 0.65-3.1 |
| | | Mean±SE | 0.0033±0.0016 | 0.0062±0.0024 | 0.23±0.1 | 0.06±0.024 | 1.9±0.39 |
| | Spinach (n=3) | Median | 0.0016 | 0.0047 | 0.18 | 0.048 | 3.6 |
| | | Ranges | 0.0013-0.0018 | 0.0045-0.021 | 0.12-0.29 | 0.015-0.082 | 2-6.2 |
| | | Mean±SE | 0.0016±0.0002 | 0.01±0.0056 | 0.2±0.051 | 0.048±0.033 | 4±1.2 |
| Legume | French Bean (n=3) | Median | 0.0023 | 0.025 | 0.91 | 0.02 | 5.2 |
| | | Ranges | 0.0009-0.023 | 0.002-0.047 | 0.21-3.2 | 0.02 | 2.6-13 |
| | | Mean±SE | 0.0086±0.007 | 0.025±0.023 | 1.4±0.89 | 0.02 | 7.1±3.3 |
| | Runner Bean (n=8) | Median | 0.0017 | 0.0034 | 0.3 | 0.017 | 2.6 |
| | | Ranges | 0.0007-0.47 | 0.0008-0.0084 | 0.16-0.82 | 0.008-0.075 | 0.023-3.2 |
| | | Mean±SE | 0.0083±0.0056 | 0.0038±0.0011 | 0.37±0.078 | 0.028±0.011 | 2.2±0.39 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Cucurbit Fruiting** | Courgette (n=11) | Median | 0.001 | 0.01 | 0.19 | 0.012 | 1.5 |
| | | Ranges | 0.0005-0.015 | 0.0008-0.052 | 0.051-0.62 | 0.005-0.022 | 0.14-2.9 |
| | | Mean±SE | 0.0034±0.0017 | 0.018±0.0085 | 0.28±0.064 | 0.012±0.002 | 1.4±0.25 |
| | Cucumber (n=3) | Median | 0.0099 | 0.0019 | 0.19 | 0.011 | 1.5 |
| | | Ranges | 0.0008-0.011 | 0.0014-0.0024 | 0.066-0.27 | 0.005-0.016 | 1.2-1.8 |
| | | Mean±SE | 0.0074±0.0033 | 00019±0.0005 | 0.18±0.06 | 0.011±0.006 | 1.5±0.32 |
| **Solanaceous Fruiting** | Tomato (n=10) | Median | 0.001 | 0.0045 | 0.26 | 0.008 | 1.2 |
| | | Ranges | 0.0005-0.004 | 0.0063-0.016 | 0.061-0.66 | 0.006-0.041 | 0.43-4.7 |
| | | Mean±SE | 0.0015±0.0005 | 0.0065±0.002 | 0.3±0.74 | 0.014±0.007 | 1.9±0.48 |
| **Fruits** | Apple (n=11) | Median | 0.0019 | 0.0025 | 0.49 | 0.009 | 1.5 |
| | | Ranges | 0.0007-0.008 | 0.0012-0.0058 | 0.1-0.96 | 0.008-0.046 | 0.3-3.8 |
| | | Mean±SE | 0.0026±0.0007 | 0.0031±0.0008 | 0.48±0.08 | 0.018±0.009 | 1.8±0.33 |
| | Currant (n=3) | Median | 0.0044 | 0.018 | 0.33 | 0.061 | 3.4 |
| | | Ranges | 0.0008-0.0086 | 0.0016-0.027 | 0.31-0.96 | 0.03-0.38 | 1.6-3.5 |
| | | Mean±SE | 0.0046±0.0022 | 0.015±0.0074 | 0.53±0.21 | 0.016±0.11 | 2.8±0.63 |
| | Pear (n=2) | Median | 0.01 | 0.0039 | 0.32 | 0.024 | 0.99 |
| | | Ranges | 0.0018-0.019 | 0.0012-0.0066 | 0.078-0.55 | 0.024 | 0.52-1.5 |
| | | Mean±SE | 0.01±0.0085 | 0.0039±0.0027 | 0.32±0.24 | 0.024 | 0.99±0.48 |
| | Raspberry (n=14) | Median | 0.0026 | 0.0092 | 0.58 | 0.018 | 2.4 |
| | | Ranges | 0.0011-0.04 | 0.0024-0.056 | 0.1-2.1 | 0.007-0.057 | 0.37-11 |
| | | Mean±SE | 0.0076±0.0038 | 0.014±0.0045 | 0.67±0.12 | 0.023±0.005 | 3.2±0.78 |
| | Rhubarb (n=24) | Median | 0.0013 | 0.0072 | 0.15 | 0.015 | 1.2 |
| | | Ranges | 0.0005-0.0091 | 0.001-0.032 | 0.02-0.95 | 0.005-0.088 | 0.24-21 |
| | | Mean±SE | 0.023±0.0005 | 0.0091±0.0018 | 0.25±0.051 | 0.022±0.005 | 2.8±0.91 |
| | Strawberry (n=3) | Median | 0.0041 | 0.0033 | 0.19 | 0.056 | 1.4 |
| | | Ranges | 0.0022-0.006 | 0.0023-0.0043 | 0.11-0.27 | 0.0340.078 | 1.2-1.6 |
| | | Mean±SE | 0.0041±0.0019 | 0.0033±0.001 | 0.19±0.081 | 0.056±0.022 | 1.4±0.18 |

**Table S4** Descriptive statistics (mg 100g-1; FW; Se in µg 100g-1; FW) of essential minerals (Ca, Cu, Fe, K, Mg, Mn, P, Se and Zn) in food crop edible parts grown on urban horticultural soils across five cities in the UK.

