Carbon in urban, brownfield and heavy metal contaminated soils

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Abstract

This thesis is comprised of a collection of work on urban, brownfield and heavy metal contaminated soils carried out within the North West of England from March 2007 to December 2009. Field and laboratory based experiments were used to determine the amount of carbon stored in urban soils and fluxes of dissolved organic carbon and soil respiration. The effects of added organic amendments on carbon storage and mobility as well as the onward implications to heavy metals and arsenic mobility and the impact of earthworms on these processes were also investigated.

A city-wide topsoil survey of parkland and road verges in Liverpool showed that carbon storage ranged from < 3 to > 10 kg total organic carbon m^{-2} whilst physico-chemical characteristics and heavy metal and arsenic concentrations also varied considerably. The abundance of technogenic material restricted organic carbon storage and flux to the upper 30 cm of an inner city lawn soil studied in greater detail. Brownfield soil carbon storage and fluxes were enhanced by adding a small amount of greenwaste compost to these soils but large applications did not greatly increase carbon storage further. Enhanced losses of carbon by dissolved organic carbon leaching and increased soil respiration rates were consequences of greenwaste compost additions, although these effects were highly seasonal, occurring in greatest magnitude at the warmest periods of the year. Proportionately, the annual losses of carbon to soil respiration were far greater than those to dissolved organic carbon.

An amendment consisting predominantly of woody material and a biochar amendment had a lower impact than composted greenwaste on dissolved organic carbon mobility, and the co-mobilisation of heavy metals and arsenic in a soil from a previously heavily industrialised centre of population. Earthworms reduced dissolved organic carbon when inoculated with compost and biochar amended soil, but increased this soluble fraction of carbon in woody amended soils, with attendant consequence to trace metal and arsenic mobility. Zinc and cadmium mobility were largely independent of changes in soluble carbon, but arsenic, copper and lead were heavily influenced by added carbon. Biochar amendment proved very effective in reducing concentrations of soluble cadmium and zinc in a heavy metal contaminated soil by adsorption, as well as having the added benefit of reducing total and bioavailable polycyclic aromatic hydrocarbon (PAH) concentrations.

It is concluded that carbon storage in urban soils can potentially be increased by applying organic amendments, although longer-term carbon storage may only be substantially enhanced with repeated applications of amendments. However, in urban soils with significant residual pollution, it can be questioned whether this practice is environmentally sound, regarding mobilisation of potentially harmful trace elements. Biochar and larger woody fraction amendments to soils may be more efficacious.

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Declaration

I declare that the material contained within this thesis, unless stated to the contrary, is my own work carried out in the Faculty of Science, Liverpool John Moores University, from February 2007 to March 2010, under the supervision of Professor Nicholas Dickinson, and has not been submitted for any other academic award.

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Research objectives	Section of the thesis
-	*Chapter 1.* **Introduction**
-	*Chapter 2.* **Urban and brownfield soils**
1. Determine how much C is present in urban, brownfield and heavy metal contaminated soils.	2.1 Carbon storage and trace element concentrations in city parkland and road verge topsoils *
2. Examine the effects of different organic soil amendments on C storage and major fluxes.	2.2 Short-term carbon dynamics in urban soils amended with greenwaste compost [1]
3. Develop a predictive model of the major C fluxes.	2.3 Annual respiratory losses of carbon from a city centre urban lawn soil *
4. Study the mobility of carbon and heavy metals and arsenic through soil profiles.	2.4 Carbon and trace element mobility in an urban soil amended with greenwaste compost [2]
5. Analyse the effects of different amendment and earthworms on C and heavy metals and arsenic.	2.5 Carbon and trace element fluxes in an urban soil with compost and biochar amendments, inoculated with earthworms [3]
-	*Chapter 3.* **Heavy metal contaminated soil**
6. Discover whether organic amendments can be used to reduce the mobility of heavy metals and arsenic.	3.1 Mobility of arsenic, cadmium and zinc in a multi-element contaminated soil profile assessed by in-situ soil pore water sampling, column leaching and sequential extraction [4]
-	3.2 Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil [5]
-	3.3 Cadmium and zinc immobilisation and retention by biochar [6]
-	*Chapter 4.* **Overall conclusions**
	Appendix. Supplementary material [2457]

Superscript references key

* Papers marked with this symbol are reports of experimental work intended to be written into research papers following additional work in the future.

[1] Beesley, L., Jones, J.M., Dickinson, N.M. Short-term carbon dynamics in urban soils amended with greenwaste compost. Soil Use and Management (under review)

[2] Beesley, L., Dickinson, N. 2010. Carbon and trace element mobility in an urban soil amended with greenwaste compost. Journal of Soils and Sediments 10, 215-222

[3] Beesley, L., Dickinson, N.M. Carbon and trace element fluxes in an urban soil with compost and biochar amendments, inoculated with earthworms. Soil Biology and Biochemistry (accepted for publication with corrections)

[4] Beesley, L., Moreno-Jimenez, E., Clemente, R., Lepp, N., Dickinson, N. 2010. Mobility of arsenic, cadmium and zinc in a multi-element contaminated soil profile assessed by *in-situ* soil pore water sampling, column leaching and sequential extraction. Environmental Pollution 158, 155-160

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[6] Beesley, L., Marmiroli, M. Cadmium and zinc immobilisation and retention by biochar. Environmental Science and Technology (under review)

[7] Rawlinson, H., Putwain, P., Dickinson, N., Beesley, L., Sparke, S., Jones, J. 2010. Organics program-final report. Cross Lane Tip and Chorley former royal ordnance facility. Waste and Resources Action programme. Banbury, Oxon (in press).

Table 1. Glossary of major abbreviations used throughout this thesis.

Glossary of major abbreviations	
SOM	Soil Organic Matter
OM	Organic Matter
LOI	Loss on ignition
SOC	Soil Organic Carbon
SIC	Soil Inorganic Carbon
OC	Organic Carbon
C	Carbon
TC	Total Carbon
TOC	Total Organic Carbon
N	Nitrogen
WSC	Water soluble carbon
WSTC	Water Soluble Total Carbon
WSOC	Water Soluble Organic Carbon
WSN	Water soluble Total nitrogen
DTC	Dissolved Total Carbon
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DTN	Dissolved Total Nitrogen
WHC	Water holding capacity
PAH	Polycyclic Aromatic Hydrocarbon
SEM/EDX	Scanning Electron Microscope/X-ray emission detection
ICP/MS	Inductively coupled plasma/mass spectroscopy

Chapter 1:
Introduction

This chapter provides a brief general introduction to some of the major processes influencing carbon in soils, reviews recent literature on urban soil carbon storage and flux, examines trace element distribution in urban soils, and discusses the advantages and disadvantages of adding soil amendments. An overview of the study sites used in this thesis is also provided at the end of this section but a detailed description is provided in each paper.

1.0 Importance of soils to C storage

The most current estimate suggests that upwards of 95 percent of the UK's land carbon stock is contained in soils (Ostle et al, 2009) providing an impetus to progress our understanding of their further carbon storage potential, to advance our understanding of how to tackle climate change. Carbon sequestration is the practice of locking-up C and can be considered equally beneficial wherever it occurs (Brainard et al, 2003) in that one tonne of carbon stored in urban soils is equally environmental beneficial to one tonne stored in forest soil. The added benefit of exploring the C storage potential of urban soils is that they may require augmentation with organic materials to counteract degradation, disturbance and residual contamination. Furthermore, unlike agricultural or forest soils, they are not generally required to sustain food production or ecosystem services.

In this thesis existing carbon storage across a range of urban soils is calculated by means of topsoil survey and more detailed profile analysis, and the potential to further enhance the carbon stock by adding a variety of soil amendments is explored. The effects of amendments on heavy metal mobility are examined in the context of the risks associated with the application of organic soil amendments to brownfield and other urban soils.

1.1 Fractions of C in soils

In the solid phase of soils, C exists in both inorganic and organic forms. Inorganic carbon (SIC) consists of primary minerals originating from parent material and secondary minerals which have been transformed from primary minerals by environmental processes (Bronick and Lal, 2005). Over tens to hundreds of years, inorganic C changes negligibly because processes of chemical weathering occur slowly. In contrast, soil organic carbon (SOC) is derived from dead plant and animal matter and faecal material. Organic matter in soils is impacted measurably upon over shorter time periods and is particularly important to soil quality because organic matter regulates key processes in soils such as the formation of soluble and insoluble complexes with metals, aggregate formation, water retention and many key biological processes (Haynes, 2005).

The amount and stability of SOC is dependent on time and chemical composition of the organic material from which it is formed (Lou and Zhou, 2006). Degradation rates of SOC vary from days to centuries (Stevenson and Cole, 1999), which determines long-term soil nutrition and C storage (Franzluebbers and Stuedemann, 2002). Labile fractions of organic material, which are those with the most rapid degradation times, are transient and easily disrupted by environmental change (Marland et al, 2004) because they consists of material in transition between fresh residues and stabilised organic matter (Hayes, 2005). A significantly smaller proportion of carbon in soils is water soluble (Cao et al, 1999). Water soluble C is that which can be de-sorbed from soil particle surfaces (Tao and Lin, 2000) and is mobile within soils, where it can be transported, relocated or exported from the soil matrix. Dissolved organic carbon (DOC) is organic carbon in solution that will pass though a 0.45 µm pore size membrane (Buckingham et al, 2008); this sub-fraction of water soluble C represents both the most bioavailable (Marschner and Kalbitz, 2003) and actively cycled soil C pool (Andreasson et al, 2009). Lastly, soil respiration, the below ground proportion of ecosystem respiration, is the process of CO_2 exchange between soil components and the atmosphere, and plays a critical role in regulating climate dynamics in the earth system (Lou and Zhou, 2006). Further, more detailed components of carbon in soils, humic and fulvic acids and black carbon for example, although important in determining storage, gains and losses of C from the soil system, are not measured in the experimental work in this thesis but are discussed briefly in this literature review where appropriate.

1.2 Factors controlling carbon storage in soils

1.2.1 Aggregation and soil texture

About 58% of organic matter is C (Grimshaw, 1989; Stevenson and Cole, 1999), the proportion depending on pedogenic factors, such as soil type (Grimshaw, 1989), soil depth, parent material (Cresser et al, 2007), aggregation and texture. The latter two of those factors are mechanisms by which organic matter can be physically protected from degradation in soils. For example, SOC was found to increase with an increase in mean aggregate size in a silty agricultural soil (John et al, 2005). Ferreras et al (2006) found that water-stable aggregates increased in proportion to the organic matter input to soil whereas Abivien et al (2007) found that no trend was consistent between the rate of organic input and aggregate stability, indicating some uncertainty in the relationship. Bronick and Lal (2005) suggested that aggregation, and association of organic matter with soil texture was a function of the amount of organic matter in the soil; that is to say that when organic matter was low, aggregation with clay minerals became dominant in aggregate stability rather than organic matter itself. Muller and Hoper (2004) found that under conditions of identical organic matter input to soils, soils with a higher clay content showed reduced organic matter degradation because organic matter is often found to be intimately associated with silt and clay content in soils (Six et al, 2002). Hassink et al (1993) had previously suggested that this process is two-fold. Organic matter can be protected from degradation by its physical location within small pore spaces in fine-textured soils, like clays, whereas in coarse-textured sandy soils, adsorption onto clay particle surfaces could offer most protection of organic matter. McLaughlan (2006) studied organic carbon in abandoned agricultural soils with variable clay contents (5 – 45%) and found no relationship between clay and easily degradable or more stable C. In forest soils, Hagedorn et al (2001) compared soil samples from depth increments in 100 cm soil profiles from two textural classes. Unlike the acid loam soil, in the calcareous sandy soil sampled, organic C content varied little with depth because soil conditions, such as pH were homogenous throughout the profile.

1.2.2 Soil pH

Soil pH is a regulator of many soil processes. In the previously mentioned study by Hagedorn et al (2001) the low pH of the acid loam soil restricted mineralization in the surface 30cm, leading to a higher organic C content in this horizon. Kemmitt et al (2006) found similar depth effects in silty clay loam and sandy loam soils because more acidic conditions restrict decomposition. This is a self-perpetuating process, because organic acids are produced in the decomposition process, further reducing soil pH (Ross, 1989). In a study of over 600 soil samples, to establish predictive functions for SOC content, soil pH variations only accounted for 5% of the variation in SOC (Bell and Worrall, 2009). In that study, soil series accounted for only a small proportion of the variation in SOC (< 10%), suggesting that abiotic parameters could have been more influential than soil chemical or soil-specific effects.

1.2.3 Abiotic influences

An intimate relationship exists between organic matter cycling in soils and ambient environmental factors, such as soil moisture and temperature. Rawls et al (2003) found that organic matter positively influenced water retention in soils with high organic matter, whereas soil texture influenced water retention in soils with lower organic matter; organic matter was the dominant force behind soil moisture retention. Excess soil moisture can prevent the decomposition of organic matter. This is exacerbated further by soil texture and degree of compaction. Brevik et al (2002) found that compaction effectively confined fresh organic carbon at the surface of soil, limiting C storage in lower horizons because the translocation of organic materials from where they were deposited had not taken place. Smith et al (2003) reported that soil organisms responsible for turnover of soil C and therefore C turnover itself are limited predominantly by soil moisture content. Soil moisture becomes a limiting factor for decomposition because soil organisms cannot respond to temperature variations without sufficient soil moisture to sustain their communities. This is why the potential of soils to sequester C is generally found to be greater in cooler conditions (Lal, 2003) whereas nearly 70% of organic matter added to soil can be mineralized within the first year given mild conditions (Bernal et al, 2006).

1.3 Water-soluble (WSC) and dissolved organic carbon (DOC)

Water-soluble C forms only a small proportion of the total C pool in soils. For example, Nelson et al (1994) found that 1% of solid phase C was water soluble in the upper 20 cm of soil and only 0.4 % below 80 cm. Corvasce et al (2006) found similar trends in a study of eight 200 cm deep soil profiles, which they attributed to soil textural differences with depth. Actual concentrations of both WSC and DOC are reported widely. Briefly, Chantigny (2003) reviewed a substantial body of literature on both WSC and DOC. Values of WSC for forest and agricultural soils are reported as 1000-3000 mg l^{-1} and 5-900 mg l^{-1} respectively whilst DOC is far lower at 5-440 mg l^{-1} and 0-70 mg l^{-1} for the same soils.

In terms of the production and transport of C in solution, Cao et al (1999) discovered that during the early stages of leaching soil (in leaching columns), high concentrations of WSC was generated, with extraction rapidly tailing off to a background level in a short time period. Here, water soluble carbon, initially in pore spaces is rapidly flushed from soil followed by desorption of aggregate-protected C and finally slowly degrading compounds produce a steady background level of WSC. Qualls (2000) successively leached the same soil, finding that the pool of WSC is partially replenished after leaching, which could indicate that some C in solution was re-adsorbed to soil particle surfaces. Dissolved organic carbon, in contrast to WSC, originates from leaching of above or below ground plant litter and the decomposition activity of soil microflora (Haynes, 2005) rather than simply what is de-sorbed from soil particle surfaces. The vertical transport of DOC within soil profiles has been shown to vary greatly. Neff and Asner (2001) found that, in a clay soil, up to 90% of DOC was lost from the surface organic horizon to the mineral soil below. On the other hand Borken et al (2004) applied an organic amendment (mature compost) to the surface of a forest soil and found that only 5% of DOC was leached to 10 cm depth and less than 0.5% to 100 cm depth, after 32 months. Guggenberger and Kaiser (2003) reported that DOC leaching from organic surface soils could account for as much as 38 g OC m^{-2} yr^{-1}, the vast majority of this (31 g OC m^{-2} yr^{-1}) being adsorbed in the mineral horizons below, so that only a small fraction could be potentially lost or exported from the soil system, for example to groundwater.

Bundt et al (2001) explored the transport of DOC through the soil profile and its implications for storage of C. They found that SOC can be enriched by up to 70% along preferential flow paths (the most abundant pathways of soil solution and DOC transport through the soil matrix), creating spatially distinct areas of the profile with regards to C storage. The age of the soil could further influence this process as Lilienfein et al (2004) reported that older soils can adsorb more DOC than younger, less well developed soil. The ability of soils to adsorb organic matter has a substantial effect on dissolved organic matter in soil (Haynes, 2005). Jones et al (2008), in a study of DOC in temperate forest soils, hypothesised that DOC might be progressively more recalcitrant as it moves down the soil profile, diminishing its potential priming effect with depth. This effect is discussed further in section 1.7.2.

1.4 Soil respiration

The CO_2 measured at the soil surface can be considered to represent total below ground respiration. On the importance of soil respiration to turnover of SOC on a global scale, Raich and Schlessinger (1992) summarised data on respiratory losses of C from various ecosystems. Temperate grasslands and forests lost ~440-700 g C m^{-2} yr^{-1}. Tundra lost only 60 g C m^{-2} yr^{-1} whilst tropical lowland forests lost > 1000 g C m^{-2} yr^{-1}.
Several biochemical pathways contribute to total soil respiration measured at the soil surface. They are root respiration, microbial respiration, further enhanced by the decomposition of litter, and the oxidation of organic matter (Kuzyakov et al, 2006, Lou and Zhou, 2006). Both Buchmann (2000) and Wang et al (2009) found that the majority of total respiration was root-derived in a sandy loam forest soil and temperate grassland soil respectively. Root respiration specifically is not measured in the experimental work in this thesis so will not be discussed in this chapter.

1.4.1 Abiotic factors influencing soil respiration

Soil temperature and moisture have been studied extensively as factors influencing soil respiration, because they are general drivers of microbiological activity in soils. When soils are at field moisture capacity soil micropores are largely filled with water, whilst macropore spaces are largely filled with air so that further increases in soil moisture can push trapped CO_2 out of the soil. Additionally, above field moisture capacity anaerobic conditions can occur, limiting microbial activity and soil respiration (Lou and Zhou, 2006). Smith et al (2003) found that the factors controlling respiration are seasonal, affected by soil moisture deficits in dry periods of the year. Wang et al (2009) found that microbial respiration was closely related ($r^{-2} = 0.94$) to soil temperature in a humid temperate grassland soil, where soil moisture deficits are unlikely. These effects can be depth dependant. Nakadai et al (2002) showed that the surface 10cm of a bare agricultural soil could contribute about 70% to total soil respiration in summer but only 40% in winter because of the differences in the thermal gradient around the soil surface. It has been suggested that microbial communities contributing to soil respiration can acclimate to temperature changes, regulating their metabolism to suit, so that respiration rates return to similar levels after particular changes in soil conditions (Davidson and Janssens, 2006).

Examining the effects of repeated wet-dry cycles on soil respiration can be an effective way to mimic annual or inter-annual respiration trends. Butterly et al (2009) found that, with increasing numbers of drying and rewetting cycles, a chromic luvisol responded with pulses of soil respiration, decreasing in magnitude with each successive wet-drying cycle. The amount of extractable organic carbon remained the same, even under conditions of reduced respiration, so the authors attributed the changes to the microbial biomass community, rather than intrinsic soil properties.

1.4.2 Biotic and soil specific factors influencing soil respiration

In a study of forest soils, when soil temperature was kept constant, soil pH was an important influence on respiration rates (Vanhala, 2002). Koizumi et al (1999) found correlations between soil respiration and temperature in peat and clay soils whereas in well-drained coarse textured sandy soil, moisture retention was low and no correlation was found. In fine textured soil Wang et al (2003) found no correlation between clay content and soil respiration. In their study total organic carbon (TOC) content of soil was found to account for 75-81% of the variability in respiration. Borken et al (2004) found mixed results when organic matter, in the form of compost, was applied to forest soils, possibly because the soil already had substantial organic matter content. In a similar study, Clark et al (2007) used various amendments on sodic clay subsoils, finding that the amount of WSC influenced soil respiration. In laboratory trials by Liu et al (2006) similar significant correlation was observed between WSC and soil respiration. Soil respiration can be further influenced by soil macrofauna. In a microcosm experiment, Speratti and Whalen (2008) found that earthworms were indirectly responsible for 7-58 % of the total CO_2 evolved from soil, not through their own respiratory activity, but by ingesting large quantities of soil, altering the composition of the burrowed soil and excreta (Lou and Zhou, 2006).

1.5 Carbon in urban soils

Having considered some of the main factors generally influencing C storage and major fluxes in soils, the following section reviews previous studies specifically related to urban soils.

1.5.1 Definitions and characteristics of urban soils

Definitions of urban soils are broad, reflecting varied levels of anthropogenic influence, disturbance and heterogeneity. For example, Hollis (1991) describes anthropogenic soils as those 'whose profile composition have been so strongly altered by direct human action that the original soil horizon sequence has been mostly destroyed'. This is certainly the case where soils have been deepened historically through waste disposal (Davidson et al., 2006; He and Zhang, 2006). Urban soils can often contain large amounts of coarse material, which affect macropore size, structure and moisture flow characteristics (Schleuß et al, 1998). Furthermore, the chemical composition or the organic matter in urban soils may also be very different to that of native soils. Beyer et al (2001) studied soils from 4 profiles in an urban area in Northern Germany. They found that plant-derived material formed a similar proportion of SOM in both urban and native soil but urban soils contained lower amounts of extractable humic compounds. The urban soils contained higher amounts of aromatic C, probably associated with the deposition of fossil fuel combustion residues.

1.5.2 Historical distribution of C in urban soils

Bellamy et al (2005) reported the results of a study that measured soil C in 5600 topsoils (0-15 cm), re-sampling a subset of those soils 25 years later, to determine whether C storage changed over time. Net losses of soil C were found in 92% of soils surveyed, especially soils that had high organic matter contents initially but there was no correlation between soil C losses and soil texture, land use changes or rainfall. Significant negative correlations were found however between the rate of C loss and the original C content. In that study, 'Man made' soils as they were defined, which had initially low soil C, showed only small overall losses over the 25 year period. In fact the authors found that those soils with < 30 g C kg^{-1} showed net gain in C over 25 years whereas soils <100 g C kg^{-1} showed large net losses, so that soils low in carbon could act as stores for additional C. Meersmans et al (2009) examined data from 2276 soil profiles in Belgium that were first sampled in 1960 and again in 2006. SOC was found to have decreased in most soils in the upper 30 cm; a mean decrease of 0.69, 0.01 and 0.02 kg C m^{-2} in cropland and two grassland soils respectively. However in grassland soils there was a net increase of SOC of up to 0.8 kg C m^{-2} over the total measured soil depth (100 cm), indicating potential relocation, rather than large net losses, in the soil C stock.

1.5.3 Amounts of C in urban soils

Pouyat et al (2002) measured C storage in soils along a rural- urban gradient, finding that soils in urban areas contained up to 17.2 kg C m^{-2}, similar to that previously found by Jo and McPherson (1995) (18.5 kg OC m^{-2}). Pouyat et al (2006) reported C storage of 1.5 – 16.3 kg OC m^{-2} across a range of soils in different countries and subject to different land management practices, providing a large dataset of baseline values of C storage in urban soils. In this study the highest amounts of C were consistently found in residential lawns which the authors attributed to careful lawn management and supplementation of nutrients. The work of Golubiewski (2006) supported this, finding that urban green spaces contained twice as much C as native grasslands or cultivated fields. Tomlinson and Milne (2006) applied meta-analysis to soil C data, assuming that urban soils contained half as much C as equivalent soils under pasture, although they did not measure C in urban soils directly.

1.5.4 Depth distribution of C in urban soils

The properties and C densities of urban lawn topsoils were compared to adjacent agricultural topsoils by Kaye et al (2005) at two soil depths: 0-15 cm and 15-30 cm. They found that a clear distinction in C storage existed between those two depths in urban, but not in agricultural soils, due to heavy and regular disturbance. Urban soils stored more than twice as much C in the 0-15 cm soil than 15-30 cm with C densities of 4.8 kg OC m^{-2}, in the range of Morrisada et al (2004), who reported C densities of 3.9 – 13.8 kg OC m^{-2} with 48% of organic carbon stored in soils from 0-30 cm depth from the 100 cm profile.

1.6 Trace metals and arsenic in urban soils

1.6.1 Concentrations and distribution

In a survey of 31 topsoil samples (0-20 cm) in parks in Seville, Spain, Madrid et al (2002) found that Zn and Pb were the two metals found in the highest concentrations. This work was expanded to include different urban centres by Madrid et al (2007), sampling 63 soils across 3 cities. Zinc and Pb levels were, again, higher than other heavy metals in 2 out of 3 cities (at 210 mg kg^{-1} and 237 mg kg^{-1} Zn and Pb respectively in aqua regia). Ruiz-Cortes et al (2005) measured total metal concentrations (by aqua regia) in 51 soils from 0-10 cm depth, in urban areas of Seville, Spain. Zinc and Pb were also present in greatest concentrations (137 mg kg^{-1} and 725 mg kg^{-1} respectively). Cadmium was also measured, with values in the range 0.18 – 4.85 mg kg^{-1}. In this study a sequential extraction found that Cd extracted by the water extractable phase of a sequential extraction accounted for 74% of the total soil concentration whereas, for Zn and Pb, water extractable concentrations only accounted for 40 and 63% respectively. This explains why concentrations of Zn in the soil solution are very low (Kiekens, 1995) and similarly why little evidence has been found that Pb is readily lost from soil profiles by leaching (Davis, 1995).

Hursthouse et al (2004) examined the metal concentrations of soils from 0-20 cm in urban parks, gardens and allotments in three countries. Samples taken in allotment and garden plots in the UK (Glasgow) had substantially greater levels of Zn and Pb (max. 1004 and 7051 mg kg^{-1} of Zn and Pb respectively) than soils in Italy and Spain. Dabkowska-Naskret (2004) examined the mobility of Zn, Cu, Pb and Cd in 5 garden soils in Poland by sequential extraction, finding that all but Cu exceeded background levels by a significant margin although water soluble and exchangeable fractions were generally low. Labile Cd was especially low because of associations between this metal, organic matter and Mn oxides. Copper showed highest affinity to organic matter with up to 32% of the total in the organic matter-associated fraction. The authors conclude that metals were largely immobilised in the soils studied because of high pH and organic matter.

1.6.2 Speciation and geochemical association

The above mentioned studies demonstrated various geochemical associations can ensure that high total concentrations of trace elements in soils are not necessarily equal to high water soluble or mobile concentrations. In a study of 32 soil samples taken from the soil surface (0-15 cm) of a moderately contaminated former industrial, brownfield[1] site in Wolverhampton, UK, Thums et al (2008) performed a five stage sequential extraction to determine geochemical associations. Lead was found to be associated with the most stable phases, whilst Cu was primarily associated with the organic phase. Conversely Zn was associated with the least stable phases, this being attributed at least in part to a strong negative relationship between pH and Zn in the easily exchangeable phase. Ge et al (2000) had previously approached the assessment of geochemical association of Cd, Pb, Zn, Cu and Ni in a different way. In their study, of soils from 0-15 cm in 3 urban railway yards, soil solution had been extracted by centrifuging soil pastes, finding that elements were largely immobilised at the soil particle surface because of high pH and organic matter. Cadmium was present as free ions in solution, whereas Cu, Zn and Pb were predominantly complexed with fulvic acid with little present as free ions. However these figures varied greatly between the 3 soils sampled, with associated difficulties in extrapolating the results.

1.7 Effects of organic amendments to soils

Adding organic materials to soils can influence general soil conditions, C storage and both trace metal and As behaviour. In this section priming effects and soil C saturation are also included, because they are relevant in terms of adding organic amendments to soils.

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[1] Definition of brownfield land is 'Previously-developed land is that which is or was occupied by a permanent structure, including the curtilage of the developed land and any associated fixed surface infrastructure.' (Planning Policy Statement 3, (PPS3) Annex B, 2006).

1.7.1 General benefits

There are well defined beneficial properties of organic soil amendments, such as decreases in bulk density, increases in water holding capacity (Bernal et al, 2006), assistance in the release of nutrients to soil, pH buffering capacity (Saebo and Ferrini, 2006) and erosion stabilization (Craul, 1999). This can aid plant establishment as well as recycling C to soils (Ros et al, 2003).

Organic materials such as biosolid wastes (manures for example), contribute to more labile pools of C (Clemente et al, 2007) whilst wood-derived amendments have a greater affinity to bind soil particles (Palumbo et al, 2004) and could contribute more substantially to longer term C storage. Zmora-Nahum et al (2007) examined the properties of composts made from woody material compared to garden green waste. Greater organic matter, N and DOC were found in garden green waste compost. Perez-Piqueres et al (2006) mixed green waste compost in a ratio of 20% amendment to 80% clay and a sandy-silt clay soil and measured CO_2 for 8 hours following the application of the compost. In the clay soil the compost did not significantly increase basal respiration (that is the total respiration from soil including micro and macro organisms and root) whereas basal respiration was significantly increased in the sandy soil.

1.7.2 Priming effects and carbon saturation point

Potentially negative effects on the stability of existing C in soils have been identified when new organic material is applied to soil. Priming effects are strong, short-term changes in the turnover of organic matter caused by comparatively moderate treatments to soil (Kuzyakov et al, 2000) and have relatively recently been discussed in the literature. Fontaine et al (2003) suggested that the communities of micro-organisms involved in this process become specialised, growing and adapting quickly to decompose only the fresh organic matter inputs to the old soil. Fontaine et al (2004) conducted laboratory trials, adding cellulose to ^{13}C labelled soil and studying decomposition of native SOC. Their findings indicate that the supply of fresh C may accelerate the decomposition of native SOC and induce a negative C balance. Hamer and Marschner (2005) repeatedly added substrate to soils to induce priming effects in two forest soils finding that repeated additions had greater effects than single additions showing that the effect was repeatable.

The authors suggested that the labile pool of C may not be the only pool to be affected by priming, because the effect was repeatable. In subsequent work by Fontaine et al (2007), fresh C additions to soil were shown to increase the decomposition of deep layers of old soil C, previously largely recalcitrant. Chabbi et al (2009) identified so called 'carbon tongues' within deeper soil horizons (60-140 cm depth). In these distinctively different zones of deeper soil, ^{14}C dating found modern age C compared with C aged several thousands of years in adjacent matrix soil. The authors suggested that preferential flow paths in this case have led to twice the amount of C in these spatially distinct areas of the profile, compared to matrix soil.

Carbon storage can reach saturation point in soils which is the realistic maxima of carbon storage beyond which further inputs produces no net gain in C storage. Recently, Stewart et al (2008 a,b) found that soils with low C content are furthest from their C saturation level, and therefore potentially have the greatest efficiency for storing C. Kimetu et al (2009) suggested that, in soils with a high SOC contents, organic matter can be mineralised more quickly due to the presence of already highly adapted and active microbial communities, which can quickly reduce the C storage potential of soils high in organic matter.

1.7.3 Trace metal and arsenic stability and mobility

The linkage between soil C, urban soil degradation and trace metals and As studies can be found where soil amendments are concerned. Bernal et al (2006) state that soluble OM and decomposition of OM to which metals are bound form two such mechanisms directly related to the application of organic amendments to soils by which trace elements are affected. Composts with a high quantity of humic acids can decrease bioavailability of metals by adsorption and their molecular size and structure limits their transport through soils, meaning that mobility and leaching of metals complexed with humic acids is generally low. Song and Greenway (2004) examined the adsorption capability of a compost consisting of wood, straw and vegetable waste, discovering that the affinity of elements to bind to compost was almost identical to that of humic acid (Pb >Cu >Cr > Ni > Cd > Zn > Co > As). Clemente and Bernal (2006) amended contaminated acid and calcareous soil with humic acid extracted from peat and compost. In the acid soil the humic acid immobilised Zn and Pb but mobilised small amounts of Cu and Fe. A muted effect was observed in calcareous soil, with slight mobilisation and redistribution among phases in soil. O' Dell et al (2007) explored the application of green waste compost to a Cu and Zn contaminated mine spoil soil, finding that the compost had high binding capacities for both metals: 96% removal of Cu at DOC concentrations exceeding 500 mg l^{-1} and 50-70% removal at < 300 mg l^{-1} DOC. The authors calculated a binding capacity of 0.17 g Cu / g C but <0.09 g Zn / g C. Businelli et al (2009) examined the response of Cu, Zn, Pb, Ni, Cr and Cd to a single dose of compost applied to a landfill covering soil over a 10 year period. Compost was found to induce large fluxes of WSC which migrated downwards in the profile over the 10 year period. Metals transported vertically were adsorbed to lower mineral strata over time but levels of metals returned to background concentrations in the enriched lower strata after 10 years. The effect of DOC on metal mobility has been found to be dependent on the pH of the soil. Kalbitz and Wennrich (1998) discovered that, at low pH, metals were already mobile, so DOC had little effect on their further mobilisation. These same elements were less mobile at higher pH, so DOC induced increases in mobility at soil pH > 4.5. This indicates a hierarchy of influential mechanisms on trace element mobility.

Zhao et al (2007) used a column leaching experiment to examine the movement of Cu and Zn from contaminated topsoil overlying acid and calcareous subsoils. Stark concentration gradients were observed for both metals suggesting that fast mobilisation occurs at the soil surface. In fact the authors identify that a boundary of only 2 cm thickness existed, below which Cu and Zn concentrations were not affected. Ruttens et al (2006) conducted lysimeter studies on industrially contaminated soil, under natural conditions following a 5% compost application to the soil. The results found distinctly different behaviours of Zn and Cd compared to Cu and Pb. Compost reduced Zn and Cd in leachate whereas Cu and Pb leaching was increased 17 and 30 times respectively. Farrell et al (2010) studied the leaching of Cu, Pb and Zn from a contaminated acidic soil (pH 2.2) which had been amended with green waste compost, noting that sharp increases in metal mobility after amendment application were related to high levels of leached salts rather than DOC.

Arsenic is known to be more mobile in alkaline conditions (Fitz and Wenzel, 2002), but is also affected by organic matter. Kumpiene et al (2008) reviewed the work of other authors showing that DOM can mobilise As by displacing the more weakly complexed As bound to Fe oxides. Wang and Mulligan (2009) investigated this further in column studies where soils were leached with solution of distilled water at pH 11 and a solution of 0.1% humic acid. Humic acid was found to mobilise As and significant correlation was observed between the mobilisation of Fe and As, probably by the formation of aqueous Fe-humate complexes.

1.8 Study sites overview

Five main field study sites were used in this work, all within the North West of England.

Study sites A and B (Fig 1.1), 'Byrom Street' and 'St Helens', are located in two major centres of population. Byrom Street is a university campus whilst the St Helens site is a garden attached to a Quaker Meeting House. The Byrom Street site features in papers 2.2, 2.3, 2.4 whilst St Helens forms paper 2.5 in the 'urban and brownfield soils' chapter.

Study sites C and D (Fig 1.1), 'Cross Lane' and 'Chorley' are brownfield soils, formerly municipal waste disposal and munitions manufacturing sites respectively. These sites feature in paper 2.2 in the 'urban and brownfield' soils chapter, with further work in the appended material.

Study site E (Fig 1.1) is 'Kidsgrove', a heavy metal contaminated sediment-derived soil located in the proximity of previous industrial activity, between two canals. This site is used for papers 3.1, 3.2 and 3.3 in the 'heavy metal contaminated soil' chapter.

Not included in the study sites map (Fig 1.1) are the locations sampled for the survey of urban soil characteristics and carbon storage (2.1 'Carbon storage and trace element concentrations in city parkland and road verge soils'). The reasons for the choices of study site, details of the known histories and any previous studies are detailed in the methods section of each paper.

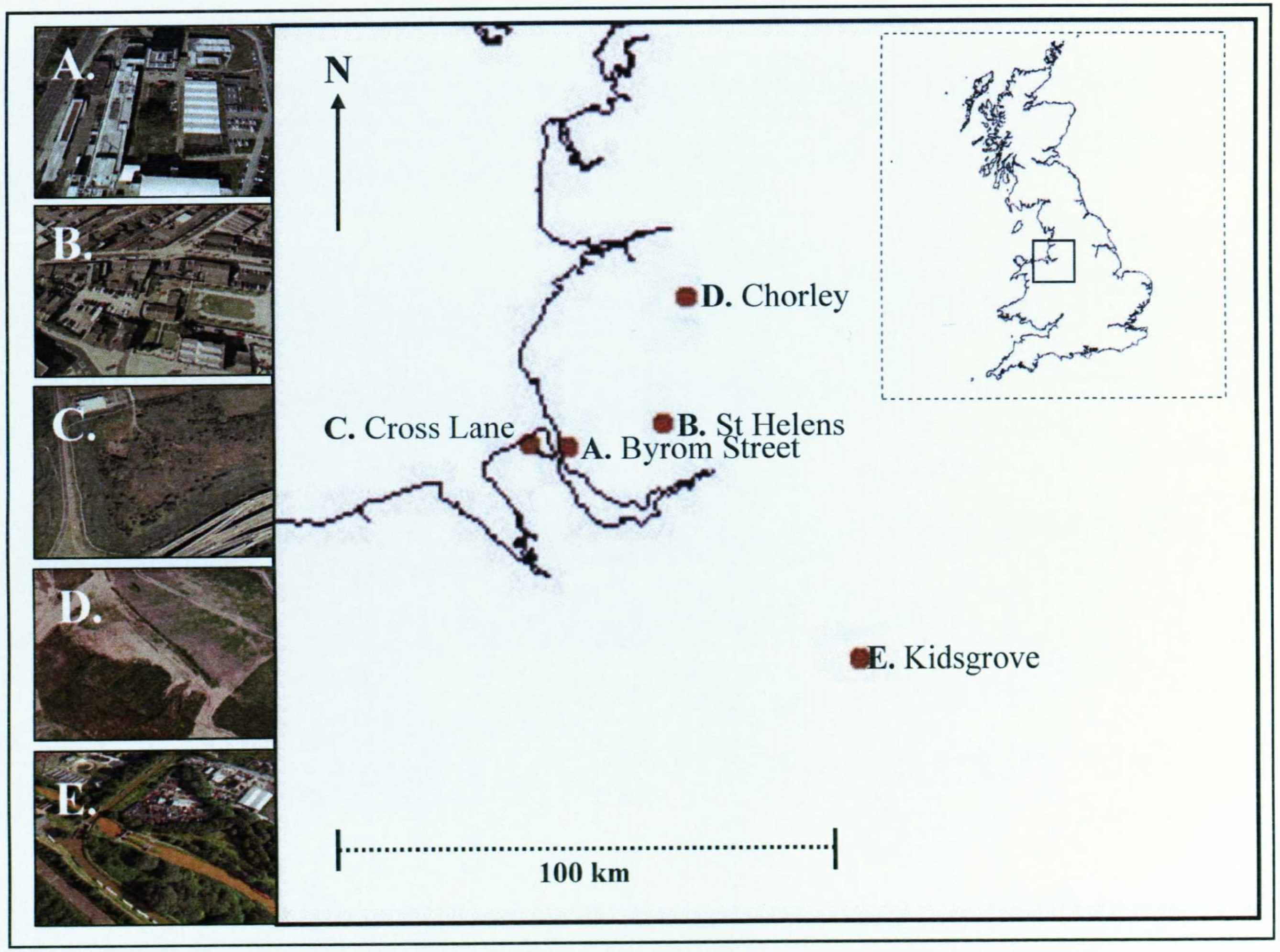


Figure 1.1. Outline map and aerial photographs of study site locations within Northwest England (photographs from Google earth).

