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Quantification of black carbon in urban soils

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Dedication

For my mother Rachel whose achievements continue to inspire me.

Abstract

Black carbon (BC), which comprises partially combusted organic material such as char and soot, is a hazardous pollutant and contributor to global warming, but is also highly stable, and once deposited in soil contributes to long-term stocks of sequestered carbon. The effects of land use and proximity to emission sources on the quantities of BC stored in soil have heretofore received little scientific attention. Quantification of BC in soils has proven problematic as it is difficult to chemically or physically distinguish between thermally altered (BC) and unaltered organic carbon fractions. This thesis presents studies leading to the development of an improved method for soil BC measurement, employing chemooxidation, which was rigorously tested using additions of a range of major types of BC to soil. The method was applied to measure soil BC in gardens and non-domestic greenspaces, under grass and tree cover in a representative UK city (Leicester), and in agricultural land within 7.5 km of the city. Soil BC was also measured in transects away from one of the main roads in the city, to determine whether vehicle emissions interacting with tree cover, potentially intercepting particles, can locally affect BC concentrations. BC provided 28.1 % of the total soil carbon in the city, twice the concentration found in agricultural land. Soil BC was negatively correlated to distance from the main road, implicating vehicle emissions as important local sources, but effects of trees on this relationship were inconclusive. Positive correlations were found between soil BC and non-pyrogenic soil organic carbon concentrations, soil nitrogen, and the soil carbon to nitrogen ratio, suggesting that BC may increase recalcitrance and sequestration of organic carbon. It is concluded that BC represents a significant and distinct carbon pool in urban soils, and may have a considerable influence on soil biogeochemical cycling and carbon sequestration.

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Chapter 1: Introduction to black carbon as a component of the carbon cycle and a pollutant within urban soils.

The incomplete combustion of biomass and fossil fuels produces a continuum of carboniferous particles known collectively as black carbon (BC). BC encompasses soot, charcoal, bio-char, graphite, activated carbon (C), and elemental C, and each term denotes a particular manifestation of a partially-combusted organic compound. BC is ubiquitous in every natural reservoir: earth, air, and water. It occurs naturally as a result of wildfires and the erosion of graphitic rocks, but is of special scientific interest as an anthropogenic pollutant (Goldberg, 1985). Relatively small BC particles can remain in the atmosphere for weeks after production, with various effects on the environment (Ramanathan and Carmichael, 2008), but the vast majority of BC is deposited immediately in the vicinity of its source, leading to particularly high BC concentrations in urban soils (Lorenz and Kandeler, 2005). This research proposes to focus on the detection, dispersal and storage of BC in the soils of built-up areas, and the impact of BC on belowground biogeochemistry.

Black carbon: physical and chemical characteristics

BC is defined as a material produced by the incomplete combustion of biomass and fossil fuels, containing at least 60 % C, and typically the accessory elements hydrogen (H), oxygen (O), nitrogen (N), and sulphur (S) (Goldberg, 1985). Within the atmosphere of urban areas, high levels of BC form a significant proportion of all particulate pollution. For example, Novakov (1982) found BC to comprise 97% of aerosols in New York City air samples. BC is also ubiquitous in soils and sediments due to atmospheric and fluvial distribution and deposition (Forbes *et al.*, 2006). BC has generally been considered a particularly refractory form of organic C due to its highly aromatic structure. BC is the

slowest-cycling of soil C pools, and BC in marine sediments was found to have a ^{14}C age several millennia older than concurrently-deposited sediment, indicating a long residence time in soil or the water column (Masiello and Druffel, 1998).