| Food crops | | Ca | Cu | Fe | K | Mg | Mn | P | Se | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| | Median | 17 | 0.02 | 0.27 | 116 | 8.70 | 0.07 | 7.70 | 0.16 | 0.32 |
| **Beetroot** (n=5) | Mean±SE | 58±38 | 0.17±0.06 | 0.33±0.13 | 183±76 | 7.4±1.6 | 0.066±0.02 | 16±4.5 | 0.25±0.1 | 0.32±0.03 |
| | Ranges | 7.1-206 | 0.03-0.38 | 0.04-0.80 | 47-477 | 1.2-10 | 0.01-0.11 | 3.3-30 | 0.02-0.8 | 0.29-0.35 |
| | Median | 57 | 0.03 | 0.95 | 253 | 16 | 0.17 | 33 | 0.28 | 0.71 |
| **Onion** (n=4) | Mean±SE | 161±124 | 0.59±0.31 | 1.1±0.51 | 239±27 | 20±7.7 | 0.19±0.07 | 35±6.7 | 0.3±0.1 | 0.71±0.51 |
| | Ranges | 2.1-530 | 0.17-1.5 | 0.15-2.2 | 163-287 | 8.1-42 | 0.05-0.4 | 20-53 | 0.05-0.6 | 0.20-1.2 |
| | Median | 3.80 | 0.03 | 0.20 | 206 | 12 | 0.05 | 26 | 0.14 | 0.23 |
| **Potato** (n=10) | Mean±SE | 10±3.7 | 0.42±0.01 | 0.31±0.12 | 234±60 | 13±3.2 | 0.059±0.01 | 28±7 | 0.33±0.2 | 0.30±0.06 |
| | Ranges | 1.0-34 | 0.02-1.4 | 0.02-1.3 | 23-685 | 0.62-30 | 0.01-0.13 | 2.1-71 | 0.06-1.4 | 0.17-0.52 |
| | Median | 51 | 0.02 | 0.31 | 188 | 9.90 | 0.07 | 26 | 0.99 | 0.23 |
| **Chard** (n=4) | Mean±SE | 46±9.8 | 0.26±0.092 | 0.53±0.29 | 228±56 | 11±36 | 0.11±0.04 | 25±6.7 | 1.2±0.6 | 0.24±0.03 |
| | Ranges | 21-62 | 0.06-0.49 | 0.11-1.4 | 142-393 | 3.9-19 | 0.06-0.22 | 6.7-39 | 0.07-2.7 | 0.19-0.33 |
| | Median | 32 | 0.01 | 0.31 | 159 | 6.30 | 0.06 | 11 | 0.041 | 0.25 |
| **Lettuce** (n=6) | Mean±SE | 53±21 | 0.23±0.10 | 0.32±0.06 | 169±35 | 7.4±1.6 | 0.059±0.01 | 20±7.2 | 0.04±0.01 | 0.24±0.03 |
| | Ranges | 3.6-141 | 0.05-0.68 | 0.04-0.49 | 75-325 | 3.7-15 | 0.03-0.08 | 9.2-53 | 0.03-0.06 | 0.16-0.31 |
| | Median | 27 | 0.03 | 0.39 | 211 | 17 | 0.08 | 27 | 0.57 | 0.30 |
| **Runner Bean** (n=8) | Mean±SE | 52±22 | 0.37±0.08 | 0.39±0.07 | 251±4 | 18±3.4 | 0.10±0.02 | 31±7.2 | 0.71±0.2 | 0.42±0.12 |
| | Ranges | 1.9-183 | 0.16-0.82 | 0.08-0.75 | 81-550 | 5.9-38 | 0.03-0.23 | 10-77 | 0.07-2.1 | 0.17-1.3 |
| | Medium | 16 | 0.02 | 0.25 | 130 | 11 | 0.05 | 18 | 0.08 | 0.19 |
| **Courgette** (n=11) | Mean | 20±5.5 | 0.28±0.64 | 0.25±0.05 | 154±24 | 9.9±1.2 | 0.10±0.05 | 18±3.2 | 0.23±0.1 | 0.20±0.02 |
| | Ranges | 2.2-67 | 0.05-0.62 | 0.08-0.61 | 44-341 | 2.9-16 | 0.01-0.54 | 4.5-39 | 0.003-1.3 | 0.15-0.29 |
| | Median | 11 | 0.03 | 0.27 | 151 | 11 | 0.06 | 19 | 0.09 | 0.38 |
| **Tomato** (n=10) | Mean±SE | 15±4.3 | 0.30±0.07 | 0.29±0.07 | 177±35 | 11±2.1 | 0.06±0.01 | 21±3.5 | 0.11±0.03 | 0.4±0.04 |
| | Ranges | 0.51-45 | 0.06-0.66 | 0.06-0.77 | 26-337 | 1.7-22 | 0.01-0.11 | 3.5-39 | 0.01-0.4 | 0.34-0.47 |
| | Median | 10 | 0.05 | 0.17 | 194 | 12 | 0.06 | 18 | 0.27 | 0.25 |
| **Apple** (n=11) | Mean±SE | 17±4.7 | 0.48±0.08 | 0.25±0.06 | 190±30 | 12±2.5 | 0.06±0.02 | 25±4.7 | 0.23±0.06 | 0.26±0.04 |
| | Ranges | 1.7-48 | 0.10-0.96 | 0.06-0.62 | 46-360 | 2.8-29 | 0.01-0.20 | 7.0-45 | 0.01-0.4 | 0.15-0.38 |
| | Median | 14 | 0.06 | 0.35 | 246 | 17 | 0.09 | 37 | 0.24 | 0.25 |
| **Raspberry** (n=14) | Mean±SE | 21±5.2 | 0.67±0.12 | 0.34±0.03 | 288±45 | 21±4.4 | 0.16±0.04 | 32±3.9 | 0.38±0.2 | 0.38±0.09 |
| | Ranges | 5.6-81 | 0.10-2.1 | 0.14-0.51 | 92-671 | 4.3-69 | 0.02-0.49 | 8.3-48 | 0.004-2.3 | 0.16-1.1 |
| | Median | 24 | 0.02 | 0.20 | 112 | 6.4 | 0.06 | 12 | 0.08 | 0.41 |
| **Rhubarb** (n=24) | Mean±SE | 36±8.1 | 0.25±0.05 | 0.22±0.03 | 157±3 | 9.1±1.6 | 0.09±0.02 | 16±2.7 | 0.27±0.09 | 0.53±0.18 |
| | Ranges | 0.82-164 | 0.20-0.95 | 0.01-0.64 | 34-528 | 0.70-28 | 0.01-0.49 | 1.7-57 | 0.08-2 | 0.15-2.1 |

**Table S5** Nutrient content expressed as percentage of the reference nutrient intake (% RNI for adults) derived from the consumption of UH produce grown on urban horticultural soils across five cities in UK and commercial horticultural crops commonly consumed across EU. The % RNI for adult females and males are presented for Ca, Cu, Fe, K, Mg, P, Se and Zn for '5 a day' (400g F&V) diet.

| **Female** | UH | | EU | |
|---|---|---|---|---|
| | **Mean (%)** | **SEM** | **Mean (%)** | **SEM** |
| Calcium | 25.37 | 10.66 | 18.73 | 1.42 |
| Copper | 12.98 | 1.93 | 19.69 | 1.66 |
| Iron | 12.38 | 2.86 | 22.22 | 4.2 |
| Potassium | 23.47 | 2.15 | 28.43 | 1.11 |
| Magnesium | 19.63 | 2.39 | 26.66 | 2.24 |
| Phosphorus | 18.32 | 1.85 | 24.39 | 0.98 |
| Selenium | 2.194e-003 | 6.56e-004 | 2.16 | 0.42 |
| Zinc | 11.47 | 2.83 | 16.93 | 1.31 |
| **Male** | | | | |
| Calcium | 25.37 | 10.66 | 18.73 | 1.42 |
| Copper | 12.98 | 1.93 | 19.69 | 1.66 |
| Iron | 21.06 | 4.88 | 37.79 | 7.15 |
| Potassium | 23.47 | 2.15 | 28.43 | 1.11 |
| Magnesium | 17.67 | 2.15 | 24 | 2.02 |
| Phosphorus | 18.32 | 1.85 | 24.39 | 0.98 |
| Selenium | 1.755e-003 | 5.25e-004 | 1.73 | 0.33 |
| Zinc | 8.45 | 2.08 | 12.47 | 0.96 |

**Table S6** Results of unpaired t-test between the daily intake of essential minerals (Ca, Cu, Fe, K, Mg, P, Se and Zn) from UH produce and commercial horticultural crops in two diets: '5 a day' (400g F&V) and '10 a day' diets (800g F&V).

| | **'5 a day'** | **'10 a day'** |
|---|---|---|
| **Calcium** | $p < 0.0001$; $U = 2680$ | $p < 0.0001$; $U = 1206$ |
| **Copper** | $t(198) = 21.02$ ;$p < 0.0001$, | $t(198) = 35.87$ ;$p < 0.0001$, |
| **Iron** | $p < 0.0001$; $U = 481$ | $p < 0.0001$ |
| **Potassium** | $t(198) = 15.57$ ;$p < 0.0001$, | $t(198) = 22.42$ ;$p < 0.0001$, |
| **Magnesium** | $t(198) = 8.87$ ;$p < 0.0001$, | $t(198) = 19.81$ ;$p < 0.0001$, |
| **Phosphorus** | $p < 0.0001$; $U = 971$ | $p < 0.0001$; $U = 127$ |
| **Selenium** | $p < 0.0001$ | $p < 0.0001$ |
| **Zinc** | $t(198) = 13.70$ ;$p < 0.0001$, | $t(198) = 27.10$ ;$p < 0.0001$, |

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# Opening the black box: Soil microcosm experiments reveal soot black carbon short-term oxidation and influence on soil organic carbon mineralisation

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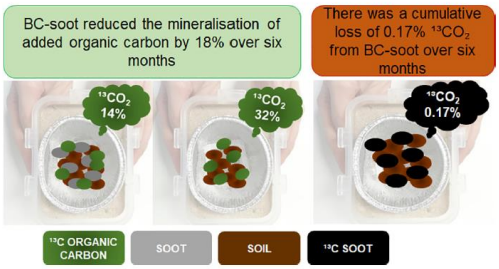
## HIGHLIGHTS