Chapter 2:

Urban and Brownfield soils

This chapter contains five papers on urban and brownfield soils. Paper 2.1 introduces some general properties, carbon storage and trace metal and arsenic concentrations in a range of city topsoils. This is a report which could be expanded for publication with more data. Papers 2.2 and 2.3 examine depth distribution of carbon and enhancing carbon storage in urban and brownfield soils using green waste compost. Paper 2.3 is a report which could be expanded for publication with more detailed analysis of data and developed modelling. Papers 2.4 and 2.5 follow by determining in greater detail the mobility of soluble carbon in pore water and co-mobilisation effects to trace metals and arsenic.

2.1 Carbon storage and trace element concentrations in city parkland and road verge topsoils.

2.1.1 Abstract

Parkland and road verge topsoils are a suitable starting point for assessing carbon storage and key properties of soils in the urban environment, because they are readily accessible and easily sampled. The aim of this exploratory study was to survey key physico-chemical parameters, carbon storage (carbon density) and selected trace metal and arsenic concentrations in topsoil (0-15 cm depth) samples taken from parks and road verges in the city of Liverpool, UK. Carbon storage varied considerably over the city wide scale with C densities of 3 – 10 kg total organic carbon (TOC) m^{-2}. Soil texture had a negligible influence on other soil parameters because all soils were predominantly sandy. Organic carbon formed the majority of the labile, water-soluble C pool in these soils, but was not accurately predictable from TOC data alone. Copper and lead concentrations were correlated with organic matter and TOC, whereas zinc appeared to be dependent only on soil pH. Cadmium concentrations were not affected by any measured parameter. Arsenic was related positively to organic matter, but negatively to pH. Inter-relationships between all trace metals and As existed, but were strongest between Cu and As and Cu and Pb,

suggesting the potential importance of organic matter in the stability and dispersal of these elements in the urban soils of Liverpool.

2.1.2 Introduction

In the 1970's, surface soils in urban areas were first surveyed to readily and reliably measure and monitor aerially deposited trace metals. An example of this was a detailed 650 km^{-2} soil sampling programme undertaken in 1975 in the county of Merseyside, UK. Concentrations of the biologically significant metals Pb, Cd, Cu and Zn were determined and mapped on a 2 km grid basis across the county and sorted according to land use (Parry et al, 1981). The survey of 200 samples found that Pb and Zn hotspots correlated with the general extent of urbanisation whilst Cu and Cd were localised, mainly associated with industrial activity. One of the land use categories which the 1975 study surveyed was parkland. Parkland and road verge soils, compared to garden and allotment soils, are much less likely to have been frequently disturbed, exported or sealed during the constant development of the post-war era and could represent a reliable indicator of the properties of urban soils. Furthermore they are readily accessible for soil survey.

Land use in urban areas is transient and rapidly changing even on decadal timescales and soil properties reflect these short-term changes. Often containing large amounts of coarse material (Schleuß et al, 1998), many urban soils have been augmented or deepened through past waste disposal (Davidson et al., 2006; He and Zhang, 2006). This undoubtedly leads to the large heterogeneity in soil properties found in urban soils (Hollis, 1991). In urban topsoils, physico-chemical characteristics and concentrations and speciation of trace elements have been shown to vary considerably over relatively small geographical scales and between centres of urbanisation (Madrid et al, 2002, Madrid et al, 2007). Variability such as this makes it difficult to establish whether urban soils are consistently as effective at storing carbon as has been found previously (Golubiewski, 2006). Several previous studies have reported carbon storage in urban soils (Jo and McPherson, 1995; Pouyat et al, 2002, 2006, 2009; Kaye et al, 2005). In some cases, urban soils have been found to contain twice as much organic carbon in the upper 15 cm of soil than below this depth because, unlike agricultural soil for example, urban topsoils have not been regularly and systematically worked (Kaye et al, 2005). Morrisada et al (2004) analysed soils from 0-100 cm in Japan finding that 48% of organic carbon was stored in the upper 30 cm of soil.

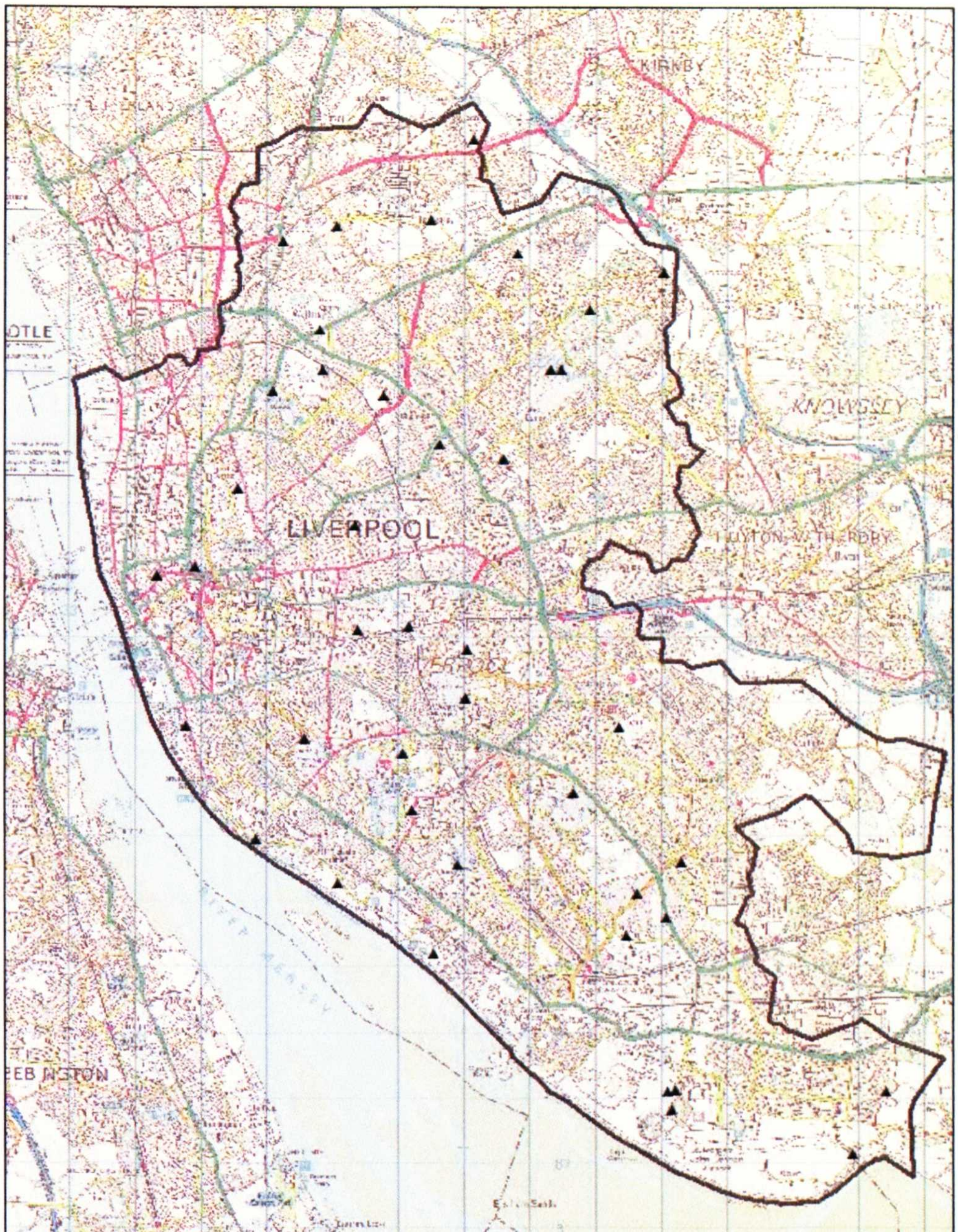
Meersmans et al (2009) examined data from over 2000 soil profiles in Belgium, finding that the upper 30 cm of soil showed net losses of C since they were first surveyed more than forty years previously. By contrast, across the entire 100 cm profile, there had been small net gains in carbon storage. However, difficulty surrounds extrapolating the results of these studies to other cities, where the soil properties and characteristics may be very different.

The aim of this study was to evaluate the extent to which urban parkland and road verge topsoils in the city of Liverpool varied in their carbon storage, their labile, water-soluble pool of C and concentration and association of trace metals and arsenic with other soil properties.

2.1.3 Study sites and methods

2.1.3.1 Sampling locations and soil sampling

During a 6 month period between March and November 2007, 53 topsoil samples (0 – 15 cm depth) were taken from urban parkland and road verges within the city boundaries of Liverpool, UK. Sampling locations in parkland were chosen according to the least likelihood of recent soil disturbance; for example, away from paths, roads and other through routes. Newly created green spaces were avoided because soils could have been recently disturbed or imported. Road verge samples were taken in areas where vehicles had not been parked, roadworks debris dumped or other clearly obvious recent disturbances. At each location, duplicate samples of topsoil were taken by inserting and carefully withdrawing steel cylinders, 2.5 cm in diameter and 20 cm in length into the surface 15 cm of soil. After the samples were taken, the ends of the cylinders were capped and the samples returned to the laboratory for analysis. 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 equal coverage of the whole city (see Fig 2.1.1).



This work is based on data provided through EDINA UKBORDERS with the support of the ESRC and JISC and uses boundary material which is copyright of the Crown.
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Figure 2.1.1 Soil sampling locations in the city of Liverpool. Note that a small number of points were on the boundary of the city limits and cannot be seen on this map.

2.1.3.2 Sample preparation and analysis

Bulk density was determined by measuring the volume of air-dried soil (20-25°C for 48 hrs) in each cylinder of soil. Soil was then lightly crushed and sieved to < 2 mm. Material greater than 2 mm was negligible in all samples, so this was not included in particle size classification. Particle size distribution was determined using a Beckman Coulter LS 13 Laser Diffraction Particle Size Analyser: 2mm – 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.

Organic matter was determined by the loss on ignition method (LOI) and total (TC) and inorganic carbon (IC) were determined using a TOC-SSM (Shimadzu, Tokyo, Japan). Total organic carbon (TOC) was 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 hours in an orbital shaker and allowed to settle for 45 minutes. After pH analysis the suspension was centrifuged at 3000 rpm for 10 minutes and the resultant supernatant was passed through a nylon filter to remove any suspended particulate matter which could interfere with analysis. These 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). Soil C densities (kg TOC m^{-2}) were calculated according to the soils' bulk density (g cm^{-3}) and TOC content (%) given the soil sampling depth (15 cm).

Pseudo-total concentrations of trace elements were determined after microwave assisted digestion of 0.2g air dried soil samples (< 2 mm) in concentrated 14 M, GPR grade HNO_3 by ICP-MS (XSERIES 2 ICP-MS; Thermo Scientific, MA, USA). Rhodium (1 ppm) was added to each sample as an internal standard, to compensate for varying instrument response during analysis.

2.1.3.3 Statistical analysis and mapping

All statistical analyses were carried out in SPSS v.14 for Windows. The sample location map (Fig 2.1.1) was created using ArcGIS 9.3.1.

2.1.4. Results and discussion

2.1.4.1 Physico-chemical characteristics

Clay content was low in all samples (< 3.5%), whereas sand was consistently high (mean 78%; data not shown). Mean soil pH was 5.9, but the range was large, with as low as pH 3.9 recorded at a wooded site. In common with other parameters, bulk density ranged greatly from 0.6 g cm^{-3} to 1.9 g cm^{-3} (Fig 2.1.2 B).

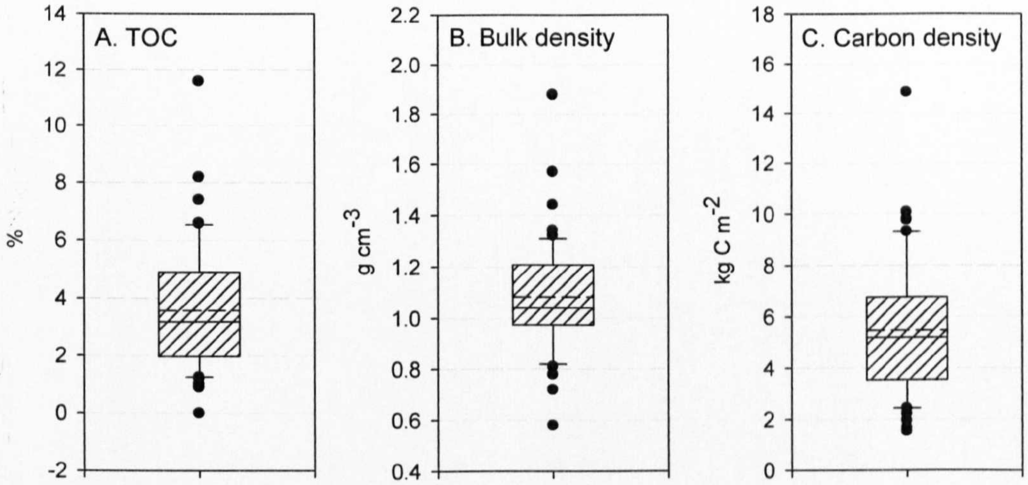

Figure 2.1.2. Mean and range of TOC, A), Bulk density, B) and carbon density, C) of urban soils. Dashed line is the mean value, solid line is median, box is the upper and lower quartile and whisker is the 10th and 90th percentile

2.1.4.2 Carbon density and labile C pool

Soils taken from across the city (Fig 2.1.1) varied considerably in their C density, from 3 – 10 kg TOC m^{-2} (Fig 2.1.2 C; discounting outlying values). This was due to the large variation in TOC and bulk density (Fig 2.1.2 A and B). These carbon densities fall within the range reported by Pouyat et al (2006) when reviewing data from urban soils studied in the United States; 1.5 – 16.3 kg TOC m^{-2}. Unlike older soils, or where considerable annual litter inputs are allowed to recycle to soil, the urban soils collected in the present study contained no visible organic horizon.

Both organic matter and TOC showed strong negative correlations to bulk density (Table 2.1.1). Decomposing biological residues have a lower density than mineral soil constituents; for example, bulk density of surface mulch applied green waste compost was previously reported to be more than 2.5 times lower than urban topsoil (Beesley and Dickinson, 2010). Sand and silt content had no significant influence on organic matter, but clay was negatively correlated with TOC (Table 2.1.1). Hassink et al (1993) suggested that, in coarse textured soils, such as those in the present work, with low clay content, adsorption onto clay particle surfaces can protect small amounts of organic matter against decomposition.

Table 2.1.1 Pearson correlations between key physico-chemical parameters in 53 parkland and road verge topsoils. * $p < 0.05$; ** $p < 0.01$; NS = Not statistically significant

	Bulk density	pH	Sand	Silt	Clay
pH	0.300 *	-	NS	NS	NS
OM	-0.725 **	-0.410 **	NS	NS	NS
TOC	-0.649 **	-0.361 **	NS	NS	-0.319 *

WSOC is an important constituent of the total C pool in soil because of its mobility and reactivity, and its capability to influence physical, biological and chemical processes in soil (Scaglia and Adani, 2009). In the 53 soils sampled in the present study, mean WSTC was not substantially greater than mean WSOC (Fig 2.1.3), leaving only a small soluble inorganic fraction. This was surprising given the lack of regular litter inputs to many of these soils. The lack of annual returns of C would indicate that the C pool in these soils could be easily diminished and may explain why extractable nitrogen was low. Total organic carbon (TOC) and WSOC were positively correlated (Fig 2.1.4) but TOC could not be considered to be an accurate predictor of the labile pool of C in these topsoils. This relationship would probably vary with soil depth as found by Nelson et al (1994) and Corvasce et al (2006). Mean total nitrogen in water extracts was only ~37 mg l^{-1} (Fig 2.1.4 inset) giving a wide mean C:N ratio in solution of 20.8:1. In circum-neutral, well drained soils, C:N ratios of 10:1 could typically be expected (White, 1997).

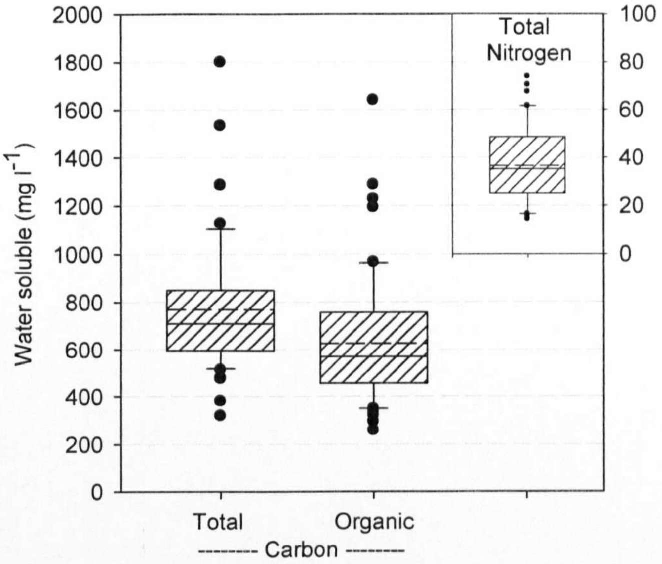

Figure 2.1.3. Mean and range of water soluble total and organic carbon and water soluble total nitrogen (inset) taken from aqueous extraction of soils. Dashed line is the mean value, solid line is median, box is the upper and lower quartile and whisker is the 10th and 90th percentile

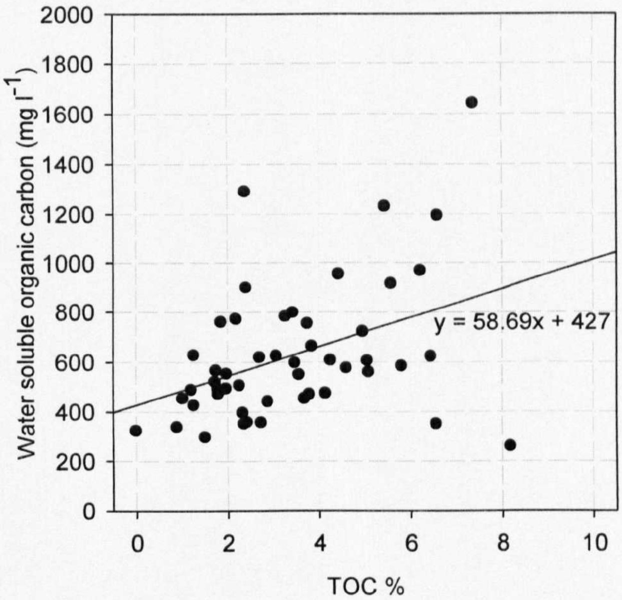

Figure 2.1.4. Relationship between TOC and WSOC in 53 soil samples, showing relationship between solid and water-soluble phases ($r^{-2} = 0.366$, $P < 0.01$).

2.1.4.3 Pseudo-total trace element concentrations

Zinc and Pb were found in the highest pseudo-total concentration in the 53 sampled soils, followed by Cu, As and Cd (Fig 2.1.5). In the survey of 1975, Parry et al (1981) found that available Zn and Pb levels in parkland soils were also the highest of elements determined for this land use type. Pseudo-total Cu and As distribution in the present study could be explained by their relationship with organic matter (Table 2.1.2).

Table 2.1.2. Pearson correlations between key physico-chemical parameters and trace elements in 53 urban parkland and road verge soils. * $p < 0.05$; ** $p < 0.01$; NS = Not statistically significant

	Cu	Zn	As	Cd	Pb
pH	NS	0.422 **	-0.299 *	NS	NS
OM	0.587 **	NS	0.633 **	NS	0.547 **
TOC	0.655 **	NS	0.682 **	NS	0.613 **

In similar, previous studies, Madrid et al (2007) sampled 63 soils across 3 cities finding that Zn and Pb levels were higher than other heavy metals in 2 out of 3 cities (at up to 210 mg kg^{-1} and 237 mg kg^{-1} Zn and Pb respectively in Aqua Regia). Ruiz-Cortes et al (2005) similarly measured total metal concentrations in 51 soils from 0-10 cm depth, again in urban areas of Seville, Spain, finding that Zn and Pb were present in greatest concentrations at up to 137 mg kg^{-1} and 725 mg kg^{-1} respectively. In that study Cd was also measured, with values in the range 0.18 – 4.85 mg kg^{-1}. Importantly, rather than the method of extraction and concentration, the element hierarchy of concentrations across these studies largely mirrors that of the present study in Liverpool.

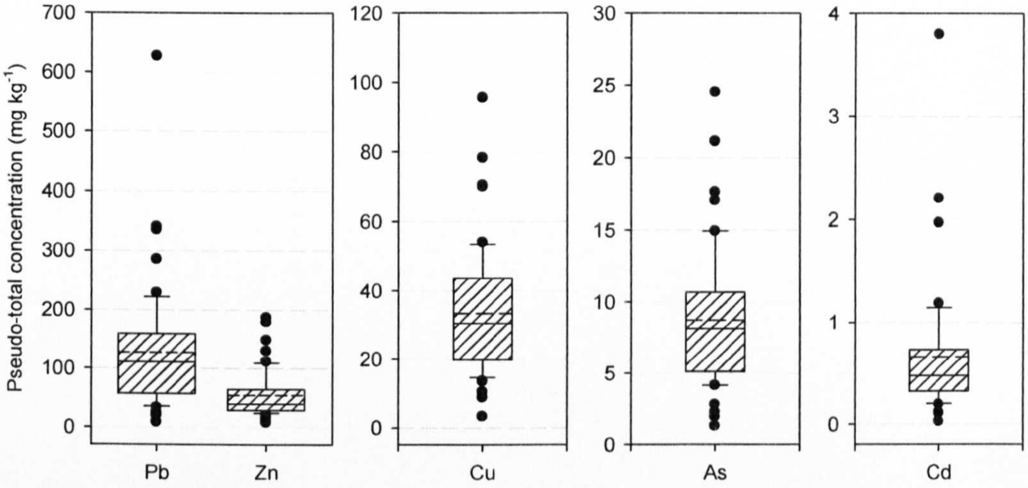

Figure 2.1.5. Mean and range of trace element pseudo-total concentrations in urban soils. Dashed line is the mean value, solid line is median, box is the upper and lower quartile and whisker is the 10th and 90th percentile

2.1.4.4 Interrelationships between measured soil characteristics

There were significant negative correlations between pH and OM/TOC (Table 2.1.1) because higher pH is generally more favourable for OM decomposition, which generates organic acids. Soil pH was positively correlated with bulk density because in less dense soils, aeration and porosity were probably increased, aiding organic matter decomposition. This also explains why OM and bulk density are negatively correlated (Table 2.1.1).

Trace metal associations with other soil properties included a strong positive correlation between OM and Cu; Thums et al (2008) noted intimate association of Cu with the organic phase in urban soils, determined by sequential extraction. In the present study similarly strong positive correlations were found between OM and both Pb and As. Zinc distribution was not related to OM or TOC, whilst Cd was the only element not to be correlated with any measured soil parameter. Inter-element correlations were found between all the analysed elements but were strongest between Cu, As and Pb (Table 2.1.3), probably because of the strong association with OM previously discussed (Table 2.1.2). In addition, some elements are likely to have originated from the same source, explaining their synonymously distribution.

Table 2.1.3. Pearson correlations between pseudo-total trace metals and arsenic in 53 urban parkland and road verge soils. * $p < 0.05$; ** $p < 0.01$; NS = Not statistically significant

	Cu	Zn	As	Cd	Pb
Cu	-	0.594 **	0.914 **	0.429 **	0.845 **
Zn	-	-	0.495 **	0.462 **	0.697 **
As	-	-	-	0.402 **	0.812 **
Cd	-	-	-	-	0.465 **

2.1.5 Conclusions

This exploratory soil survey, covering predominantly sandy parkland and road verge topsoils showed that carbon densities in the city of Liverpool are comparable to the general range found by previous workers studying carbon storage in urban soils. The results further suggest that the water soluble, labile pool of carbon was predominantly organic which, given the associations of some trace elements with organic matter, could impact negatively on trace element mobility.

2.2 Short-term carbon dynamics in urban soils amended with green waste compost

2.2.1 Abstract

This paper presents data on the temporal dynamics of carbon in urban soils and examines the potential to build and maintain urban soil carbon stocks using green waste compost. Carbon storage, leaching of dissolved organic carbon (DOC) and soil respiration were measured in a 35 year old urban lawn soil that had received a surface mulch application of compost, and in two topsoils created by mixing soil with green waste compost. In the old lawn soil, organic carbon storage was largely limited to the upper 15 cm depth, with material below 30 cm consisting of substantial amounts of building debris and technogenic material. Leaching of DOC from the compost mulch at the soil surface was readily mobile to soil below. In the newly created topsoils, mixing of small amounts of compost increased C storage from < 2 to 6 kg total carbon (TC) m^{-2}. Medium compost application rates reduced bulk density, with the effect only of maintaining C storage at ~6 kg TC m^{-2}. The highest application rates increased C density, but also most rapidly increased DOC leaching. In terms of the annual carbon balance, soil respiration was found to account for the greatest flux (20%), with losses corresponding to peak annual soil temperatures, whereas DOC accounted for only a small ($\leq$ 0.5%), but potentially important proportion of the annual loss. Repeated applications of small amounts of compost are probably most effective at building and maintaining C storage over the medium to long-term in these urban soils.

2.2.2 Introduction

Urban soils represent an emerging area of soil science. The need to better understand these soils has been recognised for some years (Bullock and Gregory, 1991) but an acknowledgement of their potential environmental value and interest is surprisingly recent (Scharenbroch et al., 2005; Lorenz et al., 2006; Lehmann and Stahr, 2007; Lorenz and Lal, 2009). Historic and continuing degradation of urban soils has been associated with diminished soil quality and a lesser provision of ecosystem services (Barrios, 2007; Tratalos et al., 2007). Nevertheless, certain urban land uses have been shown to increase the amount of C stored in soils (Pouyat et al., 2002) such as established urban green spaces, which have been reported to contain larger carbon pools, more than twice the size of those in native grasslands and cultivated fields (Golubiewski, 2006). Despite some studies reporting C storage in urban and degraded soils (Jo and McPherson, 1995; Pouyat et al, 2002; 2006; 2009; Tomlinson and Milne, 2006; Churkina et al, 2010) more detailed information on the dynamics of C in these soils is somewhat sparse (Beesley and Dickinson, 2010).

Definitions of urban soils are necessarily broad, reflecting varied levels of disturbance and heterogeneity. Hollis (1991) describes urban, anthropogenic soils as those in which the profile composition has been so strongly altered by direct human action that the original soil horizon sequence has been mostly destroyed. This is certainly true of many urban soils that have been deepened historically through waste disposal (Davidson et al., 2006; He and Zhang, 2006). In these circumstances subsoil horizons could be enriched with buried organic and black carbon (Lorenz and Kandeler, 2005; Lorenz et al., 2006). Alternatively, adding carbon to degraded soils with an already low carbon content has much greater potential to increase C storage than the amendment of more developed soils, that are closer to their carbon saturation level (Stewart et al., 2008 a,b). Urban soils in residential areas, receiving regular management inputs and lacking regular soil disturbances, create conditions conducive to net C storage (Pouyat et al, 2006) but urban landscapes that are managed for aesthetic purposes, without regular returns of carbon to soils, such as from litter degradation, could require alternative provision of soil C input. Adding organic amendments, such as composted green waste, to soils, has been found to provide large increases in soil organic carbon (SOC) within the first year of application (Leroy et al., 2008) whilst improving physico-chemical characteristics and functionality (Bernal et al, 2006). There is potential to use this material to enhance C storage in urban soils.

In this paper we measure carbon storage and two major fluxes in three urban soils with green waste compost amendment. By collating the results we derive a basic mass balance of C for these soils, to establish the potential for building and maintaining carbon storage in the year following green waste compost amendment.

2.2.3 Materials and methods

2.2.3.1 Field study sites[2]

Three study sites were chosen for this investigation. The first site, Byrom Street, was a relatively undisturbed urban lawn located on the university campus grounds in the city centre of Liverpool (Lat/Long: 53° 24'45.10" N, 2° 58'50.60" W). Disturbance in the past 35 – 40 yrs has been minimal apart for periodic mowing, the grass clippings being removed and disposed of elsewhere. A soil trench (100 cm x 50 cm x 100 cm depth) was excavated on an area of the lawn away from tree roots in such a way that two profiles were revealed on opposite sides of the trench. By the nature of urban soils, in centres of dense population, site selection and location of trial pits in this study were discrete, so only a single pit was excavated, replication provided by opposite faces of the trench. Above one profile, a 30 cm deep surface mulch of green waste compost (Whitemoss Horticulture, Merseyside) was applied whilst the opposite profile remained as a control, without the surface application of compost. The trench was left for 2 months before experimental work commenced in January 2008, allowing time for the compost mulch to equilibrate to field conditions.

The two other sites, Cross Lane and Chorley, were both newly created urban soils, part of a project funded by the Waste and Resources Action Program (WRAP) to examine the benefits of manufacturing topsoils using green waste compost. Cross Lane, Wirral (Lat/Long: 53° 24' 58 67" N, 3° 04' 26 30" W) was a former municipal landfill, taking general household refuse until the 1970's, whilst the Chorley site, Lancashire (Lat/Long: 53° 40' 38 76" N, 2° 39' 05 03" W), was a munitions manufacturing works that was fully decommissioned within the last 5 years. The topsoil creation, which took place between March and April 2007, mixed soil-forming materials (Cross Lane) or existing site subsoil (Chorley) with green waste compost to create new topsoil to replace existing topsoil which had been prior removed as part of the sites' remediation. At the Cross Lane site, only a shallow covering of topsoil overlay landfill waste, meaning that locally sourced sand and silt were mechanically mixed with green waste compost on a volume basis to produce new topsoil.

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[2] Note that more details of work on the study sites in this section can be found in the appended material (4).

Compost incorporation volumes here were 15, 30 and 45% compost, which were the low to medium application rates for this study. At Chorley the existing topsoil, containing munitions waste, was removed and disposed of safely elsewhere, whilst the non-contaminated subsoil was mixed in the same way as above, to give the high application rates of 50 and 65% compost. Both sites had a control of soil only, and a mulch treatment, of 30 cm compost on the soil surface (as at Byrom Street). All soil mixtures and the mulch were placed, using an earthmover, to 30 cm depth in triplicate, randomized experimental plots of 5m x 5m (Figure 2.2.1 inset). Due to the large size of the plots after triplications, two sites were required to incorporate the variety of compost mixtures for this study. Vegetation was annually cut-back and removed from the plots during the experimental work, but no other maintenance was carried out on the plots. In common with the Byrom Street site, it was only possible to excavate one trench on each replicate treatment, because the sites were open to public access. Shallow, 15 cm deep trenches were excavated for experimental work and two months was allowed after soil mixing and placement for soils and compost to equilibrate before soil sampling and experimental work started in April 2007.

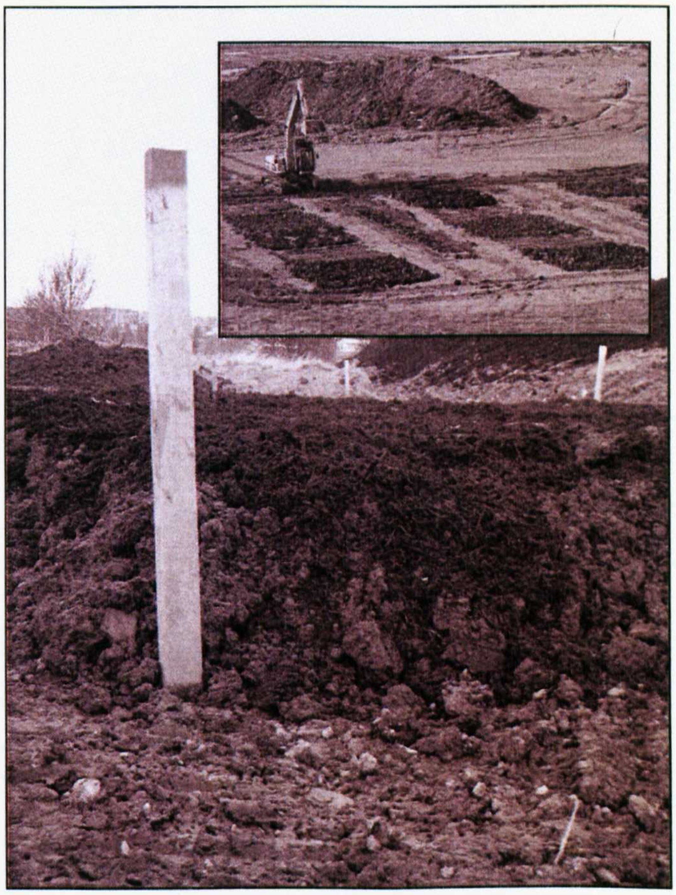

Figure 2.2.1. Newly manufactured topsoil following placement at Cross Lane site (showing mulch treatment) and triplicate experimental plots viewed from above (inset).

2.2.3.2 Soil sampling and physico-chemical analysis

Triplicate bulk soil samples were collected by inserting steel cylinders, 250 mm in diameter, horizontally into the soil profile at 15, 30, 50 and 75 cm depth at Byrom Street, and at 15 cm in the shallow trenches in the new topsoils at Cross Lane and Chorley. Samples were air dried at 20-25°C for 2 weeks in the laboratory before dry bulk density determination. Soil at Byrom Street was found to contain significant quantities of debris and other material greater than 2 mm particle size so this was also included in overall particle size determinations and classified as stones. Soil samples were then crushed and sieved to < 2mm for the following analysis.

Particle size was determined using a Beckman Coulter LS 13 Laser Diffraction Particle Size Analyser according to the following classification: > 2mm (stones), 2mm – 63 μm (sand), 62.9 – 2 μm (silt) and < 2 μm (clay). Owing to the relatively low organic matter content of the soils analysed for particle size, organic matter was not removed prior to analysis. Organic matter content was determined by the loss on ignition method (LOI) and total carbon (TC) and inorganic carbon (IC) were determined using a TOC-SSM (Shimadzu, Tokyo, Japan). Total organic carbon (TOC) was calculated as TC minus IC. Soil pH was measured by a Jenway pH meter with an SIS electrode, in a 1:10 soil and de-ionised water suspension, shaken for 3 hours in an orbital shaker and allowed to settle for 45 minutes. After pH measurement the suspension was centrifuged at 3000 rpm for 10 minutes and the resultant supernatant was passed through a nylon filter to remove any suspended particulate matter which could interfere with analysis (following Beesley et al, 2010a). These extracts were analysed for total water soluble carbon (WSC) using a TOC-VE (Shimadzu, Tokyo, Japan). Soil C densities (kg TC/TOC m^{-2}) were calculated according to the dry bulk density (g cm^{-3}) and TC content (%) based on a soil depth of 15 cm.

2.2.3.3 Experimental procedures

a.) Dissolved Organic Carbon

Dissolved organic carbon (DOC), which is operationally defined as the soluble organic carbon passing through a filter of 0.45 µm pore size (Buckingham et al., 2008), was sampled for one year using duplicate rhizon pore water samplers (Eijkelkamp Agrisearch Equipment, Netherlands) inserted into the soil profiles at 15 and 30 cm depths at Byrom Street, with samples taken from the profile beneath the compost amendment and the profile without amendment. Additional rhizon samplers were placed in the compost amendment itself and sampled in the same way. Pore water was sampled for one year from January 2008 to January 2009 at two weekly and, latterly, monthly intervals using removable needles and vacuum tubes (following Beesley and Dickinson, 2010). Samples were analysed for DOC using a Shimadzu TOC-VE. Daily rainfall, evaporation and soil temperature data were collected from the Met Office weather station at Ness Botanical Gardens, Neston, Wirral (Lat/Long: 53° 20' N, 3° 5' W), located 12 km southwest of the Byrom Street study site. Total throughflow was calculated by taking evaporation away from rainfall for each of the sampling periods. Soil temperature measurements were recorded in the upper 20 cm of soil at the weather station and a mean calculated for each sampling period. DOC here, in pore water at Cross Lane and Chorley, was measured over a 2 year period from April 2007 to April 2009. DOC was sampled and analysed as previously described, except that rhizon samplers were only placed at 15 cm depth, to sample pore water from the new topsoils at intervals of 3 months, 4 months, 8 months, 1 year and 2 years from the start of experimental work.

b.) Soil respiration

Soil respiration was measured under both controlled conditions in the laboratory and under field conditions in this study to investigate its response to temperature and moisture variation when soil was amended with different volumes of compost. Weekly measurements of soil respiration and soil temperature were taken over a 6 month period at 6 points within a 200 cm radius of the trench at Byrom Street, using a portable open chamber soil respirometer (ADC Bioscientific, Herts, UK). In the laboratory, bulk soil excavated from 0-15 cm depth of the trench at the same site, was mixed with compost on a vol:vol basis (15, 30 and 45% compost). These mixtures were placed into triplicate PVC cylinders (500 mm high and 150 mm internal diameter) which were stabilised in a bed of sand that would not influence the respiration measurements. Soils were kept in darkness to prevent vegetation establishment, in an environmental chamber (Conviron, USA) where temperature and relative humidity could be controlled accurately. Steel collars, which effectively provided a seal onto the soil surface, were pre-inserted into the soils both in the field and in the cylinders, and soils were equilibrated for 2 months in each case prior to respiration measurements. Soil respiration measurements in the laboratory controlled conditions were taken weekly over a 7 month period with soil temperature adjusted from 15°C > 10 °C > 5°C < 10 °C < 15°C. Measurements were taken for 4 weeks at each temperature, leaving 2 weeks between temperature changes for equilibration to the new conditions. To stabilize soil moisture and prevent soil from drying during this experiment, soils were periodically wetted with de-ionised water, whilst relative air humidity was maintained at 60%. In a parallel experiment, identical to that used to study soil temperature and respiration, soils were saturated, allowing the following 48 hours for the soils to reach field capacity (mean moisture content in control soil of 18.9%). Soils were kept at a constant temperature of 10°C, but soil was not re-wetted, and humidity was not controlled, to allow soil moisture to gradually decrease. In this experiment soil respiration was measured as the soils dried, to establish the influence of soil moisture. Soil moisture measurements were recorded simultaneously using a HH2 moisture meter (Delta T LTD, UK).

2.2.3.4 Mass balance calculations

A mass balance calculation of C storage and potential losses of C from soil was derived from carbon density, dissolved organic carbon and soil respiration data from the urban lawn soil; presented in Figure 2.2.7. The highest value of carbon density measured in soil following compost amendment from all soils was used to represent an uppermost estimate of C storage for the urban soils used in the mass balance, whilst all the other data was measured in the Byrom Street lawn soil. Mean soil respiration rates were multiplied from their measurement unit, μmol CO_2 m^{-2} s^{-1}, to kg C m^{-2} yr^{-1}. For DOC losses, the concentration of DOC in pore water was multiplied by the sum of throughflow data for the days between the collections of each pore water sample, assuming that 1 mm throughflow was equal to 1 litre of throughflow for a square metre of soil. The sum of these data was used to approximate an annual leaching value and produce a mass balance of C. The proportion of C flux, in the first year following compost application, to soil respiration and DOC leaching was then calculated as a percentage of the C density measured in the soil at the beginning of the experimental work.

2.2.3.5 Statistical analyses

All statistical analysis was carried out using SPSS v.14 for windows. Data were analysed for the influence of compost application on DOC concentrations by Kruskal-Wallis tests (data was non-parametric) whilst soil respiration data were log transformed to perform MANOVA analysis, to identify the significant effects of soil temperature and compost on respiration rates.