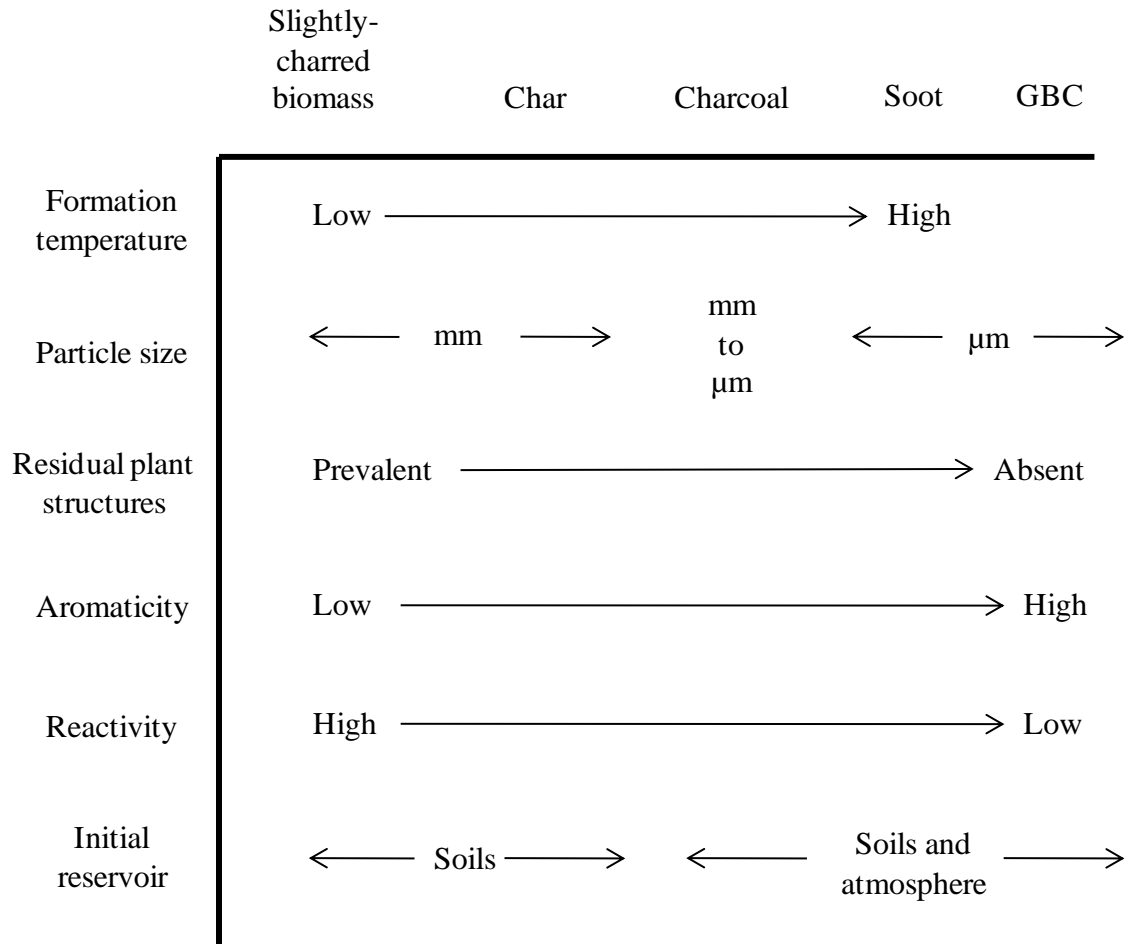


Figure 1.1. The BC combustion continuum (adapted from Hedges *et al.*, 2000; Masiello, 2004).

BC ranges from less-altered forms such as slightly charred biomass to highly aromatised structures like charcoal and soot (Fig. 1.1). Slightly charred biomass has a low formation temperature, a particle size that typically exceeds 1 mm, and contains remnant structures from its parent organic matter (OM). Thus, this type of BC is still somewhat reactive, and tends to settle immediately onto the soil surface after formation due to its large size (Hedges *et al.*, 2000). At the other end of the continuum, soot is created by

condensation reactions of gaseous combustion products that form solid assemblages of aromatic C rings (Kennedy, 1997). Soot particle size is much smaller, on the scale of submicrons, so it can remain airborne for days or weeks before settling onto the soil (Masiello, 2004). It is possible to determine the parent material of charred biomass and charcoal by studying its chemical structure, but soot is so altered by the gaseous intermediate phase of its production that its original material cannot be identified (Hedges *et al.*, 2000). The structure of a soot particle consists of stacked lattices of hexagonal C rings, which agglomerate to form particles (for a diagram of soot structure, see Ogren and Charlson, 1983). Graphitic black carbon (GBC) is formed belowground as organic material is heated and pressurised in the absence of oxygen, being highly aromatic and almost pure C; as such it is the most stable form of BC.

The C cycle

The global C cycle is the system by which C is converted between its various forms, both mineral and organic, via environmental and biological processes in atmospheric, aquatic, and terrestrial biospheres (Fig. 1.2). Organic carbon (OC) molecules are derived from living organisms, contain C-C or C-H (hydrogen) bonds, and are therefore available for assimilation by other organisms. By definition, BC is a form of OC. Inorganic carbon (IC) is mineralised C, such as carbon dioxide (CO₂), calcium carbonate (CaCO₃), and carbon monoxide (CO). IC is actively cycled by environmental and geological processes, and converted to OC by biological ones.