- Black carbon (BC) influence on soil organic carbon mineralisation was studied.
- The stability of BC in soil over short timescales was investigated.
- BC-soot reduced the mineralisation of added organic carbon by 18%.
- BC-biochar did not influence the mineralisation of added organic carbon.
- There was a cumulative loss of 0.17% $^{13}C$ from BC-soot over six months.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Soils hold three quarters of the total organic carbon (OC) stock in terrestrial ecosystems and yet we fundamentally lack detailed mechanistic understanding of the turnover of major soil OC pools. Black carbon (BC), the product of the incomplete combustion of fossil fuels and biomass, is ubiquitous in soils globally. Although BC is a major soil carbon pool, its effects on the global carbon cycle have not yet been resolved. Soil BC represents a large stable carbon pool turning over on geological timescales, but research suggests it can alter soil biogeochemical cycling including that of soil OC. Here, we established two soil microcosm experiments: experiment one added $^{13}C$ OC to soil with and without added BC (soot or biochar) to investigate whether it suppresses OC mineralisation; experiment two added $^{13}C$ BC (soot) to soil to establish whether it is mineralised in soil over a short timescale. Gases were sampled over six-months and analysed using isotope ratio mass spectrometry. In experiment one we found that the efflux of $^{13}C$ OC from soil decreased over time, but the addition of soot to soil significantly reduced the mineralisation of OC from 32% of the total supplied without soot to 14% of the total supplied with soot. In contrast, there was not a significant difference after the addition of biochar in the flux of $^{13}C$ from the OC added to the soil. In experiment two, we found that the efflux $^{13}C$ from soil with added $^{13}C$ soot significantly differed from the control, but this efflux declined over time. There was a cumulative loss of 0.17% $^{13}C$ from soot over the experiment.

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These experimental results represent a step-change in understanding the influence of BC continuum on carbon dynamics, which has major consequences for the way we monitor and manage soils for carbon sequestration in future.



## 1. Introduction

There is approximately three times more carbon found in soils than is held in the atmosphere as $CO_2$ (Fischlin et al., 2007; Lal, 2004; IPCC, 2019). However, global shifts in land-use from natural and semi-natural ecosystems to agricultural and urban land, along with agricultural intensification have heavily degraded soils, with the resultant loss of an estimated 40 to 90 Pg of soil organic carbon (SOC) (Smith, 2007). As a direct response, signatories of the Kyoto Protocol are required to quantify the amount of carbon stored in soils, in order to monitor the net carbon emissions to the atmosphere by changes in land management or land-use. In spite of the critical role soils play in the global carbon cycle, we fundamentally lack detailed mechanistic understanding of the turnover of major soil organic carbon pools, particularly so-called black carbon (BC). This limits our ability to integrate soils into policies for a net zero future.

Black carbon is the product of the incomplete combustion of biomass and fossil fuels (Masiello, 2004; Hedges et al., 2000; Kuhlbusch and Crutzen, 1995). As such, the term BC describes a continuum of particles from slightly charred biomass to highly condensed and refractory soot and graphite (Bird et al., 2015; Hedges et al., 2000; Kuhlbusch and Crutzen, 1995). Slightly charred particles are generally dominated by small polycyclic aromatic hydrocarbons (PAHs) (2-7 rings) and labile carbon forms and, whereas soot particles are mainly comprised of gas phase re-condensed highly aromatic molecules (PAHs >7 rings) and stable carbon forms (Bird et al., 2015; Koelmans et al., 2006; Meredith et al., 2012). Black carbon occurs ubiquitously in the environment, playing an important role in a wide range of biogeochemical processes (Talukdar et al., 2019; Bond et al., 2013; Flanner, 2013; Masiello, 2004), and it has been suggested that it may influence the turnover of more labile ecosystem-derived SOC, defined as decaying plant residues, soil biota and exudates (Liu et al., 2018; Edmondson et al., 2015; Liang et al., 2010; Major et al., 2010). Overall, it is estimated that global BC soil stocks range between 54 and 109 Pg, representing the largest pool in the BC cycle (Bird et al., 2015). BC has been demonstrated to contribute to a significant portion of the total organic carbon (TOC) pool; e.g. in urban soils >20% (Edmondson et al., 2015; Hamilton and Hartnett, 2013; Liu et al., 2011; Rawlins et al., 2008) and in agricultural soils between 2 and 42% (Lavallee et al., 2019; Hamilton and Hartnett, 2013; Skjemstad et al., 2002). However, the methods used to determine soil carbon stocks do not consistently quantify BC, with the current state-of-the-art deploying CN elemental analysis which does not distinguish between ecosystem-derived carbon and BC (Edmondson et al., 2015). In contrast, alternative approaches such as dichromate oxidation mostly target the more labile ecosystem-derived carbon (Reisser et al., 2016; Knicker et al., 2007). As a direct result, the differential outputs of current analytical methodologies render national carbon inventories incomparable. For example, across Continental Europe and Northern Ireland BC is quantified as part of the TOC pool via elemental analysis (de Brogniez et al., 2015; Xu et al., 2011), while BC is not accounted for in England, Wales (Bradley et al., 2006) and the Republic of Ireland (Cruickshank et al., 1998) where soil carbon measure are derived from dichromate oxidation.

Although BC is ubiquitous in soils globally, our understanding of its contribution to the SOC cycle and the biogeochemical global carbon cycle is poorly resolved (Smith et al., 2015). Understanding of the influence of BC on the SOC cycling and its stability in soils is crucial for climate change mitigation policies due to its potential to offset carbon emission and increase carbon sequestration and to increase the accuracy of global carbon models simulating carbon cycling under different climate change scenarios (Cotrufo et al., 2016).

Research on the influence of BC on the turnover of more labile, ecosystem-derived SOC, include both suppression and stimulation of SOC mineralisation (Whitman et al., 2015). Liu et al. (2018) reported that addition of biochar (a form of BC) to the soil decreased the cumulative emission of $CO_2$ between 72% to 88% compared to control without biochar. Similarly, Liang et al. (2010) observed that total carbon mineralisation in BC-rich soils was 25.5% lower than in BC-poor adjacent soils. In contrast, Major et al. (2010) observed that 41% and 18% more carbon was respired when biochar was added to the soil compared to control, in two consecutive years. BC represents a largely stable pool of carbon turning over on geological timescales (Lehmann, 2015; Singh et al., 2012; Preston and Schmidt, 2006; Masiello, 2004; Goldberg, 1985). However, studies have reported soil BC mineralisation at shorter timescales (Major et al., 2010; Cheng et al., 2006; Hamer et al., 2004), although most of this work is carried out in the context of the more labile biochar, as opposed to soot, which is the more recalcitrant component of the BC continuum, but is a major feature of soils in the industrialised world (Hamilton and Hartnett, 2013; Liu et al., 2011; Sánchez-García et al., 2012; Stanmore et al., 2001). To date, no studies have investigated the stability of soot in soils and its role in the mineralisation of ecosystem-derived organic carbon. To provide a fundamental advance in our understanding of the extent to which BC represents an active component in the soil carbon cycle, we established two microcosm experiments in combination with isotope tracer technology and gas analysis to address two fundamental questions: a) Does BC (soot and biochar) influence the mineralisation of ecosystem-derived carbon pools? and b) Is BC in the form of soot mineralised in soils over short time scale?