2.2.4 Results and Discussion

2.2.4.1 Soil properties

Soil pH was lower at Byrom Street than either Cross Lane or Chorley (Table 2.2.1). Organic matter and TOC decreased with soil depth at Byrom Street, with a lack of organic carbon below 15 cm reflecting the composition of the lower material in the profile, which was largely technogenic. At Cross Lane and Chorley, organic matter, TOC and WSC were increased with the rate of compost incorporation (Table 2.2.1). WSC was lower at Byrom Street than at the other two sites, but despite a reduction in TOC with soil depth, WSC was greater with depth, reflecting possible leaching and immobilisation effects on soluble carbon from the surface soil to lower depths in this profile. The ability of soils to adsorb dissolved organic matter (DOM) has been shown to increase with age (Lilienfein et al, 2004), and at Byrom Street the disturbance and burial of older soils could have caused a sharper boundary between younger and older soils in the profile than would be found in chronosequences in naturally developed, undisturbed soils. Clay content increased slightly with depth in the profile, which may have further immobilised WSC at lower depths on particle surfaces. A notable characteristic of the soil in this profile was the substantial amount of stones and pieces of building debris, which meant that a variable proportion of the material at each depth was > 2 mm. Soil at 30 - 50 cm depth had the greatest proportion of stones, which explains the higher bulk density at this depth (Table 2.2.1). Soils at Cross

Lane and Chorley had a higher proportion of silt and clay (Table 2.2.1) than the urban lawn soil at Byrom Street.

Table 2.2.1. Physico-chemical properties of soils and compost amendment (mean ±SE, n =3) by soil depth (Byrom Street) and compost application volume (Cross Lane and Chorley). Soil samples at Cross Lane and Chorley were taken after newly manufactured topsoils had equilibrated to field conditions for 2 months. ND = Below limit of detection.

*Note that material > 2 mm was also included in particle size distribution at Byrom Street.

Byrom Street	Soil	---------------	---------------	-------------	*Compost*
	0-15 cm	15-30 cm	30-50 cm	50-75 cm	
pH	6.65	6.85	8.56	8.63	*8.1*
Organic Matter %	6.64 (0.67)	4.06 (0.28)	2.44 (0.16)	2.45 (0.04)	*23.1 (0.49)*
TOC %	2.09 (0.01)	0.48 (0.01)	ND	ND	*12.3 (0.16)*
WSC mg l^{-1}	393 (18.8)	418 (14.0)	482 (16.0)	360 (25.4)	*3175 (192)*
Bulk density (g cm^{-3})	1.29 (0.02)	1.28 (0.02)	1.73 (0.08)	1.68 (0.08)	*0.47 (0.05)*
*Stones %	16 (0.8)	-	44 (1)	24 (0.5)	
Sand %	67.9 (0.4)	-	43.6 (0.7)	59.3 (1)	-
Silt %	15 (0.4)	-	11.1 (0.4)	14.7 (0.7)	-
Clay %	1.09 (0.37)	-	1.3 (0.36)	1.75 (0.13)	-

Cross Lane	Soil	---------------	---------------	-------------	-------------
	0% compost	15%	30%	45%	Mulch
pH	7.52	7.7	7.6	7.81	7.91
Organic Matter %	3.92 (0.0)	8.18 (0.29)	7.41 (0.14)	11.7 (0.07)	11.6 (0.27)
TOC %	0.09 (0.04)	2.79 (0.11)	1.46 (0.09)	3.63 (0.25)	2.61 (0.06)
WSC mg l^{-1}	531 (22.5)	871 (30)	630 (36.4)	1224 (34)	1164 (7)
Bulk density (g cm^{-3})	1.55 (0.1)	1.14 (0.03)	1.13 (0.28)	0.91 (0.06)	1.22 (0.87)
Sand %	60.6 (0.33)	-	-	-	-
Silt %	37.6 (0.56)	-	-	-	-
Clay %	3.97 (0.06)	-	-	-	-

Chorley	Soil	-	---------------	-------------	-------------
	0% compost		50%	66%	Mulch
pH	8.95	-	8.50	8.27	8.58
Organic Matter %	2.01 (0.03)	-	16.8 (0.19)	21.2 (0.65)	27.9 (0.83)
TOC %	0.17 (0.04)	-	5.06 (0.24)	6.24 (0.31)	7.88 (0.28)
WSC mg l^{-1}	226 (14.6)	-	792 (91.4)	993 (145)	2122 (422)
Bulk density (g cm^{-3})	1.55 (0.76)	-	1.06 (0.17)	0.89 (0.09)	0.86 (0.23)
Sand %	37.2 (0.68)	-	-	-	-
Silt %	58.6 (0.71)	-	-	-	-
Clay %	6.84 (0.19)	-	-	-	-

2.2.4.2 Soil carbon storage

Total soil C storage (carbon densities) at Byrom Street ranged from 1.5 - 5 kg TC m^{-2} (Figure 2.2.2) with a depth decrease, most notably in the organic fraction (Table 2.2.1). The constituents of this soil lower in the profile included cement, residues of construction waste and the original parent material and, whilst this increased bulk density, their inorganic composition restricted TC density. Carbon density in the upper 15 cm of soil was at the lower end of that reported elsewhere for other urban soils (Jo and McPherson, 1995; Pouyat et al, 2006; Tomlinson and Milne, 2006). At Cross Lane and Chorley, C densities in soils with no compost added, were also at the lower end of reported values in the above literature (< 2 kg TC m^{-2}) but, following compost addition, there was a very important and opposing effect of adding compost to carbon storage. The addition of the lowest volume of compost mixed in with soil (15%) at the Cross Lane site, raised C density to approx. 3 times that of the control (6 kg TC m^{-2}; Figure 2.2.2). This increase was not linear with increasing compost volume. Despite the organic fraction showing slight increases when more compost was applied, there was a small reduction in total C density (Figure 2.2.2 B) because large amounts of compost reduced bulk density (Table 2.2.1). At Chorley, although bulk density was similarly low, the high compost application resulted in higher C densities (~12 kg TC m^{-2}). Further bulk density measurements, taken in February 2008, showed that bulk density had reduced or remained the same at Cross Lane since the experimental work began, but had increased slightly in the uppermost compost application (65%) at Chorley (data not shown), an effect that would have influenced C densities over the year. Some of the increase in C density observed could also have been related to the higher clay content of the Chorley soil (Table 2.2.1). In clay soils, organic matter located in small pore spaces can be physically protected from degradation (Hassink et al, 1993) and, where there is identical organic matter input, a higher clay content reduces organic matter turnover, resulting in higher SOM levels (Muller and Hoper, 2004). This may explain the greater C densities in soil at Chorley since the lower volume of compost application in this soil was not greatly different to the upper application volume at Cross Lane, and without compost application, C densities were similarly low at both sites (< 2 kg TC m^{-2}, Figure 2.2.2).

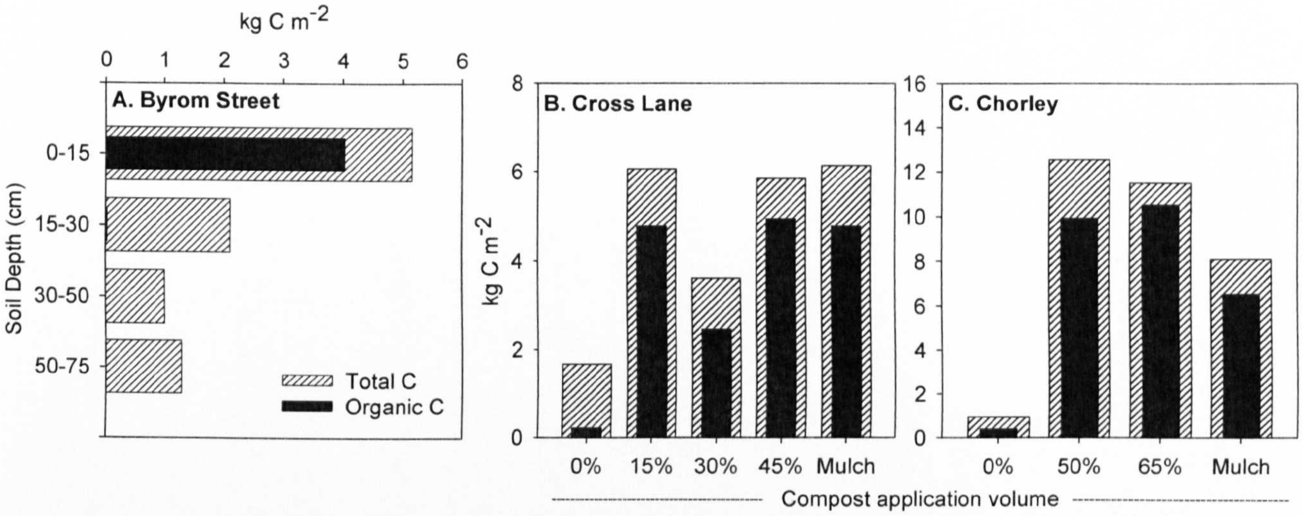

Figure 2.2.2. Total and organic C density in the soil profile at four depths at A) Byrom Street, and B and C) in the upper 15 cm of soil and compost mixtures and mulches at Cross Lane and Chorley.

2.2.4.3 Dissolved organic carbon in the urban lawn soil

Concentrations of DOC in pore water sampled directly from compost amendment applied to the surface of the urban lawn soil at Byrom Street fluctuated considerably, with temporal differences in DOC concentration of > 400 mg l^{-1} over the year (Figure 2.2.3A). Dissolved organic carbon comprises a mixture of biological residues at various stages of decomposition (Wallage et al, 2006) and considerable production was therefore expected from compost, especially under favourable conditions of moisture and temperature experienced in the summer and early autumn periods in which samples were taken (Figure 2.2.4). Soil moisture deficits are infrequent as a result of relatively high and regular rainfall in the maritime climate of the northwest of England, but some periods of zero throughflow and high soil temperature were seen in summer (Figure 2.2.4). In such conditions, of relatively high soil microbial activity, DOC production would probably increase but with limited transport through the soil because of limited rainfall and low throughflow. During any subsequent period of high throughflow, the larger concentrations of DOC accumulated in pore spaces, would be flushed through the soil (Figure 2.2.3B).

Leaching of DOC from compost to soil below was indicated by an immediately elevated concentration of DOC at 15 cm depth at the start of the experimental period (Figure 2.2.3B). Subsequently, there was clear influence of rainfall and temperature on DOC production and transport from compost during the year. In the first 4 months of the year, soil temperature was lowest (Figure 2.2.4) and DOC was readily leachable after compost was applied. Towards the middle of the year peak concentrations of DOC leached to 15 cm depth were ~230 mg l^{-1} compared to ~100 mg l^{-1} in the control soil profile (Figure 2.2.3B and C), indicating rapid transport of this mobile C fraction. Finally, at the end of the year, when production of DOC from compost was lowest, concentrations at 15 cm began to reduce, due to the lack of DOC supply from compost but continued throughflow. The increase in DOC concentration due to the addition of compost in soil at 15 cm was significant ($p < 0.001$). Other workers sampling pore water by the same method, albeit in soils without supplementary organic additions, have similarly reported wide ranging DOC concentrations (Knight et al, 1998; Clemente et al, 2008). In the present soil, a boundary existed at 15 cm, below which leaching of DOC was much lower, with peak concentrations of DOC in the compost amended soil at 30 cm greater than those of the control soil at 30 cm only in the summer period, corresponding to peak DOC production from compost (Figure 2.2.3C); concentrations in the latter third of the year reduced to similar levels in both control and compost amended soil (< 100 mg l^{-1}). The mean increase in DOC concentration at 30 cm was also significant ($p < 0.01$), probably an effect induced in the first half of the year, when the highest concentrations of DOC were produced by compost and readily leached. Throughflow variations with soil depth could provide an explanation for this variance in DOC leaching, since moisture would be retained for longer in the upper depth, where organic matter was greatest (Table 2.2.1). In a study by Borken et al (2004), where mature compost was applied to forest soils, only 5% of DOC was leached from the compost mulch to 10 cm soil depth below and less than 0.5% was leached to 100 cm. Guggenberger and Kaiser (2003) had previously reported that DOC leaching from organic surface soils could be as high as 38 g m^{-2} yr^{-1}, the vast majority of this being adsorbed in the mineral horizons below, so that only a small fraction could be potentially lost from the soil system. The present study appears to support this, also finding restricted vertical mobility of DOC.

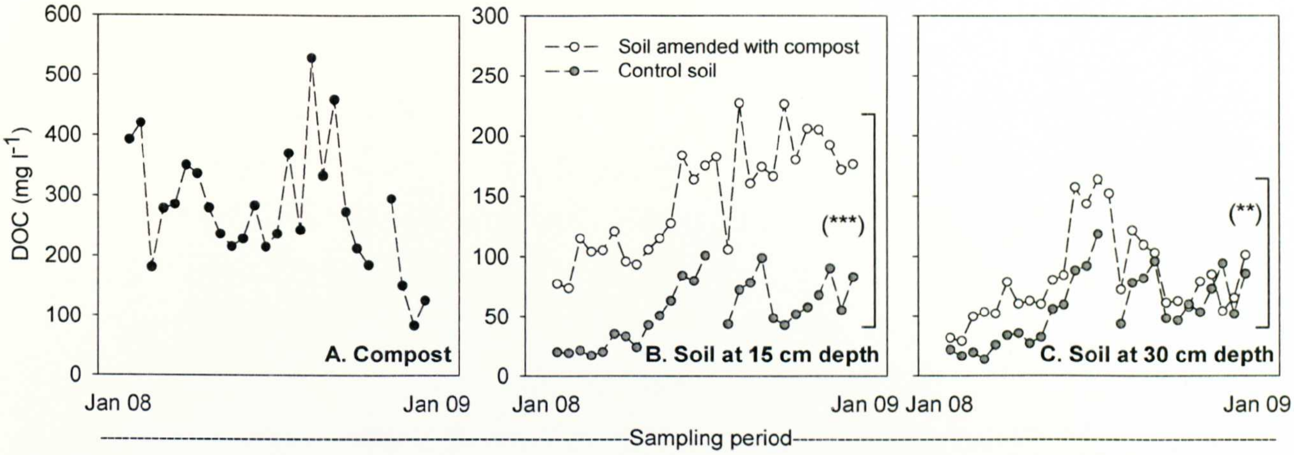

Figure 2.2.3. Dissolved Organic Carbon (DOC) in soil pore water at Byrom Street from A) compost amendment, B) soil at 15 cm depth in the profile and C) soil at 30 cm depth in the profile. Significant differences between mean DOC concentration for the whole experimental duration between control and compost amended soil are indicated by ** $p < 0.01$ and *** $p < 0.001$ (Kruskal-Wallis).

As previously discussed, the elevated WSC, measured at lower soil depths in the profile, appears contradictory at first, but may be related to DOC leaching. Adsorption onto mineral surfaces could immobilise C in solution as it travels from the topsoil, where it is abundantly mobile (Figure 2.2.3B) through the residues and debris in the subsoil. In this case DOC would not be free in solution in pore water, but could be desorbed from soil by more aggressive aqueous laboratory extraction methods. In such circumstances only very high throughflow would impact on the mobility of soluble C at lower depths. Were this to occur, an enhancement of organic carbon in soil solution may provide a biological stimulus to the decomposition of recalcitrant fractions of C lower in the profile; for example through N fertilisation or from the minor proportion (<10%) that consists of simple organic compounds such as organic acids, amino acids and saccharides (Green et al., 2006). This effect has been found in older soils, where forests have been converted to agriculture (Fontaine et al., 2007). Such priming effects as they are termed, are unlikely to be deleterious to deeper soil carbon in the present soil as TOC was below the limit of detection at the lowest soil depths, but these mechanisms might be important in other urban soils, with a considerable proportion of their carbon stored at lower depths.

2.2.4.4 Dissolved organic carbon in the newly created topsoils

At Cross Lane and Chorley, where soils were manufactured using compost, initially high concentrations of DOC in the first 3 months of sampling were superseded by far lower concentrations after 1 year (Figure 2.2.5) in common with the rapid reduction in DOC seen in pore water from the compost mulch, applied to the surface of the soil at Byrom Street (Figure 2.2.3A). Dissolved organic carbon concentrations peaked at 400-500 mg l^{-1} at Chorley (Figure 2.2.5B), which also corresponded to the peak DOC concentration in the pore water sampled directly from compost at Byrom Street (Figure 2.2.3A). At both Cross Lane and Chorley, rapid reduction in DOC concentrations in pore water occurred following environmental exposure of the newly created topsoils, probably driven by soil temperature and throughflow as previously discussed.

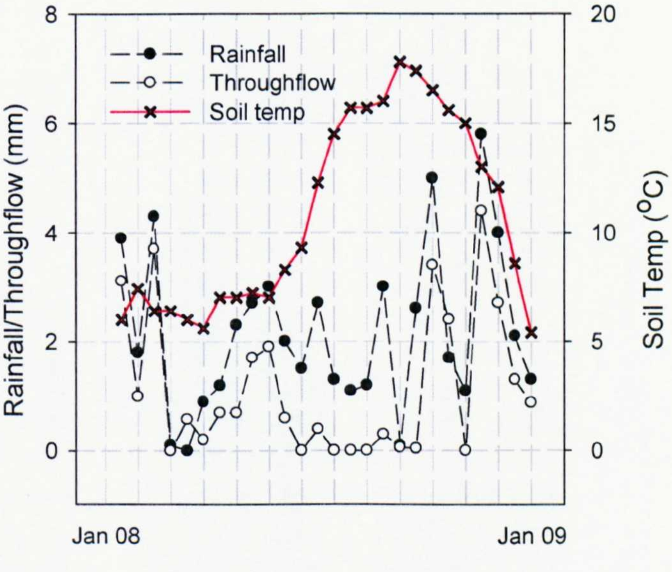

Figure 2.2.4. Rainfall, throughflow and mean soil temperature corresponding to each of the pore water sampling periods at Byrom Street. Rainfall and throughflow is a sum of daily measurements in each sampling period divided by days between each sampling period. Soil temperature is a mean over each sampling period.

After 1 year, concentrations of DOC reached similar background levels at Cross Lane and Chorley (≤ 100 mg l^{-1}) indicating that, irrespective of the amount of compost that was applied to the soil, DOC stabilised with time. Only the highest compost application rates (50 and 65%), at the Chorley site, significantly increased mean DOC concentrations in pore water over the entire 2 year experimental duration (Figure 2.2.5; $p < 0.05$). This indicates that lower compost applications, although inducing immediate leaching of DOC, did not have significant effects on the leaching of DOC over the entire 2 years; in mass balance terms DOC only accounted for small annual losses of C (Figure 2.2.7). Soluble C in soil pore spaces, produced rapidly as micro-organisms decompose the fresh organic material immediately following compost application, was probably leached first from these new topsoils. This would be followed by the desorption of some aggregate protected C leaving the gradual degradation of the more insoluble fractions of C that provide a steady soluble C input (Cao et al, 1999). Slightly greater eventual background concentrations of DOC could have been expected where compost was added, because of the greater potential for protection of C by aggregation and the small proportion of lignified material in the compost, which would decompose slowly; lignin degradation has been shown to be an important control on dissolved organic matter production (Kalbitz et al, 2006).

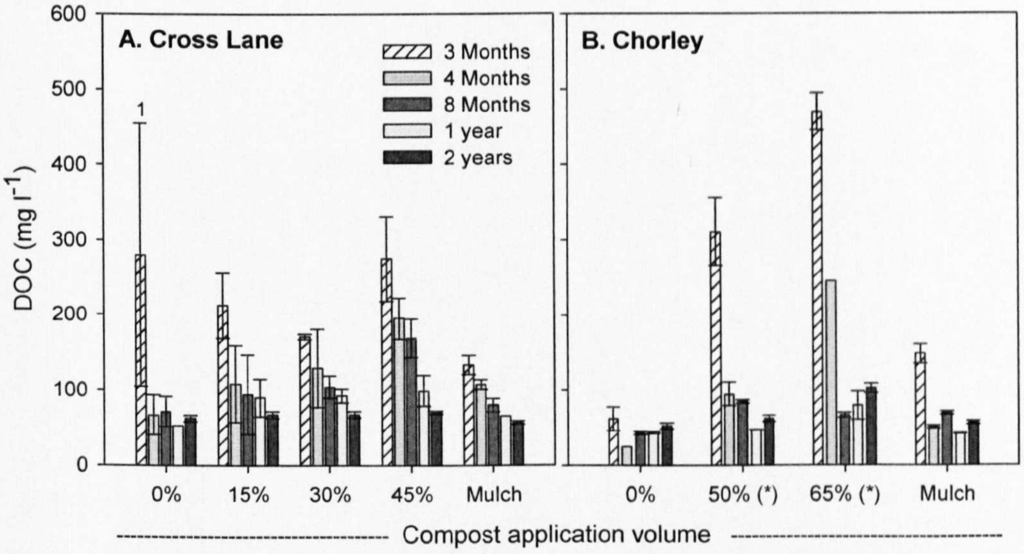

Figure 2.2.5. Dissolved Organic Carbon (DOC) in pore water from 15cm depth in soil at A) Cross Lane and B) Chorley sampled 3, 4, 8 months, 1 and 2 years after soil and compost mixing. Note the high variability between replicates in the control at the beginning of sampling at Cross Lane, denoted by the large error bar. Statistically significant increases in mean DOC concentration measured after compost application, after the 2 year experimental duration, are indicated by * on the X axis (Kruskal-Wallis; $p < 0.05$). [1] Note that this result was omitted from statistical analysis because of the large error.

2.2.4.5 Soil respiration

Soil respiration was measured in soil excavated from the urban lawn, at Byrom Street, mixed with compost to the same volumes as at Cross Lane. In the laboratory experiment, decreasing soil temperature significantly decreased mean soil respiration rate in the control and compost amended soils (MANOVA; $p < 0.01$) whilst also reducing the range (Figure 2.2.6). A similar temperature response was measured in the field at 10 and 15°C, although vales were slightly lower than laboratory values, probably because soil in the field had not been disturbed. At 5°C field values were much lower than laboratory values for control soil (Figure 2.2.6), indicating that laboratory results may have overestimated field respiration rates at cooler times of year. It was unlikely that this was a soil moisture effect, as this parameter varied little, the increases in which could solely be attributed to the addition of compost to this sandy soil (data not shown). Soil moisture governs the influence of other factors, such as soil temperature, on soil respiration (Lou and Zhou, 2006), but soil moisture deficits are unlikely in the UK, given the regular rainfall and cool soil temperatures, and were sparsely seen during the year (Figure 2.2.4). Although soil respiration rates were a function of temperature, the response of soil respiration to soil temperature was not linear. In this respect, following the decrease in soil temperature in the laboratory experiment, during the subsequent increase in temperature, respiration rates did not mimic those recorded at the same temperature previously. Only small increases in mean respiration rate and a much narrower range of respiration rates were recorded as temperature was increased. This effect could be associated with a lag phase in microbial activity, whilst soil micro organisms adapt to changing soil conditions. Coupled with the mortality of some ill adapted soil organisms during the temperature reductions, and combined with the inevitable reduction in available substrate for the remaining soil organisms, there would be an overall net decrease in soil respiration activity even though temperature was increased; it has been suggested that soil microbial communities can adapt their metabolism in response to changing soil conditions and disturbances (Davidson and Janssens, 2006).

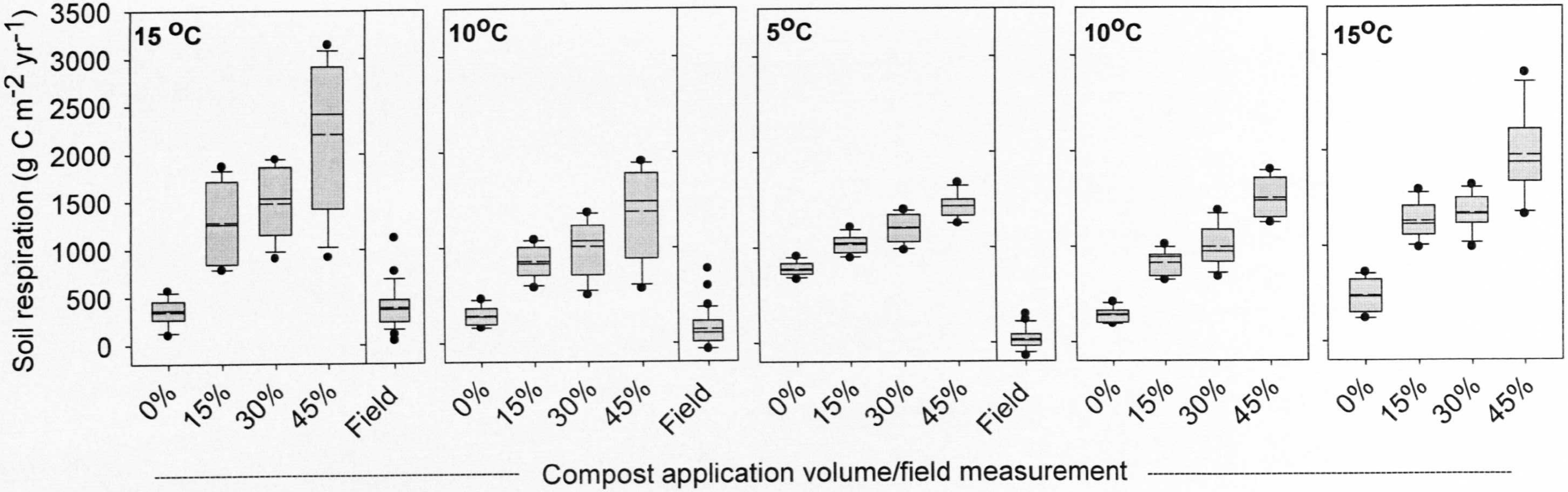

Figure 2.2.6. Mean and range of soil respiration rates measured from soils at Byrom Street under field conditions and in a laboratory using different soil and compost mixtures and soil temperatures (soil moisture constant). Dashed line is the mean value, solid line is median, box is the upper and lower quartile and whisker is the 10th and 90th percentile. Field values are grouped and presented according to soil temperature measured in the field. Note that both increasing soil temperature and adding compost significantly increased soil respiration rates (MANOVA; $p < 0.001$ and $p < 0.01$ for compost and temperature respectively).

Wang et al (2003) previously found that total organic carbon content of soil accounted for 75-81% of the observed variability in soil respiration, which would explain why compost induced increased respiration rates. In the present study, adding compost increased soil respiration rates significantly (MANOVA; $p < 0.001$), so reductions in available substrate as decomposition occurs would reduce respiration rates during the 6 months experiment. Furthermore, dissolved organic carbon reduced rapidly in the first months following the addition of compost to soils in this study (Figure 2.2.3A; Figure 2.2.4), which further explains why soil respiration rates did not respond similarly in the first months of the laboratory experiment as in the last months, despite the same soil temperatures and moisture conditions. Increases in water-soluble carbon have previously been found to enhance soil respiration rates (Clark et al, 2007). Furthermore, priming effects, immediately following the addition of compost to soils for example, are known to affect short term CO_2 production (Kuzyakov, 2006), which could have artificially enhanced respiration rates in the early stages of the experiment. Although there was some discrepancy between field and lab respiration rates at low soil temperature in the present study, soil respiration accounted for 20% of the annual loss of C from this lawn soil (Figure 2.2.7); to be considered as an upper estimate. Because compost addition increased C storage in soil, whilst increasing respiration rates, adding compost did not greatly affect the proportional total annual loss of C to respiration (Figure 2.2.7).

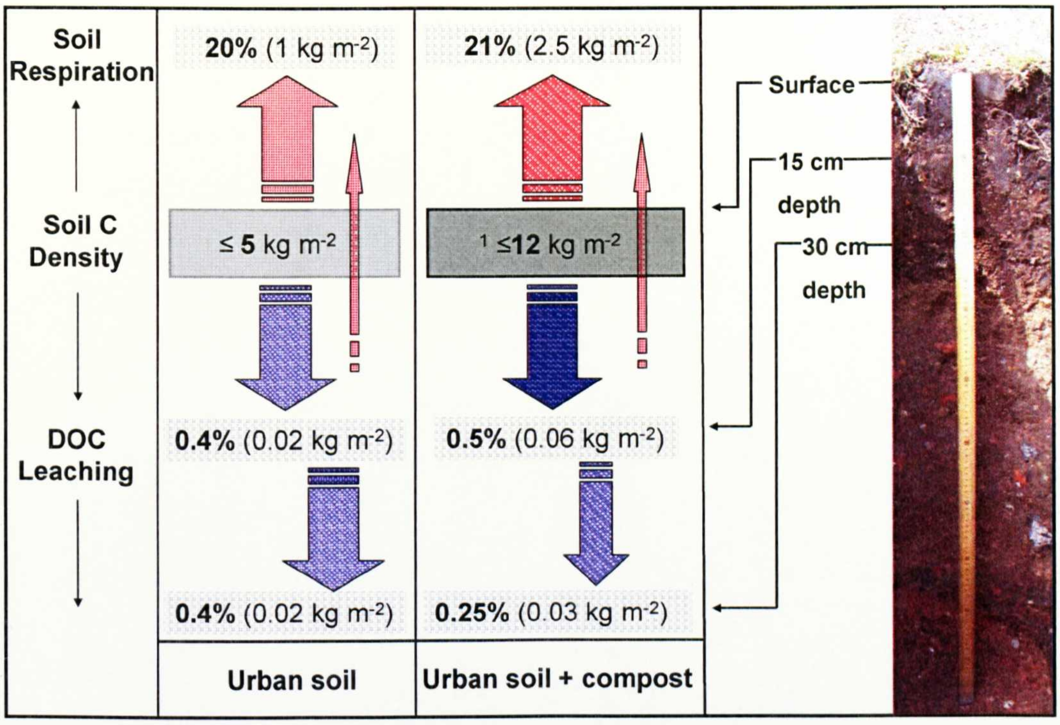

Figure 2.2.7. Mass balance of C for the first year after compost amendment of a 35 year old urban lawn soil at Byrom Street, showing C storage (C density) and the proportion (%) of C lost to soil respiration and DOC leaching. ^{1} Note that C density was the uppermost value recorded in all of the urban soils in this study. Photograph is the soil profile at Byrom Street.

2.2.5 Conclusions

Without the addition of green waste compost, C densities were low in two recently created urban topsoils and did not exceed 2 kg TC m^{-2}, falling short of the amount stored in the topsoil of a more established, older lawn soil (~5 kg TC m^{-2}). Small amounts of compost were most effective at increasing C density in the newer soils but medium applications reduced bulk density with no net increase in C storage, so that only very high application rates further increased C storage (~12 kg TC m^{-2}). Substantial changes in concentration of DOC occurred during the first year after compost was applied to soil, largely influenced by seasonal climatic variations, yet the proportional annual loss of C from soil via DOC were low (≤ 0.5%). Soil respiration was dependent on both soil temperature and volume of compost added to soil, and contributed ~20% of annual C loss by this pathway. Compost greatly enhanced respiration rates, but not annual losses, because increases in C storage by adding more compost largely offset increased respiration losses.

It appears that only small C inputs, such as plant litter and root exudates, would be required to maintain C stocks in some urban soils. Adding compost increases carbon storage, but can also enhance annual losses, so repeated applications of compost are required to build and maintain longer-term carbon storage. Therefore, in urban areas, adding small amounts of composted green waste regularly could maintain soil C stocks at more than double their current levels.

2.3 Annual respiratory losses of carbon from a city centre urban lawn soil.

2.3.1 Abstract

This paper presents the results of soil respiration measurements taken from an inner city soil over a 6 month period, at laboratory controlled variable soil temperatures, moistures and application rates of composted green waste. Data were analysed using a three variable parametric model in MATLAB to predict annual soil respiration rates based on meteorological data. Total annual loss of C to soil respiration was calculated using two contrasting soil moisture scenarios. Soil temperature was found to be the primary driver of seasonal trends in soil respiration. Total annual respiration (T_{ar}) from soil was < 1200 g C m^{-2} yr^{-1} at low moisture but more than doubled at high soil moisture, with the majority of this difference occurring during summer months when soil moisture was the limiting factor in warm soils. The predicted T_{ar} fitted well with that reported previously in 2.2 and represents an annual loss of C from this soil of ~25 - 50%, depending on soil moisture. Applying green waste compost to the soil significantly increased respiration rates but more data would be required to ensure the accuracy of the model in predicting respiration rates when compost application is included as a variable. Furthermore, the effects of decomposition also need to be included into the model as this influenced soil respiration measured in the laboratory.

2.3.2 Introduction

Soils are the largest terrestrial store of carbon (C) with those currently below their capacity a repository for additional stocks (Stewart et al., 2008b) given appropriate management. The close proximity of urban soils to centres of population means that they are now gaining recognition for their distinctiveness and value as well as their C storage potential. But it is not just their convenience that makes them attractive for C storage because there is evidence that the amount of C already stored in these soils could be far greater than that of other neighbouring land uses (Golubiewski, 2006) and, in fact, urban soils have been shown to have potential to sequester large amounts of carbon (Pouyat et al, 2006). In degraded urban areas, the experimental manipulation of soils to modify their C storage capability could be an attractive option for urban soil management. One way to achieve this would be to add organic amendments. But it is not simply the case that adding more organic matter to soils increases C storage, as the mechanisms of C loss can be adjusted by the addition of fresh organic material. For example, the addition of green waste compost to an urban soil disturbed the soluble, transient pool of C (Beesley and Dickinson, 2010) and increases in soluble carbon have been shown to stimulate soil respiration (Liu et al, 2006; Clark et al, 2007).

The breakdown of carbon-based organic substrates produces CO_2, the exchange of which, between soil and atmosphere, plays a crucial role in climate dynamics of the earth system (Lou and Zhou, 2006). Physico-chemical characteristics, pH, organic matter content and soil texture influence soil respiration rates (Koizumi et al, 1999; Vanhala, 2002) mediated by temporal soil moisture and temperature changes (Lou and Zhou, 2006). The amount of carbon in soils also significantly influences soil respiration rates. Wang et al (2003) found that as much as 80% of the variability in soil respiration could be attributed to the soil's carbon content. At the biochemical level, C release from soils, as respiration, simply has a 1:1 molar relationship with carbon substrate consumption (Lou and Zhou, 2006). The inter-relationships between factors controlling soil respiration at the ecosystem level however, are far more complex and difficult to elucidate. In the context of urban soils, that may have been disturbed, deepened or supplemented (Davidson et al., 2006; He and Zhang, 2006), the multiple drivers of respiration might require even more careful consideration.

The aim of the present study was to develop a predictive model of annual soil respiration rates from an inner-city urban lawn soil. Seasonal variations in soil respiration were examined in response to annual soil temperature changes and moisture and compost variations using a three variable, parametric modelling approach. Total soil respiration values were calculated to determine the annual losses of C by respiration for this soil system.

2.3.3 Methods

2.3.3.1 Soil collection and experimental work

Soil was collected from the grounds of the university campus within the city centre of Liverpool, UK (Lat/Long: 53° 24'45.10" N; 2° 58'50.60" W). The 35 year old urban lawn site has also been studied in relation to mass balance of C (see 2.2) and fluxes of soluble C and trace metals (see 2.4; Beesley and Dickinson, 2010). The area had been minimally compacted by occasional recreational use within the last 35 years, but there was no evidence of soil importation or exportation. Topsoil only was used for experimental work (0-15 cm) and was collected by digging a shallow trench of 100 x 50 cm to a depth of 15 cm in a secluded area of the site. Any biological debris, earthworms and material > 2 mm was removed from the bulk soil. Material < 2mm was retained for inclusion in particle size distribution characterisation, to be classified as stones. The remaining soil was air dried at 20-25°C for 2 weeks prior to analysis.

Green waste compost, sourced from Whitemoss Horticulture (Kirkby, Merseyside) was thoroughly mixed mechanically with the soil on a vol:vol basis to give a low, medium and high mixture of compost and soil (15, 30 and 45 % compost respectively). Triplicate PVC cylinders of 50 cm height and 15 cm internal diameter (Fig 2.3.1) were filled with each soil and compost mixture and a control with soil only. The base of the cylinders were covered with a geotextile material, so that soils could drain freely. Cylinders were kept in darkness to prevent any vegetation establishment, in an environmental chamber (Conviron, USA), where temperature and relative humidity could be controlled accurately. Stainless steel soil respiration collars were inserted into the soil in each cylinder, to effectively form a seal on the soil surface. Before any measurements were taken, 2 weeks equilibration time was allowed after inserting the collars.

Soil respiration was measured weekly for a 6 month period whilst soil temperature was adjusted firstly in a decreasing cycle from 15°C to 10 °C to 5 °C and then increased in the same increments (following the method detailed in 2.2). Measurements were taken for 4 weeks at each temperature, leaving 2 weeks between measurements, for soils to equilibrate to the new temperature. To keep soils moist whilst temperature was adjusted, soils were prevented from drying by periodically wetting them with de-ionised water (pH 5.5) and relative air humidity was maintained at 60%. In a second, parallel experiment, using the same experimental design as above, soils were saturated and allowed to drain for 48 hours to imitate field capacity (mean moisture content of soil 18.3%). Soils were kept at a constant temperature of 10 °C in the environmental chamber, but humidity was not controlled in this case, to allow soil to dry gradually. In this experiment soil respiration was measured weekly, for 2 months, as the soils dried from field capacity. Soil moisture measurements were taken simultaneously using an HH2 moisture meter (Delta T LTD, UK) inserted into pre-drilled holes in each soil cylinder at 30 cm depth.

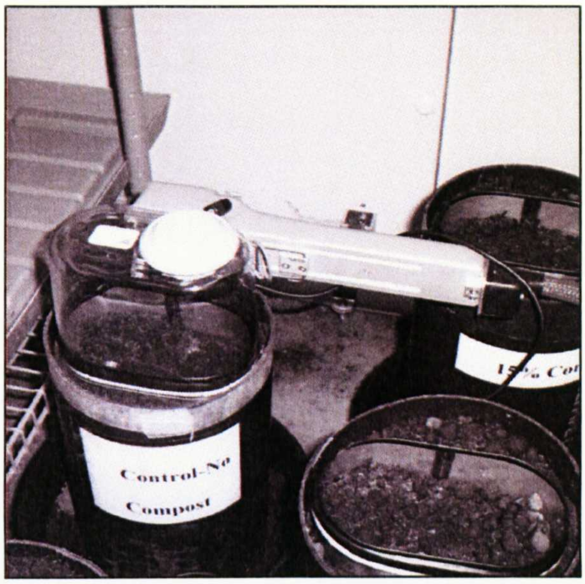

Figure 2.3.1. Soil respiration measurement in progress under controlled conditions in an environmental chamber.

2.3.3.2 Physico-chemical soil characterisation

Samples of soil, compost and each soil mixture were retained for the following physico-chemical analysis. Particle size was determined using a Beckman Coulter LS 13 Laser Diffraction Particle Size Analyser according to the following classification: > 2mm (stones), 2mm – 63 μm (sand), 62.9 – 2 μm (silt) and < 2 μm (clay). Owing to the low organic matter content of the soil (data not shown) organic matter was not removed prior to analysis. Total organic carbon (TOC) was determined using a TOC-SSM (Shimadzu, Tokyo, Japan). Soil pH was measured by a Jenway pH meter with an SIS electrode, in a 1:10 soil and de-ionised water suspension, shaken for 3 hours in an orbital shaker and allowed to settle for 45 minutes. After pH measurement the suspension was centrifuged at 3000 rpm for 10 minutes and the resulting supernatant was passed through a nylon filter to remove any suspended particulate matter which could interfere with analysis. These extracts were analysed for water soluble organic carbon (WSOC) using a TOC-VE (Shimadzu, Tokyo, Japan).