Plant photosynthesis is a key driver of the C cycle, as this biological process fixes atmospheric CO₂ into bioavailable carbonic compounds. The majority of this C is lost back to the atmosphere as CO₂ through the process of heterotrophic and autotrophic respiration. The balance of a terrestrial ecosystem as a net sink or source of atmospheric CO₂ depends

on the relative rates of productivity and decomposition (Schimel, 1995). Plants are an ephemeral store of C, and contain only a small portion of the C stored in a terrestrial ecosystem, but decomposition and humification of plant detritus can convert this OM into a longer-term pool of C in the soil.

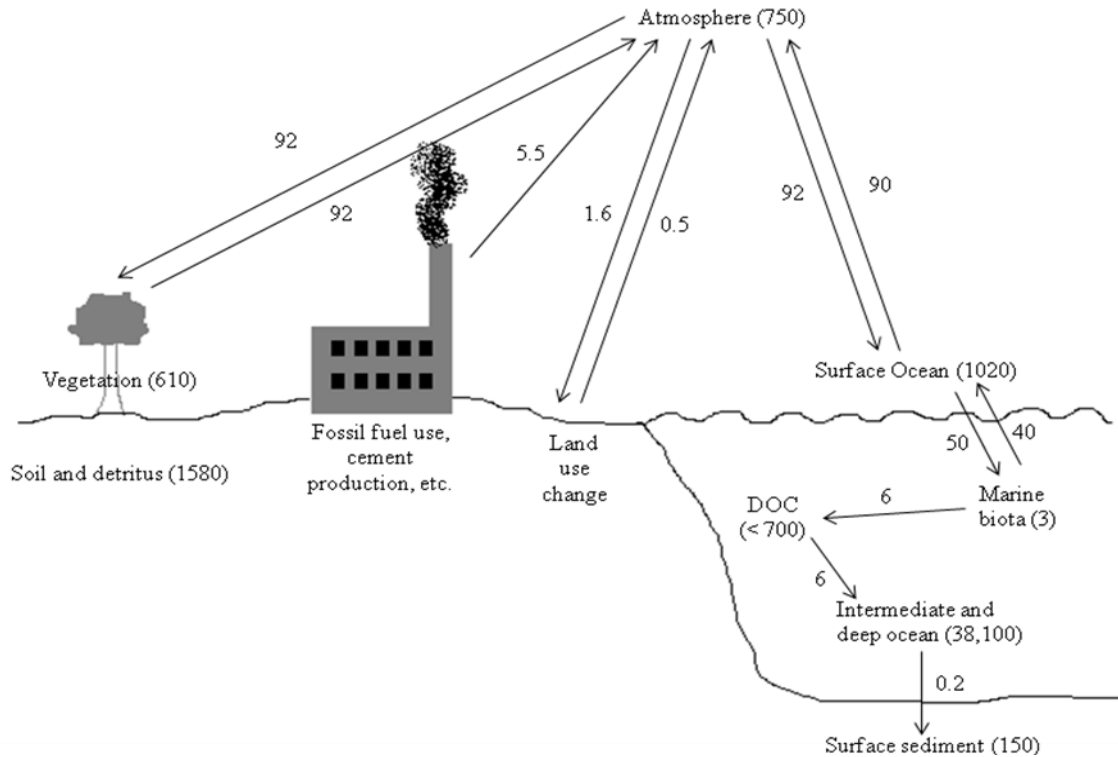


Figure 1.2. The C cycle, depicting mean C stocks in brackets (in Gt C) and fluxes (Gt C yr⁻¹) estimated for the years 1980-1989, from Schimel (1995).

In terrestrial systems, two-thirds of OC on average is stored below ground, and this C pool has much slower turnover rates than aboveground C (Schlesinger, 1977). Currently, the majority of global temperate grasslands are considered to be C sinks – reservoirs in which C inputs exceed losses (Bruce *et al.*, 1999; Conant *et al.*, 2001; Vleeshouwers and Verhagen, 2002). Soil OC has been split into three distinct pools based on residence time, particularly for the purpose of soil C models; these are labile (< 10 years), slow-release (10-10³ years), and passive (> 10³ years) (Lal *et al.*, 2001). A C pool, simply stated, is C of homogeneous chemical structure with uniform bioavailability to plants and microbes

(Smith *et al.*, 2002). Rapidly cycling OM (e.g. plant litter, microbial biomass) makes up 3-5 % of soil organic matter (SOM) (Darrah, 1996), but the average residence time of SOM is on the scale of decades (Jones and Donnelly, 2004). Decomposition is hindered, increasing soil residence time, when soil forms protective aggregates that encapsulate SOM (Fig. 1.3). Roots, fungal hyphae, microbial debris and clay minerals are the main contributors to this aggregation.