## 2. Material and methods

### 2.1. Experimental microcosm soil

Soil for the microcosm experiment was sampled, in triplicate, from an arable farm in Lincolnshire, UK (53°18' 52.1" N, 0° 26' 17.6" W), in February 2019. The soil samples were subsequently mixed, air-dried and passed through a 2 mm sieve. Prior to analyses, a subsample of this soil was homogenised in an agate ball-mill and sieved to 2 mm to remove any stones. Soil texture was determined by Laser Scattering Particle Size Distribution Analyser (Horiba LA 950): prior analyses, TOC was removed by addition of $H_2O_2$ (9.8 M) to 10 g of soil (Mikutta et al., 2005). Soil pH was measured in a 1:2.5 soil to water solution. Soil TOC concentration was determined in a CN analyser (Vario EL Cube, Elementar, Hanau, Germany) (Edmondson et al., 2012). Before TOC analyses, inorganic carbon was removed by addition of 700 μl of HCl (6 M) to 90 mg of soil (Rawlins et al., 2008). Soil BC concentration was analysed by hydropyrolyses (HyPy), described in detail elsewhere (Meredith et al., 2012). The microcosm soil had a pH of 6.73 and a sandy loamy texture. Soil TOC was 28.72 ± 0.84 mg $g^{-1}$, of which more than 95% was ecosystem-derived organic carbon (26.64 ± 0.91 mg $g^{-1}$), with a BC concentration of 2.08 ± 0.09 mg $g^{-1}$.

### 2.2. Soot and biochar production and characterization

Samples of soot particulate matter (PM) were generated from methane gas under pyrolysis conditions in an electrically heated flow tube reactor. The equipment and method of particulate generation has been

described previously (Eveleigh et al., 2014), and adaptations have been made to the equipment to collect soot PM onto filter papers (Dandajeh et al., 2017). Separate soot PM samples were collected from methane of natural isotopic composition (BOC, UK), and isotopically labelled $^{13}C$ methane (99% $^{13}C$, Sigma Aldrich). The reactor temperature was controlled to 1200 °C gas temperature at the reactor centreline. Flow rates of 20 l $min^{-1}$ nitrogen and 207 ml $min^{-1}$ of methane were metered by mass flow controllers, resulting in 10,000 ppmv methane concentration. The flow rates resulted in a residence time through the reactor zone of constant heating of ~1 s. Particulate matter was sampled from the reactor centreline and drawn through a stainless-steel sampling tube under vacuum and filtered through glass fibre filters (70 mm filter, 0.7 μm pore size) onto which soot PM was deposited. A total mass of about 0.55 g particulate was collected onto several filters (a total of about 100 mg per filter), for both natural and isotopically labelled methane.

Biochar samples were produced from willow chips using a laboratory pyrolysis unit at the UK Biochar Research Centre at the University of Edinburgh. Approximately 30 g of willow chips were placed in a laboratory batch pyrolysis unit with a vertical quartz tube (inner diameter 50 mm) externally heated by a 12 kW infra-red gold image furnace (P610C; ULVAC RIKO, Yokohama, Japan) described in detail elsewhere (Mašek et al., 2018; Crombie et al., 2013). Before pyrolysis, the reactor was purged with nitrogen to eliminate any residual air within the system. The nitrogen purge was maintained at a rate of 0.3 l $min^{-1}$ for the duration of the experiment. The willow chips were pyrolyzed at a heating rate of 20 °C $min^{-1}$, with the highest treatment temperature (HTT) of 450 °C, and a residence time of 30 min at HTT. After pyrolysis, the system was cooled down under nitrogen flow to prevent oxidation of the biochar.

Soot and biochar samples were analysed using HyPy (Meredith et al., 2012). HyPy tests were performed using the procedure described previously by Ascough et al. (2009). The soot and biochar samples were first loaded with 10% by weight of molybdenum (Mo) catalyst using an aqueous/methanol solution of ammonium dioxydithiomolybdate [$(NH_4)_2MoO_2S_2$] and placed within borosilicate sample holders to allow for the accurate weight loss during pyrolysis of each sample to be determined (Haig et al., 2020). The samples were pyrolyzed with resistive heating from 50 °C to 250 °C at 300 °C $min^{-1}$, and then from 250 °C to 550 °C at 8 °C $min^{-1}$, before being held at the final temperature for 2 min, under a hydrogen pressure of 15 MPa. A hydrogen sweep gas flow of 5 l $min^{-1}$, measured at ambient temperature and pressure, ensured that the products were quickly removed from the reactor, and subsequently trapped on dry ice cooled silica (Meredith et al., 2004).

The dichloromethane soluble products desorbed from the silica were then analysed on an Agilent GC–MS (7890B GC; 5977A MSD), scanning in the mass range of *m/z* 40-400 (EI 70 eV, source temperature 200 °C). Product separation was performed on an HP-5MS column (30 m × 250 μm × 0.25 μm). The GC oven temperature was initially held at 50 °C for 0.5 min, then heated to 300 °C at a rate of 4 °C $min^{-1}$, where it was held for 5 min. Individual compounds were identified using a NIST MS library and published data.

The soot appeared to be very similar in composition to the n-hexane soot described in the BC ring trial (Hammes et al., 2007), with a carbon content 93% (compared with 92.9%), and an atomic H/C of 0.21 (compared with 0.19). As expected, the soot was very stable under HyPy conditions ($BC_{HyPy}$ = 69%), although as with the ring trial soot there was a small but significant labile fraction. The biochar carbon concentration was 73% and an atomic H/C of 0.61, similar to atomic H/C of biochars produced at equal pyrolysis temperature (Xiao et al., 2016). Compared to soot, biochar was less stable under HyPy condition ($BC_{HyPy}$ = 52%), however within the range of $BC_{HyPy}$ reported in Meredith et al. (2017) for biochars produced at similar temperature.

GC–MS of this labile non-$BC_{HyPy}$ fraction of the soot was dominated by 4-6 ring parent PAHs structures (Fig. 1). This is probably a reflection of the relatively high temperature of formation of the soot, which is known to increase the degree of condensation, and so result in a more restricted distribution of PAHs that are able to be cleaved off by HyPy (Mcbeath et al., 2015; Meredith et al., 2017). For this soot, the formation temperature of 1200 °C has appeared to suppress 2-4 ring PAHs in preference to 5-6 rings, in addition to the much larger clusters that form the stable $BC_{HyPy}$ fraction.

GC–MS of the labile non-$BC_{HyPy}$ fraction of the biochar show it to be very similar to the soot one, dominated by 4-6 rings PAHs structures (Fig. 2), however soot also presented 7 rings PAHs structures (e.g. Coronene, Fig. 1). The labile biochar fraction contained more alkyl-substituted PAHs resulting in multiple clusters of peaks and an

