

Article

Carbon and Metal(loid)s in Parkland and Road Verge Surface Soils in the City of Liverpool, UK

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Abstract: Urban soils are at the interface between land and people and provide a wide variety of important ecosystem services to highly populous areas. The aims of this soil survey were (1) to measure the bulk density, carbon (C) storage and pH of surface soils (0–15 cm depth) from public spaces (parks and road verges) in the city of Liverpool, UK, and (2) to determine the likely impact of these master variables on heavy metal concentrations (As, Cd, Cu, Pb and Zn). The bulk densities and organic matter contents varied considerably in the predominantly sandy textured soils within the city boundary, resulting in diverse C densities from 1–10 kg C m². Organic carbon formed the majority of the labile, water-soluble and extractable C pool in these soils, a fact not easily elucidated from their organic matter or C content alone. The copper and lead concentrations in the sampled soils were correlated with organic matter and organic carbon in water-extracts. Cadmium and zinc appeared to be dependent only on soil pH, whilst arsenic was related positively to organic matter, but negatively to pH. Interrelationships, and hence synonymous distributions, of all metal(loid)s existed, but were strongest between Cu and As, and Cu and Pb. These results suggest that the diverse bulk densities, and hence carbon storage, of the urban soils surveyed influenced the dispersal of metals and arsenic.

Keywords: urban soils; carbon sequestration; bulk density; heavy metals

1. Introduction

Land use in urban areas is transient and rapidly changing on decadal timescales with the constant cycle of development. Often containing large amounts of coarse material [1], many urban soils have been augmented or deepened through past waste disposal [2,3] reflecting short term change and large-scale heterogeneity. In urban topsoils, the physico-chemical characteristics and concentrations of trace elements have been shown to vary considerably over relatively small geographical scales and between centres of urbanization [4,5]. Likewise, previous studies have also reported variable carbon storage in urban soils [6–11]. Notwithstanding their large variability, urban soils are increasingly recognized as having the potential to store more carbon (C) than agricultural or ‘natural’ soils [12]. For example, Vasenev and Kuzyakov [13], compiling data from over 700 urban soils, revealed that C accumulation in urban soils extended far greater in depth than in ‘natural’ soils, resulting in a net 3- to 5-fold greater C storage in the urban than in the ‘natural’ soils sampled. Some urban soils have been found to contain twice as much organic carbon in the upper 30 cm of soil than below this depth, because unlike neighbouring agricultural soils, urban topsoils are less likely to have been as regularly and systematically worked [14], and conditions conducive to the accumulation of C are extant.

Physico-chemical interactions between the organic matter in soils and metal(loid)s may also influence the distribution of contaminants in soils. Parry et al. [15] surveyed 200 samples across

the county of Merseyside (greater Liverpool area), finding that Pb and Zn hotspots correlated with the general extent of urbanization, whilst Cu and Cd were localized, and mainly associated with the industrial emission of particulates and associated dispersal and deposition [16,17], which is not surprising in this formerly industrially active region. Further investigation into the transport of metal(loid)s through local soil profiles in this region indicated that the mobility of metal(loid)s is strongly correlated with water-soluble carbon [18,19]. Thus, it follows that urban soils in formerly industrialized areas may exhibit strong correlations of contaminants within hotspots of C rich soils.

The aim of this study was to evaluate the extent to which urban public parkland and road verge topsoils in the city of Liverpool varied in their key properties. The bulk density and organic matter were determined for 92 soils, whilst a subset of 52 were analysed in more detail to determine their labile, water-soluble pool of C, and concentration and association of trace metals and arsenic with other soil properties. The interrelationships between soil properties and metal(loid)s are discussed, with specific reference to the management of urban soils.

2. Study Sites and Methods

2.1. Sampling Locations and Soil Sampling

A total of 92 topsoils (0–15 cm depth) were sampled from urban parklands and road verges within the city boundaries of Liverpool, UK. Sampling locations were identified according to the least likelihood of recent soil disturbance (i.e., without any form of obvious tillage, disturbance, or addition or subtraction of material). At each sampling location, a 6-figure grid reference was taken using a Garmin Etrex handheld GPS in order to map the locations and ensure good coverage of the whole city during the rolling sampling. The sample locations and extent of city coverage are shown in Figure 1a, and location of the study area within the UK (Figure 1b). A free survey method was preferable here, rather than a grid scheme, because of the obvious ubiquity of sealed surfaces within the city environment (Figure 1c). By this method, soils were obtained away from paths, roads and other through routes, and newly created green spaces were avoided because soils could have been recently disturbed, imported or otherwise improved. Road verge samples were taken in areas where vehicles had not been parked, roadworks debris had not been dumped or where other clearly obvious recent disturbances had not occurred.