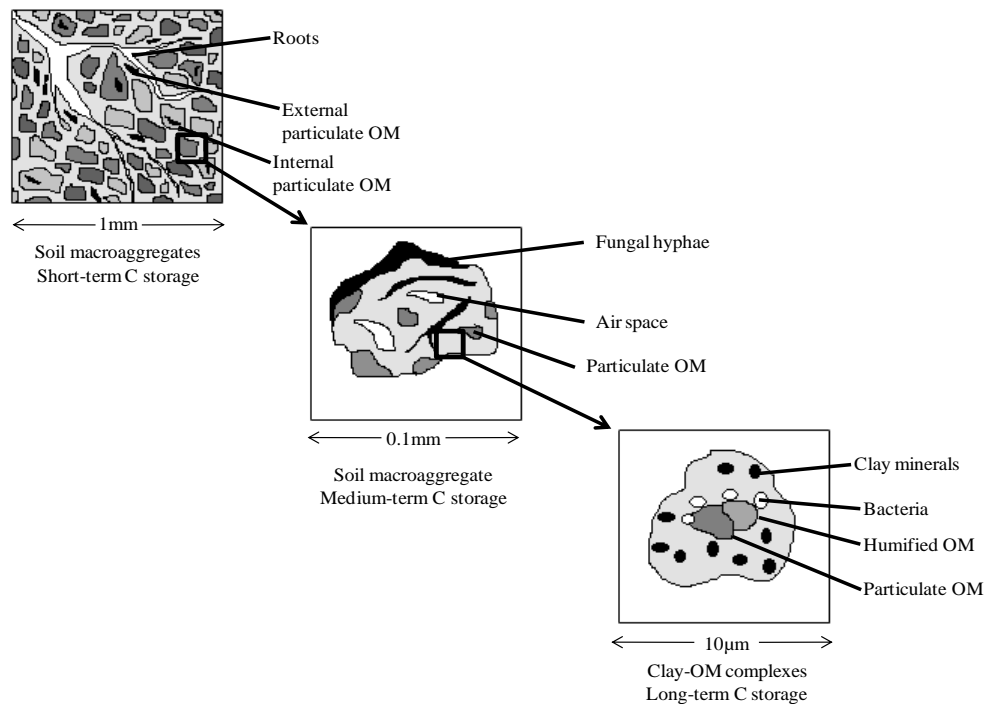


Figure 1.3. The structure of soil aggregates, adapted from Jones and Donnelly (2004).

Stabilisation of SOM into more recalcitrant molecular structures occurs by three main mechanisms: chemical binding of SOM with soil minerals, biochemical stabilisation by reactions with biologically-derived compounds such as glomalin and lignin, and physical aggregation that creates barriers against microbes and their extracellular enzymes (Jones and Donnelly, 2004). SOM can also be transferred to deeper layers of the soil, by leaching and the vertical mixing performed by soil organisms such as earthworms. At depth, decomposition rates are decreased by less favourable conditions, such as reduced

oxygen and water saturation of pores. The amount of C stored by a soil system depends on many factors, including climate, vegetation, hydrology, topography, and nutrient availability (Gupta and Rao, 1994), although soil BC inputs represent a means of increasing C storage capacity independent of biological loss processes.

Human impacts on the C cycle

Globally, the soil C pool is estimated at 2200 Pg, of which approximately 70 % is soil OC (Lal, 2003). Anthropogenic disturbance of the natural C cycle has been, and is currently, altering the amount of C the earth is able to sequester. In the terrestrial biosphere, land management such as fertilisation and irrigation can increase inputs to the SOM pool. However, soil OC has also been deleteriously affected by humans. For example, Bellamy *et al.* (2005) reported a mean annual loss of 4.44 TgC in English and Welsh soils. These losses were attributed to such land use changes as conversion of grassland to farmland (both arable and pasture), burning of upland vegetation, afforestation on wet soils, and increased erosion and leaching due to drainage schemes and loss of vegetative cover. Deforestation and other land-use change (such as a shift from semi-natural to agricultural land cover) can result in a C loss from the biotic pool, photosynthetic CO₂ assimilation is further reduced by certain agricultural practices such as fallowing (Houghton, 1991).

In addition to natural mechanisms of CO₂ release, activities such as fossil fuel burning and cement production have caused the amount of CO₂ generated by humans to increase from approximately 280 ppm in pre-industrial times to 379 ppm in 2005 (IPCC, 2007). Rising concentrations of CO₂ and other respiration-derived greenhouse gases such as methane (CH₄) and nitrous oxides are of particular scientific interest because of their impact on climate change. Anthropogenic CO₂ is thought to be a primary cause of increasing average global temperatures, because of its ability to absorb and re-emit the

sun's infrared radiation, causing an elevated portion of solar energy to be retained in the atmosphere as heat rather than escaping into space (Burroughs, 2007).