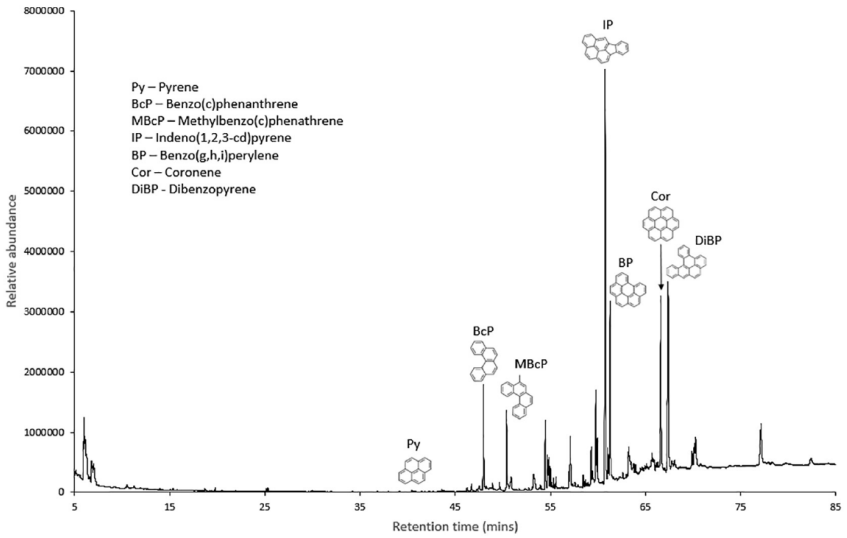


**Fig. 1.** Total ion chromatogram of the labile non-$BC_{HyPy}$ of the soot.

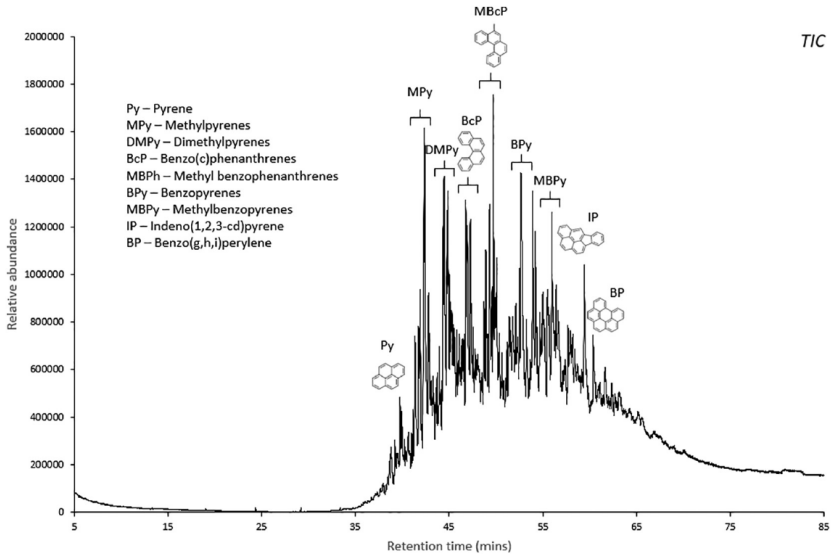


**Fig. 2.** Total ion chromatogram of labile non-$BC_{Hy/Py}$ of the biochar.

unresolved complex mixture beneath the baseline (Fig. 2). Biochars and charcoals, especially those formed at relatively low temperatures are typically dominated by 2-4 ring structures (Rombolà et al., 2016; Ascough et al., 2010). In this biochar, the 4 rings structures are the most abundant and the 2-3 rings compounds seems to be suppressed at 450 °C.

### 2.3. Microcosm experiments

Two microcosm chamber experiments were conducted over 168 days: experiment one added $^{13}C$ labelled organic carbon to soil with and without added BC (soot or biochar) to investigate the influence of soot and biochar on organic carbon mineralisation; experiment two added $^{13}C$ soot to soil to investigate the mineralisation rate of soot in soil.

Experiment one treatments were: control (organic carbon) (soil with 19.42 mg $^{13}C$ organic carbon - 99% $^{13}C$ Sucrose, Sigma Aldrich catalogue number 605417); organic carbon and soot (soil with 19.42 mg $^{13}C$ organic carbon and 25 mg of unlabelled soot) and organic carbon and biochar (soil with 19.42 mg $^{13}C$ organic carbon and 25 mg of unlabelled biochar). Soot and biochar were added into the soil at rate of 10 t $ha^{-1}$ which represents a common rate of application in soil-BC research experiments (O'Connor et al., 2018; Jeffery et al., 2011). Sucrose, glucose and fructose are often identified as the most abundant low molecular weight carbon compounds present in root exudates, across all ecosystems (Girkin et al., 2018; Shi et al., 2011). Thus, sucrose was selected for this experiment as a common photosynthetically derived form of labile organic carbon found in soils across all ecosystems (Canarini et al., 2019; Girkin et al., 2018; Shi et al., 2011). Sucrose was added at the rate of 3.88 mg C $g^{-1}$ dry soil which falls between low and medium root exudates input rates previously reported in literature (Basiliko et al., 2012; Girkin et al., 2018; Shi et al., 2011). Experiment two treatments were: control (soil) and soot (soil with 25 mg of $^{13}C$ soot). All treatments were thoroughly mixed into 5 g dry weight equivalent of soil to homogenise and replicated four times. Each treatment was set up in a 180 ml air-tight plastic container and kept in a controlled environment at constant temperature of 18 °C for the duration of the experiment. Ultra-pure water was added to each experimental unit throughout the duration of the experiment to maintain soil moisture at field capacity. Experiment one ran for 168 days and experiment two ran for 154 days, with measurements at set up and after 1, 7, 14, 21, 28, 35, 42, 49, 56, 70, 84, 98, 112, 126, 140, 154 and 168 days. $^{13}CO_2$ gases were sampled through a one-way stopcock valve with a 10 ml syringe. To avoid anoxic condition, each experimental unit was opened to oxygenate at each sampling point. Gas samples were analysed for $^{13}C$ content by continuous flow isotope ratio mass spectrometry (SERCON ANCA GSL 20-20 IRMS). According to convention, $^{13}C$ enrichment was expressed as $\delta^{13}C$ (relative to the Pee Dee Belemnite international standard) using Eq. (1) (Boström et al., 2007).

$$\delta^{13}C\ (‰) = \left( \frac{\left(\frac{^{13}C}{^{12}C}\right)_{Sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{Standard}} \right) \times 1000 \quad (1)$$

The cumulative percentage of the $CO_2$ respired from $^{13}C$-labelled soot or organic carbon was calculated by pool dilution using Eq. (2).

$$C_l = \sum_{n=n^{th}}^{t} \left[ \left( \frac{A_r - A_a}{A_s} \right) x100 \right] \quad (2)$$

where $C_l$ = Cumulative percent $CO_2$ lost; t = sampling time point; n = $n^{th}$ sampling time point; $A_r$ = atom% of the $^{13}C$-$CO_2$ respired (see Table S2 and S4); $A_a$ = atom% of $^{13}C$-$CO_2$ (natural abundance; $A_a$ = 1.09 atom%); $A_s$ = $^{13}C$ atom% of the labelled soot or organic carbon added to the soil.

### 2.4. Statistical analyses

Linear mixed-effect models were used to analyse the differences between $\delta^{13}CO_2$ fluxes in the incubation experiment with or without $^{13}C$ soot and to test for an effect of soot and biochar on $^{13}C$ organic carbon mineralisation over time. The mixed-effect model was applied using the package 'nlme' (Zuur et al., 2009) in R v.3.6.1 (R Core Team, 2017), where the random effect variable was replicate, the fixed effect

variables were treatments and duration of the experiment (Days) and method of estimation Maximum Likelihood (ML). The Akaike information criterion (AIC) was used to compare the performance of different models and identify the best fitting model. To improve normality, δ $^{13}CO_2$ modelled data of experiment one were log-transformed prior to statistical analyses. Data below IRMS limit of detection were treated as missing values and thus exclude from the analyses.

## 3. Results

### 3.1. Effect of soot and biochar on the mineralisation of added organic carbon

The addition of soot significantly decreased the flux of δ $^{13}CO_2$ from the organic carbon added to the soil ($F = 30.152$; d.f. = 1,89; $p < 0.0001$; Fig. 3a). Although the flux of δ $^{13}CO_2$ from the organic carbon decreased significantly over time there was a significant interaction between experimental duration (Days) and treatment. The difference between the organic carbon and organic carbon with soot increased over time ($F = 67.372$; d.f. = 2,89; $p < 0.0001$; Fig. 3a). The significant reduction in the flux δ $^{13}CO_2$ from organic carbon with soot addition resulted in a reduction in cumulative loss of carbon supplied over the duration of the experiment from 32% without soot to 14% with soot (Fig. 3b). In contrast, there was not a significant difference after the addition of biochar in the flux of δ $^{13}CO_2$ from the organic carbon added to the soil ($F = 2.402$; d.f. = 1,92; $p = 0.1246$; Fig. 3c). However, there was a significant interaction between experimental duration (Days) and treatment. The difference between the organic carbon and organic carbon with biochar slightly increased over time ($F = 23.921$; d.f. = 2,92; $p < 0.0001$; Fig. 3c).

### 3.2. Mineralisation of soot in soil

The addition of $^{13}C$ soot significantly increased the flux of δ $^{13}CO_2$ when compared to the control ($F = 234.7715$; d.f. = 1,98; $p < 0.0001$; Fig. 4a), however the δ $^{13}CO_2$ flux $^{13}C$ soot added decreased significantly over the duration of the experiment ($F = 5.9169$; d.f. = 2,98; $p = 0.0037$; Fig. 4a). After 24 h 0.0037 mg of the added $^{13}C$ soot had been mineralised and the cumulative total of mineralised soot increased to 0.039 mg after 168 days (Fig. 4b). The cumulative loss of carbon added as soot over the duration of the experiment was 0.17% (Fig. 4b).