2.3.3.3 Climate data

Daily soil temperature records for July 2007 to July 2008 were collected from the Met Office weather station at Ness Botanical Gardens, Neston, Wirral (station number 7326; Lat/Long: 53° 20' N, 3° 5' W), located 12 km southwest of university campus. Soil temperature was taken at 30 cm soil depth to reduce surface effects. Soil moisture data used for modeling respiration rates were obtained by taking the minimum and maximum recorded soil moisture (HH2 moisture meter, Delta-T devices LTD, UK) from triplicate cylinders, identical to those described above, placed outside at the field location under natural environmental conditions. Measurements were taken monthly for 6 months and a mean value calculated, avoiding taking measurements following periods of heavy rainfall.

2.3.3.4 Data analysis and modeling

Measured soil respiration data were sorted according to compost application volume, soil temperature and soil moisture giving a data population of 312. A three variable parametric model was created using MATLAB, producing the following equation for the determination of respiration rate:

$$\text{Respiration rate } (\mu g\ C\ m^{-2}\ s^{-1}) = [0.1596\ (T) + 0.0779\ (M) + 0.0667\ (CV) - 0.0044\ (T^2) - 0.0041\ (M^2) - 0.0004\ (CV^2) + 0.0209\ (T \times M) + 0.0020\ (T \times CV) - 0.0042\ (M \times CV)]$$

Where T is soil temperature (°C), M is soil moisture (%) and CV is compost application volume (%). Two way ANOVA statistical analyses were performed using SPSS v.14 for windows.

2.3.4 Results and Discussion

2.3.4.1 Characteristics of soil and compost

Soil contained a significant proportion of stones, probably associated with previous construction activity at the site (Table 2.3.1) as discussed by Beesley and Dickinson (2010 (see 2.4)). Soil texture was sandy, explaining the low minimum recorded soil moisture both in the laboratory (Fig 2.3.3) and under field conditions (Table 2.3.1). Soil pH was circum neutral, whilst the pH of compost was mildly alkaline. Water soluble organic carbon (WSOC) and TOC were almost 5 and 6 times greater respectively in compost than in soil without compost addition (Table 2.3.1), reflecting the contribution of organic matter from the compost (Table 2.3.1).

Table 2.3.1. Physico-chemical characteristics of soil, compost and compost mixtures (mean ± SE; n = 3)

Soil treatment	Soil (no compost)	Low	Medium	High	Compost
pH	6.65	7.53	7.65	7.86	8.1
TOC %	2.09 (0.01)	2.36 (0.16)	3 (0.26)	3.39 (0.14)	12.3 (0.2)
WSOC mg l^{-1}	357 (14)	495 (32)	742 (40)	954 (57)	1724 (32)
Min recorded soil moisture %*	16.1	-	23.3	-	-
Max recorded soil moisture %*	36.6	-	52.8	-	-
Particle size distribution (%):	--------------	------------	------------	-------------	-------------
Stones (> 2 mm)	16 (0.8)	-		-	-
Sand (2 mm – 63 µm)	67.9 (0.4)	-	-	-	-
Silt (62.9 µm – 2 µm)	15 (0.4)	-	-	-	-
Clay (< 2 µm)	1.09 (0.37)	-	-	-	-

*Note that soil moisture was measured under field conditions in soil and soil with 30% compost application in conditions of uncontrolled soil temperature.

2.3.4.2 Measured soil respiration rates

Increasing soil temperature caused a significant overall increase in mean respiration rates (ANOVA; $p < 0.001$), but the magnitude of this effect varied according to whether or not compost was incorporated. In soil without compost mean respiration rate was higher at 5°C than at the higher temperatures, but the range was lower (Fig 2.3.2a). Mean respiration rates significantly increased when compost was applied to soil (ANOVA; $p < 0.001$) whilst the range of values also increased (Fig 2.3.2 b, c and d). Gregory and Vickers (2003) also found that respiration increased in proportion to compost application rate of a single dose of woody green waste compost. At low and medium applications, respiration rates at 5°C in the present study were higher than at 10°C, in common with the control soil. Increasing soil temperature to 15°C increased both the mean and range above that of the lower temperatures (Fig 2.3.2 b and c). The Q_{10} (quotient of change in respiration caused by a 10°C change in temperature) was 1.2 for low and medium compost applications, but increased to 1.5 at the highest compost application. Lou and Zhou (2006) report that Q_{10} values of less than 1 indicate soil systems with a low sensitivity to temperature changes; high sensitivity systems are those where a 10°C temperature increase would cause respiration rates to increase by 10 times. Janssens and Pilegaard (2003) measured soil respiration *in-situ* for one year in a Danish beech forest soil and calculated the Q_{10}. They discovered that absolute soil respiration was lower in winter than summer, but Q_{10} was nearly 6 times greater ($Q_{10} = 23$) in the winter time (at lower temperatures). Similarly, in that study, soil moisture was inversely related to Q_{10}. In the present study Q_{10} was measured from 5 to 15°C only, so it is likely that the values derived for the responses of soil with compost to soil temperature only represent those that could be found during distinct times of the year.

Due to the fact that respiration rates were measured in a decreasing followed by an increasing temperature cycle, measurements at 10 and 15°C were taken both at the beginning and end of the 6 month experimental period. In contrast, measurements at 5°C were taken only in the middle of the 6 month period. During the course of the experimental period organic matter would have decomposed, meaning that those data recorded at 15°C would represent earliest and latest stages of this decomposition, whereas the narrower time period in which data at 10°C and especially that at 5°C were recorded could have caused an overestimation of respiration rates. This could have particularly been the case in the soil, whose pool of available substrate for decomposition was lower than in compost (Table 2.3.1). As well as the larger amounts of decomposable substrate provided by compost to soil microorganisms, the quality of the substrate would also have influenced respiration rates. In the soil there would have been more recalcitrant material, because the organic matter in the soil would be older. The more simple sugars in the younger organic matter in compost can more easily be converted to CO_2 by microbial activity (Lou and Zhou, 2006), increasing respiration rates.

Increases in soil moisture generally increase respiration rates in aerobic conditions (Lou and Zhou, 2006). Fang and Moncrieff (2001) incubated intact soil cores from farmland and forest soils from Scotland, with soil moisture contents between 20 and 50% finding that moisture had no obvious effect on respiration rate. Similarly, Vanhala (2002) found that maintaining constant soil moisture levels (at 60% of WHC) buffered variations in respiration rates. In the present study, soil moisture significantly affected soil respiration rates in the narrow range of moisture values recorded for this sandy soil ($p < 0.01$; Fig 2.3.3). Moisture values recorded from the soil with compost in the field were far higher than those measured in the laboratory respiration experiment (Table 2.3.1; Fig 2.3.3). In this respect it was difficult to elucidate the individual effect of moisture, given that compost application so strongly influenced respiration rates even at the low soil moisture value.

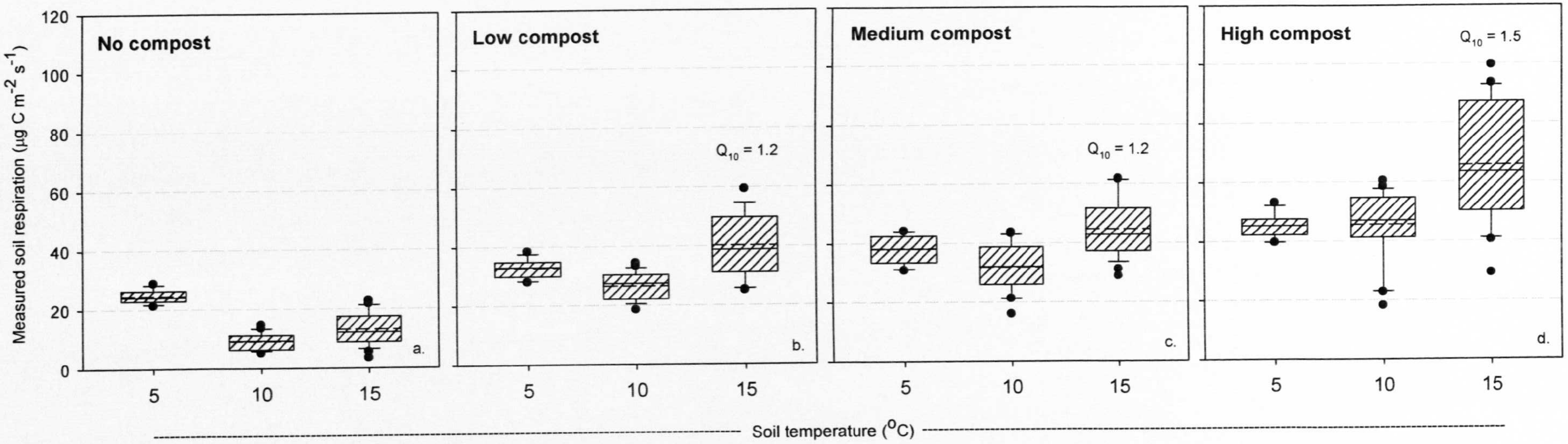

Figure 2.3.2. Measured mean and range of soil respiration rates by varying soil temperature and compost application rate. Dashed line is the mean value, solid line is median, box is the upper and lower quartile and whisker is the 10th and 90th percentile. Note that increasing compost application increased both mean and range of respiration values and temperature response (Q_{10}).

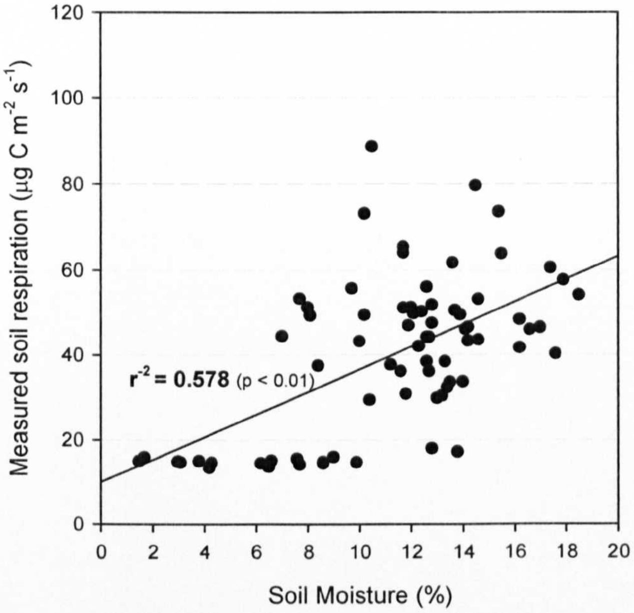

Figure 2.3.3. Relationship between soil moisture and measured respiration rates ($n = 72$) at 10°C.

2.3.4.3 Modelled annual respiration rates from soil

Soil temperatures taken from Met Office measurements fitted well with those used in the laboratory respiration experiment, with summer peaks of 18°C and winter lows of 4°C (Fig 2.3.4a). When soil respiration rates were modeled based on these daily soil temperatures, clear seasonal patterns of high summer respiration and low winter respiration rates could be observed from soil without compost (Fig 2.3.4a). During winter, when soil temperatures were ~5°C, respiration rates at both minimum and maximum soil moisture fitted well with those measured in the laboratory (20 – 40 µg C m^{-2} s^{-1}). During the warmer periods of the year there were clear limitations of moisture on respiration rates, with rates < 100 µg C m^{-2} s^{-1} and > 140 µg C m^{-2} s^{-1} at minimum and maximum moisture respectively. When compost application rate was factored into the model an interesting and somewhat opposing effect was observed, which was initially difficult to explain. With increasing compost application there was a tendency for high moisture to reduce respiration rates to 0 µg C m^{-2} s^{-1} during the winter months, when soil temperatures were low (Fig 2.3.4b, c and d). Negative soil respiration rates have been observed previously, in field measurements by Li et al, (2010), but a mechanism of calcite formation requiring CO_2 consumption by soil was thought to be the reason for this (Xie et al, 2009). In the present study such biological, chemical or physical mechanisms can be ruled out because zero or negative respiration rates were not measured in the laboratory (Fig 2.3.2). Seasonal variability in respiration rates has previously been described by Smith et al (2003), with both soil temperature and moisture acting as the limiting factors in respiration during distinct times of year. In the present study, temperature, moisture and compost volume were positive functions in the model, relating to the significant positive effects of each parameter on measured respiration rates (Fig 2.3.2), whereas moisture multiplied by compost volume function was negative meaning that increases in both compost application and soil moisture, combined with reductions in soil temperature, produced artificially low respiration rates (Fig 2.3.3 b, c and d). This was purely a modeling problem.

Total annual C losses to respiration (T_{ar}) from soil were 1113 and 2767 g C m^{-2} yr^{-1} at minimum and maximum moisture, respectively (Fig 2.3.4a), based on the sum of daily respiration rates. Raich and Schlesinger (1992) reported annual C losses to respiration from different ecosystems, with peak values of 1092 g C m^{-2} yr^{-1}; similar to the lower values in the present study. Kaye et al (2005) reported annual soil respiration rates up to 5 times greater in fertilised and irrigated urban lawn soil (~2800 g C m^{-2} yr^{-1}) than neighbouring agricultural soils; the upper annual C flux for soil in the present study, at maximum moisture, fits well with those urban lawn data of Kaye et al (2005).

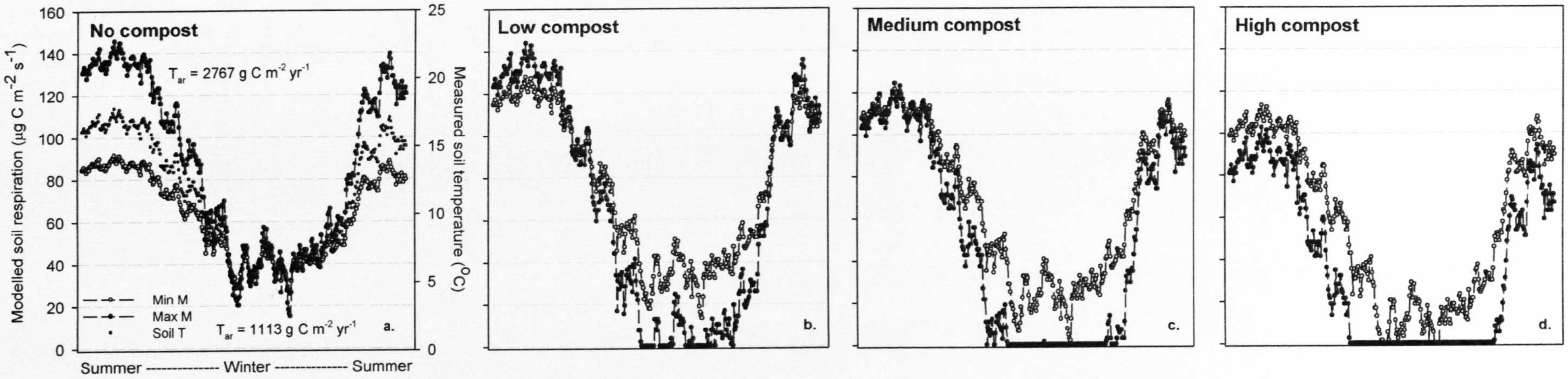

Figure 2.3.4. Soil respiration modelled from measured soil temperature, compost application volume and minimum and maximum measured soil moisture values. T_{ar} denotes total annual respiration.

2.3.4.4 Limitations and improvements to this approach

Measured soil respiration rates take account of the various responses of respiration to cycles of temperature increase and decrease, moisture variations and compost incorporation. Soil temperature, compost application and moisture all significantly influenced respiration rates in the laboratory. In urban areas, where it may not be practical or possible to obtain large continuous datasets in field conditions, modeling respiration rates based on controlled laboratory experiments is a useful way of calculating annual C losses by this pathway. Modeling annual variability in respiration rates based only on this relatively small dataset of 3 parameters should only be considered as a starting point because the modeled results extrapolate on the narrow range of conditions at which soil respiration was measured. In the present study, modeled respiration rates in soil without compost were low in winter, limited by low soil temperature, but soil moisture limited rates in summer. Larger datasets are required to improve this approach, preferably with continuous sampling of both day and night time respiration rates. Secondly, annual measured soil moisture data would also improve the model, rather than relying just on two contrasting moisture scenarios. Furthermore, some measure of decomposition of available substrate for microorganisms should also be factored into the model to reduce overestimations.

2.3.5 Conclusions

Total annual C losses to respiration (T_{ar}) from soil were calculated as 1113 and 2767 g C m^{-2} yr^{-1} at minimum and maximum soil moisture respectively, based on the sum of daily respiration rate. These values fitted well with those reported previously in the literature. This modeling approach has demonstrated clear potential to assess annual respiratory losses of C from urban soils, accounting for climatic variability. However further refinements to the model and larger datasets are required to accurately assess the extent to which the application of green waste compost enhances soil respiration.

2.4 Carbon and Trace Element Mobility in an Urban Soil Amended with Green waste Compost

2.4.1 Abstract

The amendment of degraded urban soils using recycled organic wastes offers potential improvements to physico-chemical status and functionality, but there is a paucity of knowledge on the potential impact on residual contaminants in soil. The aim of this study was to evaluate the mobility of trace metals and arsenic through an urban soil following amendment with greenwaste compost over an annual cycle. Rhizon soil pore water samplers were inserted into the sides of a soil pit located in a relatively undisturbed urban lawn, which was amended with a surface mulch of greenwaste compost. Regular sampling and analysis of pore water from the compost and at varying soil depths was carried out, in comparison to an adjacent profile which had not been amended. Rapid dissociation of As from compost was found following its surface deposition as a mulch. Periods of high rainfall enhanced As mobility through upper soil horizons to deeper technogenic layers with higher pH. Copper concentrations in soil beneath compost were substantially elevated and strongly correlated with dissolved organic carbon (DOC) released from compost into pore water. Seasonal biological activity, rather that soluble carbon, determined the patterns of mobility and release of Zn in both compost amended and control soil. Location of more stable concentrations of Pb at lower depths reflected reduced atmospheric fallout or the composition of the lower strata. Flushes of DOC from compost also enhanced mobility of residual Cd in soil. Amendment of urban soils with greenwaste compost mulches impacts on residual trace element contaminants and may enhance the mobilisation of harmful elements to the wider environment, meaning that caution is needed when applying compost to soils with elevated levels of trace metals.

2.4.2 Introduction

Urban soils exhibit a diversity of *in-situ* and *ex-situ* development, with wide-ranging properties and mixtures of artefacts such as construction residues and wastes (Lehmann and Stahr, 2007). Within this strongly anthropogenically-impacted matrix, urban soils generally also contain trace element concentrations that are significantly elevated above background levels (Wong et al., 2006). The stability of contaminants amongst these trace elements may have considerable bearing on risks to human health; for example, disturbance may enhance pathways of potentially toxic metals and metalloids thorough dust blow or through solubilisation towards groundwater (Thums et al., 2008). Within this context, clearly it is important to understand how land management practices may influence the mobility of residual pollutants in urban soils.

By definition, urban soils are located in areas of high and continuing human disturbance, occupying the margins and supporting the green infrastructure of the built environment. Soil disturbance, translocation, replacement and improvement are often supplemented with the importation of organic matter derived from composted wastes. This has multiple benefits of improving vegetation establishment and growth, reducing compaction, increasing water holding capacity (Bernal et al., 2006) and protecting against erosion by increasing aggregate stability (Craul, 1999, Whalen et al., 2003). Additionally, recycling of materials with a high organic matter content to soil removes them from waste streams, such as landfills, and can potentially increase carbon storage in otherwise degraded soils (Dickinson and Pulford, 2005, Pouyat et al., 2006). Degraded soils with low carbon contents may have the greatest efficiency to store added carbon, because they are further from their saturation level (Stewart et al., 2008ab), but research has also drawn attention to some misguided assumptions about whether organic matter applications to soil necessarily increase the pool of stored carbon; in some circumstances there may be a negative relationship between C input and soil C conservation (Fontaine et al., 2004, 2007).

Soil pore water, the aqueous phase to which plants and microorganisms are exposed (Nolan et al., 2003), contains variable amounts of dissolved organic carbon (DOC), which is the most bioavailable fraction of organic matter in soils (Marschner and Kalbitz, 2003). Leaching by water transports this soluble C fraction into the lower soil matrix and represents a small, but potentially important pathway by which ecosystem C could be lost (Neff and Asner, 2001) with DOC fluxes at 90-100 cm depth probably representing the net export of DOC by leaching from the soil matrix (Guggenberger and Kaiser, 2003). Borken et al (2004) found that up to 5% of DOC from compost was leached to 10 cm and less than 0.5% leached to 100 cm depth, within a forest soil amended with compost. Given the obvious significance of pore water in the transport of DOC and trace elements through soils there are surprisingly few reports of its sampling *in-situ* under field conditions (for example; Geibe et al., 2006; Buckingham et al., 2008; Clemente et al., 2008). Clemente et al (2008) sampled pore water from an urban woodland soil finding that DOC exerted a strong influence on the mobility of Cu, Zn and Pb. The restricted mobility of As compared to other elements was attributed to its low solubility in this soil, which was strongly acidic (pH 4.03 - 4.44); conditions known to reduce the solubility of As (for example; Fitz and Wenzel, 2002).

The aim of the present study was to examine the stability and mobility of C and trace elements in an urban soil, through detailed analysis of soil pore water throughout an annual cycle following the application of greenwaste compost.

2.4.3 Methods and Materials

2.4.3.1 Site description

The sampling location was within the grounds of the university campus within the city centre of Liverpool (Lat/Long: 53° 24’45.10” N; 2° 58’50.60” W). Soil sampling took place on an area of lawn with little disturbance over the last 35 years. The area has been minimally compacted by occasional recreational use, but is within private grounds, so has not been used as a dog walking area for example. The site was selected because it represents an urban soil that has been subject to relatively light disturbance. A soil pit of 1 x 0.5 m and a depth of 1m was excavated by hand, revealing a soil profile of topsoil (0-30 cm depth) over miscellaneous construction residues and subsoil (30-100 cm), with a clear definition between these two zones. For replication, opposite faces of the exposed soil profile were used for analysis, with one face assigned for control purposes and the opposite face, for studying the influence of the addition of recycled greenwaste compost. A mulch amendment of compost, sourced from local household collections of green garden waste (Whitemoss Horticulture, Kirkby, Merseyside), was applied to the soil surface of one face of the profile to a depth of 30 cm and left to equilibrate to field conditions for 2 months (November 2007 to January 2008). Whilst this is a high application rate it was recognised that decomposition and compaction of the compost would occur and a high application rate could be required to avoid the need for a second application of compost to the soil and to optimize the effects of the compost throughout the year long experimental duration. The opposite, control profile was not amended but was sampled routinely in the same way.

2.4.3.2 Soil sampling, preparation and analysis

Representative samples of bulk soil (1 kg) were excavated by hand using a trowel from the soil pit in triplicate at depths of 0-30 cm, 30-50 cm and 50-75 cm then air dried at 20-25 °C for two weeks. These sample depths represent the topsoil zone (0-30 cm) and the layers of subsoil containing building rubble below (30-75 cm) previously mentioned. Large debris was removed and the remaining material was broken up carefully by hand before being passed through a 2 mm sieve to determine the proportion of the material from each depth consisting of stones. Remaining soil was analysed for particle size using a Beckman Coulter LS 13 Laser Diffraction Particle Size Analyser. Owing to the relatively low organic matter content of the soil, organic matter was not removed prior to particle size analysis.

For bulk density determination fresh soil was sampled using steel cylinders (250 mm diameter) inserted laterally into the exposed soil profile at 0-15 cm, 15-30 cm, 30-50 cm and 50-75 cm. Sampling was in triplicate. This soil was air dried as previously described. Following the determination of bulk density, soil was crushed and sieved to < 2mm for the remaining analysis. Soil pH was analysed by a 1:10 aqueous solution, shaken for 3 hours. Samples were then centrifuged for 10 minutes at 3000 rpm and the supernatant filtered through a fine nylon mesh (approx 60 μm) to remove suspended particulate matter. Extracts were analysed for water soluble total and organic carbon and water soluble total nitrogen using a TOC-VE (Shimadzu, Tokyo, Japan). Organic matter was determined by loss on ignition (LOI) and total organic carbon (TOC) was determined using a TOC-VE 'SSM' (Shimadzu, Tokyo, Japan). Microwave digestion in HNO_3 and subsequent analysis by ICP-MS was used to determine soil pseudo-total metal and arsenic concentrations. The same procedure of pseudo-total metals and As analysis was applied to the compost amendment before and after the experimental work.

2.4.3.3 Pore water sampling and analysis

Soil pore water was sampled by duplicate 'Rhizon' samplers (Eijkelkamp Agrisearch Equipment, Netherlands), inserted laterally into both soil profiles at 15 cm and 30 cm depth (Fig 2.4.1). These were sampled at regular intervals from January 2008 to January 2009 using removable needles attached by a Luer-Lock mechanism to the sampler and vacuum tubes to extract soil pore water from the sampler. Additionally paired rhizon samplers were inserted into the compost amendment. From March 2008 duplicate samplers were added at 50 cm depth in the amended soil profile for additional information on soil pore water at this lower soil depth. Samples were analyzed for trace metals and As using ICP-MS and diluted to 1:10 using de-ionised water and analysed for DOC analysis using a TOC-VE (Shimadzu, Tokyo, Japan). Occasionally faulty samplers were replaced; data points were omitted from figures in these cases. Mean rainfall (mm) for the days preceding sample collection was calculated from daily rain gauge measurements and mean soil temperature (°C) from daily soil temperature records by the Met Office Monitoring station at Ness Botanical Gardens, Wirral, Cheshire (station number 7326; Lat/Long: 53° 20' N, 3° 5' W) located 12 km southwest of the study site.

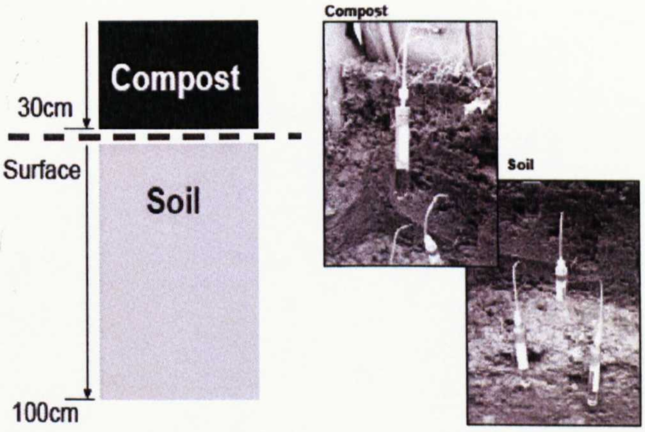

Figure 2.4.1. Experimental field design, showing the placement of rhizon pore water samplers in the soil profile.

2.4.3.4 Statistical analysis

All statistical analyses were carried out in SPSS v.14

2.4.4 Results and Discussion

2.4.4.1 Initial characteristics of compost and soil

The compost amendment had higher OM, TOC, WSTC and WSTN than soil. In the soil profile a consistent decrease with depth in these parameters was observed (Table 2.4.1). Soil pH was notably higher below 30 cm, probably reflecting the presence of building rubble. Soil predominantly consisted of sand, with silt and clay accounting for only a small proportion of the particle size distributions in the profile (11-15% and 1-1.75% respectively). The proportion of stones was markedly greater at 30-50 cm (Table 2.4.1), whereas sand accounted for the majority of the particle size distribution at 0-30 cm and 50-75 cm. Pseudo-total As, Zn and Cu concentrations were higher in compost than soil, but Cd was at highest concentrations at 15-30 cm and Pb below 30 cm in soil. These trace metal and As concentrations appear fairly typical of some urban soils (for example; Hartley et al., 2008, Thums et al., 2008), exceeding background rural levels but below the levels deemed contaminated under UK legislation (DEFRA, 2002, CL:AIRE, 2008).

2.4.4.2 DOC in pore water

Elevated concentrations of DOC in pore water collected from compost fluctuated considerably over the sampling period (Fig 2.4.2A) with an apparent general decrease over time. There was a clear pattern of leaching of DOC to soil beneath compost, to peak concentrations of ~230 mg l^{-1} compared to ~100 mg l^{-1} in the control soils and to depths of 50 cm (Fig 2.4.2B and C). Fluctuating concentrations of DOC in the control soil are likely to be related to soil temperature and moisture influences on biological activity and decomposition (Fig 2.4.3). Soluble organic carbon within the soil matrix would be expected to be slowly desorbed from aggregates, providing a supply of soluble C that diffuses into pore spaces (Cao et al., 1999). Pore structure, size, vertical and lateral distribution are bound to result in variable desorption and transportation of DOC through soils; organic C, N and cation exchange capacity (CEC) have been shown to be significantly increased within preferential flow paths through soils that create biological hotspots (Bundt et al., 2001). In the present study, bulk soil at 50 cm was low in TOC and WSTC but varying concentrations of DOC in pore water with depth show that factors controlling DOC within the soil matrix are related to leaching from upper horizons, probably the result of differences in particle size distribution through the profile (Table 2.4.1) and through the influence of temperature and moisture on biological activity and decomposition affected by seasonal rainfall patterns (Fig 2.4.3).

Table 2.4.1. Properties of surface compost amendment and soil from 0-15 cm, 15-30 cm, 30-50 cm and 50-75 cm (mean ±SE, n =3) prior to pore water sampling. ND = Below limit of detection. (Note that, for particle size analysis, data are from soil from 0-30 cm, 30-50 cm and 50-75 cm).

Sample depth	Compost	Soil			
		0-15 cm	15-30 cm	30-50 cm	50-75 cm
pH	8.1	6.65	6.85	8.56	8.63
Organic Matter (LOI) %	23.1 (0.5)	6.64 (0.67)	4.06 (0.28)	2.44 (0.16)	2.45 (0.04)
Bulk Density g cm^3	0.47 (0.05)	1.29 (0.02)	1.28 (0.02)	1.73 (0.08)	1.68 (0.08)
TOC %	12.3 (0.2)	2.09 (0.01)	0.48 (0.01)	ND	ND
WSTC mg l^{-1}	3175 (192)	482 (16)	360 (25)	221 (5.2)	188 (2)
WSTN mg l^{-1}	403 (28)	16.4 (1.1)	15.6 (2.2)	ND	ND
Particle size distribution (%)					
Stones (> 2mm)	-	16 (0.8)		44 (1)	24 (0.5)
Sand (2mm-63µm)	-	67.9 (0.4)		43.6 (0.7)	59.3 (1)
Silt (63 µm-2µm)	-	15 (0.4)		11.1 (0.4)	14.7 (0.7)
Clay (<2µm)	-	1.09 (0.37)		1.3 (0.36)	1.75 (0.13)
Pseudo total (mg kg^{-1})					
Cu	61.6 (1)	29.0 (3.4)	19.3 (0.3)	50.0 (25.1)	19.1 (1.2)
Zn	163 (8)	101 (1)	46.6 (1.4)	54.0 (4)	48.9 (1.2)
As	9.1 (0.6)	6.4 (0.4)	5.73 (0.32)	5.37 (0.2)	5.20 (0.10)
Cd	0.8 (0.06)	3.79 (1.99)	6.58 (3.8)	2.65 (0.44)	2.22 (0.29)
Pb	142 (1)	58.3 (7.4)	71.2 (112)	86.4 (4.8)	81.9 (0.4)

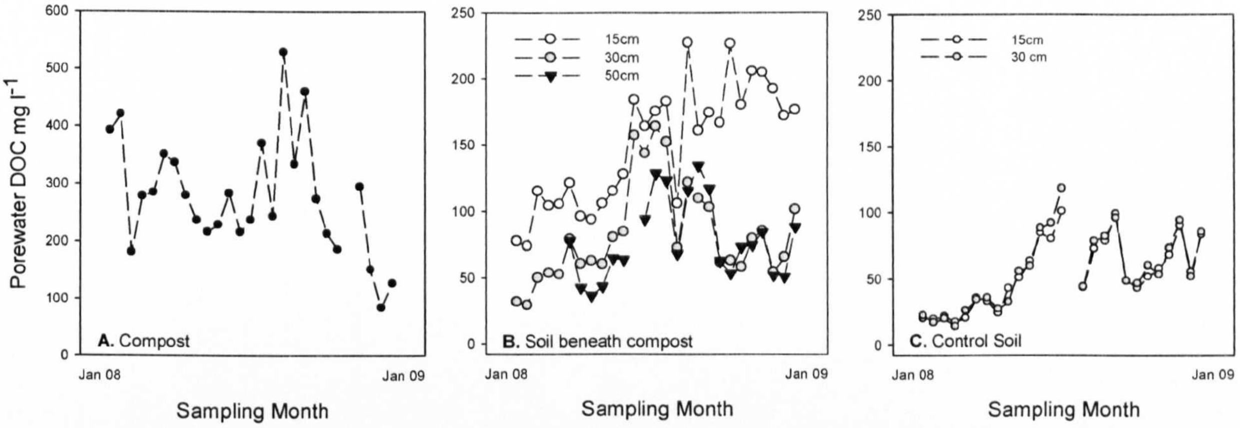

Figure 2.4.2. Dissolved organic carbon (DOC) in porewater from compost, soil beneath compost at 15 cm, 30 cm and 50 cm and control soil at 15 cm and 30 cm depth from January 2008 through to January 2009 inclusive. Note the differing scales between compost and soil.

2.4.4.3 Trace metals and arsenic in pore water

At the beginning of the sampling period As had much greater solubility than other elements, with up to 3.5% soluble in pore water (Table 2.4.2) as similarly found by Song and Greenway (2004). These authors attributed this to the fact that As does not complex as strongly as other elements with humic acids or other ligands in compost. In the present study, As was rapidly released from compost in the early stages of the experiment and then declined through the year (Fig 2.4.4A), apparently independently of soil temperature and rainfall (Fig 2.4.3). Pore water As was elevated in soil beneath compost at 15 cm depth and 50 cm depth compared to 30 cm depth (Fig 2.4.4B), a first explanation being that the metalloid's mobility is determined by differing soil pH with depth (Table 2.4.1); unlike most metals, As mobility is enhanced at high pH (O'Neill, 1990). On this basis soil pH in the surface 30 cm, being substantially lower (pH 6.7-6.9) than in both the compost above (pH 8.1) and soil at 50 cm below (pH 8.6) would tend to immobilise As at 0-30 cm depth as rainwater transports dissolved As through the soil. However, there would be an obvious exception to this during large flushes of rainfall, with increased throughflow of water offering less opportunity for binding of As and immobilisation by the lower soil pH in the upper 30 cm of the soil. Additionally, due to a greater mean particle size in the soil at 30-50 cm in the profile (Table 2.4.1) an even more rapid movement of water through the profile in this zone would likely increase the leaching of As from the soil above at periods of high rainfall. Indeed some corroboration is provided by the peak rainfall and peak As in pore water from 50 cm occurring together towards the end of the year (Fig 2.4.3 and 2.4.4B). However, given the slight difference in pseudo-total concentration of As with soil depth and the greater bulk density of soil at lower depths (Table 2.4.1) it is likely that the material at lower soil depths, consisting of building debris, is a significant source of the enhanced As in pore water at 50 cm depth.

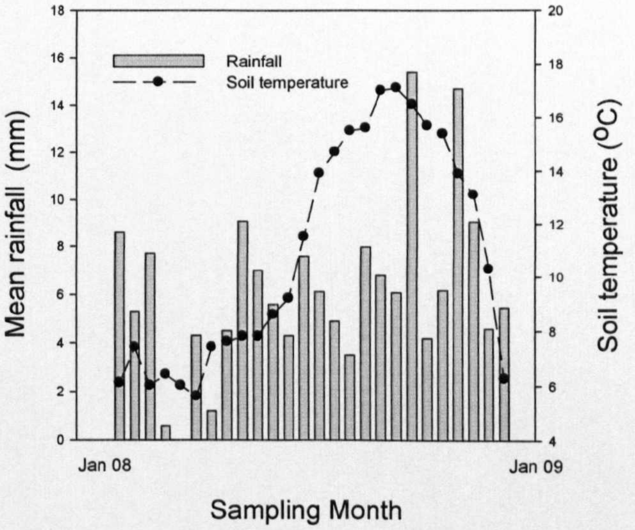

Figure 2.4.3. Mean rainfall and soil temperature at each sampling period within the experimental period

A further driver of As mobility is likely to be an enhanced release of P, concentrations of which are always elevated in compost (for example; Curtis and Claassen, 2009). Increased solubility of As was also noted by Clemente et al (2008) from similar use of rhizon pore water sampling in an urban woodland, attributed there to higher WSOC in the upper, organic horizon, although no correlation was observed between DOC and As in pore water. Relevant parallels can be drawn to the surface application of compost in the present study in which As was positively correlated with DOC in compost but there was no significant correlation in the soil beneath compost. However, these two parameters were negatively correlated in control soil where DOC inputs are only marginal (Table 2.4.3). Thus, the present study strongly points to the removal of dissolved As and DOC from compost, likely due to a combined flush of these elements in response to rainfall variations annually (Fig 2.4.3). Ge et al (2000) studied metals in soil solution from urban railway yards, concluding that Cd, Cu, Nickel (Ni), Pb and Zn were largely immobilised at the soil particle surface because of high pH, indicating that the effects observed in the present study may be specific to As, exacerbated by its high solubility.

In common with As, Cu in pore water was negatively correlated with DOC in control soil. In soil beneath compost Cu and DOC were positively correlated (Table 2.4.3) with Cu concentrations up to 10 times those of control soils (Fig 2.4.4E). Pore water concentrations of Cu were also found to be positively correlated with DOC in compost, supporting the results of other studies linking Cu closely with organic matter including recent studies on urban soils; sequential extraction for example, has shown Cu to have highest extractable concentration (median 48%) associated with the organic phase (Thums et al., 2008). Copper concentrations in pore water at 15 cm depth in amended soil (Fig 2.4.4E) had a delayed response to compost addition, but the correlation with DOC in compost and soil beneath compost closely link organic matter with soluble Cu nonetheless. Zinc pseudo-total concentrations in bulk soils showed a clear depth profile (Table 2.4.1) but there was no correlation between pore water Zn and DOC in the compost, soil beneath compost or control soil (Table 2.4.3) indicating that Zn may be retained in more stable complexes in soil. Nevertheless, Zn solubility was much greater in compost than in soil (Table 2.4.2), as evident in flushes of this element from compost being quickly reflected at lower soil depth (Fig 2.4.4G and H). Higher pseudo-total Zn concentrations were found in compost after the experimental year (Table 2.4.2), probably related to decomposition processes in the compost; studies have shown that organic matter decomposition can strongly influence Zn, especially at alkaline pH (Kiekens, 1995). Similar but more muted peaks of Zn in pore water occurred in control soil (Fig 2.4.4I) indicating that the influence of natural processes, for example, rates of biological activity and decomposition, primarily determine Zn mobility. A combination of rainfall and soil temperature conditions in early summer and autumn could have increased Zn mobility, enhanced by the presence of compost (for example through moisture retention).