The resultant change in temperature is the cause of rising sea levels due to melting polar ice, altered rainfall and increased storm events that induce drought in some regions and floods in others, and disrupted ecosystem function caused by selection against native species. These and other related issues have worldwide ecological ramifications, and also create serious problems for human food production and harvest (Borroughs, 2007). Rising global temperatures have resulted in positive feedback loops whereby the effects of climate change augment its causes. For example, warming of the earth's oceans has caused a decreased aquatic solubility of gases, including CO₂ and CH₄, effecting the release of these greenhouse gases into the atmosphere. In another instance, warming on land causes an increase in soil microbial respiration, with similar consequences of increased emissions (Prentice, 2001).

In order to mitigate these problems, efforts are being made to decrease CO₂ emissions and enact ecosystem management practices that will promote long-term C storage. For example, changes to agricultural practices could result in a decrease in the incidence of wildfires, C leaching and erosion, and improvements to soil structure could increase soil C sequestration (Lal, 2004). Minimising soil disturbances such as those caused by tilling or construction will promote the continued existence of soil aggregates and their relative inaccessibility to microbes. Permanent grassland has been found to sequester more C than agricultural land, and soil supporting perennial crops is favourable to annual crops. The introduction of earthworms to soil may also be of benefit as their casts encase SOM and aid in the conversion of light fraction soil to heavy fraction (Jones and Donnelly, 2004).

The ability of an ecosystem to store C in a recalcitrant form is currently of intense scientific interest (IPCC, 2007). Although biomass and SOM can be degraded very quickly, biomass-derived C can also be converted into forms that are much less degradable, and remain unchanged in one pool for hundreds or thousands of years (Prentice, 2001). Herein lies the importance of BC: rather than having been released during combustion as atmospheric CO₂, BC is C that has been converted into a stable, recalcitrant stock of soil OC (Goldberg, 1985). This is because of the conversion of C-containing molecules such as carbohydrates, fats, and proteins into stable, aromatised structures. However, much is yet unknown about BC cycling, distribution, and global production, and thus its role in the global C cycle and climate change remains unclear.

Urbanisation and urban soils

Urban ecosystems are an important, yet understudied, facet of ecology that are of increasing importance due to globally rising urbanisation (Grimm *et al.*, 2008), and an environmental impact that extends beyond the physical limits of urban areas. Cities create distinct anthropogenic conditions to which traditional ecological models may not apply (Collins *et al.*, 2000). The gaps in research are surprising, considering that urban development constitutes 14 % of British land use (DEFRA, 2004), and that urban residence is on the rise, with currently over 50 % of people worldwide living in cities (Grimm *et al.*, 2008).

The functioning of urban ecosystems is highly disrupted: they contain increased impervious surfaces, a large proportion of non-native species, reduced vegetation and water cover, and higher average temperatures than the surrounding area (Pavao-Zuckerman, 2008). This last item is termed the urban heat island effect, and is attributed to the low albedo and high heat capacity of paved surfaces and buildings, reduced area for evaporative

cooling by plants and water, greater surface area for heat absorption created by multi-storey buildings and a canyon-like, heat-trapping topography. BC deposition can also increase the light absorption of urban surfaces, thereby increasing their temperature, a phenomenon which will be explained further on. Urban areas contain high levels of atmospheric pollutants, and as a result often experience modified cloud cover and precipitation (Grimm *et al.*, 2008). However, anthropogenic changes to the environment are not always considered to be negative and certain ecosystem services can be enhanced by human activity. For example, non-native species of earthworm can increase soil C storage, and non-native plants may increase an ecosystem's productivity (Hansen and Defries, 2007).

Urban soils are heavily influenced by human activity and are often so altered as to have lost much of their ecosystem function altogether (DeKimpe and Morel, 2000). However, soils in cities provide many important ecosystem services, such as modulating water flow and filtering pollutants, providing a substrate for buildings, roads, gardens, and recreation grounds, storing C, and enabling domestic-scale agriculture (Rawlins *et al.*, 2008). The highly altered state of urban soils, when compared to non-urban soils, can be attributed to elevated temperatures, artificial mixing and landfilling, and also compaction and surface sealing that obstruct atmospheric and aboveground inputs (Lorenz and Kandeler, 2005). Most of these sealants (gravel, pavement, etc.) are efficient absorbers and conductors of heat, creating an additional warming influence on the underlying ground (Byrne *et al.*, 2008). Urban soils may also exhibit increased concentrations of heavy metals, altered hydrologic regimes, and elevated N and S inputs (Pavao-Zuckerman, 2008). A high level of disturbance due to building and road construction, and underground piping and cables systems, destroys aggregates and the microhabitats they create. Urban soils often contain large quantities of anthropogenic material such as sludge, ash, garbage,