At each location, a sample of topsoil was taken by inserting and carefully withdrawing a steel triaxial cylinder, 2.5 cm in diameter and 20 cm in length, into the top 15 cm of soil. After the sample was taken, the ends of the cylinder were capped, and the samples were returned to the laboratory for analysis.

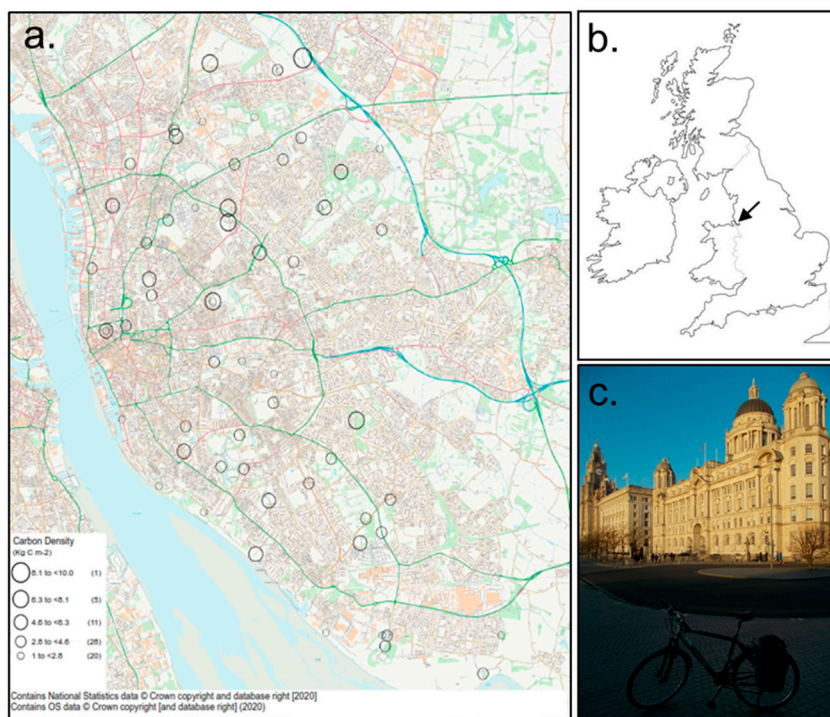


Figure 1. (a) Sample locations, selected by free survey, displaying the carbon (C) density of soils ($n = 92$). (b) The location of the study area within the UK (shown not to scale) and (c) the difficulty in locating soils in some areas due to the extent of sealed surfaces.

2.2. Sample Preparation and Analysis

Once at the laboratory the soil samples were divided into two for analyses, with all of the samples collected ($n = 92$) analysed for organic matter and bulk density, whilst a subset ($n = 52$) were additionally analysed for pH, soil texture, total organic carbon, water-soluble total and organic carbon, water-soluble total nitrogen and metal(loid) concentrations. This was done due to the time constraints of analysing all samples for all parameters.

All samples ($n = 92$): Bulk density (BD) was determined by measuring the volume/mass of air-dried soil (20–25 °C for 48 h) in each cylinder. Soil was then lightly crushed and sieved to <2 mm. Organic matter (OM) was determined by the loss on ignition method (LOI), whereby the difference in air-dried soil mass and soil mass after heating to 550 °C was calculated.

Subset ($n = 52$): The particle size distribution was determined using a Beckman Coulter LS 13 Laser Diffraction Particle Size Analyser: 2 mm–63 µm (sand), 62.9–2 µm (silt) and <2 µm (clay). Owing to the relatively low organic matter content of the soils, organic matter was not removed prior to particle size analysis. Total (TC) and inorganic carbon (IC) were determined using a TOC-SSM (Shimadzu, Tokyo, Japan), and total organic carbon (TOC) was subsequently calculated as TC minus IC. Soil pH was measured in a 1:10 soil and de-ionised water (pH 5.5) suspension, shaken for 3 h in an orbital shaker and allowed to settle for 45 min. After pH analysis, the suspension was centrifuged at 3000 rpm for 10 min, and the resulting supernatant was passed through a nylon filter to remove any suspended particulate matter that could interfere with analysis. These sample extracts were analysed for total water-soluble carbon (WSTC), water-soluble organic carbon (WSOC) and water-soluble total nitrogen (WSTN) using a TOC-VE (Shimadzu, Tokyo, Japan).