Higher pseudo-total concentrations of Pb in lower depths within the soil profile (Table 2.4.1) probably reflect either atmospheric fall out before the phasing out of leaded petrol more than a decade ago or more likely the presence of elevated levels of this metal in the lower strata of construction residues. Low solubility of this element (Table 2.4.2) corresponds with the results of other studies (for example; Davies, 1995) and, apart from a positive correlation with DOC in compost and soil, there appears to be a similar influence of biological activity to that observed for Zn (Fig 2.4.4J, K and L).

Table 2.4.2. Proportion of dissolved trace metals and As in pore water from compost and control soil (percentage of pseudo-total that is dissolved in pore water as measured at the beginning of the sample period; Jan 2008) and changes in pseudo-total concentrations prior to (January 08) and following (January 09) pore water sampling (mean ±SE, n =3).

Solubility	Compost	Soil	-------------	------------	Pseudo-total concentrations	Compost	Compost
%	Surface	0-15 cm	15-30 cm	30-50 cm	mg kg^{-1}	January 08	January 09
As	3.544	0.040	0.031	0.080	-	9.1 (0.59)	5.61 (0.27)
Cu	0.282	0.059	0.042	0.018	-	61.6 (1.3)	42.5 (0.2)
Zn	0.089	0.001	0.006	0.005	-	163 (8)	262 (49)
Cd	0.101	0.004	0.002	< 0.001	-	0.8 (0.06)	33.3 (4.8)
Pb	0.030	< 0.001	< 0.001	< 0.001	-	142 (1)	119 (25)

Cadmium was the only element lower in concentration in compost than in soil at the start of the experiment, both in pseudo-total (Table 2.4.1) and in pore water (Fig 2.4.4M, N and O) and was highest in bulk soil at 15-30 cm (Table 2.4.1). Flushes of Cd from compost caused some enhancement of Cd mobility in pore water in soils beneath compost during spring and summer months (Fig 2.4.4N), probably due to the combined effect of greater solubility in compost (Table 2.4.2) and correlation with DOC in soils (Table 2.4.3), where peaks in autumn months are likely a result of high rainfall (Fig 2.4.3). In common with the solubility of As (Table 2.4.2) and the sharp decrease in concentrations of Cu and Pb in pore water from compost over the sampling period (Fig 2.4.4B and 2.4.4J), the pseudo-total concentrations of these elements in the compost remaining after the experiment showed a concomitant decrease (Table 2.4.2). However, in the case of Zn and Cd the pseudo-total concentrations in compost were higher after the experiment (Table 2.4.2) which could explain the unexpected and sporadic peaks of these elements dissolved in pore water during the year (Figs 2.4.4G, M and O).

Table 2.4.3. Correlations between DOC and trace metals and As in pore water from compost, soil beneath compost and control soil (control samples are a combination of 15 and 30 cm depths; soil beneath compost samples are a combination of 15, 30 and 50 cm depth).

	Compost	Control	Soil beneath compost
As	0.295*	-0.351**	ns
Cu	0.543**	-0.392**	0.507**
Zn	ns	ns	ns
Cd	ns	0.435**	0.367**
Pb	0.376**	0.328**	0.260**
n	*48*	*89*	*132*

** $p < 0.01$; * $p < 0.05$; ns = not statistically significant

Most urban and brownfield soils are multi-element contaminated, therefore the association between trace metals in soils and in pore water is also worthy of consideration with relation to the behaviour of dissolved elements in the soil. There were no significant correlations between elements in soil pseudo-totals from the soil profile, probably because, unlike many industrially contaminated soils, the origin of the elements present is not solely derived from one source. However some significant correlations were observed between elements in the pore water, further indicating that behaviour of elements dissolved in soil pore water can be independent of the pseudo-total concentration. In general the behaviour of Cu was found to be most indicative of that of other trace metals in pore water whether in compost or in soil; Cu concentrations were positively correlated with As, Cd and Pb ($p < 0.01$) in pore water from compost. In soil beneath compost pore water Cu was similarly correlated with pore water As, Cd, Pb and, additionally with Zn ($p < 0.01$). In control soils there were moderate, positive correlations between Cu and Zn ($p < 0.05$) and Cu and As ($p < 0.01$). Zn mobility was consistently related to both Cd and Pb ($p < 0.01$) in control soil whereas, in compost and soil beneath compost As was positively correlated with Pb ($p < 0.01$).

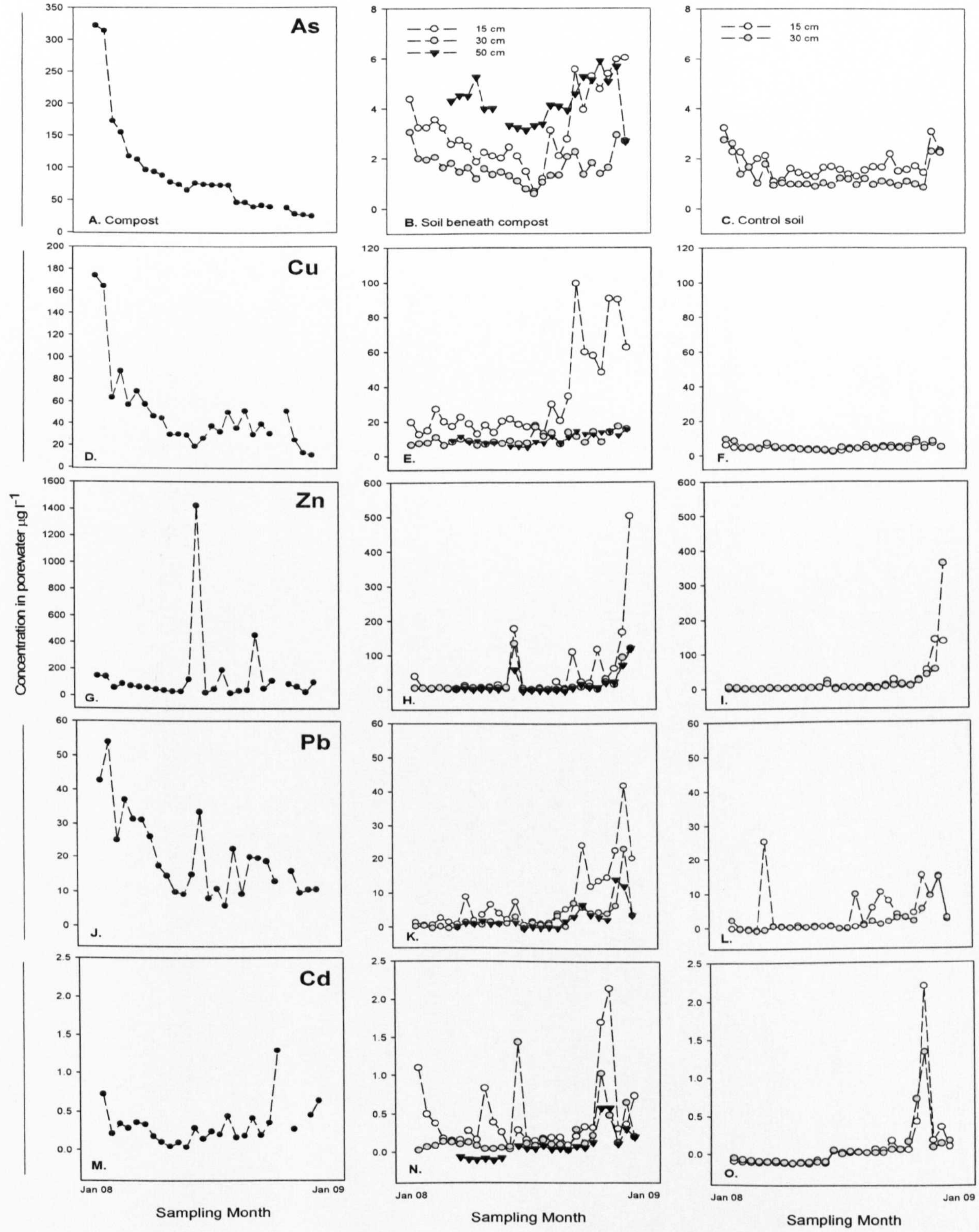

Figure 2.4.4. Trace metal and arsenic concentrations in soil porewater from compost, soil beneath compost at 15 cm, 30 cm and 50cm and control soil at 15 cm and 30 cm depth from January 2008 through to January 2009. Note differing scales between compost and soils except for Pb and Cd.

2.4.5 Conclusions

This simple field experiment, in which compost was added to an urban soil, has enhanced knowledge of the potential risks of using this organic material as mulches and amendments. Compost amendment causes large and immediate fluxes of DOC in pore water that influence residual contaminants in various ways, with a combination of effects that could be unique to anthropogenic urban and other technogenic soils. High solubility meant that As was transported rapidly from the compost amendment but could be immobilised in soil, determined by pH and throughflow of water. Copper provided the most direct evidence of mobility being dependent on the release of DOC from compost. In the cases of Zn and Pb, mobility was also enhanced by compost, but rates of release were additionally determined by temperature and moisture conditions that mediate biological activity and decomposition. Cadmium concentrations were lower in compost than in soil initially, but the effects of a flush of DOC through soil were to enhance the mobility of this residual contaminant in soil additionally exacerbated by the influence of seasonal atmospheric fallout. Therefore, whilst applying recycled greenwaste compost to urban soils may be hugely beneficial to physico-chemical characteristics, including potentially increased sequestration of carbon, the results of the present study indicate that some caution should be exercised when remediating soils that contain residual trace element contaminants with this organic material There may be increased risk of enhancing the mobility of potentially harmful metals and As to human health receptors and the wider environment.

2.5 Carbon and trace element fluxes in an urban soil with compost and biochar amendments, inoculated with earthworms.

2.5.1 Abstract

Amendment of soils using composted organic wastes could enhance carbon storage but may mobilise harmful pollutants commonly found in frequently degraded urban soils. In the present study, carbon and trace element fluxes in soil pore water were studied in response to the addition of composted green waste, non-composted woody amendment, and biochar, in an urban soil profile and in mesocosms inoculated with the earthworm *Lumbricus terrestris*. The effect of earthworms on soil respiration was also measured. All amendments enhanced dissolved organic carbon (DOC) leaching both in the soil profile and mesocosms. The effect of compost was most pronounced on DOC, dissolved nitrogen (DTN) and trace metals, especially Cu and Pb. Zinc mobility was independent of changes in soil properties induced by any of the amendments. Biochar enhanced As, Cu and Pb mobility in the mesocosms, whilst the woody amendment neither greatly increased DOC nor As, Cu, Pb or Zn mobility. In contrast to the other amendments, earthworm inoculation increased DOC and Cd mobility when soils were amended with the woody material. Earthworms also increased soil respiration, especially at higher soil temperatures, in response to more favourable soil moisture conditions. In wider environmental terms, compost may be the most effective amendment at improving general soil conditions, and increasing soluble nitrogen, but the alternative amendments have a lower impact on DOC and trace element mobility. Careful consideration should be given to the characteristics of the urban soils to which each of the amendments is applied to maximise benefits to soil quality whilst minimising the mobilisation of potentially harmful trace metals and arsenic.

2.5.2 Introduction

As much as 95% of the total carbon stored on land is in soils (Ostle et al, 2009). Net losses of C from UK soils have been discovered over relatively short time periods (Bellamy et al, 2005), suggesting that improved soil management is required to maintain C storage at current levels. In the UK, urban soils form an ever-increasing proportion of soils but have received sparse attention with regards to C storage and fluxes, despite increasing evidence to suggest that the urban C pool may be substantially greater than neighbouring native soils

(Golubiewski, 2006). Another recognisable feature of many urban soils is elevated levels of heavy metals and As (Hursthouse et al, 2004, Thums et al, 2008) associated with previous industrial fallout and waste disposal activity.

Organic amendments, such as green waste composts, are known to have immobilising effects on some heavy metals because humic acids bind elements such as Pb, Cu and Cr (Song and Greenway, 2004; O'Dell et al, 2007). Whilst this generally encourages the use of these amendments on contaminated land, it might also have potential drawbacks. For example, dissolved organic carbon (DOC), abundantly leached from freshly applied green waste compost, has been shown to enhance the downward mobility of trace metals and As in soils (Businelli et al, 2009, Beesley and Dickinson, 2010). An alternative is to utilize the residual woody lignified material remaining after compost is produced. Practical uses or disposal of this material are difficult compared to composted products because demand is low and disposal or recycling costs high. Applying this material to soils could be effective at improving the physical properties of some degraded soils, especially where compaction has occurred. It could also offer greater potential to store carbon in a relatively stable and slowly degrading recalcitrant form compared to composted green waste.

Biochar, which is charcoal produced by pyrolysis of biological residues, is another alternative to composted wastes. Amongst the beneficial effects already demonstrated by the application of this material to soils are improved soil fertility (Novak et al, 2009) water holding capacity (Thies and Rillig, 2009) and enhanced C storage (Lehmann, 2007 a,b). Application of charcoal to soils can sequester more C than non-charred organic matter (Glaser et al, 2002). There is also evidence to suggest that biochar can adsorb and immobilise selected soil pollutants (Novak et al, 2009, Smernik, 2009). Earthworms are known to have beneficial influences on the properties of soils through increasing water-soluble nutrients (Roithmeier and Pieper, 2009) and carbon storage (Don et al, 2008) by working and mixing soils. Their potential to mobilise soil contaminants has also been previously identified (Sizmur and Hodson, 2009) but information on their influence on carbon and trace element mobility in urban soils is somewhat lacking, despite the fact that they have demonstrated benefits to the regeneration of degraded soils elsewhere (Ma et al, 2003, 2006).

This aim of the present study was to compare carbon and trace element fluxes in an urban soil, in response to surface mulch or mixed applications of green waste compost, a non-composted woody material, and biochar. Parallel field soil profile studies and mesocosm trials were undertaken to examine fluxes of C and impacts on soluble trace elements. The additional influence of the earthworm *Lumbricus terrestris* was examined in relation to each soil amendment, by their inoculation with the soils in the mesocosms.

2.5.3 Study sites and methods

2.5.3.1 Soil profile

The field study site was located in the grounds of a Quaker Meeting House in St Helens, Merseyside, UK (Lat/Long: 53° 27' N, 2° 43' W) which was constructed during the 17th century. There was no evidence of major soil disturbance within the last century because the site has been largely closed to public access, and the only known disturbance has been the occasional tillage and removal of vegetation during general site maintenance.
In a secluded area of the site, three timber matrices, each with five equal enclosures of 30 x 50 cm and a height of 30 cm, were constructed to contain replicates of each soil treatment and a control, containing only soil (Fig 2.5.1 A). Between the 3 matrices, 2 soil trenches were excavated by hand to a depth of 100 cm, exposing a soil profile beneath the amendments. Soil excavated from these trenches was retained for the mesocosm experiment. Along with the control, containing only soil, treatments in the matrices consisted of green waste compost, from household green waste collections, and the woody residual material (called oversize) separated during the composting process. The latter was screened to 10 – 20 mm. These materials were sourced from Whitemoss Horticulture, Kirkby, Merseyside, UK. A third amendment, biochar, was produced by pyrolysis of hardwoods native to England and Wales (Oak, Ash, Sycamore and Birch) at 400°C in steel ring furnaces (Bodfari Charcoal, Denbigh, North Wales, UK).

Within the 4 soil profiles, on opposite sides of each trench, rhizon pore water samplers were inserted at 25, 50 and 75 cm below each amendment (Fig 2.5.1 A inset). Samplers were also placed directly into each amendment but these samplers failed to collect sufficient volumes of pore water for analysis. Two months equilibration time was allowed before pore water was collected by removable vacuum tubes. Samples were taken bi-monthly from February 09 to December 09.

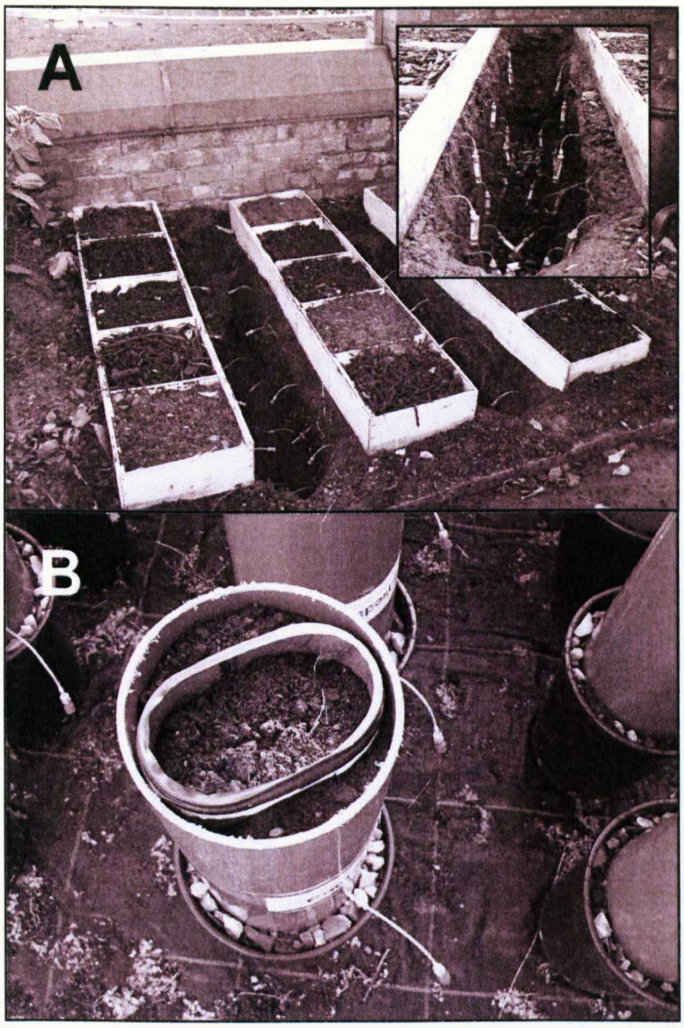

Figure 2.5.1 A. Soil treatment matrices and experimental trenches showing placement of pore water samplers (inset) and B), showing soil cylinders with respiration collars and pore water samplers incorporated.

Large items and biological debris, including roots and earthworms, were removed from the soil excavated from the trenches described earlier. Soil was mixed with the amendments on a vol:vol basis (30:70 amendment to soil ratio) rather than by weight, because the density of the individual amendments was very different. Mixtures were placed into PVC cylinders (50 cm height by 20 cm internal diameter) in 6 replicates (Fig 2.5.1 B). The base of each cylinder was covered with a fine, porous, geotextile material to allow water drainage whilst retaining soil in the cylinders. Fifteen juvenile *Lumbricus terrestris* (Ecology Earthworms, Suffolk, UK) were added to 3 replicate mesocosms of each of the treatments, with the remaining 3 containing no earthworms. Straw (5g) was added to the surface of each soil as a feedstock for this vertically burrowing, anecic earthworm. The same amount was also applied to soils without earthworms. Rhizon pore water samplers (as described previously) were inserted into small holes drilled into the mesocosms at 25 cm depth and pore water was collected as detailed previously. The mesocosms were placed in a designated area on the university campus in Liverpool (Lat/Long: 53° 24'45.10" N; 2° 58'50.60" W), 28 km west of the Quaker House, in a single-block, fully randomised arrangement. Two months equilibration time was allowed before pore water samples were collected monthly from July to December 2009.

2.5.3.2 Soil sampling and analysis

For soil profile characterisation, triplicate samples of soil were collected prior to the addition of soil amendments, from the profiles excavated in the field using a small hand auger, 5cm in diameter, inserted laterally into the face of the profiles. Soil was withdrawn from 25, 50, and 75 cm depth and air dried at 20-25°C for two weeks, before being ground and sieved (< 2 mm) prior to analysis. The oversize amendment was milled to 1 mm before analysis.

For both soil and amendment samples, pH was determined in a 1:10 solution of soil to de-ionised water, shaken for 3 hours and allowed to settle for 45 minutes. Particle size distribution of the soil was determined by a Beckman Coulter Laser Diffraction particle size analyser the following size classification: Sand (2 mm-63 µm), silt (62.9 µm-2 µm) and clay (<2 µm). Owing to the low organic matter content of the soil, pre treatment to remove organic matter was not considered to be necessary prior to this analysis. Samples were sonicated during particle size analysis to minimise flocculation. Organic matter was determined by Loss on Ignition (LOI). A Shimadzu SSM-TOC instrument (Shimadzu, Tokyo, Japan) was used to determine Total Organic Carbon (TOC). To determine water soluble organic carbon (WSOC), a suspension of 1:10 (soil/amendment: water) and shaken for 3 hours and centrifuged at 3000rpm for 10 minutes. The resulting supernatant was screened through a fine nylon mesh to remove particulates capable of interfering with the function of analytical equipment and extracts were analysed using a Shimadzu TOC-VE.

Aliquots of 0.2 g samples of the soils, green waste compost and milled woody oversize amendment were microwave digested in 10ml of concentrated (14M) HNO_3 and analysed for pseudo-total As, Cd, Zn, Pb, Cu and Fe using ICP-MS (XSERIES 2 ICP-MS; Thermo Scientific, MA, USA). A rhodium standard was added to each sample to monitor and compensate for changes in instrument sensitivity during analysis. Certified reference material (CMI 7004) was used to verify accuracy, with recoveries of > 75% for all elements. Due to the high carbon content of biochar, it could not be analysed using microwave assisted acid digestion. Pore water samples were analysed for dissolved organic carbon (DOC) and dissolved total nitrogen (DTN) using the same instrument as WSOC and for Cu, Zn, Pb, Cd and As using the same instrument as for pseudo-total elements.

2.5.3.3 Soil moisture and respiration

Soil moisture (%) was recorded using a HH2 soil moisture meter (Delta T devices, UK), inserted to 5 cm depth in each mesocosm. A portable open chamber soil respirometer (ADC Bioscientific LTD) was used to measure *in-situ* soil respiration from soil mesocosms (Fig 2.5.1B). For each mesocosm the respirometer was operated for a minimum of 6 minutes on each soil and the mean value of values recorded at 4, 5 and 6 minutes calculated. Respiration measurements were taken from the mesocosms with soil and soil with green waste compost mixed because the respirometer collars would not effectively form a seal on the soil mixed with the larger oversize or biochar. During soil respiration analysis, soil temperature (°C) was recorded by the respirometer and respiration values were grouped according to the soil temperature they were recorded at. Measurements were taken weekly, for 10 weeks, from Aug 09 to Nov 09, when soil temperature and moisture were variable.

2.5.3.4 Statistical analysis

General linear model analysis was performed to evaluate the influence of amendments, earthworms and time on DOC and As, Cd, Cu, Pb and Zn concentration in pore water and soil respiration in the soil mesocosms. Soil amendments and earthworms were included as fixed factors whilst sampling time was included as a random factor. All analyses were carried out using SPSS v.14 for windows.

2.5.4. Results and Discussion

2.5.4.1 Physico-chemical characteristics of soil and amendments

Soil was predominantly sandy, with a circum-neutral to slightly alkaline pH (Table 2.5.1). All major soil parameters and pseudo-total concentrations of trace elements decreased with depth, supporting the expectation that the origin of metals and As was atmospheric. Concentrations of trace metals were significantly higher in green waste compost than oversize, most notably Zn and Pb, although neither amendment contained concentrations that could be considered excessive. The pseudo-total concentrations of these elements in biochar were not determined, although water-soluble concentrations were subsequently found to be very low (see 3.3). Oversize had much greater organic matter (by LOI) content than the other amendments but biochar had the highest TOC, reflecting the fact that the majority of the organic matter in biochar was carbonised. In oversize, this proportion was less than half, explaining its lower WSOC content than biochar (Table 2.5.1).

Table 2.5.1. Characteristics of soil collected from the field profile and soil amendments prior to experimental work (mean ± S.E; n = 3).

Soil depth (cm)	Soil 0-10	- 10-30	- 30-75	Oversize	Green waste compost	Biochar
pH	7.9 (0.1)	7.1 (0.2)	7.0 (0.3)	7.11 (0.01)	8.1 (0.02)	9.9 (0.0)
Sand %	------------------83 ------------------			-	-	-
Silt %	------------------ 16 ------------------			-	-	-
Clay %	------------------ <1 ------------------			-	-	-
OM (LOI) %	8.6 (1.2)	5.7 (0.8)	3.2 (0.7)	84 (0.16)	24 (0.49)	56 (2.4)
TOC %	5.8 (0.1)	3.3 (1.2)	1.3 (0.4)	40 (0.5)	12 (0.7)	53 (2.4)
WSOC mg l^{-1}	329 (27)	263 (14)	284 (27)	6541 (783)	1724 (32)	11723 (182)
Pseudo-total mg kg^{-1}	-	-	-	-	-	-
As	27 (2.8)	6.3 (0.75)	3.7 (0.66)	4.1 (0.6)	9.1 (0.6)	ND
Cd	35 (9.1)	14 (2.4)	5.3 (1.3)	0.6 (0.1)	0.8 (0.06)	ND
Zn	357 (91)	112 (26)	39 (1.3)	54 (9.1)	163 (8)	ND
Pb	449 (47)	119 (22)	73 (5.3)	66 (15)	142 (1)	ND
Cu	170 (6.8)	55 (9.2)	27 (2.6)	23 (3.4)	62 (1)	ND
Fe (%)	2.9 (0.33)	1.5 (1.06)	1.2 (0.05)	ND	1.3 (0.1)	ND

ND = Not determined

2.5.4.2 DOC mobility in the field soil profile

The amendments affected DOC mobility in the zone of soil immediately below the amendments (25 cm) by raising concentrations of DOC above 100 mg l^{-1} (Fig 2.5.2 b, c and d). Oversize amendment had the least overall impact on DOC concentrations in the upper 25 cm of soil, with concentrations of only 100-200 mg l^{-1} (Fig 2.5.2 c). Green waste compost raised DOC in pore water to concentrations of > 300 mg l^{-1}, measured in August 09. Compost was the only amendment to raise the concentration of DOC above 100 mg l^{-1} below 25 cm depth, although the response to its application to soil was delayed (Fig 2.5.2 b). Previously, in an urban landfill soil, underlying mineral horizons depleted in organic matter, were found to retain soluble organic matter leached from a surface compost amendment (Said-Pullicino et al, 2010), which may explain the lower DOC concentrations in pore water at lower depths in the present study. Biochar showed a delayed response to its application to soil, with concentrations of DOC, initially (Feb 09), only slightly greater than the control. In the following months, mean concentrations increased close to those of green waste compost (Fig 2.5.2 d). Biochar is known to have a high water holding capacity (Thies and Rillig, 2009) and had a very high WSOC content (Table 2.5.1), which could have resulted in very slow throughflow and delayed leaching of DOC to the soil below. Large error bars associated with the different DOC concentrations in the upper 25 cm of soil between replicates of the same treatment could indicate differences in preferential channels of water flow between relatively small areas of the soil matrix, meaning that certain regions of the soil may be more thoroughly leached than others (Beesley et al, 2010a).

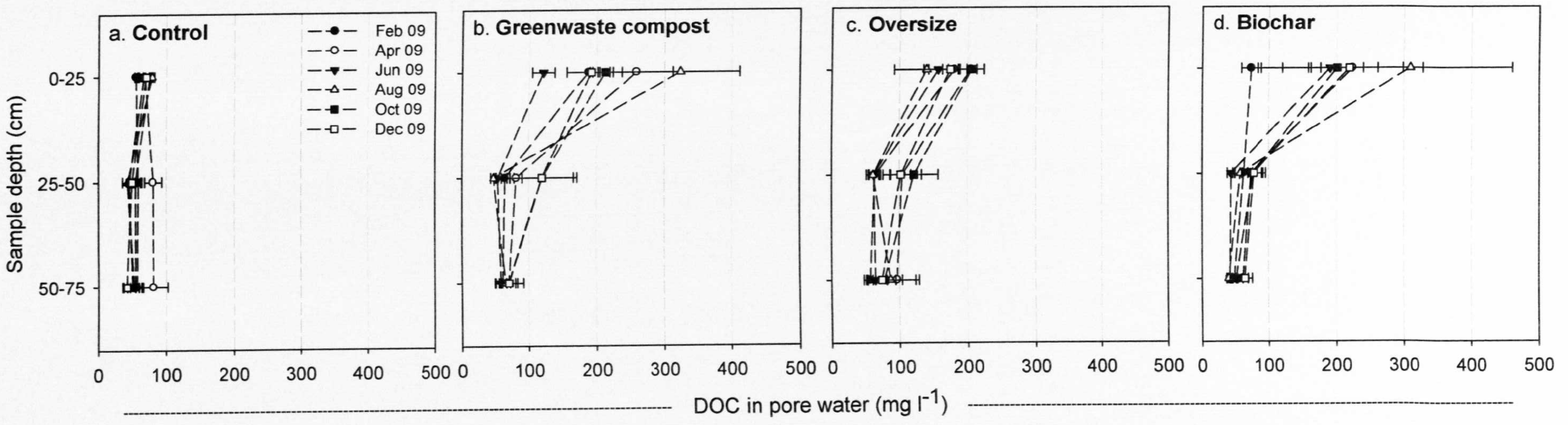

Figure 2.5.2. Concentration of dissolved organic carbon (DOC) in pore water collected from 3 soil depths when soil amendments were applied as a surface mulch above an urban soil profile.

2.5.4.3 Trace element mobility in the field soil profile

The upper 25 cm of the soil was also where the addition of soil amendments had the greatest influence on trace element concentrations in pore water, with little observable difference below this depth (data not shown). In earlier work, Beesley and Dickinson (2010) had similarly found that adding compost as a surface mulch most greatly affected DOC concentrations in soil pore water collected from the upper depth of soil. In the present study, green waste compost mobilised Cu, Cd and Pb most potently (Fig 2.5.3 b, c and d) with strong positive correlations between these metals and DOC (Table 2.5.2), suggesting this association as the means of transport of trace elements through the soil profile. Enhanced solubility of Cu and Pb associated with DOC has previously been found in soil pore water extracted from an urban soil with a high organic matter content (Clemente et al, 2008).

Zinc was the least dynamic of the trace elements in pore water with peak concentration, common to the control and all amendments, appearing only to be related to soil disturbance (data not shown). Apart from some enhancement of Cu concentrations in later months (Fig 2.5.3 b) only arsenic was influenced by biochar to any great extent, with this amendment increasing the concentration of this metalloid in pore water to > 300 $\mu g\ l^{-1}$ (Fig 2.5.3 a). This could have been related both to correlations of Cu and As with DOC (Table 2.5.2) and an increase in the pH of the pore water associated with biochar application (> pH 8); higher solubility of As has been noted at the more alkaline end of the pH range of 3-8 (Fitz and Wenzel, 2002).

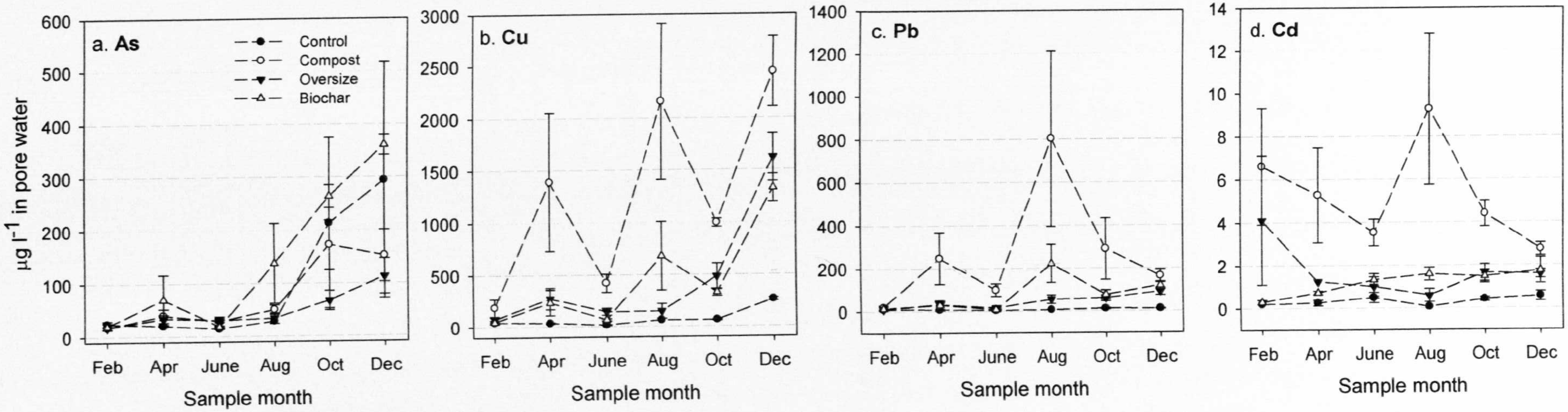

Figure 2.5.3. Concentrations of arsenic (a.), copper (b.), lead (c.) and cadmium (d.) in soil pore water collected from the upper depth (0-25 cm) of the field soil profile as influenced by soil amendments applied as a surface mulch. Note that Zn concentrations are not shown because this element did not respond to the amendments.

2.5.4.4 DOC and DTN in the mesocosms

Concentrations of DOC in pore water from the control soil in the mesocosms did not fluctuate greatly over the sample period with earthworm inoculation appearing to have little further effect (Fig 2.5.4 a). Adding amendments to the soil significantly increased DOC in pore water (Table 2.5.3) with compost increasing DOC most rapidly in the first 3 months (Fig 2.5.4 b). Concentrations declined in the latter 3 months of the experiment, probably associated with reductions in soil temperature and microbial activity in the months after September. Biochar immediately elevated concentrations of DOC in pore water (Fig 2.5.4 d), which reduced in the latter months of the experiment for the reason previously mentioned. In the field profile a delayed response of DOC to biochar addition was seen, unlike the mesocosms, which could have been related to the previously discussed water retention effect of the biochar, which was muted when biochar was mixed and incorperated into the soil. Oversize amendment increased mean DOC concentrations the least of the three amendments (Fig 2.5.4 c). Only the compost amendment contributed to consistently elevated DTN in pore water, with rapid reductions in its concentration between July-August (Fig 2.5.4 f), which could have been an effect of the physical disturbance of the soil after the compost was mixed, even after the equilibration period. For biochar and oversize alike, DTN was not detectable in pore water in soil without earthworms but worms liberated small amounts of DTN in pore water in early months (Fig 2.5.4 g and h). In common to the amended soils, small initial increases of DTN in pore water from control soil were probably related to disturbance, an effect which earthworms would have enhanced.

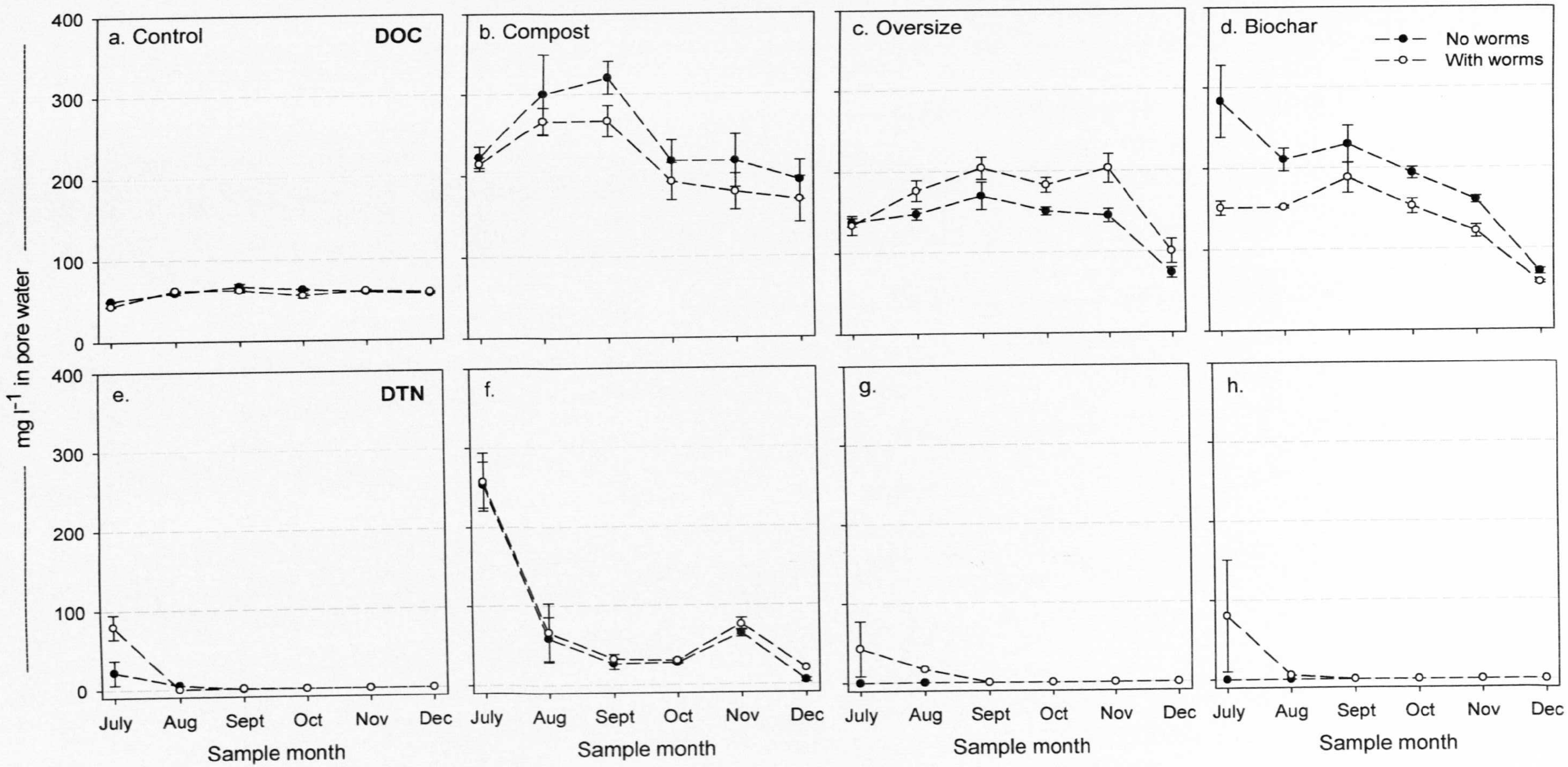

Figure 2.5.4. Changes in concentration of DOC (a-d) and DTN (e-h) in pore water collected from the mesocosms. Note that only in the oversize treatment (c.) did DOC increased with earthworm presence.

The affect of earthworms on DOC concentrations in pore water was significant, although less so than the magnitude of the effect of adding soil amendments (Table 2.5.3). Earthworms more effectively assimilate carbon from recently deposited fractions of organic matter (Edwards and Bohlen, 1996) rather than older, recalcitrant organic matter, which may explain their lack of influence on DOC in the control soil (Fig 2.5.4 a). In soil amended with compost and biochar, earthworms reduced DOC concentrations, although the difference narrowed towards the end of the 6 month experimental period for biochar (Fig 2.5.4 d). Contrasting affects of earthworms on carbon have previously been found, with the earthworm *E. albidus* increased DOC in soil extracts (Roithmeier and Pieper, 2009) whilst Amador et al (2003) found that *L. terrestris*, the species used in the present study, most strongly affected C dynamics only in the first weeks of incubation with soil. However, earthworms have also been found to adsorb water-soluble organic compounds in their gut (Edwards and Bohlen, 1996) by mixing organic and inorganic materials, offering greater physical protection to organic matter in the excreta (Scullion and Malik, 2000). The reductions in DOC in pore water from soil mixed with compost and biochar in the present study (Fig 2.5.4 b and d) suggest that adsorption in the earthworm gut could have immobilised C from these amendments whereas they may not have ingested the larger oversize material, explaining the opposite trend (Fig 2.5.4 c).