sewage, bricks, oil, and concrete (Lorenz and Lal, 2009). Due to high levels of disturbance, the absence of roots and fungal hyphae impedes the formation of soil aggregates, and an increased level of soil erosion is observed (Groffman *et al.*, 2003). Soil particles are transported across the soil surface by natural processes such as wind and water movement, but also at an increased rate due to human activities like soil removal, tillage, vehicular or foot traffic, and irrigation.

BC is a particularly interesting anthropogenic amendment to degraded urban soils, and a challenge to understanding urban soil ecology and C storage. Although cities constitute only 3 % of land use worldwide, they produce 78 % of the world's C emissions (Brown, 2001), which indicates that BC emissions are likely to be concentrated in urban areas. BC has been found to constitute up to 70 % of OC in urban soils (Lorenz *et al.*, 2006). A study of BC in three industrial British cities – Coventry, Stoke-on-Trent, and Glasgow – found that the median BC soil concentrations were 0.46, 0.59, and 1.77 %, respectively (Rawlins *et al.*, 2008). The recalcitrance of BC signifies that it should be considered not just a pollutant, but also an opportunity for managing and improving soil C sequestration in cities. However, as yet the role of BC in increasing soil C content and the effects it has on soil function are not fully understood.

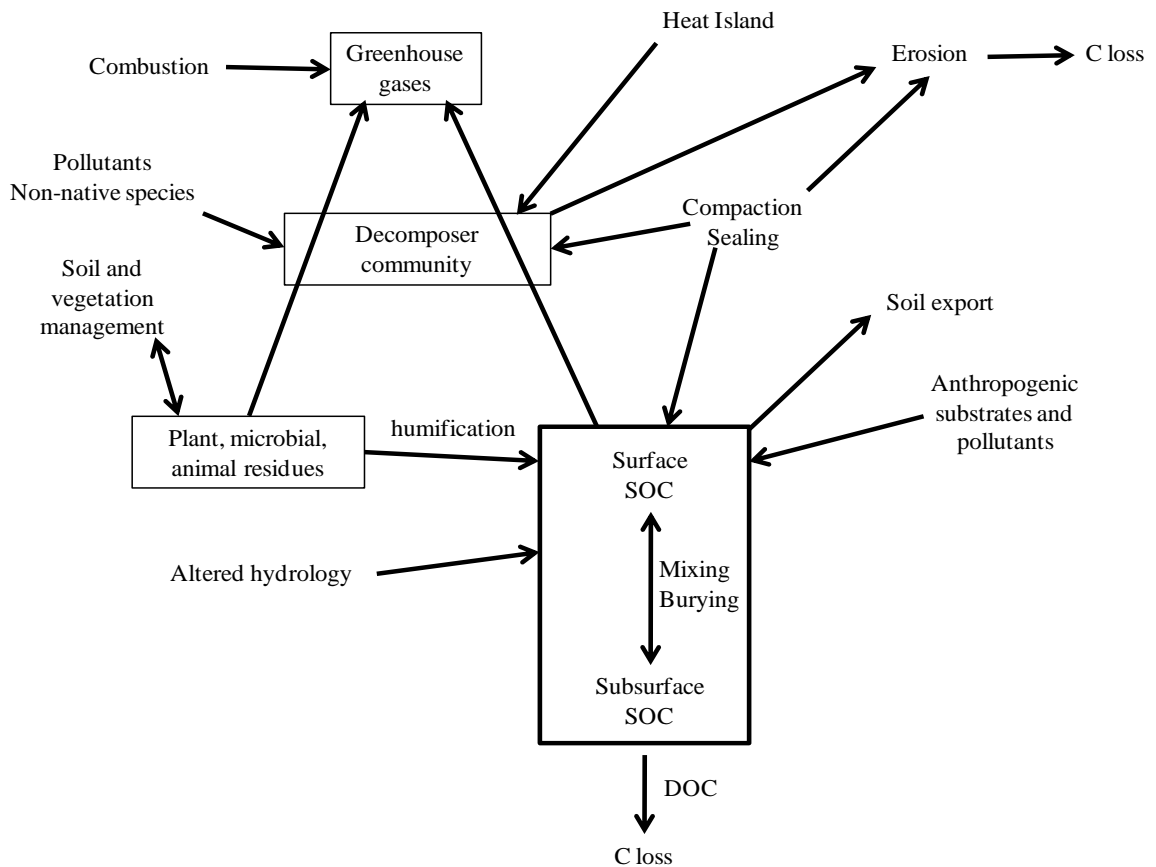


Figure 1.4. The effects of urbanisation (in bold) on soil organic carbon (SOC) dynamics, adapted from Lorenz and Lal (2009).