## 4. Discussion

It is estimated that the global BC soil pool ranges between 54 and 109 Pg, this is the largest pool in the global BC cycle (Bird et al., 2015) with the soot fraction of this BC pool considered to be the most recalcitrant (Masiello, 2004; Hedges et al., 2000; Kuhlbusch and Crutzen, 1995). Here we show, for the first time, that BC in the form of soot supresses the mineralisation of labile organic carbon in soils, with 18% less $^{13}CO_2$ produced when soot is added to the soil. In addition, we show that BC in the form of soot can be, to some extent, mineralised in soils and contribute to soil $CO_2$ effluxes. Together, these findings cast doubt on the widely held assumption that BC in the form of soot plays a passive role in soil carbon dynamics. Black carbon represents an important component of the carbon cycle that is not accounted for

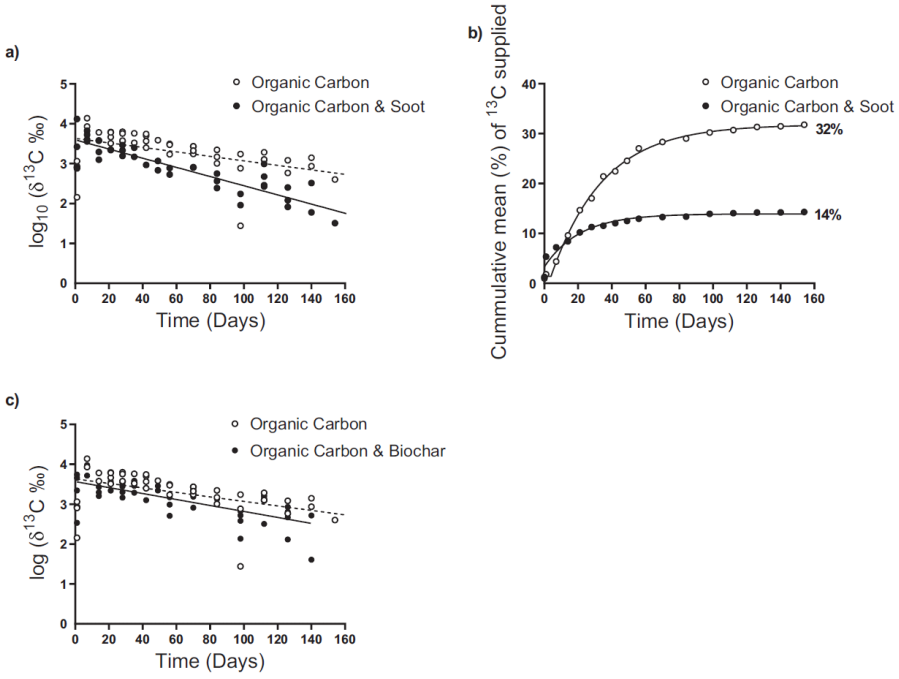


**Fig. 3.** The effect of the addition of soot and biochar to soil on the evolution of $CO_2$ from $^{13}C$ labelled organic carbon over time, a) $\log_{10}$ δ $^{13}C$ evolution from soil with added $^{13}C$ labelled organic carbon and $^{13}C$ labelled organic carbon and soot, b) mean cummulative loss of $^{13}C$ supplied as sucrose; standard error bars are too small (see Supporting Information Table S2 for standar error values), c) $\log_{10}$ δ $^{13}C$ evolution from soil with added $^{13}C$ labelled organic carbon and $^{13}C$ labelled organic carbon and biochar and. Open circles represent soil with $^{13}C$ organic carbon and closed circles represent soil with $^{13}C$ organic carbon and BC added.

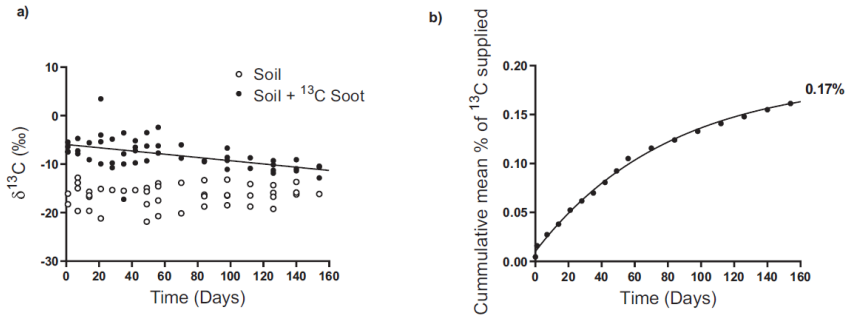


**Fig. 4.** a) The δ $^{13}C$ flux from soil with added $^{13}C$ labelled soot (closed circles) compared to control soil (open circles), and b) mean cumulative loss of $^{13}C$ soot supplied from soil for the duration of the experiment; the standard error bars are too small (see Supporting Information Table S4 for standar error values).

in current models of dynamic carbon fluxes between soils and the atmosphere (Cotrufo et al., 2016). This finding is thus fundamental to our understanding of the soil carbon cycle.

While the mechanisms underpinning the suppressive effect of soot on the mineralisation of labile organic carbon need further investigation, the high surface area of soot and the high abundance of surface binding sites (surface groups) increase the reactivity and capability of soot to interact with labile organic carbon (Lehmann, 2015), thus potentially explaining this result. Indeed, it has been demonstrated that BC presents a high sorption affinity for organic carbon compounds (Kasozi et al., 2010), making them less accessible for soil microbes. In particular, adsorption and encapsulation have been suggested as potential mechanisms by which BC may suppress the mineralisation of labile organic carbon (Liu et al., 2018; Whitman et al., 2015; Lu et al., 2014; Zimmerman et al., 2011). In the first mechanism, encapsulation, the organic carbon is adsorbed within the pore of black carbon which became physically unavailable for microbes degradation. In the second mechanism, adsorption, the organic carbon is adsorbed on the large surface area of the black carbon which became less accessible to soil microbes. This result corroborates the previously observed correlation between ecosystem-derived soil organic carbon and soil BC concentration, which in the urban context of this study, was most likely soot (Edmondson et al., 2015; Hamilton and Hartnett, 2013; Liu et al., 2011). Additionally, our findings are supported by research demonstrating a suppressed mineralisation of ecosystem-derived organic carbon in BC (biochar) amended soils (Wang et al., 2016; Cross and Sohi, 2011; Liang et al., 2010). In contrast, the addition of BC in the form of biochar did not affect the mineralisation of labile organic carbon. Similar results were found by other studies, where no significant effect on the soil organic carbon mineralisation was observed following biochar addition (Wang et al., 2016; Kuzyakov et al., 2009). To understand the mechanisms underpinning the differences between soot and biochar effect on labile organic carbon mineralisation, further research is needed. However, it has been suggested that the decrease in soil organic carbon mineralisation due to the sorption properties of BC could be associated with its more recalcitrant fractions (Whitman et al., 2015). This is also what our findings potentially suggest. The HyPy analyses on soot and biochar showed that soot was more stable under HyPy condition than biochar, with a larger recalcitrant fraction compared to biochar, 69% and 52%, respectively. Potentially suggesting that driving the differences between soot and biochar effect on organic carbon mineralisation might be the presence of a greater recalcitrant fraction in soot compared to biochar. However, further analysis is needed to investigate this hypothesis. Additionally, previous research has demonstrated that the suppression of soil organic carbon increases with increased biochar concentration (Liu et al., 2018). Particularly, in Liu et al. (2018) a significant decrease in soil organic carbon mineralisation was observed only after biochar application rate of about 67 t $ha^{-1}$. Thus, explaining the differences between soot and biochar effect on soil organic carbon mineralisation might also be the rate of biochar applied in this experiment (10 t $ha^{-1}$). However, further research is needed to investigate this. While we show that soot influences the dynamics of labile carbon mineralisation, we have also demonstrated that it is mineralised itself and therefore represents a hitherto overlooked component of the carbon cycle. As suggested by Bird et al. (2015), BC degradation processes in soil can be seen as continuum ranging from more labile lightly charred materials to highly recalcitrant condensed aromatic molecule, although our analyses suggest that even at the recalcitrant end of this continuum a proportion of BC is still mineralizable over short timescales. The chemical analysis of our labelled soot revealed that around 30% of the soot is potentially labile and composed of aromatic hydrocarbons, such as pyrene and phenanthrene, that are known to be readily mineralised by the soil microorganisms (Couling et al., 2010). These PAHs are still likely to represent the minor portion of the soot that was able to be mineralised over the course of the experiment (Couling et al., 2010). Our experimental results also indicated that soot mineralisation declined with time. While the mechanisms behind the decrease in soot mineralisation need further research, microbial toxicity induced by PAHs associated with soot could have played a role in the slowdown of the soot mineralisation (Patel et al., 2020). Similarly, soot addition could have caused a change in soil pH, unfavourable for soil microbes, thus changing their biomass, composition and activity and consequently reducing soot mineralisation (Thies et al., 2015; Lehmann et al., 2011).