2.5.4.5 Trace element mobility in the mesocosms

Biochar influenced arsenic mobility to a greater extent than the other amendments (Fig 2.5.5 d) whose effects were minimal (Fig 2.5.5 b and c). This could have been related to the pH of the pore water as previously discussed (which was < 7 in the control soil but > 8 in the biochar mixed soil (data not shown). In common with the mulch experiment, levels of Zn in pore water appeared mainly related to soil disturbance because peak concentrations in pore water occurred at the start of the experiment and decreased thereafter to similar levels (Fig 2.5.5 e-h). Neither soil amendments nor earthworms significantly influenced Zn concentrations in pore water (Table 2.5.3). Copper and Pb were similarly influenced by DOC in the mesocosms (Fig 2.5.5 i-p) as in the field experiment (Fig 2.5.3), with each amendment increasing concentrations in pore water in tandem with DOC; strong positive correlations of these metals with DOC were found in samples from the soil profile (Table 2.5.2). Cadmium concentrations in pore water were exclusively affected by oversize, (Fig 2.5.5 s). This is an effect not seen when the amendments were added as a mulch to the soil surface (Fig 2.5.3 d), suggesting soil disturbance could have influenced this metal.

Table 2.5.2. Pearson's correlations of trace metals and As with DOC in pore water samples from the uppermost sampled soil depth (25 cm) in the field profile (data are a mean of all pore water samples collected over the experimental duration from Feb 09 to Dec 09). * = p <0.05, ** = p <0.01, ns = not significant.

Correlation with DOC	Control	Oversize	Green waste compost	Biochar
- Cu	ns	ns	0.602**	0.609**
- Zn	ns	ns	0.570**	ns
- As	ns	0.438*	ns	0.510*
- Cd	ns	ns	0.669**	ns
- Pb	ns	ns	0.809**	0.740**

Trace element mobility was variously affected by earthworms, with a general reduction in concentration probably associated with close correlations between some of the elements with DOC as previously discussed. Statistical analyses of the pore water samples suggested that Cu was most significantly influenced by earthworms (Table 2.5.3), which was also the element most closely correlated with DOC in the field study (Table 2.5.2). Sizmur and Hodson (2009) reported that earthworm worked soils have been found to be richer in humic acids than soils not worked by worms; humic acids are known to increase metal availability (Bernal et al, 2006). In contrast, earthworms are known to accumulate heavy metals in their tissues (Edwards and Bohlen, 1996). In the present study, with the exception of Cd, concentrations of all elements in soil pore water were reduced, suggesting the latter of those mechanisms affecting trace element mobility was the most important in this soil.

Table 2.5.3. Statistical significance of soil amendments (SA), earthworms (EW), and time (T) as factors influencing DOC and trace element concentrations in pore water and soil respiration in the mesocosms. Level of significance of each factor influencing each parameter is indicated by * = p <0.05, ** = p <0.01, *** = p <0.001, ns = not significant

	SA	EW	T
DOC	***	*	*
As	***	n.s.	*
Cd	***	**	n.s.
Cu	***	***	*
Pb	***	n.s.	n.s.
Zn	n.s.	n.s.	***
Soil Respiration*	***	***	*

*Note that soil respiration was only measured in control soil and soil with compost, with and without earthworms.

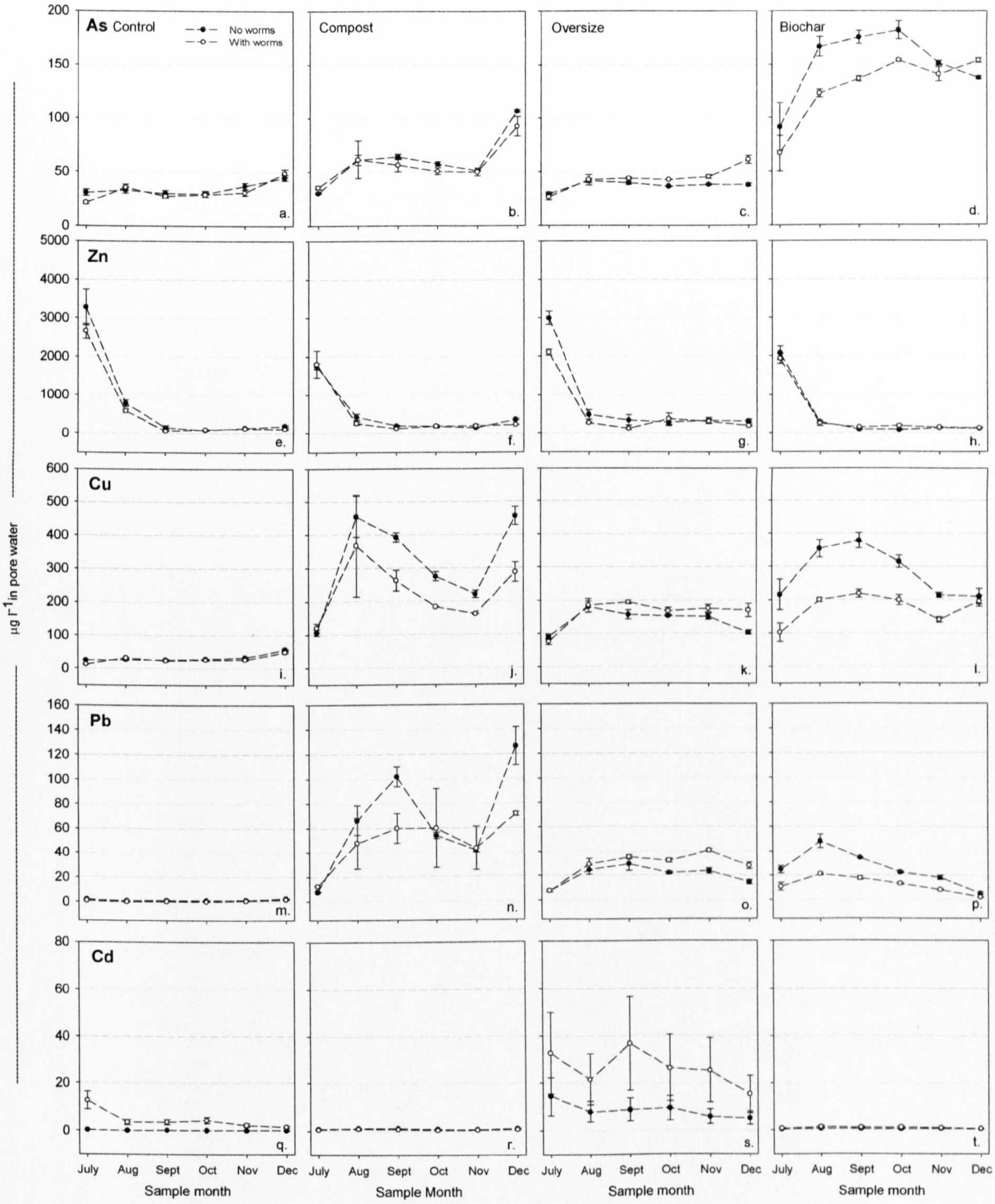

Figure 2.5.5. Variation in trace metal concentrations in pore water collected from the mesocosms in response to different soil amendments, earthworms and time (a-t).

2.5.4.6 Influence of amendments on soil moisture and respiration

Moisture was poorly retained by this sandy soil before amendment (Fig 2.5.6 a) and both incorporating amendments and earthworms increased mean moisture content of the soil. Compost and biochar were most effective at increasing soil moisture retention (5-10 % above the control; Fig 2.5.6 a). Biochar has a very high water holding capacity (Thies and Rillig, 2009) with narrow but consistently high soil moisture values recorded in the present study. Earthworms reduced both mean and range of moisture values with biochar (Fig 2.5.6 a), but it was not clear in this study the extent to which this material was ingested by earthworms, which could alter its moisture retention capability by disrupting its fine pore structure. Oversize material produced the broadest range of moisture values, probably representing its limited long term moisture retention due to its large size.

Soil temperature and moisture drive soil respiration (Lou and Zhou, 2006) and soil respiration is a good indicator of the activity of soil micro-organisms, which affects the production of DOC. Both the additions of compost and earthworms significantly influenced soil respiration (Table 2.5.3). Soil respiration increased when compost was added to soil (Fig 2.5.6 b and c), probably the result of more available substrate for feeding micro-organisms but also more favourable soil moisture conditions for this process. The increase in respiration in the control soil at > 15°C, compared to < 15°C could be due mainly to greater activity of the microbial community in soil at higher soil temperatures. When earthworms were inoculated with the control soil, the measured increase in soil respiration was probably due to increased moisture retention (Fig 2.5.6 a) whereas the increase in the compost amended soil was probably due to greater earthworm activity in the presence of greater amounts of organic matter. Bohlen and Edwards (1995) found that the earthworms *L. terrestris* and *A. tuberculata* increased soil respiration in organically amended soil, both due to an increase in microbial activity and directly by earthworm respiration. Speratti and Whalen (2008) later found that earthworms were responsible for 7-58% of total CO_2 flux, in a microcosm experiment on a sandy loam incubated with earthworms for 28 days. An additional influence in the present study could be the higher DOC concentrations consistently found in the compost amended mesocosms (Fig 2.5.4), indicating continued decomposition after compost addition, which would explain the increase in soil respiration; Liu et al (2006) discovered significant correlation between soluble carbon and soil respiration.

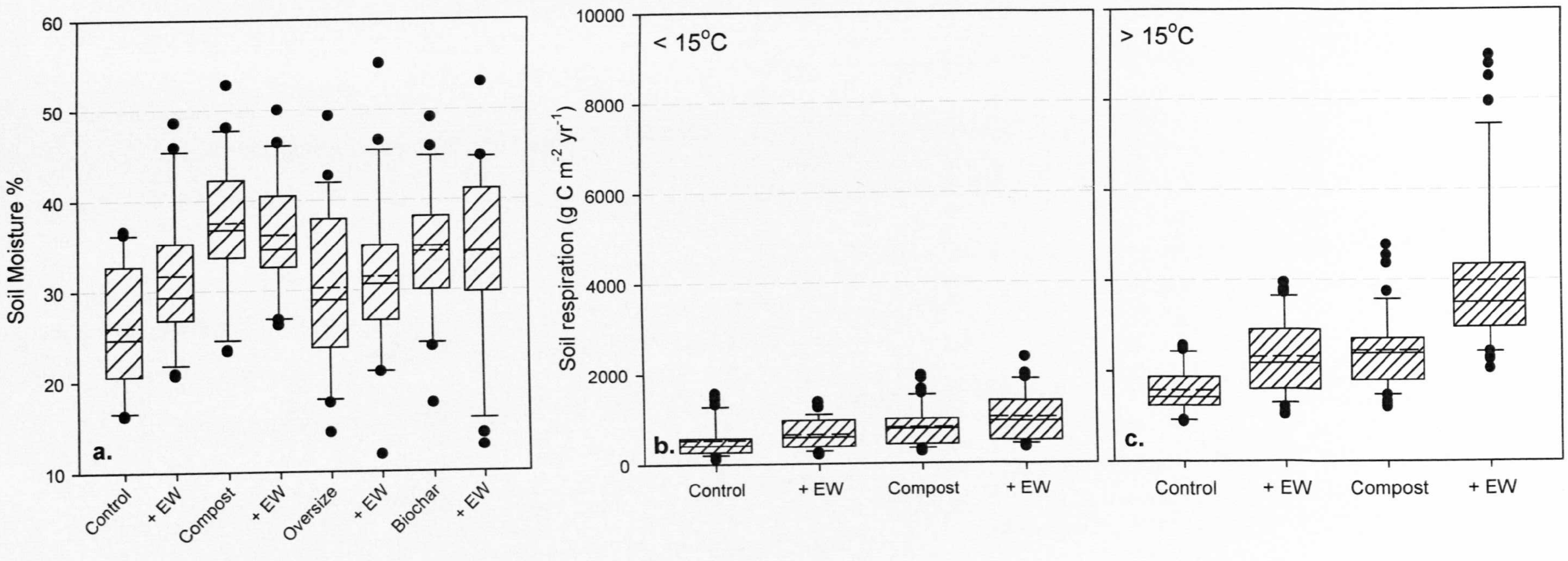

Figure 2.5.6. Combined effects of soil amendments and earthworms on soil moisture; n = 21 (a) and the effects of compost and earthworms on soil respiration in the mesocosms measured over a 10 week period. Data are sorted according to measured soil temperatures; less that 15°C (b) and greater than 15°C (c). Dashed line is the mean value, solid line is median, box is the upper and lower quartile and whisker is the 10th and 90th percentile; n = 45

2.5.5 Conclusions

Compost and non-composted organic materials enhance carbon cycling in urban soils, with increased mobility of soluble carbon and increased soil respiration. Composted green waste increased DOC and trace metal mobility the furthest of all of the amendments, whilst, unlike the non-composted amendments, also enhancing dissolved total nitrogen in soil pore water. Biochar increased As mobility when applied to the surface of the soil profile and when mixed, identifying a potential drawback of adding this material to As contaminated soils. The woody oversize amendment had least impact on DOC and As, increasing Cd mobility in the earthworm worked mesocosms, but with minimal impact on any trace elements without earthworm inoculation. Earthworms increased soil respiration by increasing soil moisture but decreased DOC mobility and the mobility of those trace elements closely correlated with this soluble fraction of carbon in pore water. Although it appears that biochar and woody amendments could improve degraded urban soils, with less impact on the mobilisation of DOC and trace elements than composted green waste, further long term field trials are now needed. These need to address the impact of biochar on arsenic contaminated soils and the interactions of earthworms with this material, as well as the further consequences to long-term soil quality of each of the alternatives to composted green waste amendment presented here.

Chapter 3:

Heavy metal contaminated soil

This chapter presents three papers on a multi-element contaminated soil. In 3.1, the solubility and mobility of arsenic, cadmium and zinc are studied in field and laboratory tests. In 3.2 the immobilisation of these elements is examined by green waste compost and biochar, whilst the final paper (3.3) specifically focuses on the mechanisms of element retention by biochar in the context of its high pH and soluble carbon content.

3.1 Mobility of arsenic, cadmium and zinc in a multi-element contaminated soil profile assessed by in-situ soil pore water sampling, column leaching and sequential extraction[3].

3.1.1 Abstract

Three methods for predicting element mobility in soils have been applied to an iron-rich soil, contaminated with arsenic, cadmium and zinc. Soils were collected from 0-30 cm, 30-70 cm and 70-100 cm depths in the field and soil pore water was collected at different depths from an adjacent 100 cm deep trench. Sequential extraction and a column leaching test in the laboratory were compared to element concentrations in pore water sampled directly from the field. Arsenic showed low extractability, low leachability and occurred at low concentrations in pore water samples. Cadmium and zinc were more labile and present in higher concentrations in pore water, increasing with soil depth. Pore water sampling gave the best indication of short term element mobility when field conditions were taken into account, but further extraction and leaching procedures produced a fuller picture of element dynamics, revealing highly labile Cd deep in the soil profile.

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[3] Sequential extraction procedure carried out by Eduardo Moreno

3.1.2 Introduction

The characteristics of soils in urban, contaminated and brownfield areas are poorly defined, especially in relation to the stability and mobility of inorganic pollutants. Some urban soils, in areas of recent or historical perturbation, are difficult to classify as soils in the traditional sense because they are heavily disturbed and have a variable content of imported materials, such as construction residues or wastes (Lehmann and Stahr, 2007). In such soils, many of which are heavily contaminated with a variety of pollutants, we have limited knowledge of the characteristics that regulate both the residence time and potential movement of metals and metalloids. Field based techniques to measure the mobility of trace elements such as the sampling of interstitial pore water, could have significant potential for ecotoxicology testing (Tiensing et al., 2001) at such sites, although there are only a few reports of the use of this method in field experiments (Farley and Fitter, 1999; Geibe et al., 2006; Buckingham et al., 2008; Clemente et al., 2008). In the case of soils that are derived from sediments or have a substantial component that originates from waste products, such as in former industrial or urban areas, the examination of element behaviour and movement in soils should be as representative as possible of processes naturally occurring in-situ, which could be unique to individual substrates or soils. In these cases, measurements taken in the field could provide valuable supplementary information when used in conjunction with laboratory based methods to examine the behaviour of trace elements.

The aim of the present study was to assess the labile fractions of cadmium, arsenic and zinc in a multi-element contaminated soil profile, in relation to the short and longer term behaviour of these elements, by directly comparing two commonly used laboratory methods with measurements taken on the same soil under field conditions. After a sequential extraction procedure to identify the geochemical associations of the elements, a laboratory leaching test was carried out to investigate longer term mobility. Soil pore water taken in-situ from the soil profile was analysed to examine element mobility and to provide a linkage between the results of the laboratory tests and the results of the data obtained under real world conditions in the field.

3.1.3 Methods

3.1.3.1 Study site

The study site was located on an embankment that separates two canals, constructed in the first decades of the 19th century in Kidsgrove, Staffordshire, UK (Lat/Long: 53°05'23.0" N, 02°15'05.7" W). The site is composed of dredged sediment, originating from the iron-rich waters of the lower of the two canals that intersect at this location. The history of the pollution in the soil is probably associated with an adjacent manufacturer, whose effluent containing Cd and Zn may have been discharged or spilled into the lower of the two canals. The origin of the As is not known, although one possible source is the former Kidsgrove gasworks that was located near to the study site at the southern end of the embankment on the outskirts of Kidsgrove. Canal sediment was dredged and dumped onto the embankment without further treatment at an unknown period within the last century and has since become spontaneously vegetated. Today the area supports a variety of shrubs (mainly *Salix caprea* and *Salix viminalis*), and perennial herbs (Lepp and Madejón, 2007). In a previous study by Hartley et al. (2004) to examine immobilisation of arsenic by soil amendments, cadmium leaching was found to increase when this soil was treated with iron based additives. However, *Salix caprea* growing here has been known to selectively accumulate Cd in stems and leaves without apparent phytotoxic effects (Lepp and Madejon, 2007) despite high soil Fe content (Hartley et al, 2004). Further to this, Hartley et al (2008) found no obvious lack of key functional invertebrate groups in this soil, leading to the conclusion that the elevated concentrations of metals have not adversely affected soil biodiversity. In the case of arsenic very limited transfer from soil to plant has been observed (Madejon and Lepp, 2007).

3.1.3.2 Soil sampling and analysis

Two adjacent trenches were excavated to a depth of 100 cm in an undisturbed area of the site that previous studies had identified as contaminated with As and Cd. One trench was used for bulk soil removal (for subsequent column leaching and laboratory extraction procedures) and the other for sampling of soil pore water in-situ. Bulk soil samples were taken from three faces of the soil trenches providing triplicate samples of approx. 500g each at depths of 0-30 cm, 30-70 cm and 70-100 cm.

In the laboratory, larger debris was removed and the remaining soil was crushed and sieved to < 2mm prior to the following analysis. Particle size distribution was determined using a Beckman Coulter LS 13 laser diffraction particle size analyser. Samples were carefully pre-treated with hydrogen peroxide (H_2O_2 30%) to remove organic matter prior to analysis. Soil pH was determined using a Jenway 3051 pH meter and SIS electrode in 1:10 suspension of soil in de-ionised water, shaken for 3 hours and allowed to settle for 45 minutes at room temperature (22°C). Total organic carbon (TOC) in solid samples was determined using an SSM-5000A/TOC-VE analyser (Shimadzu, Tokyo). Water extracts were prepared using 1:10 suspensions, shaken for 3 hours, centrifuged for 10 min at 3000 rpm and screened using a fine nylon mesh to remove any suspended particulate material which could interfere with analysis. These extracts were analysed for total water-soluble carbon (WSC) using a TOC-VE water analyser (Shimadzu, Tokyo). Aliquots of soil (0.2 g) were microwave digested in concentrated 14 M, GPR grade HNO_3 and analysed for pseudo-total As, Cd, Zn, Fe and Al using ICP-MS (XSERIES 2 ICP-MS; Thermo Scientific, MA, USA). Certified reference material (CMI 7004) was used to verify accuracy, with 78%, 83% and 94% recoveries of Zn, As and Cd respectively.

The sequential extraction procedure used here followed that of Shiowatana et al. (2001) with minor modifications. This procedure was developed for arsenic fractionation but was also used in the present study for Cd and Zn, primarily because a standardised water-soluble extraction was required for all elements. Triplicate soil samples from each depth were bulked together and mixed thoroughly before the following analysis:

For step 1 (Water-Soluble; pH 6), 1g soil plus 30 ml of deionised water was shaken for 16 h. The soil suspension was centrifuged at 3000 rpm for 15 min and the supernatant filtered through Whatman No. 42 filter paper. For step 2 (Sodium Bicarbonate–Extractable/surface adsorbed; pH 9) the soil residue from Step 1 was re-suspended in 30 ml of $NaHCO_3$ (0.5 M) and shaken for 16 h. The soil was then centrifuged and filtered as in step 1. For step 3 (Sodium Hydroxide–Extractable/Fe and Al associated; pH 13) the soil residue from Step 2 was re-suspended in 30 ml of NaOH (0.1 M) and shaken for 16 h, then centrifuged and filtered as in step 1. For step 4 (Hydrochloric Acid–Extractable) the soil residues from Step 3 was re-suspended in 30 ml of HCl (1M) and shaken for 16 h, then centrifuged and filtered as in step 1. In the final step, step 5 (Residual), the remaining soil residue from step 4 was oven-dried at 60°C for 48 h and finely ground in an agate mortar. The HNO_3

digestion procedure described previously for pseudo-total soil concentrations was used to determine element concentration for this step. This differed from Shiowatana et al, (2001) who used hydrofluoric acid digestion for the final step.

3.1.3.3 Leaching column test and pore water sampling

a.) Leaching column test

Duplicate glass columns (XK50, Pharmacia Biotech), 20 cm long with a 5 cm internal diameter were packed with 400 g of air dried soils from each depth (Fig 3.1.1 A) from one of the soil trenches. Columns were leached upwards from their base with de-ionised water (pH 5.5) at a 0.1 ml min^{-1} continuous flow maintained by a peristaltic pump. The standard method (Dutch Environment Agency; NEN 7343: Determination of leaching of inorganic components from granular materials) was modified so that a 9 fraction series over 63 days (see Table 3.1.1) was employed rather than the standard 7 fractions. Additionally, leaching water of pH 5.5 was used instead of acidified water (pH 4) to represent as realistically as possible natural precipitation. The overall aim of this test is to simulate leaching over a long term period (3-5 years). Cellulose nitrate membrane filters (1.2 μm) were placed at the base and top of each column to remove colloidal material from leachate. Before leachate collection commenced, soils were fully saturated.

Table 3.1.1. Chronology of leaching column fraction collection

Leaching fraction	Collection days	Eluate volume (ml)
1	1	30
2	1	30
3	2	90
4	3	150
5	5	300
6	11	900
7	21	1500
8	38	2000
9	63	3000

b.) In-situ pore water sampling

In the second trench compact rhizon pore water samplers (Eijkelkamp Agrisearch Equipment, The Netherlands) were inserted at 4 depths within the soil profile (10, 25, 50 and 75 cm; Fig 3.1.1 B). Samplers were placed in triplicate at each depth and left for 1 month to equilibrate, after which pore water was collected over a period of 2 weeks using removable needles and vacuum tubes. This 2 week period was required to ensure that sufficient volumes of pore water was collected for subsequent laboratory analysis. Dissolved organic carbon in pore water was determined using a TOC-VE water analyser (Shimadzu, Tokyo) and both leaching column eluate and soil pore water were analysed for arsenic, cadmium and zinc using ICP-MS (as detailed above) with an internal rhodium standard to compensate for instrument response changes during analysis.

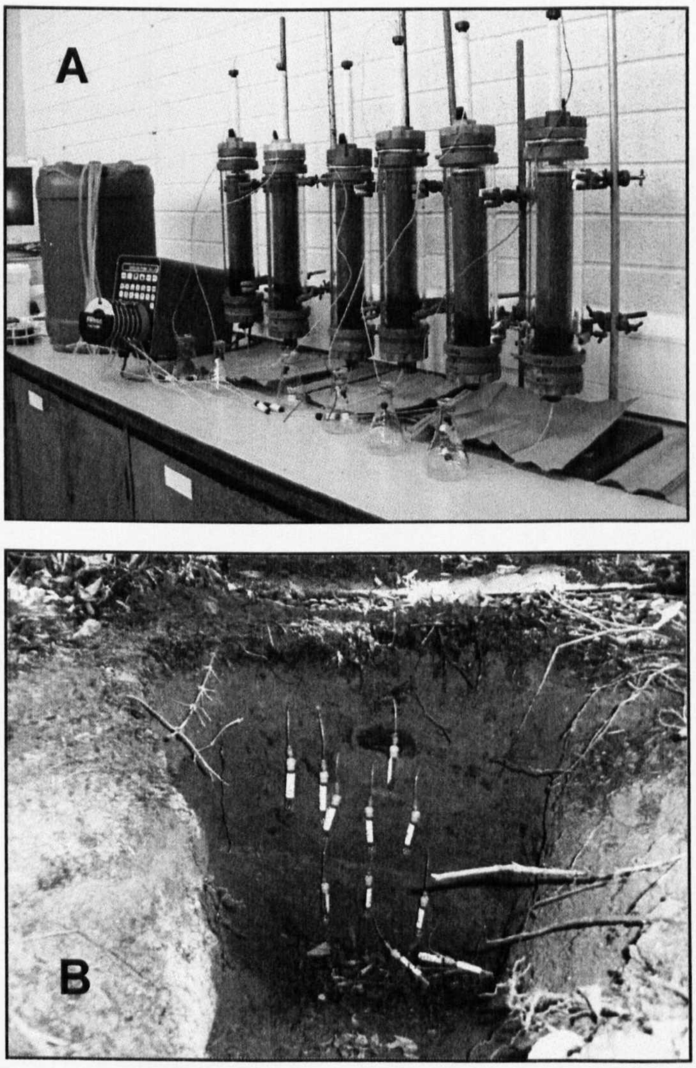

Figure 3.1.1. Leaching column set up in the laboratory (A) and rhizon pore water samplers in the soil profile in the field (B)

After analyses of all samples, the proportion of the pseudo-total As, Cd and Zn extracted by each method was calculated. In the column test, the weight of dry soil in each column (400 g) was used to calculate the total amount of element removed per kg of soil (as presented in Fig 3.1.2). For pore water data a transformation using soil moisture measurements was calculated, following Clemente et al. (2008). In a modification to this method, triplicate soil moisture measurements were taken in the field at the point of sample collection, using a portable HH2 moisture meter (Delta-T devices LTD, UK) and assuming a mean bulk density of 1.3 g cm^{-3} (Zhao et al., 2003).

Therefore calculations were made using the following equation:

$$TE_{dissolved}\ (mg\ kg^{-1}) = \frac{TE_{pw}(mg\ l^{-1}_{solution}) \cdot SM\ (l_{solution}\ l^{-1}_{soil})}{1.3\ kg_{soil}\ l^{-1}_{soil}}$$

where $TE_{dissolved}$ is concentration of element dissolved in soil pore space, TE_{pw} is absolute concentration of trace elements in pore water as sampled in the field and SM is soil moisture. The percentage of trace element dissolved in pore water was calculated by dividing $TE_{dissolved}$ by TE_{soil} and multiplying the result by 100.

3.1.3.4 Statistical analyses

Data for soil characteristics (Table 3.1.2) were analysed for differences between depths by ANOVA analysis. Where differences were found a multiple comparison of mean values was carried out by a Tukey's test. All data analyses were performed using SPSS V.14 for Windows.

3.1.4 Results and Discussion

3.1.4.1 Changes in soil properties down the soil profile

Variation in soil pH with depth was negligible (pH 6.0-6.2) and not significantly different (Table 3.1.2), with all soils slightly acidic. Soil was classified as silt loam throughout the profile, reflecting its origin as canal dredgings. No water logging was evident at any depth, suggesting free drainage within the profile and aerobic conditions. There was a general homogeneity and lack of distinct soil horizons with depth, but significantly higher TOC in the 0-30 cm zone ($p < 0.01$), which could be attributed to fallen leaf litter at the soil surface and a small zone of partially decomposed organic material in the upper 0-10 cm but there was no variation in total water soluble carbon (WSC) with depth. Pseudo-total concentrations of Cd and As were elevated at all depths (Table 3.1.2) exceeding current soil guideline values in the UK for residential areas (Cd, 1-30; As, 20 mg kg^{-1}: DEFRA, 2002). There are currently no comparable guideline values for Zn. Pseudo-total Zn ranged from 789-930 mg kg^{-1}, with the highest concentrations at 30-70 cm whilst the highest concentrations of Cd were found at 70-100 cm ($p < 0.001$). In contrast the greatest pseudo-total concentration of As was found in the 0-30 cm zone ($p < 0.001$). Iron content differed significantly throughout the profile ($p < 0.01$), whereas Al did not (Table 3.1.2). In mineral soils in the UK, iron content typically ranges from 0.5-10% (Grimshaw et al, 1989), so this element was present in high concentrations at all depths, especially between 30 and 70 cm (Table 3.1.2).

Table 3.1.2. Soil profile characteristics (mean ± S.E; n = 3). Different letters indicate significant differences between depths; ***= $p < 0.001$; **= $p < 0.01$; *= $p < 0.05$; n.s.= not significant.

Soil depth (cm)		0-30	30-70	70-100	ANOVA
pH		6.2 (0.1)	6.0 (0.04)	6.0 (0.03)	n.s.
TOC (%)		11 (0.2) b	6.2 (0.9) a	5.4 (0.6) a	**
WSC (mg l^{-1})		138 (18)	115 (4.1)	110 (2.8)	n.s.
Sand (2 mm-63 μm) %		43 (2.6) a	52 (1.9) b	47 (1.8) ab	*
Silt (62.9 μm-2 μm) %		48 (2.3)	43 (1.6)	47 (1.5)	n.s
Clay (< 2 μm) %		8.4 (0.3) c	5.2 (0.3) a	6.4 (0.3) b	**
Pseudo-total (mg kg^{-1})	As	280 (19) c	200 (13) b	96 (2.2) a	***
- -	Cd	142 (17) a	391 (12) b	862 (85) c	***
-	Zn	789 (12) a	930 (35) b	827 (33) ab	*
(%) -	Fe	9.7 (0.4) a	15 (0.6) c	13 (0.5) b	**
	Al	1.5 (0.1)	1.2(0.1)	1.2 (0.1)	n.s

3.1.4.2 Labile phases of arsenic, cadmium and zinc measured by leaching columns and in situ pore water samplers.

Greatest amounts of As were removed by the leaching column test from soils collected between 70 and 100 cm (Fig. 3.1.2) despite a soil pseudo-total As concentration of approximately one third of that in soil from 0–30 cm. This indicates the presence of a greater pool of labile As deep in the profile. Arsenic concentrations in soil pore water collected in the field were very low (< 2 µg l^{-1}), reflecting the amount that was leached in the column test (Fig 3.1.2 and 3.1.3). In the 30-70 cm zone, where pseudo-total As concentration was also high (Table 3.1.2), both column leachate and soil pore water showed that arsenic was considerably less soluble. There was no statistically significant correlation between concentrations of As and DOC in soil pore water (data not shown), indicating that soluble carbon did not affect mobilisation of As in this soil. In a similar study at Prescot (UK), in a soil with lower pH (4.0-4.4) and lower pseudo-total As concentrations (18-143 mg kg^{-1}) than in the present study, As concentrations in pore water were much higher (> 100 µg l^{-1} at 20 cm depth; Clemente et al., 2008), but no relationship with DOC was observed. Other workers have reported higher As solubility at more alkaline pH within a pH range of 3-8 (for example; Fitz and Wenzel, 2002). Soils at the present site had higher Fe and Al, and lower TOC content than those at Prescot. Oxides of both Fe and Al are known to be effective in As retention (Wenzel et al., 2001; Fitz and Wenzel, 2002; Kumpiene et al., 2008), especially in non-calcareous mineral horizons (Wenzel et al., 2002).

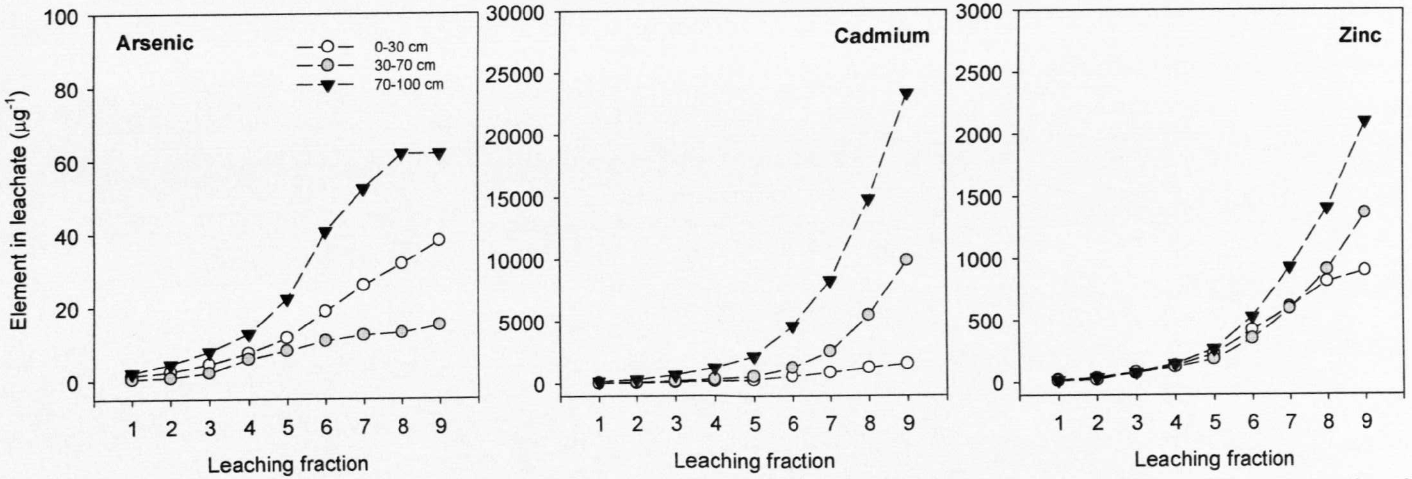

Figure 3.1.2. Cumulative amounts of leached arsenic, cadmium and zinc in three depths of a contaminated sediment derived soil profile at each of the 9 leaching fractions (n = 2). Values calculated per kg of soil from the soil weight per column. Note the higher amounts of soluble cadmium removed from deep within the profile.

In the case of cadmium, the amount leached in the column test was proportional to the pseudo-total concentration (Table 3.1.2) with an amount equating to 23.5 mg Cd kg^{-1} soil (Fig. 3.1.2) and 2.7% of pseudo-total Cd (Table 3.1.3) removed. Furthermore, cadmium was present in elevated concentrations in pore water, exceeding 2 mg l^{-1} at 25 cm and almost 5.5 mg l^{-1} in pore water from 50cm depth (Fig. 3.1.3). Over 3 mg l^{-1} was recorded at 75 cm depth; this was also the depth where most Cd was leached by the column test (Fig. 3.1.2). No significant correlation between Cd and DOC in pore water was found. Clemente et al. (2008) noted that a large proportion (1.3%) of soil Cd could be found soluble in pore water at 30 cm depth in a study on a contaminated urban woodland soil with acid pH and a peak Cd concentration of 44 mg kg^{-1}. In that work, Cd showed considerable mobility and levels in pore water were found to be a function of pseudo-total concentration of this element in the soil, soil pH and TOC. Meers et al. (2007a) also reported high relative solubility of Cd in acidic soils (0.37%, pH<7) although pseudo-total Cd concentrations of the soils in this study were far lower than in the present study (< 50 mg kg^{-1}).

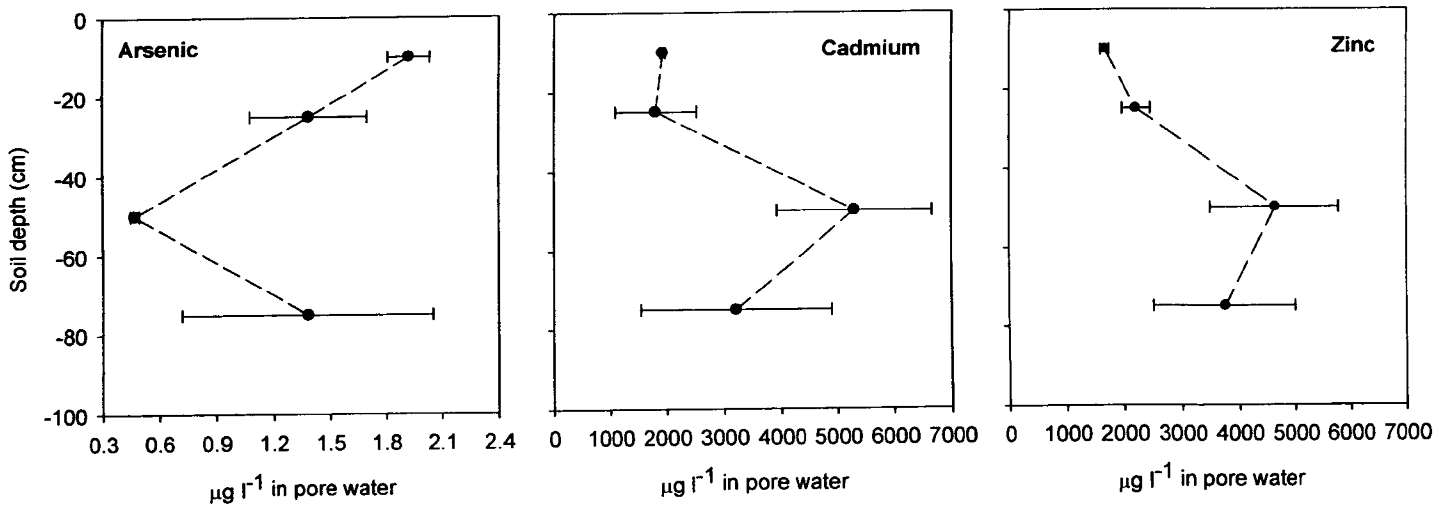

Figure 3.1.3. Concentration of arsenic, cadmium and Zn in soil pore water sampled from a contaminated sediment derived soil profile showing contrasting solubility of elements with soil depth (n = 3). Values are not corrected for soil moisture and are the actual amount extracted from the soil in the field. Note the high concentrations of cadmium throughout the profile.

An amount equating to 2.1 mg Zn kg^{-1} of soil (Fig 3.1.2) or 0.2% of the pseudo-total (Table 3.1.3) was removed by the leaching column test from the 70-100 cm zone of the profile. This was much lower than for cadmium, despite similar pseudo-total concentrations (Table 3.1.2). In common with cadmium, the peak concentration of Zn in pore water was recorded at 50 cm depth (~4.5 mg l^{-1}) and was high by comparison to the values leached in the column test (Fig. 3.1.2 and 3.1.3). There was no correlation between Zn and DOC in pore water. Similar concentrations of Zn (1-4 mg l^{-1}) were found by Clemente et al. (2008) with a significant negative relationship between pore water Zn and DOC.