The pseudo-total concentrations of trace elements were determined after the microwave-assisted digestion of 0.2 g air-dried soil samples (<2 mm) in concentrated 14 M, GPR grade HNO₃, by ICP-MS (XSERIES 2 ICP-MS; Thermo Scientific, Waltham, MA, USA). Rhodium (1 ppm) was added to each sample as an internal standard, to compensate for the varying instrument responses during analysis.

2.3. Data Analysis and Mapping

Soil carbon storage, hereafter referred to as soil C density, was determined using a conversion factor of organic matter to total organic carbon (TOC), calculated on the subset of samples on which both analyses had been carried out ($n = 52$). Firstly, the TOC for all samples was calculated by applying this conversion factor to the organic matter data for all samples ($n = 92$). The soil C densities (kg C m^{-2}) were then calculated according to the bulk density (g cm^{-3}) and TOC content (%) based on the soil sampling depth (15 cm).

To explore and simplify the interpretation of the resulting data, principal component analysis was run. This is a recognised tool to analyse complex and interrelated data sets [20] and was used in this study to evaluate the interrelationships between measured parameters. All statistical analyses were carried out in SPSS v.14 for Windows. The mapping, as shown in Figure 1a, was produced in MapInfo Pro 15.2.

3. Results

3.1. Physico-Chemical Characteristics and C Storage

The soils were predominantly sandy, loamy sand or sandy loam (64%–94% sand), with low clay content (<3.5%; data not shown). An initial visual inspection of the soils in the field revealed that, unlike soils subject to considerable annual litter inputs, these soils contained no visible O (organic) horizon, probably reflecting the large degree of continuous management in the urban environment; the removal of litter and regular mowing and removal of grass, for example. Nonetheless, the soil pH varied considerably from pH 4–8, as did bulk density (<0.6 to >1.8 g cm^{-3} ; Figure 2), reflecting the variability of soil compaction. Organic matter contents had a mean of 8.2% (Figure 2) and the carbon densities ranged from c. 1–10 kg C m^{-2} city-wide; with 45 samples having C densities of 1–4.5 kg C m^{-2} ; and of those, 20 having C densities of <2.8 kg C m^{-2} (Figure 1a).

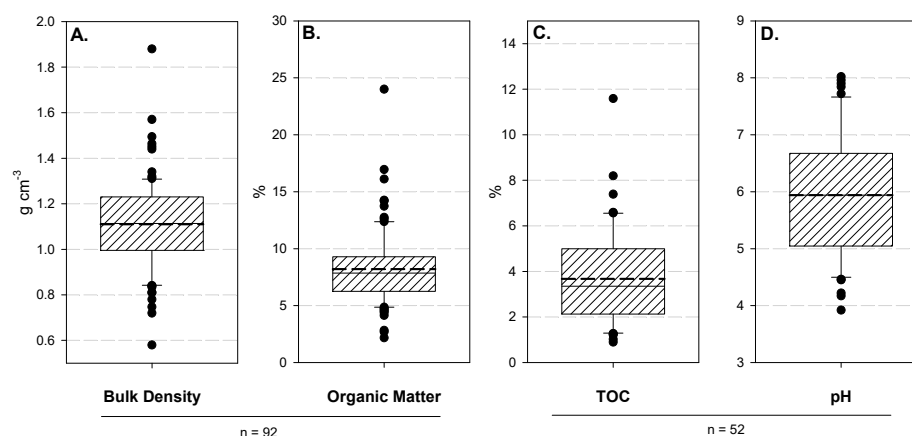


Figure 2. The mean and range of selected properties of urban soils (A and B from all samples, C and D from a subset of 52 samples). The dashed line is the mean value, the solid line is the median, the box represents the upper and lower quartiles, and the whiskers are the 10th and 90th percentiles.

Water-soluble total carbon (WSTC) was not substantially greater in concentration than mean water-soluble organic carbon (WSOC; Figure 3), leaving only a small soluble inorganic fraction.

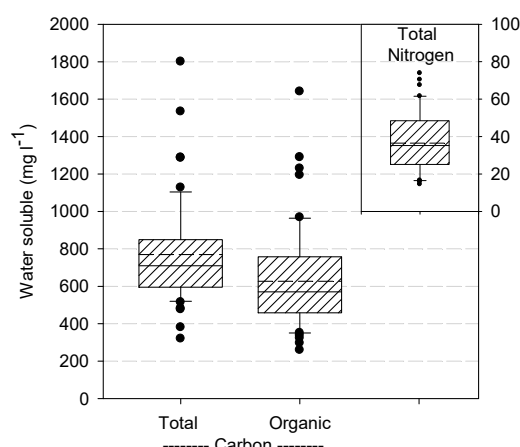


Figure 3. The mean and range of water-soluble total and organic carbon, and water-soluble total nitrogen (inset), taken from the aqueous extraction of a subset of surveyed urban soils ($n = 52$). The dashed line is the mean value, the solid line is the median, the box represents the upper and lower quartiles, and the whiskers are the 10th and 90th percentiles.