BC emissions

Anthropogenic BC emissions depend not only on the amount of fuel consumed during combustion, but also on the combustion technology. BC emission levels have declined in the UK since the 1960s due to cultural and technological advances (Novakov and Hansen, 2004). For example, the amount of BC emitted per unit fuel (the emission factor) during coal combustion in household stoves can be 10^2 or 10^3 times higher than the emission factor of coal burning in large, efficient power plants. In the UK and other industrialised countries, BC production in Britain over the last century has not only reduced in quantity but has also become much more a result of diesel fuel combustion and electric power generation rather than highly inefficient coal burning, which was historically used for

commercial, industrial, and domestic purposes. Air monitoring in New York City revealed that hourly average ambient BC levels along urban roads could be predicted from hourly average rate of diesel traffic (Patel *et al.*, 2009). At present, British BC production rates seem to have reached a steady level, but diesel fuel use is increasing. This may indicate that currently the reduction in coal burning is cancelling out the effect of higher diesel emissions, and that BC levels will soon begin to rise again. Despite the recent decline in BC emissions, even rural British BC concentrations in the atmosphere are within a range that is considered moderately to heavily polluted (Novakov and Hansen, 2004).

Global BC emissions levels and their temporal variations are not definite, as the magnitude of emissions is highly uncertain and often underestimated (Sato *et al.*, 2003; Novakov and Hansen, 2004). The trends found by Novakov and Hansen (2004) cannot be assumed to apply to much of the world, as technological progress and cultural practices vary regionally. Much of the developing world still use charcoal-burning stoves for heating and cooking, and coal-burning is a major energy source (Cao *et al.*, 2005). Ninety-five per cent of the net global population increase in the next fifty years is projected to occur in cities of developing countries (United Nations Population Division, 2006). Therefore, without significant technological and cultural changes, the global production of pollutants, including BC, is likely to continue to rise.

Airborne BC has various detrimental effects on human health. A primary component of the aromatic structure of soot is polycyclic aromatic hydrocarbons (PAHs), which are a type of persistent organic pollutant (POP) that are known carcinogens and mutagens (Masih and Taneja, 2006). Smaller BC particles are able to permeate into the alveolar region of the lungs, providing adsorption sites for other pollutants. Traffic-related

pollution has been linked to such respiratory diseases as bronchitis and asthma (Künzli *et al.*, 2000).

In an urban environment, ambient BC levels are a function of season, weather, and time of day. Time of day determines BC production by affecting levels traffic and domestic fuel use, and BC dispersal via temperature effects on the amount of vertical atmospheric mixing that occurs. Ambient BC concentrations have also been found to decrease as wind speeds increase (Sharma *et al.*, 2002). Rainfall decreased the residence time of BC in the atmosphere from an average of 7-10 days to 5 days in the city of Xi'an, China (Cao *et al.*, 2009). In the same study, winter BC concentrations were twice those observed in the summer. This is due to increased domestic heating by traditional coal-burning stoves, and a shallower surface boundary layer (the atmospheric layer closest to the earth's surface), which concentrated air pollutants.

BC in the air has a greater spatial heterogeneity than other fine particulate matter (PM_{2.5}): in New York, the difference between urban and suburban concentrations of BC was observed to be greater than the difference between urban/suburban PM_{2.5} (Patel *et al.*, 2009). Additionally, atmospheric BC concentrations in Xi'an were observed to be approximately 20-fold higher than on remote Réunion Island in the South Indian Ocean (Cao *et al.*, 2009). This heterogeneity will be reflected in BC terrestrial deposition, meaning that BC samples are indicative of their source not only in their chemical structure but also in their soil distribution, which could give an accurate idea of their point of origin. BC is deposited onto soil either immediately following combustion (if particle size is large enough) or after a period of airborne movement usually lasting no more than a few weeks. BC can also be created by the abrasion of tyres and brakes (Glaser *et al.*, 2005). Once contained within soils, it is susceptible to transport by surface runoff, and much BC

ultimately sinks into marine sediments (Kuhlbusch and Crutzen, 1995). In deltas, shelves, and slopes (the ocean floor regions experiencing the highest levels of sedimentation), BC is observed to constitute 3-10 % of sedimentary OC (Hedges and Keil, 1995).