Table 3.1.3. Proportion of pseudo-total As, Cd and Zn extracted by Step 1 (water-soluble) in the sequential extraction, leaching column test and soil pore water (* note that soil pore water values were transformed on the basis of soil moisture measured in the field and leaching column data were corrected for the soil weight per column as described previously)

		% of pseudo- total extracted by different methods		
		0-30 cm	30-70 cm	70-100 cm
As	Sequential water-soluble	0.01	0.01	0.02
	Column leaching test*	0.01	0.01	0.1
	Pore water*	<0.001	<0.001	<0.001
Cd	Sequential water-soluble	8.3	5.9	1.5
	Column leaching test*	1.1	2.5	2.7
	Pore water*	0.4	0.2	0.2
Zn	Sequential water-soluble	5.4	7.3	6.1
	Column leaching test*	0.1	0.2	0.2
	Pore water*	0.2	0.2	0.1

In the leaching column test, Cd and Zn removal, especially from soil from the 70-100 cm zone, appears to continue whereas As removal reaches a plateau (Fig. 3.1.2), suggesting that the soluble As pool had been depleted during this test. Indeed, after fraction 8 of the leaching column test no further As was removed from 70-100 cm zone soils.

3.1.4.3 Relationships between leaching and speciation of As, Cd and Zn

Both column leaching and soil pore water could be considered as simple extraction methods, identifying the water-soluble phase of As, Cd and Zn in soil. Results from the sequential extraction show that the majority of As was bound in the residual phase (65%) or associated with Fe and Al oxides (32%) so that a very small proportion (0.01-0.02 %) was water-soluble (Fig 3.1.4) at all soil depths. The uniformly low levels of As in column leachate, step 1 of the sequential extraction and pore water could be explained by the high pseudo-total Fe found at every depth in the soil profile (Table 3.1.2). Iron oxides have been shown to influence arsenic behavior in soils, retaining high quantities of arsenate, which is the main arsenic species in aerobic soils (Fitz and Wenzel, 2002; Wenzel et al., 2002). If anoxic conditions were induced at lower depths in the soil at Kidsgrove, there could be reduction of As (V) to the more mobile As (III) and a consequent increase in As solubility (Wenzel et al., 2002). However, no water logging was evident at any depth in the soil so it is likely that arsenate predominates over arsenite. This could help to explain the lack of As-uptake and phytotoxicity in the vegetation at this site observed in a previous study by Madejón and Lepp (2007), despite the high levels of soil As.

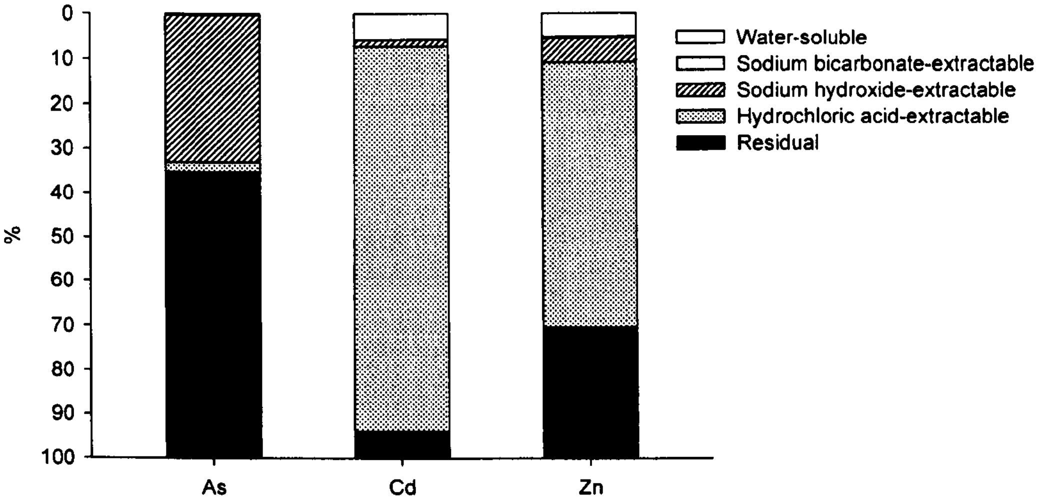

Figure 3.1.4. Speciation of Cd, As and Zn by sequential extraction (values are a mean from all soil depths). Note low water-soluble As compared to Cd and Zn.

Cadmium and zinc were scarcely extracted in steps 2 and 3 by the sequential extraction, as both use basic extractants, although due to the previous described limitations of using this method for elements other than As, it is only really realistic to consider step 1 (water-soluble) for Cd and Zn. The water-soluble Cd equated to between 1.5 and 8.3% of pseudo-total, depending on depth (Table 3.1.3), with the majority of cadmium (up to 87%) being extractable by HCl (Fig 3.1.4) and probably associated with organic matter; organic matter content throughout the soil profile was between 20 and 40% (data not shown). Therefore, in this soil, the concentrations of Cd both in soil pore water and removed by column leaching can be predominantly explained by the greater water-soluble fraction. Zinc, as with cadmium was also water-soluble (Fig 3.1.4; Table 3.1.3) in this soil, but the greatest proportion was HCl-Extractable (59.3%). The high mobility of Cd and Zn in soils has been widely reported in the literature (Knight et al., 1998; Moreno-Jiménez et al., 2009; Vamerali et al., 2009). In the context of the present soil, the rapid downward movement of the dissolved metals and lack of immobilisation through the soil profile could be viewed as beneficial to plants that root in the upper 30-50 cm of the soil. Conversely this could present risks in relation to movement towards groundwater.

3.1.4.4 Evaluation of the potential fate of As, Cd and Zn revealed by the methods used

Given the differences between the methods used in this study it was expected that step 1 of the sequential extraction would be more rigorous, extracting higher concentrations of trace elements than the column leaching or pore water based on the contact time between soil and solute. Partitioning of trace elements in soils depends on soil-to-solution ratio, duration of extraction, solutes used, and both shaking and centrifugation methods employed (Sauvé, 2001). The extended statutory leaching column test, which is continuous, extracted large amounts of Cd compared to the pseudo-total, which was not the case for Zn, where the highest extraction was only 0.2% of the pseudo-total (Table 3.1.3).

The spatial heterogeneity in pore water concentrations of As, Cd and Zn over a small area of the soil matrix is evident by the large error bars in figure 3.1.3, especially in the lower soil zones, representing the difference in concentrations of elements between replicates. This may be related to pathways of water movement through the soil in the field, percolating along lines of least resistance, so that certain regions of the soil matrix may be more thoroughly extracted than others, with an undetermined and variable contact time between soil and water in pore spaces. This demonstrates an important limitation of laboratory methods that tend to homogenize soil prior to extraction which could lead to overestimation of trace element removal; a point that is further evident when soil moisture conditions in the field are taken into account. Soil pore water collected in the field contained high levels of Cd and Zn (Fig. 3.1.3) but, when re-expressed accounting for field soil moisture content (which varied from 58% at the surface to 38% at 75 cm; data not shown) using the equation previously described, proved to extract the lowest amount of these elements (Table 3.1.3). An additional factor that may affect soil properties in the field experiment is the act of digging the trenches. This could expose the lower soil depths to additional aeration which would not normally be the case, with the potential to further enhance aerobic conditions.

Similar results to those presented here were obtained in a previous study, where pore water was found to represent the weakest extractant for Cd (Meers et al., 2007a). In that study, pore water metal concentrations showed a significant correlation with those extracted with neutral salt solutions, and neutral salt solutions are considered to be adequate to assess the impact of trace elements on plants and soil bioactivity (Kabata-Pendias, 2004). Pore water and water-soluble concentration are two methods reported in the literature for determination of phytoavailable fractions of trace elements in soils (Meers et al., 2007b; Dinelli and Lombini, 1996). The leaching column test is a valid and standardized method to assess the risk of leaching of inorganic elements, simulating the worst case scenario (Hartley et al., 2004; Hartley et al., 2009). The different methods used in the present study provided relevant and complementary information on the labile fractions of each element in this soil, which can enhance both the understanding of the dynamics of these elements, indicating the amount that is phytoavailable and the possibility of further leaching to groundwater.

3.1.5 Conclusions

The experiments reported above have directly compared laboratory and field methods that can be used to evaluate the labile phases of elements in polluted soils. The main conclusions from the study are that:

a) Cadmium was highly labile throughout this soil profile whereas arsenic was relatively immobile in the present aerobic conditions, possibly as a result of the presence of homogeneously high concentrations of Fe.
b) Step 1 of the sequential extraction (water-soluble) gives an overestimate of the soluble phase of the elements under investigation when compared to data from in-situ pore water samples.
c) Column leaching tests give a clear indication of the rates at which labile pools of each element become exhausted, indicating the longer term fate of each element; the pool of soluble As depleted relatively rapidly compared to Cd and Zn.
d) There were no relationships between element solubility and dissolved organic carbon in pore water.
e) The differences in labile fractions of elements encountered with depth may explain the lack of phytotoxicity at this site, but also indicate the attendant risk to groundwater quality.

All the methods employed here have merit when used individually, but their combined deployment produces the most holistic picture of the factors that regulate the labile phases of metals and metalloids in this soil.

3.2 Effects of biochar and green waste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil [4]

3.2.1 Abstract

Applying amendments to multi-element contaminated soils can have contradictory effects on the mobility, bioavailability and toxicity of specific elements, depending on the amendment. Trace elements and PAHs were monitored in a contaminated soil amended with biochar and green waste compost over 60 days field exposure, after which phytotoxicity was assessed by a simple bio-indicator test. Copper and As concentrations in soil pore water increased more than 30 fold after adding both amendments, associated with significant increases in dissolved organic carbon and pH, whereas Zn and Cd significantly decreased. Biochar was most effective, resulting in a 10 fold decrease of Cd in pore water and a resultant reduction in phytotoxicity. Concentration of PAHs were also reduced by biochar, with greater than 50% decreases of the heavier, more toxicologically relevant PAHs. The results highlight the potential of biochar for contaminated land remediation.

3.2.2. Introduction

Significantly elevated levels of inorganic and organic pollutants co-exist in soils from previously heavily industrialised areas. Soil characteristics as well as the individual geochemical associations of each element control whether these elevated concentrations are transferable to soluble, bioavailable and mobile fractions. Water-soluble fractions of trace metals and As in soils are the most ecologically relevant because they equate to those which are more readily mobile and bioavailable within the environment (Mench et al., 2009). Whilst the use of composted organic wastes as soil amendments, such as garden green waste, have been shown to have multiple benefits of improving vegetation establishment, reducing compaction, (Bernal et al., 2006), protecting against erosion (Craul, 1999, Whalen et al., 2003) and

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[4] Organics analysis carried out by Jose Gomez-Eyles, University of Reading, UK and linear regressions carried out by Eduardo Moreno

binding heavy metals (Song and Greenway, 2004), rapid mobilisation and vertical transport of trace metals and As was also a consequence of adding this material to soil (Beesley and Dickinson, 2010). Recent attention has been given to biochar as a soil amendment because of its potential soil conditioning properties and benefits to physico-chemical characteristics. Organic carbon contents of biochar have been reported to be as high as 90%, depending on the source material (Yin Chan and Xu, 2009), which encourages experimental application to soils to sequester C (Lehmann, 2007a,b). Further potential benefits of adding biochar to soil have also been reported; these include the adsorption of dissolved organic carbon (Pietikainen et al., 2000), increases in soil pH and key soil macro-elements, and reductions in trace metals in leachates (Novak et al., 2009). Unlike other soil amendments, biochar's longevity in soil reduces the possibility of heavy metal accumulation associated with repeated applications of other amendments (Lehmann and Joseph, 2009) such as sewage sludge.

Carbonaceous sorbents such as black carbon and activated carbon have also been shown to have a very high affinity and capacity for sorbing organic compounds (Cornelissen and Gustafsson, 2005; Lohmann et al., 2005; Oen et al., 2006; Brandli et al., 2008). There are a number of studies that indicate that these materials can reduce the bioavailability of polycyclic aromatic hydrocarbons (PAHs) in soil and sediments (Cornelissen et al., 2006; Rhodes et al., 2008). Like other carbonaceous sorbents, biochar has a large surface area, several thousand fold greater than un-charred source material (Thies and Rillig, 2009) and has also been shown to reduce the bioavailability of organic compounds (Yu et al., 2009). In this study we investigate, by simple field pot trials and laboratory experiments, whether biochar is more effective than green waste compost at reducing mobile and potentially bioavailable fractions of trace metals and As and total and bioavailable fraction of PAHs in a multi-element contaminated soil.

3.2.3. Materials and methods

3.2.3.1 Study site

Soil was sourced from an embankment that separates two canals in Kidsgrove, Staffordshire, UK (Lat/Long: 53°05'23.0" N, 02°15'05.7" W). The history of the excess concentrations of trace metals in the soil is probably associated with an adjacent manufacturing industry during the 19th century. The former Kidsgrove gasworks, located near to the study site, is one possible source of the excess As concentrations found in the vicinity and potential above-background PAH levels, although these have not been previously investigated. It is thought that canal sediment was dredged and dumped onto the embankment without further treatment at an unknown period within the last century. The site has been previously studied with regards to the spontaneous vegetation found growing there. For example, Salix caprea has been found to selectively accumulate Cd in stems and leaves without apparent phytotoxic effects (Lepp and Madejon, 2007). High soil Fe content has been found to increase soluble Cd in this soil, in laboratory experiments (Hartley et al., 2004) which, along with Zn, leaches abundantly, vertically in the soil profile (Beesley et al, 2010a). Arsenic concentrations are high but very limited transfer from soil to plant has been observed (Madejon and Lepp, 2007) because only a small fraction of the pseudo-total concentration of this metalloid was present in pore water (Beesley et al, 2010a).

3.2.3.2 Experimental design and procedure

Soil was collected from 15-30 cm soil depth on the canal embankment, avoiding a narrow litter horizon above, and sampling an area not disturbed by previous soil sampling. Soil was air-dried at 20-25°C for 2 weeks, sieved to < 2 mm and any biological debris was removed. Soil was then homogenized and thoroughly hand mixed with green waste compost (Whitemoss Horticulture, Merseyside, UK) and hardwood-derived biochar (Bodfari Charcoal, Denbigh, UK) in the following proportions, before being placed into 1000 ml PVC pots. Each treatment was carried out in triplicate.

S: 600 mL of soil per pot.
S+C: 400 mL of soil and 200 mL of compost per pot.
S+B: 400 mL of soil and 200 mL of biochar per pot.
S+C+B: 200 mL of soil, 200 mL of compost and 200 mL of biochar per pot.

Mixing was carried out on a volume basis to account for the various densities of the soil and amendments (1.8 g ml^{-1} for soil, 0.45 g ml^{-1} for compost and 0.3 g ml^{-1} for biochar). Pots were equilibrated by saturating the soils with de-ionised water (pH 5.5) for 3 days in the laboratory, after which natural drainage was allowed. One rhizon sampler (Eijkelkamp Agri-search Equipment, Netherlands) was inserted into each pot to collect pore water. The pots were then placed outdoors under environmental conditions on the university campus field location for 60 days. Pore water was collected during the 60 days field exposure, at 7, 14, 28 and 56 day intervals by connecting removable 13 ml vacuum tubes to the rhizon samplers. At the last sampling (after 56 days) some of the replicates failed to extract any pore water, but at least one sampler from each triplicate had worked. Rainfall and soil temperature data were obtained from Met Office Weather station number 7326 (Ness Botanical Gardens, Wirral (Lat/Long: 53°20'; 3°5' W) which is 12 km southwest of the university campus field location. Daily mean values were calculated for the days preceding sample collection. After the 60 day field exposure and pore water collection, the material in the pots was collected and air dried as previously described, prior to being analysed for pseudo-total trace metals and arsenic, PAHs and phytotoxicity, assessed by a bio-indicator test.

3.2.3.3 Analytical procedures for soil characterization

After soil and treatments had been initially mixed and equilibrated, but prior to field exposure, soil characteristics were determined. Soil pH was measured in a 1:2.5 suspension of soil in de-ionised water. Total organic carbon (TOC) was determined using an SSM-5000A/TOC-VE analyser (Shimadzu, Tokyo). Water extracts were then prepared using 1:10 suspensions, shaken for 3 h, centrifuged for 10 min at 3000 rpm and screened using a fine nylon mesh to remove any suspended particulate material which could interfere with analysis. These extracts were analysed for water-soluble total carbon (WSC) and water-soluble total nitrogen (WSN) using a TOC-VE water analyser (Shimadzu, Tokyo) and water-extractable trace metals and As by ICP-MS (XSERIES 2 ICP-MS; Thermo Scientific, MA, USA). Pseudo-total trace metals and As determination was by microwave digestion of 0.2 g soil samples in concentrated 14 M, GPR grade HNO_3, also analysed using ICP-MS. Certified reference material (CMI 7004) was used to verify accuracy, with recoveries consistently greater than 75%. Further details of the geochemical fractionation of Cd, Zn and As in this soil can be found in Beesley et al (2010).

Dissolved organic carbon (DOC) and dissolved total nitrogen (DTN) in pore water were determined using the same equipment as previously detailed for WSC and WSN. Trace metals and As concentrations in pore water were measured by ICP-MS as above. A rhodium standard (1 ppm) was added to each sample to verify and optimise instrument efficiency during analysis.

3.2.3.4 Analysis of total and bioavailable PAHs

Total concentrations of PAHs were determined by agitating three replicate 5 g samples of each soil after 60 days field exposure, in 10 ml of 1:1 (vol:vol) acetone/hexane mixture for 2 hours on an orbital shaker at 200 rpm. After extraction the samples were left to settle for 30 mins, after which 2 ml of solution was placed in a test tube containing 0.1 g of dry sodium sulphate before transferring to gas chromatography (GC) vials for GC-MS analysis (Gomez-Eyles et al., 2010). This method was adapted from a mechanical shaking method previously reported to give better recoveries than a Soxhlet extraction (Song et al., 2002). The bioavailable fraction was determined by cyclodextrin extractions (Stokes et al., 2005). Triplicate, 1.5 g samples of each soil after 60 days field exposure were mixed with a 25 ml solution of 60-mM HPCD (Sigma Aldrich, Poole, UK) in de-ionised water and agitated for 20 hours in an orbital shaker. The mixture was then centrifuged at 2500 rpm for 30 minutes and the supernatant discarded. The resulting soil pellet was shaken with 25 ml of de-ionised water for 10 secs, centrifuged again and the supernatant again discarded to remove any remaining HPCD solution. The soil pellet was then exhaustively extracted using the acetone/hexane mechanical shaking extraction described above and GC-MS analysis of this exhaustive extraction measured the PAHs remaining in the soil after HPCD extraction. GC-MS analysis was performed using a Thermo Trace GC Ultra system equipped with a Thermo TR-5MS capillary column (dimensions: 30 m x 250 μm x 0.25 μm; Thermo Scientific, Runcorn, UK) operating with helium as a carrier gas, coupled to a Thermo ITQ 1100 mass spectrometer (MS) through a heated transfer line (300 °C). The GC injector (220 °C) was operated in a pulsed splitless mode, 1 μl aliquots were injected using an autosampler, and the GC oven was programmed to hold 60 °C for 3 mins then raise the temperature by 15 °C/min to 290 °C, which was held for 10 minutes. The MS was operated with the ion source at 220 °C and a damping flow of 0.3 ml min^{-1}.

3.2.3.5 Phytotoxicity bio-indicator test

A shoot emergence test, using *Lolium perenne* L. var Cadix was performed on soils collected after 60 days field exposure, as a bio-indicator of phytotoxicity. Plant seed germination is sensitive to both available inorganic (Munzuroglu and Geckil, 2002) and organic pollutants (Henner et al., 1999), but, given that toxicity of inorganics is usually linked to soluble fractions but organics are poorly water-soluble, the shoot emergence test was performed directly in the soil rather than using soil extracts. Triplicate petri dishes were filled with 30g of soil collected after 60 days field exposure and watered to saturation. After 6 h, 20 seeds were placed over the soil surface. Petri dishes were incubated for 96 h under darkness at 28 °C and 60 % relative humidity in environmental chambers (Conviron, USA). Successfully emerged plants (those with shoots longer than 1 cm) were counted and the emergence success was calculated as a percentage of the 20 seeds applied to the surface of each soil whose shoots exceeded 1 cm length.

3.2.3.6 Statistical analyses

Differences between soil treatments were analysed by ANOVA using Tukey's test for means comparison ($p < 0.05$) and linear regressions were performed using concentrations of water-soluble trace elements, pH, DOC, DTN and trace elements in pore water and pseudo-total trace element concentrations in soils. All statistical analysis was carried out using SPSS v.14.

3.2.4. Results

3.2.4.1 Properties of soil and amendments

Soil pH was mildly acidic, but each amendment reduced acidity significantly (Table 3.2.1). Combining compost and biochar resulted in the greatest pH increase (to ~ pH 8). Similarly TOC and WSC (Table 3.2.1) significantly increased with the application of both of the amendments, as did DOC in pore water (data not shown). Water-soluble nitrogen (WSN) and concentrations of DTN in pore water were also elevated above those in the control soil by adding compost, but biochar had no effect on this parameter (data not shown).

Table 3.2.1. Physico-chemical characteristics and water-extractable trace metals and As in soils prior to 60 days field exposure (Different letters equal significant differences between treatments; $p < 0.05$*, < 0.01 **, < 0.001 ***, ns = not significant).

[#]Note that trace metal and As pseudo-total concentrations (in parentheses) were measured after 60 days field exposure.

	[+]S	**S+C**	**S+B**	**S+C+B**	**ANOVA**
pH	5.45 a	6.19 b	7.56 c	7.88 d	***
TOC (%)	4.6 a	6.8 b	8.1 c	12.1 d	***
WSC (mg kg^{-1})	49.4 a	65.5 b	89.3 c	129.3 d	***
Water-extractable and pseudo-total[#] (in parentheses) (mg kg^{-1})					
As	0.01 a	0.13 b	0.41 d	0.26 c	***
	(96 c)	(75 ab)	(85 bc)	(63 a)	(*)
Cd	1.10 b	0.37 a	0.38 a	0.26 a	***
	(119 b)	(77 a)	(123 b)	(73 a)	(**)
Cu	0.01 a	0.13 ab	0.27 b	0.34 b	***
	(58 b)	(46 a)	(60 b)	(47 a)	(*)
Pb	0.01 a	0.14 b	0.03 a	0.03 a	**
	(157 a)	(140 a)	(143 a)	(136 a)	(ns)
Zn	1.49 b	0.73 a	1.32 b	0.83 a	**
	(249 b)	(205 a)	(258 b)	(202 a)	(*)

[+]Soil texture was 8.4 % clay, 48 % silt, 43 % sand (after Beesley et al, 2010a).

All of the water-extractable trace metal and As concentrations were significantly affected by the amendments (Table 3.2.1). Water-extraction yielded far lower concentrations of each element in soil compared to the pseudo-total (Table 3.2.1), with Cd being the most soluble (~1 % of pseudo-total) and Zn the second most soluble (~ 0.5% of the pseudo-total). All amendments reduced water-extractable Cd significantly, but enhanced water-extractable As and Cu. There were mixed effects on both water-extractable Zn and Pb (Table 3.2.1), compost reducing the former but enhancing the latter. Pseudo-total Pb concentrations measured after field exposure were not affected by soil amendments. The other elements' pseudo-total concentrations were variously affected, Cd to the greatest extent after compost application (Table 3.2.1). Biochar and compost amendments themselves contained far lower levels of both organic and inorganic contaminants than soil;

for organics this was close to or below the limit of detection and for heavy metals and As, far below current statutory guidelines for residential soils (DEFRA, 2002).

During field exposure of the soils, rainfall was very low and soil temperature was high in the days preceding all of the pore water collections and therefore net throughflow of water in the pots was probably low (mean rainfall was less than 2 mm and soil temperature was 11.3 to 13.3 °C for each sampling time).

3.2.4.2 Trace metals and As in pore water

Cadmium and Zn concentrations were the highest of all trace elements measured in the pore water from untreated soil (Fig 3.2.1, $p < 0.05$), in common with their water-extractable concentrations (Table 3.2.1). In contrast both As and Cu concentrations in pore water were consistently very low (< 20 $\mu g\ l^{-1}$; Fig 3.2.1). Lead was increased by the addition of compost, and to a lesser extent, biochar ($p < 0.05$; data not shown). Cadmium concentrations were reduced significantly by both compost and biochar during the 56 days, with biochar having the greatest effect (Fig 3.2.1).

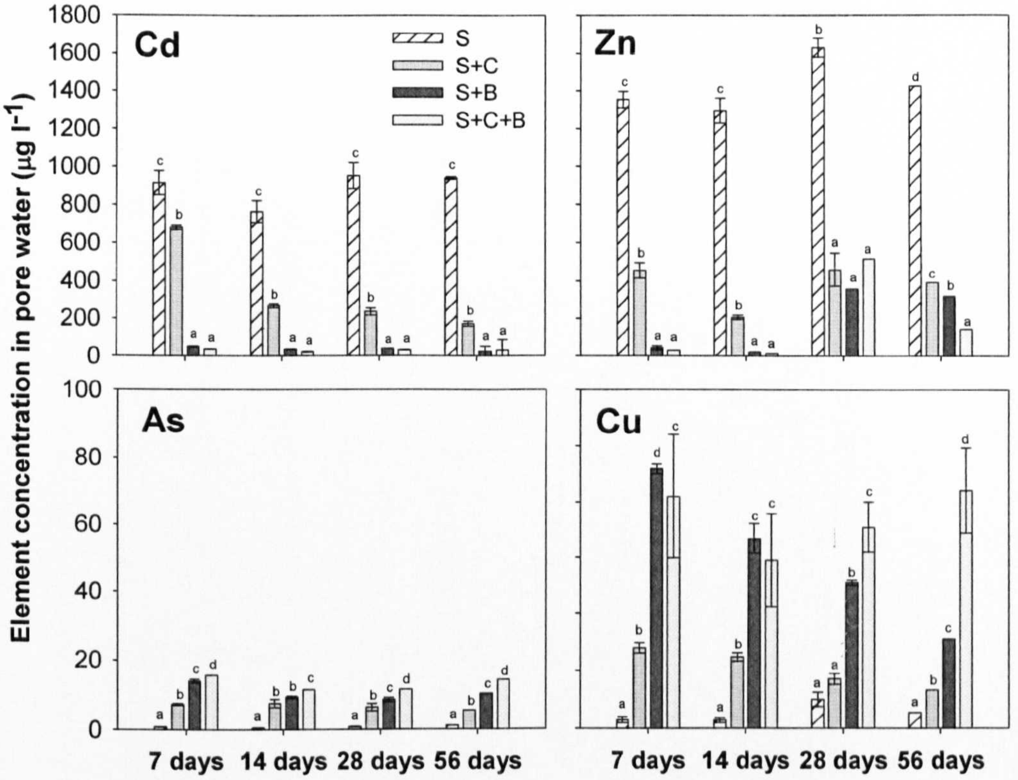

Figure 3.2.1. Concentrations of selected trace metals and As in soil pore water from soil (S), soil with compost (S+C), soil with biochar (S+B) and soil with compost and biochar (S+C+B), during 60 days field exposure (n=3; error bars represent standard error). Different letters indicate significant differences in concentration between treatments within each sampling period ($p < 0.05$).

In contrast, concentrations of Zn fluctuated, with an increase after 28 days where biochar was added, despite the initially large decrease associated with this amendment; the same effect was not seen with compost. Changes in As concentration were not time dependant as for the trace metals, but each amendment increased concentrations above that of the untreated soil. Copper concentrations responded to a greater extent to the amendments; biochar initially increased Cu in pore water, which subsequently consistently decreased over the 56 days, although concentrations were still significantly greater than the control soil ($p < 0.05$; Fig 3.2.1).

Table 3.2.2. Linear regressions between trace element concentration and other parameters (pH, DOC, and DTN) in pore water ($_{pw}$), water-extractable trace element concentrations ($_{sol}$) and pseudo-total trace element concentrations ($_{tot}$) (n=36). Parameters were ordered by significance in the model according to the independent parameter. Those parameters with least significance ($p > 0.1$) were removed from the linear model.

Model	**r**	**sig**	**F-value**
$[As]_{pw} = -11.2 + 2.28 \cdot pH + 0.022\ DOC$	0.944	***	134
$[Cd]_{pw} = 2454 - 321 \cdot pH$	0.967	***	482
$[Cu]_{pw} = -113 - 0.18 \cdot DOC + 10.9 \cdot pH + 0.99 \cdot [Cu]_{tot}$	0.940	***	81
$[Pb]_{sol} = 35.7 + 0.57 \cdot DTN - 0.28 \cdot DOC$	0.782	***	26
$[Zn]_{sol} = 3572 - 460 \cdot pH$	0.910	***	161

3.2.4.3 Total and bioavailable PAH concentrations

Following 60 days field exposure of soils, biochar treatment was most effective at reducing the concentrations of both total and bioavailable PAH groups; more than 50% relative to the untreated soil for the heavier 4- and 5-ringed PAHs and over 40% for the lighter 2- and 3- ringed PAHs (Fig 3.2.2). Differences relative to the untreated soil were only statistically significant for the total and bioavailable fractions of the 2-ringed PAHs and the total concentration of the 5-ringed PAHs ($p < 0.05$). Total PAH concentrations for all groups were reduced in the biochar treated soil significantly more than both than those in the compost and combined biochar with compost treatments, with the exception of the 5-ringed PAHs in the combined treatment ($p < 0.05$). The bioavailable PAH concentrations responded similarly but only the 2- and 3-ringed PAHs were significantly reduced after 60 days ($p < 0.05$). The compost treatment reduced both the total and bioavailable PAH concentrations by over 25% and was also generally more effective than the combined biochar with compost treatment (Fig 3.2.2). However, the total and bioavailable PAH concentrations were only significantly smaller relative to the untreated soil for the 2- and 3-ringed PAHs ($p < 0.05$).

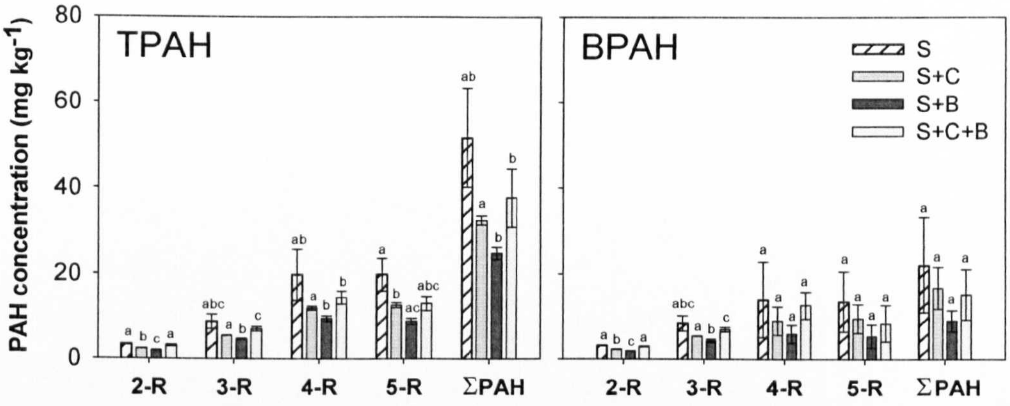

Figure 3.2.2. Total (TPAH) and bioavailable (BPAH) concentrations of 2-ringed (2-R), 3-ringed (3-R), 4-ringed (4-R), 5-ringed (5-R) PAHs and the sum of all PAHs (∑PAH) in soil (S), soil with compost (S+C), soil with biochar (S+B) and soil with compost and biochar (S+C+B) after 60 days field exposure (n=3; error bars represent standard error). Different letters indicate significant differences in concentration between treatments within each PAH group ($p < 0.05$).

3.2.4.4 Phytotoxicity assessment

Compost, biochar or the combined application of these amendments significantly ($p < 0.05$) increased shoot emergence from 61% in the untreated soil to 75-78% in the amendment treated soil (Table 3.2.3). Individual application was slightly more effective at increasing shoot length, although the difference was not significant.

Table 3.2.3. Percentage of seeds with emerging shoot lengths of > 1 cm, as an indicator of phytotoxicity (mean ± SE, n=3). Significant differences between treatments are indicated by different letters ($p < 0.05$).

	% shoot lengths of > 1 cm
S	61 ± 3 a
S+C	78 ± 4 b
S+B	78 ± 2 b
S+C+B	75 ± 4 b
ANOVA	0.033

3.2.5 Discussion

3.2.5.1 Influence of amendments on heavy metals and As in pore water

Increased Cu concentrations in pore water (Fig 3.2.1) were associated with high concentrations of DOC from compost and biochar (Table 3.2.1), with both DOC and pH influencing concentrations of this metal significantly (Table 3.2.2). Applying the amendments individually or in combination resulted in initially high Cu concentrations, but these reduced with time, reflecting the same trend in dissolved organic carbon (DOC), which also reduced in pore water over time (data not shown). Associations between Cu and DOC were previously found by Bernal et al. (2009). Increases in As in pore water (Fig 3.2.1) were associated with the increase in pH, especially where biochar and compost were applied in combination (Table 3.2.1); increased As solubility with more alkaline pH at soil $pH > 7$ has previously been reported (O'Neill, 1990, Fitz and Wenzel, 2002). In the present study, arsenic concentration in pore water was found to be both a function of pH and DOC (Table 3.2.2), although the latter was probably less influential because, unlike Cu, As concentrations did not consistently reduce with time (Fig 3.2.1). A further influence on As mobility in the presence of soil amendments could have been soluble phosphorous; P levels are generally elevated in compost (for example, Curtis and Claassen, 2009).

The contrasting effect of the amendments on Cd and Zn, compared to As and Cu, was related to the former being present abundantly as water-soluble fractions and the latter in more stable complexes in this soil (Beesley et al, 2010a). In a previous study by Clemente et al. (2006), Zn was immobilised by humic acids isolated from organic materials in acid soils while Cu mobility was enhanced by the same humic acids. Zinc and Cd are generally relatively insoluble at $pH > 7$ (Ross, 1994), so increases in pH with the application of the amendments in the present study (Table 3.2.1) would have reduced the solubility of these metals. Additionally, concentrations of Cd and Zn in pore water from environmentally exposed green waste compost are generally low (< 1 $\mu g\ l^{-1}$ and < 200 $\mu g\ l^{-1}$ respectively), whilst concentrations of Cu and As are greater (180 $\mu g\ l^{-1}$ and 300 $\mu g\ l^{-1}$ respectively; Beesley and Dickinson, 2010). Therefore it is possible that at least part of the increase in Cu and As in pore water (Fig 3.2.1) could be attributed to the direct contribution of the amendments. In comparison to green waste compost, biochar was previously found to have lower Zn but higher Cu concentrations (determined by XRF analysis; Hartley et al., 2009), which explains why Cu concentrations in pore water were increased furthest after 7 days where biochar was added to soil in the present study (Fig 3.2.1). Hartley et al (2009) also found that biochar did not significantly increase plant biomass yield. In the present study, shoot emergence (indicating phytotoxicity) was significantly increased equally by biochar and green waste compost treatment (Table 3.2.3). This was not related to changes in soluble nitrogen in soil, because only compost increased WSN and DTN above untreated soil, so it was probably predominantly due to the fact that both biochar and compost reduced water-soluble phytotoxic element concentrations sufficiently to promote successful germination.

After 60 days field exposure, pseudo-total trace metal and As concentrations were found to be significantly lower where compost amendment had been applied, but not where biochar had been used (Table 3.2.1), despite the latter reducing soluble concentrations furthest. There could have been a dilution effect of the compost, which was greater in mass than biochar applied on the same volume basis and was probably more easily incorporated into the soil during field exposure. However, as it is the soil solution concentrations, rather than the total in soil that determines the environmental impact of trace metals (Temminghoff et al., 1998), this effect was not of great importance to the interpretation of effectiveness of each of the amendments.

3.2.5.2 Influence of amendments on total and bioavailable PAH concentrations

Despite a lack of statistically significant differences between some of the treatments, the fact that biochar consistently reduced the total and bioavailable fraction to the greatest extent for all PAH groups (Fig 3.2.2) is generally encouraging in the context of remediation of PAH-contaminated soils. Other carbonaceous sorbents like activated carbon have previously been shown to reduce the bioavailable fraction of PAHs. Brändli et al. (2008) found that freely dissolved PAH concentrations measured using Polyoxymethylene (POM) strips were reduced by the addition of activated carbon whilst Yu et al. (2009) found that the sorbing properties of biochar itself reduced the bioavailability of organic pesticides to plants. However this reduction was only in the bioavailable fraction, as pesticide residues were found to persist for longer in the presence of biochar. The fact that the total PAH concentration as well as the bioavailable concentration was reduced by biochar in the present study (Fig 3.2.2) could be explained by the possibility that the

acetone/hexane extraction was not exhaustive enough to extract the PAHs that were more strongly bound to the added soil amendments, suggesting that these more strongly bound PAHs are not readily bioavailable and are thus unlike to pose an environmental risk. Alternatively the addition of biochar could have increased the degradation of PAHs; biochar has been shown to increase microbial activity in soil (Steinbeiss et al., 2009) which can stimulate PAH degradation. However, this seems unlikely as other carbonaceous sorbents (for example black carbon) have been found to decrease PAH mineralisation by reducing PAH bioavailability for microbial degradation (Rhodes, et al., 2008).
The addition of compost alone also reduced total and bioavailable PAH concentrations (Fig 3.2.2). Compost has been shown to enhance PAH degradation in a number of studies by improving soil texture, oxygen transfer, and providing energy to the microbial population (Haritash and Kaushik, 2009). It is this increased degradation potential of the microbial community that is believed to decrease PAH concentrations, not the increased sorption to organic matter (Kaestner and Mahro, 1996). Biochar and compost could therefore reduce PAH concentrations by different mechanisms in the soil which would explain why, when added in combination, they generally worked less effectively than when added individually (Fig 3.2.2). The reduced PAH bioavailability caused by the addition of biochar may have an antagonistic interaction with the increased microbial activity caused by the addition of compost by reducing the substrate available for the microbes. Although the biochar and compost were consistently found to work less effectively in combination than in isolation in both reducing the total and bioavailable PAH concentration, it is important to highlight that differences were not statistically significant, warranting the need for further investigation before drawing definitive conclusions.

Unlike pore water extraction, for which an unknown soil to solute ratio and contact time exists (Beesley et al, 2010a), some of the reduction in PAH concentrations could also have been caused by the dilution effect of adding the virtually PAH-free amendments to the soil; biochar addition of 30% by volume only constituted an addition of less than 10% by weight because the biochar was 6 times less dense than soil. However, as PAH concentrations were consistently reduced by more than 40% when biochar was added to soil, the dilution was not thought to be a largely influential mechanism of reduction.

3.2.6 Conclusions

Clear potential exists for both green waste compost and biochar to diminish water-soluble Cd and Zn fractions in this soil, significantly reducing their phytotoxic effect. However, low initial water-soluble Cu and As concentrations in this soil, combined with some mobilisation of these elements with increases in DOC and pH associated with soil amendments, make firm conclusions as to effects on As and Cu less definitive. What is clear is that both compost and biochar amendments can usefully reduce PAH concentrations, especially the heavier and more toxicologically relevant ones, with the affinity of biochar for these organic contaminants being particularly encouraging for the remediation of contaminated soils. Therefore, taken on balance, biochar has greater potential to beneficially reduce bioavailability of both organic and inorganic contaminants than green waste compost in this multi-element contaminated soil, being especially effective at reducing phytotoxic concentrations of water-soluble Cd and Zn as well as heavier PAH groups. Its targeted application to contaminated soils in field trials, as well as the mechanisms by which it immobilised selected pollutants, should now be the focus of further work.