3.2. Metal(loid) Concentrations

Zinc and Pb were found at the highest mean pseudo-total concentrations in the sampled soils, followed by Cu, As and Cd (Figure 4). The range of concentrations of all elements was large, reflecting the wide spatial distribution of the source samples, and general heterogeneous nature of these urban soils.

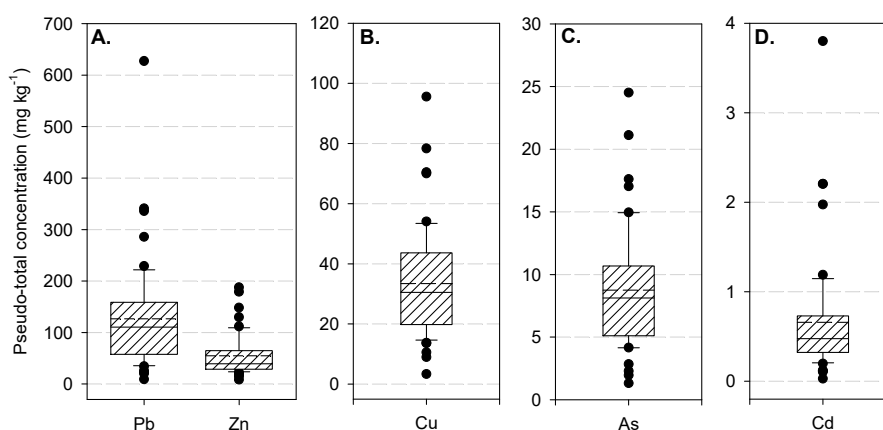


Figure 4. The mean and range of trace element pseudo-total concentrations in a subset of surveyed urban soils ($n = 52$). The dashed line is the mean value, the solid line is the median, the box represents the upper and lower quartiles, and the whiskers are the 10th and 90th percentiles.

4. Discussion

4.1. Carbon Storage and Flux

Carbon storage in soils is determined by the balance of bulk density and C content, with the trade-off between these factors resulting in increases or decreases in soil C density. The range of carbon densities of the soils of Liverpool (Figure 1a) was consistent with those of previous urban soil studies [6–8,21] that typically report 1.5–18 kg C m². Interestingly, Beesley [22] reported that manufactured urban soils, composed of green waste compost and recycled mineral materials, displayed soil C densities of 2–12 kg C m², similar to those recorded here. This demonstrates the impact of site management on soil C storage, in relation to the removal and/or addition of extraneous organic matter.

Therefore, the capacity of some urban soils to accumulate C is surprisingly high when compared to agricultural or native soils [12]. This fact is exemplified in a comprehensive review of urban soil C stocks, whereby more than 700 individual datapoints were analysed, concluding that urban soils accumulate C rapidly, resulting in their projected contribution to global soil C stocks being approx. 7%–13% [13]. It follows, therefore, that urban soils may also shed C rapidly.

Water-soluble carbon is an important constituent of the C pool in soils because of its mobility and reactivity, and its capability to influence physical, biological and chemical processes in soil [23]. The lack of fresh organic inputs to many of the unmanaged soils of Liverpool goes some way to explaining the low water-soluble nitrogen concentration, and therefore the wide range of C to N ratios (23:1 to 55:1). In circum-neutral, well drained soils, a C to N ratio of 10:1 could typically be expected, [24] and the lack of N addition to the soils sampled here would undoubtedly limit the decomposition of C, due to a lack of available labile substrate for micro-organisms to feed on. The fact that WSOC was not substantially lower in concentration than WSTC could indicate either (i) that the carbonate constituent of this soil was minimal/insoluble, or (ii) that the organic constituent was highly humified, recalcitrant and not easily extractable. Once again, managed urban soils (i.e., allotments) are likely to exhibit a more active pool of carbon, in the form of water-soluble carbon, especially when subject to recent or repeated additions of organic amendments [25]. Hence, more compacted and less worked/managed urban soils would appear to have the greatest potential for stable C storage.