Our research provided the first measure of the turnover of soot in terms of carbon cycling in soils, allowing us to measure mineralisation of soot, even in very small quantities for the first time. We estimated that the amount of carbon mineralised from soot over the course of the experiment is about 0.17%. Since small changes in TOC respiration can have significant impact on atmospheric $CO_2$ concentration (Davidson and Janssens, 2006; Schlesinger and Andrews, 2000), we contextualized this result, estimating both at global and European scale the amount of $CO_2$ related to the mineralisation of BC in form of soot. Global BC deposition rate are estimated to be of 17 Tg $yr^{-1}$ (Bird et al., 2015), whereas European BC emission are estimated to be 470 Gg $yr^{-1}$ (Bond et al., 2013). Considering a global land area of 149 $10^8$ ha (excluding ice areas) and a European land area of 10.18 $10^8$ ha we estimated that with mineralisation of 0.17% of BC per ½ year would lead to approximately 27,576 ton of $CO_2$ $ha^{-1}$ ½ $yr^{-1}$ and 0.0028 kg of $CO_2$ $ha^{-1}$ ½ $yr^{-1}$ at global and European scale, respectively. To understand the magnitude of the contribution of the soot mineralisation to the global carbon cycle, considering that global emission from land use and land use

change are estimated to be about 5.2 ± 2.6 Gt $CO_2$ $yr^{-1}$ (IPCC, 2019), we estimated that BC mineralisation in form of soot contributes to about 0.040% of these emissions.

## 5. Conclusion

This research has demonstrated for the first time that BC in the form of soot supresses the mineralisation of labile organic carbon in soils and that BC in the form of soot can be, to some extent, mineralised in soils contributing to soil $CO_2$ effluxes. This research has also shown that BC in the form of biochar has no effect on the mineralisation of labile organic carbon. These findings represent a step-change in understanding the influence of soot and other compounds on the BC continuum on carbon dynamics, providing compelling evidence that BC in the form of soot plays an active role in soil carbon dynamics. This has major consequences for the way we measure, monitor and manage soils for carbon storage and sequestration in the future. A priority for future research will be understanding which carbon pools in soils are affected by BC, for example, the influence of soot on the mineralisation of labile organic carbon in soils through rhizodeposition from plants (Hütsch et al., 2002), in addition to the microorganisms responsible for the mineralisation of BC itself in soils (Whitman et al., 2016). Further research is also needed to understand the mechanisms driving the differences between soot and biochar influence on the mineralisation of labile organic carbon.

## CRediT authorship contribution statement

**Marta Crispo:** Conceptualization, Methodology, Data curation, Formal analysis, Investigation, Project administration, Visualization, Writing – original draft. **Duncan D. Cameron:** Conceptualization, Methodology, Formal analysis, Visualization, Funding acquisition, Writing – original draft. **Will Meredith:** Formal analysis, Writing – review & editing. **Aaron Eveleigh:** Formal analysis. **Nicos Ladommatos:** Formal analysis. **Ondřej Mašek:** Formal analysis, Writing – review & editing. **Jill L. Edmondson:** Conceptualization, Methodology, Validation, Resources, Funding acquisition, Supervision, Writing – original draft.

## 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.

## Acknowledgements

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.149659.

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

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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

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(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).

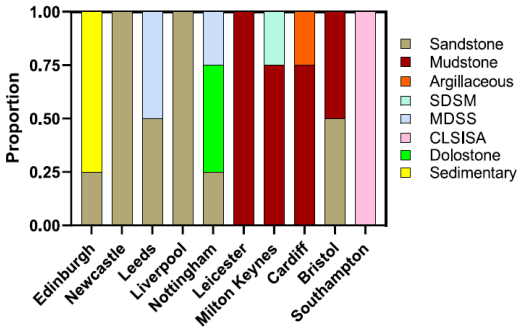


**Fig. 2.** The bedrock geology of allotments in the ten case study cities.

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 - $BC_{hypy}$.

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

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 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 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).

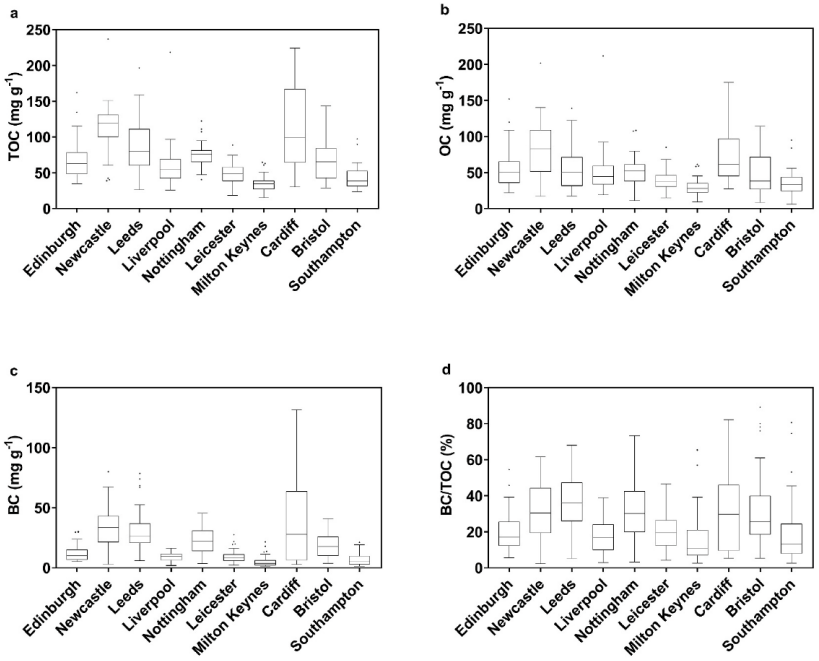


**Fig. 3.** Soil TOC, OC and BC concentrations in mg $g^{-1}$ (a, b and c) and soil BC contribution to TOC in % (d) across ten urban areas in the UK (n = 357). Boxes represent 25th, 50th and 75th percentiles; black dots represent outliers.