3.3 Cadmium and zinc immobilisation and retention by biochar [5]

3.3.1 Abstract

Water-soluble inorganic pollutants can constitute an environmental toxicity problem without measures to reduce their movement through contaminated soils, and their subsequent transfer to plants or groundwater. The capability of biochar to immobilise and retain cadmium, zinc and arsenic from a multi-element contaminated sediment-derived soil was evaluated by a column leaching experiment and by scanning electron microanalysis (SEM/EDX). Adsorption of Cd and Zn to biochar's surface reduced concentrations of soluble Cd and Zn in soil leachate 300 and 45 fold respectively. Retention of both metals was not affected by considerable leaching of water soluble carbon from biochar, and could not be reversed after continuous leaching with water at pH 5.5. Unlike Cd and Zn, retention of weakly water-soluble As on biochar's surface did not reduce leachate concentrations. It is concluded that biochar can rapidly reduce the mobility of selected contaminants in this polluted soil systems.

3.3.2. Introduction

Biochar is a low-density charred material produced by burning biomass under conditions of low temperatures and minimal oxygen. Organic carbon contents of biochar have been reported to be as high as 90% depending on the source material (Yin Chan and Xu, 2009) which has encouraged its experimental application to soils to sequester C (Lehmann, 2007 a,b). Unlike fresh organic residues, biochar does not result in significant increases in CO_2 production when it is added to soils (Spokas et al, 2009, Novak et al, 2010). Dissolved organic carbon (DOC) is adsorbed by biochar (Pietikainen et al, 2000), further supporting the relative carbon neutrality of this material. There are also wider agro-environmental benefits of adding biochar to soil, for example, increasing soil pH and reducing leaching of soluble macronutrients (Novak et al, 2009).

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[5] Scanning Electron Microanalysis carried out by Marta Marmiroli, University of Parma, Italy.

The physical structure of biochar is one of the key determinants in its soil conditioning properties because, during the charring process, the surface area of the pre-charred source material can be increased several thousand fold, greatly increasing water holding capacity (Thies and Rillig, 2009). But, although the capability of carbonaceous materials, such as biochar, to adsorb organic compounds (Oen et al., 2006; Brandli et al., 2008) and remove heavy metals and As from waste-waters (Mohan et al, 2007) has been explored, application to real world contaminated soil systems has received little systematic investigation.

Water-soluble heavy metals, rather than their total concentrations, in soils, are the most ecologically relevant and have the greatest environmental impact (Temminghoff et al., 1998). One factor influencing elemental solubility in soils is pH. Fitz and Wenzel (2002) demonstrated that As was more soluble in alkaline soils within the range pH 3-8 whereas the opposite is true of metals such as Zn (Kiekens, 1995). Some biochars have been reported to have a pH greater than 8 (Yin Chan and Xu, 2009), so there could be opposing impacts on the mobility of specific trace elements if such alkaline materials are added to contaminated soils. Furthermore, co-mobilisation of DOC and some trace metals has previously been found in soil pore water collected in field experiments (Clemente et al, 2008, Beesley and Dickinson, 2010), which raises further concerns regarding the addition of carbon-rich soil amendments, such as biochar, to contaminated soils.

The aim of this work was to establish whether biochar could effectively immobilise and retain soluble and readily mobile trace elements leached from a contaminated soil, and to establish the magnitude of the potential deleterious influences of soluble carbon and increased pH. The permanence of immobilisation effects are evaluated by examining trace metals and As in successive leachate samples from a column test and scanning electron microscope X-ray emission (SEM/EDX) element dot maps of soil and biochar before and after leaching.

3.3.3. Study site and Methods

3.3.3.1 Study site

Soil was sourced from a previously well characterised section of an embankment separating two canals, constructed in the early years of the 19th century, in Kidsgrove, Staffordshire, UK (Lat/Long: 53°05’23.0” N, 02°15’05.7” W). Sediment from the lower of the two canals that intersect at this location was placed onto the bank during dredging activity at an unknown time within the last century. Subsequently the site has been studied in relation to the transfer of Cd and Zn, both of which were found in elevated concentrations, to vegetation spontaneously colonizing the sediment-derived soil (Lepp and Madejon, 2007) and to the mobility of As, Cd and Zn in the soil solution (Beesley et al, 2010a). Despite considerable mobility of both Cd and Zn in pore water extracted from the soil profile in the field (~5 mg l^{-1} Cd and Zn) found by the latter study, limited transfer to plants was observed in the former study. Although relatively high levels of As were found heterogeneously distributed within the soil, unlike the metals, this metalloid has proven relatively insoluble in soil pore water (Beesley et al, 2010ab).

3.3.3.2 Soil sampling and characterisation

Bulk soil samples were taken from three faces of a shallow soil trench excavated by hand in a secluded area of the study site which had not been previously sampled. Triplicate samples of approx. 500g of soil were bulked and mixed in the laboratory to create a single, representative sample of the soil. Large debris and biological remnants were removed and soil was crushed and sieved to < 2mm prior to the following analysis. Particle size distribution was determined using a Beckman Coulter LS 13 laser diffraction particle size analyser, with samples having been carefully pre-treated with hydrogen peroxide (H_2O_2, 30%) to remove organic matter. Soil pH was determined in 1:10 suspension of soil in de-ionised water, shaken for 3 hours and allowed to settle for 45 minutes at room temperature (22°C). Total organic carbon (TOC) in solid samples was determined using an SSM-5000A/TOC-VE analyser (Shimadzu, Tokyo). Aliquots of soil (0.2 g) were microwave digested in concentrated 14 M, GPR grade HNO_3 and analysed for pseudo-total As, Cd and Zn ICP-MS (XSERIES 2 ICP-MS; Thermo Scientific, MA, USA). Certified reference material (CMI 7004) was used to verify accuracy, with 83 %, 94 % and 78% recoveries of these elements respectively.

Biochar was produced by pyrolysis of British native hardwood species (Oak, Ash, Sycamore and Birch) at 400°C in steel ring furnaces (Bodfari Charcoal, Denbigh, North Wales). This material was screened to leave a fraction ≤ 8 mm, thought to be a practical working size both for field application and laboratory experiments.

3.3.3.3 Leaching columns

Glass columns (XK50, Pharmacia Biotech), 20 cm long with a 5 cm internal diameter were packed with 400 g of air dried soil or to ¾ of their length with biochar. Two of the columns packed with biochar were linked, in parallel, to the preceding soil columns to allow biochar to intercept eluate directly leached from the soil (Fig 3.3.1). Eluate was collected prior to passing through the biochar by means of a small outlet at the joint between columns which remained closed at all times except during sample collection. An additional two columns were filled with biochar and leached by the same method, to provide a biochar control. Columns were leached upwards from their base for 8 weeks with de-ionised water (pH 5.5) at a 0.1 ml min^{-1} continuous flow maintained by a peristaltic pump. A cellulose nitrate membrane filter (1.2 μm) was placed at the base and top of each column to remove colloidal matter (following Beesley et al, 2010a). Eluate samples (approx 10 ml) were collected weekly from all of the columns. For the first 5 weeks (fractions 1-5) eluate was collected from both the soil and biochar filled columns. In fractions 6, 7 and 8 (weeks 6, 7 and 8) leaching of soil was terminated, but both the biochar and biochar control columns continued to be leached as previously described (Fig 3.3.1). The pH of the eluate samples from each fraction was determined as above and samples were analysed for water-soluble total (WSTC) and water-soluble organic carbon (WSOC) using a TOC-VE water analyser (Shimadzu, Tokyo). Arsenic, Cd, and Zn concentrations in the eluate samples were determined using ICP-MS (as above). A rhodium internal standard (1 ppm) was added to each sample to compensate for any decreases in instrument response over the analysis time.

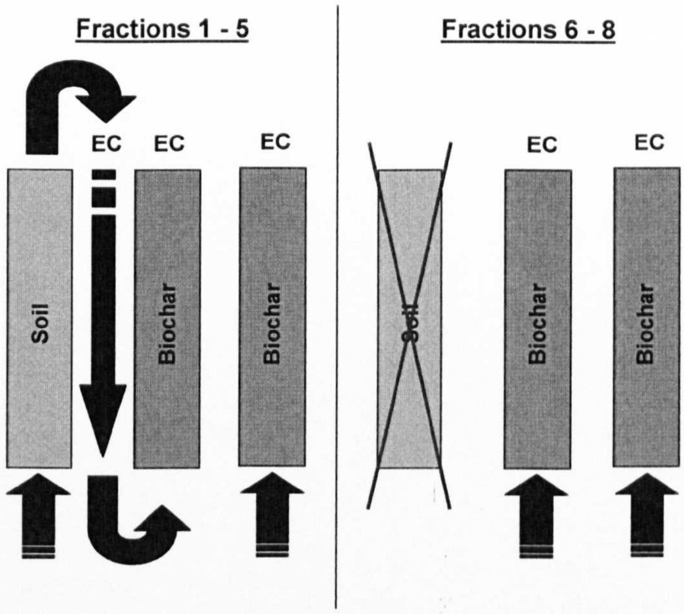

Figure 3.3.1. Schematic of laboratory leaching column experiment. EC denotes eluate collection points. Note that water is pumped from the base of the columns and eluate is collected from the top of the columns to eliminate gravitational effects.

3.3.3.4 SEM/EDX analyses

Following the collection of the last fraction of eluate from the leaching columns, 25g of soil and biochar were immediately removed from the columns and air-dried as previously described. Small sub-samples of the leached soil and biochar, along with soil and biochar that had not been leached in the columns were reduced to fine powder and deposited on scanning electron microscope slides. Each sample was placed on a single slide to avoid cross contamination. Each slide was coated, under vacuum, with colloidal graphite to ensure conductivity and analysed with a Jeol 6400 Scanning Electron Microscope (SEM; Osaka, Japan) equipped with an Oxford X-ray detector (EDX; Oxford Instruments, UK). Images and element dot maps were visualised by LINK-ISIS 4.0 software. For each analysis the voltage was set at 20 keV after Marmiroli et al (2004), whilst the working distance was 14 mm and the dead time for X-ray acquisition between 20% and 25%. The magnification and acquisition time varied according to the individual map. A colour code was applied to the element dot maps to differentiate between Cd (green), As (blue) and Zn (red). Lighter shades correspond to the higher intensity of the signal which is directly proportional to the element concentration.

3.3.3.5 Statistical analysis

ANOVA analysis of trace metals, arsenic, pH and water soluble carbon in eluate was used to determine the effects of both leaching time and biochar on these parameters, whilst Pearson correlations were used to check for relationships between parameters. All analyses were carried out using SPSS v.14 for Windows.

3.3.4. Results and discussion

Table 3.1.1. Characteristics of soil before column leaching (mean ± SE, n=3). *Note soil texture data following Beesley et al, 2010a.

Soil		
pH		6.2 (0.1)
TOC (%)		11 (0.2)
*Sand (2 mm-63 µm) %		43 (2.6)
Silt (62.9 µm-2 µm) %		48 (2.3)
Clay (< 2 µm) %		8.4 (0.3)
Pseudo-total (mg kg^{-1})	As	96 (6.6)
-	Cd	119 (1.8)
- -	Zn	249 (41)
(%) -	Fe	9.7 (0.4)
	Al	12.9 (0.9)

3.3.4.1 Eluate pH and soluble carbon

The pH of the eluate collected from the soil was mildly acidic (~pH 6), rising slightly, but not significantly, towards the end of the leaching test (Fig 3.3.2 a). Biochar increased and effectively buffered pH of the eluate at ~ 8 throughout the test (Fig 3.3.2 b) with one exception at the beginning of the leaching test (Fig 3.3.2 b); a possible consequence of the lower pH (pH < 7) of the eluate from soil (Fig 3.3.2 a) passing through the biochar. The concentration of water soluble total and organic carbon from the soil was stable throughout the test (15-20 mg l^{-1} for WSTC and 7-15 mg l^{-1} for WSOC; Fig 3.3.2 a), with no significant changes over the 5 week leaching period (Table 3.3.2). In the eluate from biochar plus soil and biochar control columns there were significant reductions in the concentrations of both total and organic C fractions (Table 3.3.2) during successive leaching. Previously, in a 67 day incubation test, the addition of biochar at application rates of 0-20 g biochar per kg^{-1} of sandy soil had no significant effect on soluble organic carbon in leachate (Novak et al, 2010). In that study biochar was mixed with soil, unlike the present study.

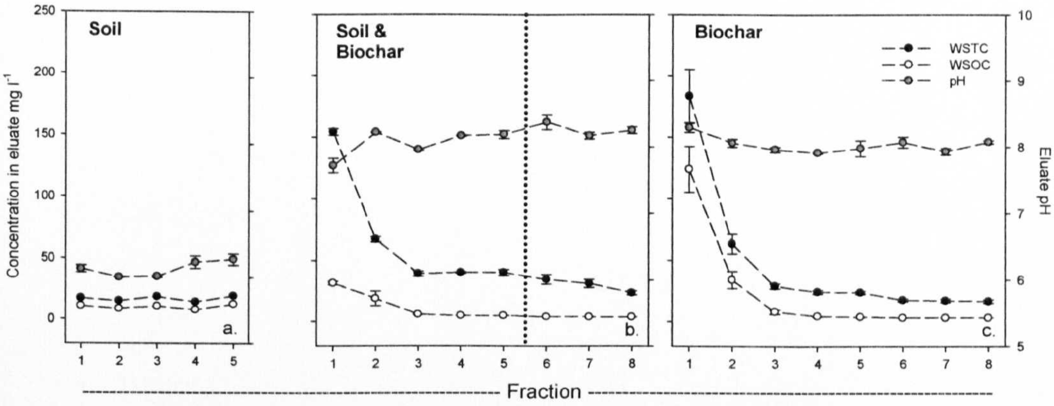

Figure 3.3.2. Water-soluble total (WSTC) and organic carbon (WSOC) in eluate from soil (a.), soil leached through biochar (b.) and biochar control (c.). Dotted, vertical line indicates where soil eluate was diverted from the leaching columns and leaching of biochar continued with de-ionised water only.

3.3.4.2 Trace elements in eluate

Arsenic concentrations were very low in eluates from soil and biochar alone (< 10 $\mu g\ l^{-1}$), but higher in the eluate from the soil with biochar than either of these individually (Fig 3.3.3 a, b and c), suggesting a cumulative leaching effect. Increased As solubility with more alkaline pH at soil pH > 7 has previously been reported (O'Neill, 1990, Fitz and Wenzel, 2002) so it was surprising that the sharp increase in the pH of the biochar eluate did not significantly mobilise this element in eluate. Neither the effect of time (Table 3.3.2) nor passing soil eluate through biochar had a significant effect on As concentration (Fig 3.3.3 a, b and c). Successive leaching of the biochar alone reduced already low concentrations of Cd and Zn in eluate further with successive fractions (Fig 3.3.3 f and i), confirming low water soluble concentrations of these elements from this material. Here there was a positive correlation between concentrations of Cd in eluate and WSOC ($p < 0.001$). This was the only element to be affected by soluble carbon throughout all of the experiment and, given that this effect only occurred in the biochar alone, where concentrations of this metal were very low, it appears that the high concentrations of soluble carbon associated with biochar did not affect element leaching.

Table 3.3.2. Effects of a 5 week leaching period on trace metals, As, pH and water-soluble carbon in eluate (ANOVA). '↑' denotes a significant increase, '↓' denotes a significant decrease at * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$. n.s = not statistically signifcant.

	As	Cd	Zn	pH	WSTC	WSOC
Soil	n.s.	↓**	↓*	n.s.	n.s	n.s.
Soil + Biochar	n.s.	n.s.	n.s.	↑**	↓**	↓***
Biochar control	n.s.	↓**	n.s.	n.s.	↓**	↓***

Cadmium and zinc concentrations in eluate from soil were high, especially in the first 2 leaching fractions (200-500 $\mu g\ l^{-1}$ in each fraction). This resulted in cumulative removals of ~ 4 mg Cd per kg^{-1} and ~ 2.5 mg Zn per kg^{-1} of soil over the 5 fractions of the test. Both metals had a similar trend to decrease successively and significantly ($p < 0.05$) after the second fraction of the leaching test (Fig 3.3.3 d and g; Table 3.3.2).Biochar significantly ($p < 0.05$) and rapidly reduced concentrations of both metals in the eluate from soil (Fig 3.3.3 e and h) with a ~300 fold decrease in Cd in the first 2 fractions. A similar effect on concentrations of these metals in soil pore water was previously seen in field conditions when biochar was mixed with this soil (Beesley et al, 2010b). A significant negative correlation between pH and Cd ($p < 0.01$) in eluate from soil when it had passed through biochar, indicated that pH may be the mechanism by which Cd was retained by biochar. The rapid increase in alkalinity of eluate following the passage of soil eluate through biochar would therefore have assisted Cd retention ($p < 0.05$; Fig 3.3.2 b). Other workers have previously noted that increases in soil pH increased retention of Cd in solution by adsorption (Azeez et al, 2010).

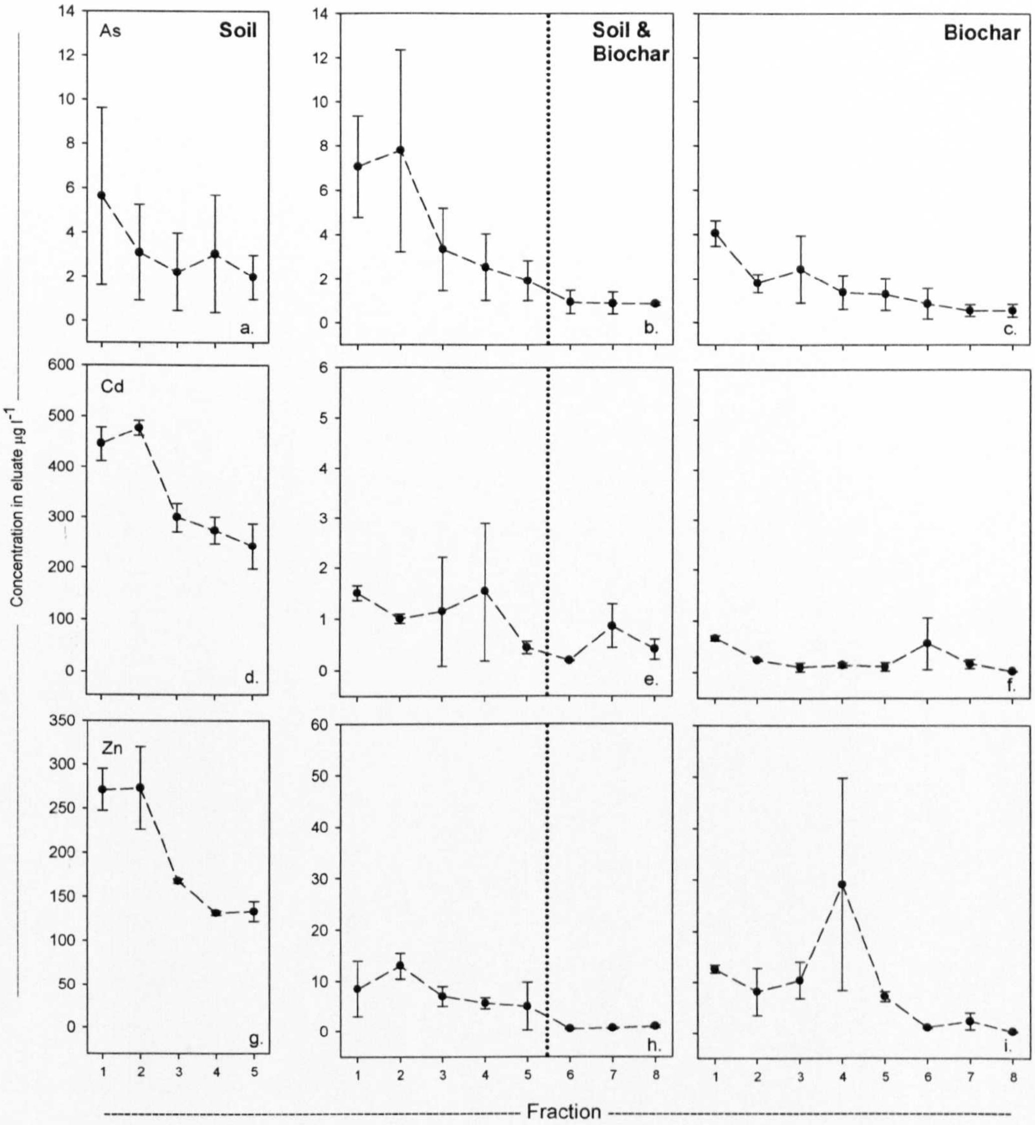

Figure 3.3.3. Concentration of arsenic (a, b and c), cadmium (d, e and f) and zinc (g, h and i) in eluate from soil, soil leached through biochar and biochar control. Note the differing scales between soil and biochar for Cd and Zn. Dotted, vertical line indicates where soil eluate was diverted from the columns and leaching of biochar continued with de-ionised water only.

In the final 3 fractions of the test (leaching fractions 6, 7 and 8, collected, 1, 2 and 3 weeks after leaching of soil was terminated) there was a small, but none significant increase in Cd in eluate from the biochar (Fig 3.3.3 e), indicating that the removal of the high concentrations of this metal previously by this material were not reversible by continually leaching it with water at pH 5.5.

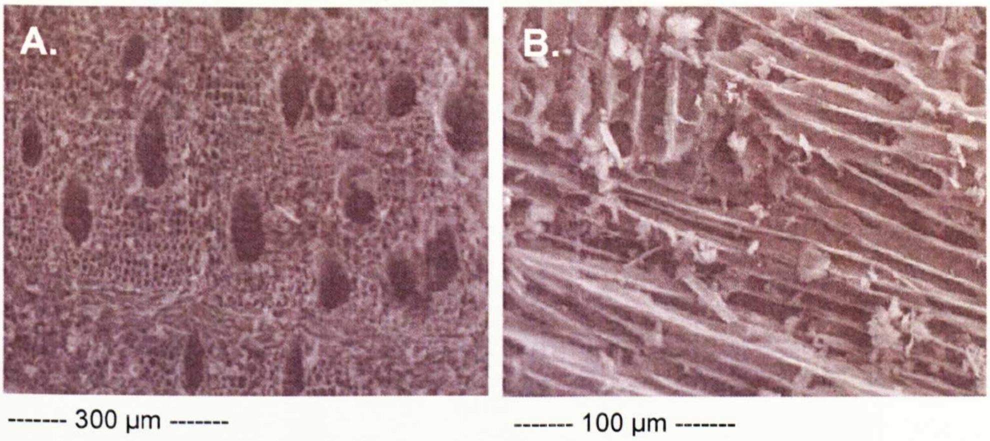

Figure 3.3.4. Scanning Electron Microscope (SEM) image of the surface of biochar at 190x (A) and longitudinal cross-section of pores at 550x magnification (B). Note both the vast surface and interior pore structure.

3.3.4.3 Desorption of trace elements from soil

Microanalysis confirmed de-sorption of Cd, Zn and As from the surfaces of the soil after it had been leached in the column test (Fig 3.3.5 B). Although pseudo-total concentration of As in this soil were also high (Table 3.3.1), it is present only in low concentrations in the water-soluble phase in this soil, and was not readily leached during the column test (Fig 3.3.3 a). Despite this it was also de-sorbed from soil during the leaching test (Fig 3.3.5 A and B) in common with Cd and Zn. In this soil the majority of As is in residual, and therefore more stable phase (> 60%), compared to Cd and Zn (residual < 5% and < 25% respectively; Beesley et al, 2010a). Since the SEM/EDX method is only effective for detecting surface adsorbed elements, from where those most weakly retained would be most readily leached, the relative decrease in concentration indicated by the element dot map is probably related to the low solubility of the metalloid. Furthermore the presence of Calcium can interfere with Arsenic detection, leading to an overestimation of the As X-ray signal. Cadmium emission lines $K_{\alpha1}$ and $K_{\beta1}$ have a high energy (23.172 and 26.093 KeV respectively), so the present study relied on the lower populated levels $L_{\alpha1}$ and $L_{\beta1}$ (3.133 and 3.316 KeV) respectively, which could have produce an underestimation of the actual number of Cd atoms in the sample, further exaggerating the presence of the other elements in comparison. Zinc $K_{\alpha1}$ and $K_{\beta1}$ can be readily measured more accurately, without interferences. The magnification used for this analysis optimized electron detection from the surface of the soil and biochar samples. However, without further destructive sample preparation, especially for biochar, which would disrupt the fine pore structure, the samples' surfaces are still rough, which can cause uneven coverage by the electron beam.

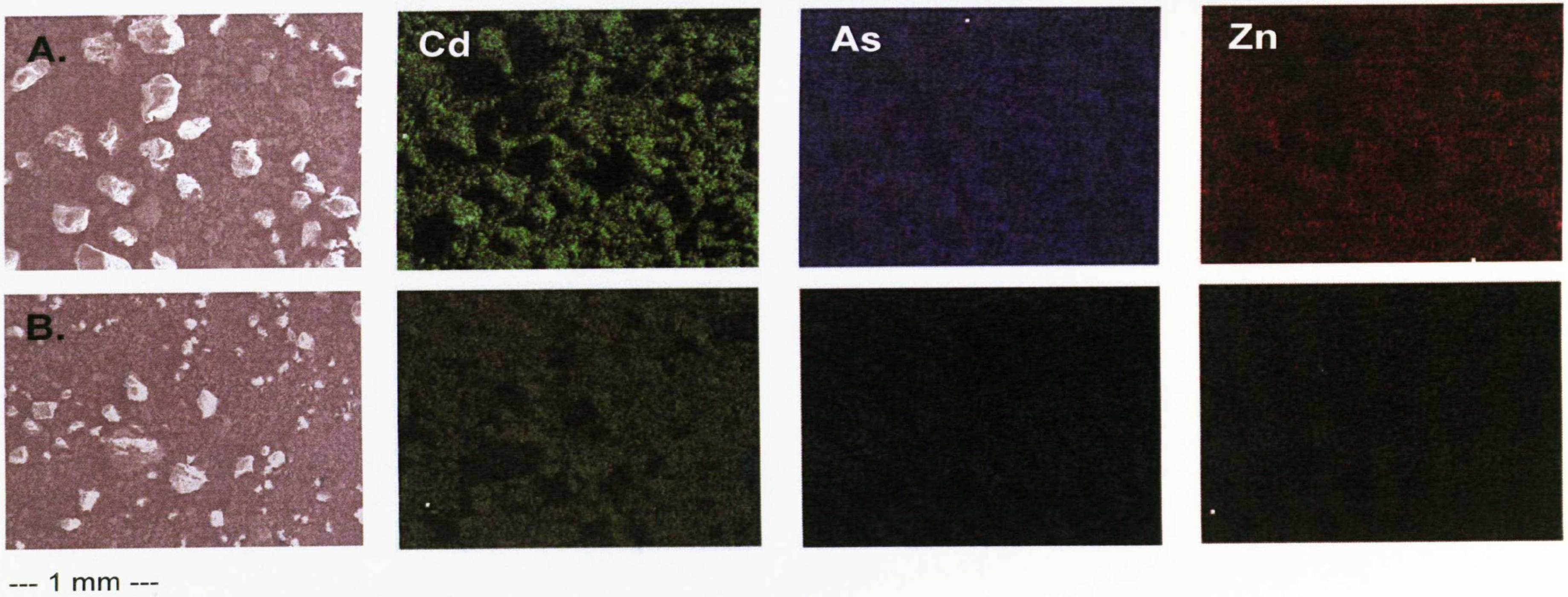

Figure 3.3.5. Scanning Electron Microscope (SEM) image and colour coded SEM/EDX dot maps (acquired at 600 frames, for 3 hours and 30mins at 40x magnification) of soil before (A) and after 5 week column leaching test (B). Note the reduction in relative concentrations of all elements after leaching, shown by darker colour shade.

3.3.4.4 Retention of trace elements by biochar

It can reasonably be concluded by eluate analysis that biochar alone is free from significant amounts of Cd, Zn and As in water-soluble form. Microanalysis revealed that these elements are not abundantly adsorbed to biochar surfaces (Fig 3.3.6 A). When Cd and Zn from soil eluate was leached through biochar, adsorption to the outer particle surface of the biochar retained these metals (Fig 3.3.6 B). Arsenic was also adsorbed to biochar (Fig 3.3.5 B), despite the small increases in concentrations in eluate (Fig 3.3.3 b). It is possible that, because of its low water soluble concentration, much of the As in solution was located only on the outer surfaces of the biochar as eluate was passed through the biochar columns. Cadmium and Zn, on the other hand, far more abundantly water soluble, and present in far higher concentrations, may have been retained both to outer surfaces and, when those retention sites were effectively saturated, further adsorbed to the network of pores and fissures that form biochar's structure (Fig 3.3.4). Differential nutrient retention and leaching effects related to pore sizes, outer and inner surfaces of biochar have previously been discussed by Major et al (2009). Such effects could explain why biochar adsorbed Cd, Zn and As, revealed by the element dot maps (Fig 3.3.5 A and B), but did not reduce water-soluble As concentrations in eluate (Fig 3.3.3 b).

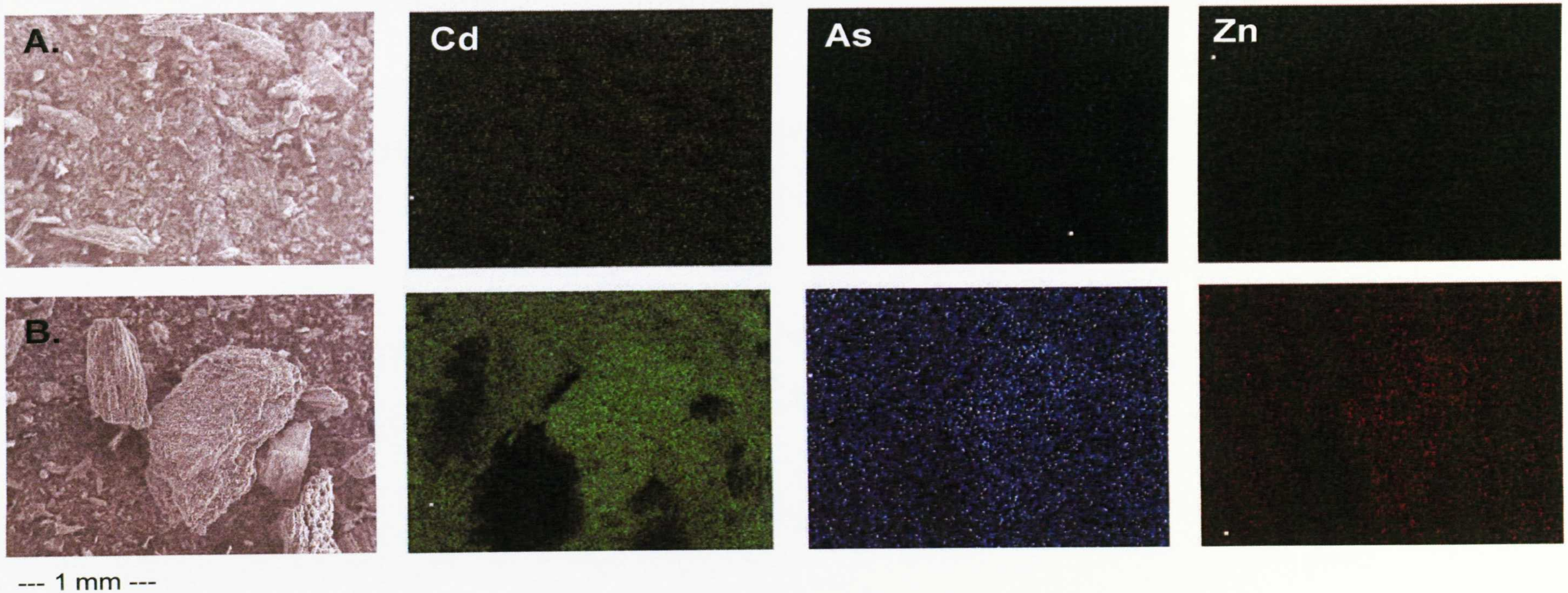

Figure 3.3.6. Scanning Electron Microscope (SEM) image and colour coded SEM/EDX dot maps (acquired at 600 frames, for 3 hours and 30mins at 40x magnification) of biochar before (A) and after leaching with contaminated soil eluate in a 5 week column leaching test (B). Note the increase in relative concentrations of all elements after leaching, shown by lighter colour shade.

3.3.5. Conclusions

Chemical measures of bulk quantities of potentially harmful elements in soil and eluate leached from soil were complemented by scanning electron microanalysis to examine the spatial distribution of each element on the complex microscopic matrix of biochar. By this simple combination of methodologies, biochar was shown to be effective in reducing concentrations of water-soluble Cd and Zn by adsorption. Biochar could be used deep in soil profiles where soluble trace metals could present environmental problems if their vertical mobility continued, or in surface soils to reduce phytotoxic concentrations, and plant transfer of metals from soil solution to the rhizosphere. The results of this study should now be expanded to determine further influences on the mechanisms of individual element retention by biochar in the light of dynamic soil physical, microbial and chemical conditions found in soils in the field.

Chapter 4: Conclusions

The aim of this thesis was to examine carbon storage and fluxes in urban, brownfield and heavy metal contaminated soils, further determining whether soil amendments could enhance carbon storage, fluxes and the attendant impacts to residual contaminants. Carbon storage and trace element concentrations in the urban soils studied in this work were heterogeneous, on a study site by site basis, across the city wide survey area and with depth in soil profiles. Soil manipulation, by the addition of organic amendment impacted on major C flux with the consequences of adding the soil amendments particularly profound with regards to soluble C. Depending upon the type and amount of amendment, the mobilisation of some trace elements by the associations of those elements with leaching soluble carbon was identified and measured.

In terms of net carbon storage, in surface topsoils across the city of Liverpool, carbon densities varied from < 3 to > 10 kg TOC m^{-2}, which was at the lower end of the range found previously. Importantly, a small but variable proportion of inorganic, anthropogenically derived material at lower depths in an urban soil profile limited the majority of organic carbon storage to the upper 30 cm, indicating that the distribution of C was site-specific depending on how the soils were previously managed. This determined the amount and type of technogenic material within them. The potential existence of deeper levels of black carbon in urban soils was not investigated in the present study, but would an important follow-up to the present work.

Adding small amounts (15% by volume) of green waste compost to urban soil or creating new soils on brownfield sites, including combining the compost with existing soils and soil-forming materials, enhanced carbon storage three fold. Larger applications (> 30% by volume) reduced bulk density, which effectively negated the benefits to additional carbon storage on a density/area basis. Small but repeated applications of green waste compost would be required to build and maintain carbon storage in these urban soils. The development of the soil profile in the years following compost application was not studied here, but remains as an interesting further aspect to be examined.

Dissolved organic carbon and soil respiration, two major pathways of soil C losses, accounted for < 1% and approximately 20% respectively of the annual loss of carbon from an urban lawn soil. Soil temperature and moisture were the drivers of these losses, with peak production and mobility of dissolved organic carbon corresponding to optimum conditions for biological activity as well as solute transport in soils. Annual carbon losses to soil respiration equated to 1 – 1.2 kg C m^{-2}, which more than doubled with compost application.

Dissolved organic carbon was increased following the application of organic amendments to soils, strongly influencing trace element solubility in soils. Copper, lead and arsenic mobility increased but cadmium and zinc were not greatly affected. For Cu and Pb this was primarily by their formation of complexes with soluble C. Green waste compost also directly contributed to increased arsenic mobility in the soil profile as it decomposed because this metalloid was highly soluble in, and rapidly dissociated from the compost during the decomposition process. In green waste compost and biochar-amended soil the earthworm *Lumbricus terrestris* reduced dissolved organic carbon mobility and the associated trace element transport when inoculated in soil. With an amendment of the remaining woody material from the compost production process, the mobility of dissolved organic carbon decreased when soil was inoculated with earthworms, which reduced the impact on trace element mobility. It was surmised that the woody amendment was too big for earthworms to ingest. Earthworms also increased soil respiration losses of C to the atmosphere most at the highest measured soil temperatures, further exacerbated by green waste compost amendment.

In a heavy metal, multi-element contaminated soil, where concentrations of cadmium and zinc in pore water were high, biochar was more effective than green waste compost at reducing pollutant mobility, but the mechanisms were distinctly different. Biochar adsorbed and immobilised both metals, whilst also effectively reducing the concentrations of some PAHs, whereas soil dilution effects could have been the reason why the compost, greater in mass at the same volume as biochar, did not have as great an effect. Although biochar generated high concentrations of soluble carbon, this did not affect cadmium or zinc retention, nor did the increased pH of biochar greatly affect mobility of As.

Taking a general overview of the work in this thesis it is clear that urban soils can store large amounts of carbon, assisted by the sensible application of suitable soil amendments. Composted green waste can mobilise trace elements into soil solution, increasing the potential risks of applying this material to contaminated urban soils. Given that repeated applications would probably be required to maintain C storage after annual decomposition fluxes, it may only be viable to apply this material to soils without residual contamination problems. Biochar, as an alternative soil amendment, can enhance carbon storage probably without frequent repeated applications and can retain potentially harmful phytotoxic trace elements present in soil solution. The focus of future research on urban soil C storage and trace element flux could therefore move in the direction of amendments that do not require repeated applications, such as biochar. An additional consideration for future work could be the combined application of green waste compost and biochar, providing the co-benefits of each amendment in one soil treatment; this has yet to be investigated in systematic, repeated trials however. Further work is urgently needed on biochar from its production, through its application to its degradation in soils to determine the efficacy of using this amendment for soil C storage. Thus far uncertainties still exist as to the C neutrality of producing soil amendments by pyrolysis versus the composting process, which is far longer established and widely accepted.

Significant opportunities exist to utilise the substantial soil resource extant within urban areas for its C storage potential. There is still more work required to say, with confidence that sustainable C storage can be enhanced by compost and biochar amendment, without, in the case of the former, de-stabilising residual contaminants and the latter, undermining C neutrality by the production of sufficient quantities of this amendment.

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Appendix: Supplementary material on CD

Copies of papers in print and in press:

Appendix 1) Beesley, L., Dickinson, N. 2010. Carbon and trace element mobility in an urban soil amended with green waste compost. Journal of Soils and Sediments 10, 215-222

Appendix 2) Beesley, L., Moreno-Jimenez, E., Clemente, R., Lepp, N., Dickinson, N. 2010a. Mobility of arsenic, cadmium and zinc in a multi-element contaminated soil profile assessed by *in-situ* soil pore water sampling, column leaching and sequential extraction. Environmental Pollution 158, 155-160

Appendix 3) Beesley, L., Moreno-Jimenez, E., Gomez-Eyles, J.L. 2010b. Effects of biochar and green waste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. Environmental Pollution 158, 2282-2287

Research report to WRAP:

Appendix 4) Rawlinson, H., Putwain, P., Dickinson, N., Beesley, L., Sparke, S., Jones, J. 2010. Organics program-final report. Cross Lane Tip and Chorley former royal ordnance facility. Waste and Resources Action programme. Banbury, Oxon (in press).