4.2. Trace Metals and As

Soil surveys of urban soils in other European cities have indicated, as was the case in Liverpool, that the concentrations of surface metal(loid)s are highly variable. Madrid et al. [5] sampled 63 soils across three cities and found higher Zn and Pb concentrations, compared to other measured elements, in two out of three cities (at up to 210 mg kg⁻¹ and 237 mg kg⁻¹ Zn and Pb respectively by Aqua Regia digestion). Ruiz-Cortés et al. [26] similarly measured total metal concentrations in 51 soils from 0–10 cm depth, also including urban areas of Seville, Spain, finding that Zn and Pb were present in the greatest concentrations, at up to 137 mg kg⁻¹ and 725 mg kg⁻¹ respectively, with Cd concentrations of 0.18–4.85 mg kg⁻¹ also recorded. The soils of Liverpool are within these ranges. It follows that, just as C densities are highly variable due to the array of measured bulk densities, thence the same physical property will manifest in vast differences in the mass of metal(loid) per unit area of soil; soil contaminant loadings expressed in these terms are, as far as we can ascertain, seldom considered, but evidently highly environmentally relevant to discrete, small but well-worked patches of urban land.

4.3. Interrelationships between Soil Parameters

It is possible that the carbon budget of soils can be directly related to, and influential upon, the concentration and distribution of some trace elements. Principal component analysis is employed here to indicate interrelationships and shows that As, Cu and Pb in the soils of Liverpool were positively related to organic matter and TOC (Table 1), which would indicate their stability and immobility, related to retention by organic matter; the strong affinity of Cu and Pb for organic matter in soils [27–32] and the retention of As by organic matter in soil [33] are well documented. However, organic materials can also release As to labile fractions [34], so that at times of high rainfall, which is the case in the maritime climate of Liverpool [18], increased mobility of this metalloid may be seen. It is also possible that the relatively high WSOC content of the soils (Figure 3) would influence the co-mobilization of metals and As associated with lighter organic fractions in the soil.

The zinc and Cd concentrations in the surveyed soils were not linked to organic matter or TOC, but rather to pH (Table 1). Both metals present similarities, from the chemical point of view and in their dynamics in soils, with their source often linked to human activities [34]. The strong mobility of both metals at pH < 5 is well known [35,36], as is their retention in the soil matrix at pH > 5 [37]. Thus, their association is quite different to that of As, Cu and Pb. Given that the surveyed soils had a mean pH of 6 (Figure 2), the mobility of Zn and Cd is likely not to be as strong as those of As, Cu and Pb.

The maritime climate of the study area may also have influenced soil Na concentrations, which were not measured here, with attendant consequences for pH and electrical conductivity that may render Cd and Zn less mobile than would otherwise be expected.

Table 1. Principal component analysis of the measured parameters from 52 urban soil samples. Data were standardized before analysis. The cumulative total explained 67% of the variance, with the remaining 33% attributable to external factors not measured in this study (factors with loadings higher than 0.6 were included in this analysis).

Factor	Component 1 (43%)	Component 2 (24%)
Bulk Density	−0.63	-
TOC	0.74	-
OM	0.64	-
pH	-	0.81
As	0.90	-
Cd	-	0.60
Cu	0.89	-
Pb	0.75	-
Zn	-	0.70

5. Conclusions

Sampled urban parkland and road verge topsoils in the city of Liverpool had C densities of 1–10 kg C m², similar to those previously reported in other urban areas. The water-soluble, labile pool of carbon was predominantly organic, which, given the associations of some metal(loid)s with C, could impact negatively on their retention in soils over the longer term. Given the diversity of factors impacting the disturbance, compaction and augmentation of soils in urban areas, the results of this study in context add to the growing body of evidence that urban soils are diverse entities, hitherto overlooked as ‘soils in their own right’. The range of metal(loid) concentrations and heterogeneous bulk densities of the soils sampled also suggest that potential contaminant hotspots may be extant where soils are rich in metal(loid)s and carbon, and also have high bulk densities. Those with responsibility for the stewardship of urban soils should therefore consider their varied and highly heterogeneous bulk densities and carbon contents, not only their metal(loid) concentration and other chemical parameters, when planning for changes of usage (for example, from parklands to allotments).

Author Contributions: L.B. and P.J. carried out the soil sampling and laboratory analysis. P.J. additionally provided mapping expertise and produced mapping output, whilst E.M.-J. was responsible for the statistical analysis. N.W.L. provided expert knowledge and guidance in the interpretation of soils data. L.B. carried out all writing and editing of the paper. All authors have read and agreed to the published version of the manuscript.

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