**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.

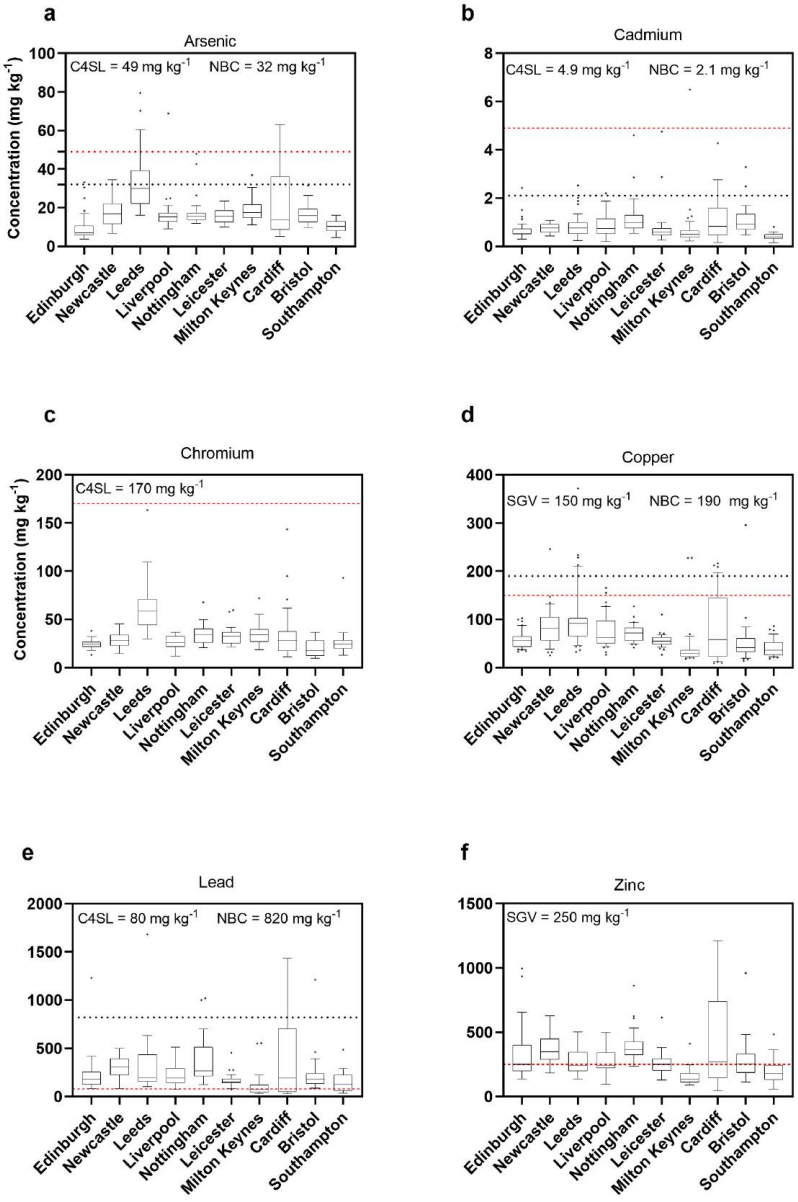


**Fig. 4.** Soil total HM concentrations (mg kg $^{-1}$) across ten cities in the UK (n = 391 composite soil samples). The concentration of As, Cd, Cr, Cu, Pb, Zn is presented in **a-f**, respectively. Boxes represent 25th, 50th and 75th percentiles; black dots represent outliers. The red dashed line 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 % (representing 16 allotment plots) and 3.5 % (representing 14 allotment plots) were also above the NBCs of Cu and Pb respectively (Fig. 4 d-e).

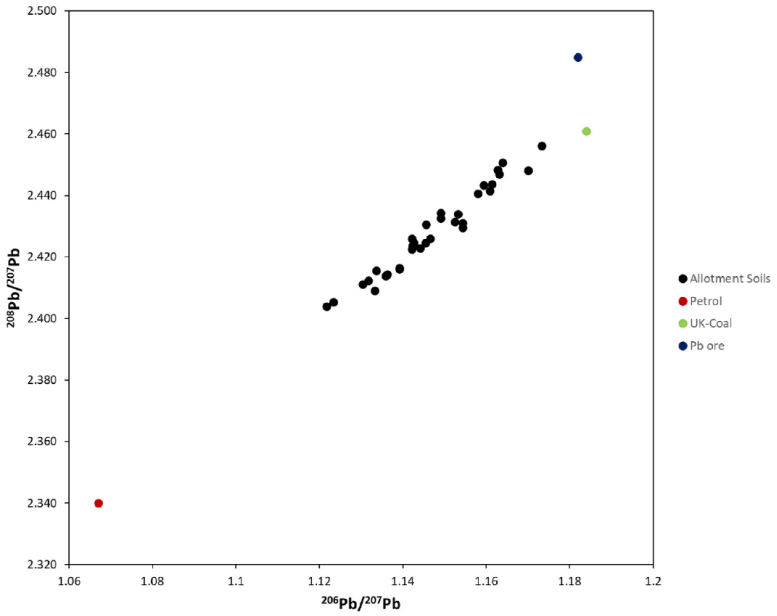


**Fig. 5.** Lead isotopic ratios in allotment soils across ten cities in the UK (n = 40). Mixing line of Pb isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) with median values for UK coal (Nottinghamshire, Yorkshire, Derbyshire), Pb ore (Galenas in Derbyshire and Leicestershire) and source 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

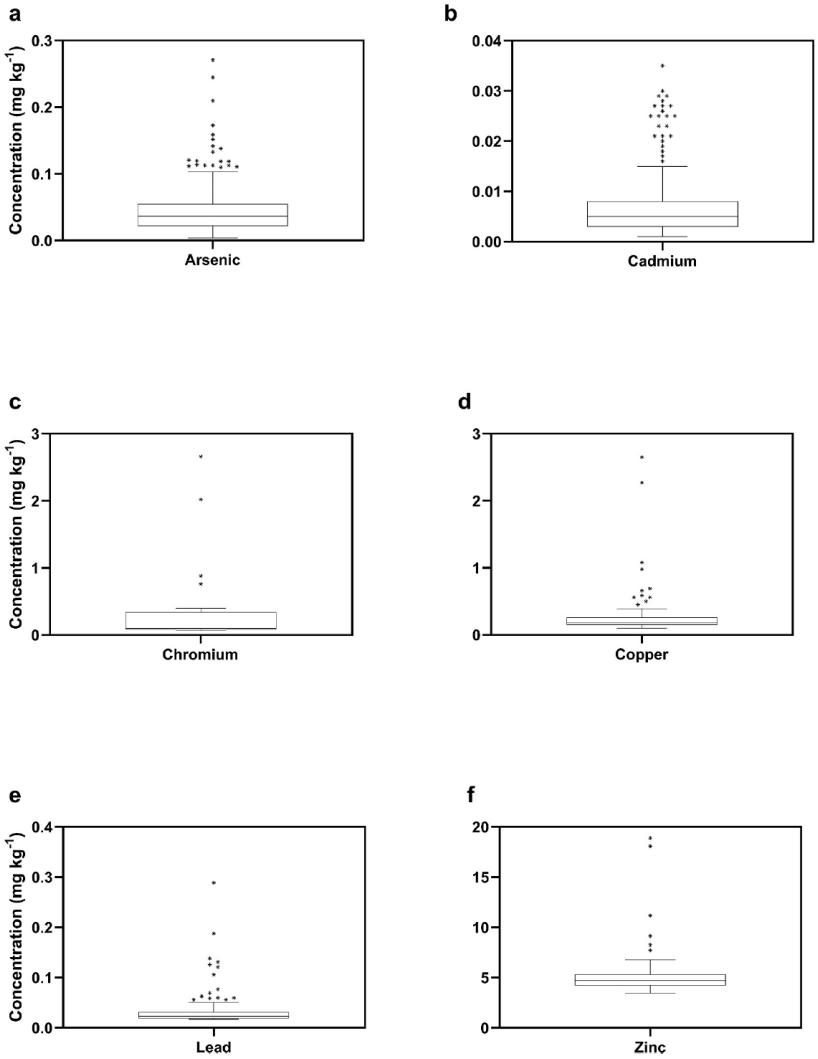


**Fig. 6.** Soil bioavailable HM concentrations (mg kg $^{-1}$) across ten cities in the UK. The concentration of As (n = 370), Cd (n = 370), Cr (n = 65), Cu (n = 147), Pb (n = 210), Zn (n = 92) is presented in **a-f**, respectively. Boxes represent 25th, 50th and 75th percentiles and black dots represent 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.

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## 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.

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