BC and climate change

Aerosol BC has various effects on the environment due to its light-absorbing properties.

Many of these effects create positive feedback loops which further exacerbate their contribution to climate change (Ramanathan and Carmichael, 2008). Soot reduces atmospheric transparency, causing a decrease in agricultural productivity that was measured at approximately 10-20 % in China and India (Chameides *et al.*, 1999). Soot deposition onto plant leaves further reduces plant productivity, by scattering and absorbing light that would otherwise be available for use by the plant (Burgin *et al.*, 2001). Reducing plant productivity causes a decrease in the amount of CO₂ that is fixed in photosynthesis, causing higher atmospheric concentrations. The absorption of light by BC warms the air, reducing the relative humidity and liquid water content, further raising air temperature. The lower relative humidity also results in reduced cloud cover, meaning a higher transmittance of sunlight to the earth's surface (Jacobson, 2002).

While contained in the atmosphere, BC has a positive radiative forcing (RF) effect, and once deposited on snow and ice it reduces surface albedo (Warren, 1984). This contributes to melting which reveals the underlying soil or water, which have a much lower reflectivity (Jacobson, 2002). This phenomenon has a greater effect on global temperature than do CO₂ emissions (Hansen *et al.*, 2005). In fact, the deposition of soot on snow and ice is thought to be the cause of approximately 25 % of global warming in the past century (Hansen and Nazarenko, 2004). Air heating alters atmospheric stability and vertical

mixing, which affects hydrologic cycles to such an extent that BC has also been correlated with regional flooding and droughts in China (Menon *et al.*, 2002).

Although aerosol BC has a net positive RF, its effects are varied and can also cause atmospheric cooling, which can also be disruptive to environmental processes. For example, as BC reduces atmospheric transparency, it decreases the amount of sunlight that reaches and heats the earth's surface, a phenomenon called global dimming, which lessens the melting of snow and ice (Ramanathan and Carmichael, 2008). Also, high concentrations of airborne particulate matter reduce the mean droplet size of cloud particles, which can lead to increased cloud formation and thus causing climatic cooling and perturbations to hydrological cycling (Tyson and Gatebe, 2001).

BC in soil

Despite the many detrimental effects of BC on human health (Künzli *et al.*, 2000; Masih and Taneja, 2006) and the atmospheric environment, deposited BC can confer certain benefits to terrestrial ecosystems. This is because of changes that occur in soil structure, chemistry, and microbiology due to the presence of BC. One such advantage is the immobilisation of many soil pollutants. Free, high-energy binding sites on BC molecules provide a binding phase for POPs, decreasing their availability in soils and water (Dachs and Eisenreich, 2000). The affinity of BC for POPs reduces biotic pollutant uptake 10- to 100-fold (Koelmans *et al.*, 2006). This is particularly relevant in urban environments where domestic food production occurs, because soil pollutants will accumulate in crops and those who consume them.

The addition of bio-char (being charcoal-BC derived from plant biomass) to agricultural soils has been observed to increase soil fertility. This is in part caused by an increase in the nutrient content of soils which results from both the nutrients contained in

the char and the ability of the char to adsorb to nutrients and organic molecules, retaining them from leaching loss (Lehmann *et al.*, 2003). Increased nutrient availability due to biochar in soils has been found to enhance primary productivity, SOM stabilisation, and SOC storage (Lehmann *et al.*, 2003; Liang *et al.*, 2010). Furthermore, BC in the form of biochar provides microhabitats for soil microorganisms, its hydrophobicity and high surface area of its micropore facilitating microbe and OM adhesion. Pietikäinen *et al.* (2000) found a three-fold increase in bacterial cells per gram in soils with a layer of biochar as compared to soils with non-adsorptive pumice. Bio-char can also harbour extraradical fungal hyphae, allowing them to sporulate and increase arbuscular mycorrhizal colonisation of plant roots by 40-80 % (Nishio and Okano, 1991; Saito and Marumoto, 2002). However, if BC is present in high levels, the high C:N ratio may cause microbial N immobilisation, reducing productivity (Lehmann and Rondón, 2003).

In a study by Uvarov (2000), European brown forest soils containing biochar from charcoal kilns were observed to have a higher rate of respiration and decomposition than soils without a BC input. Microbial activity is a good indicator of soil quality, as a high rate of decomposition will result in increased nutrient cycling rates and productivity (Knoepp *et al.*, 2000). The rate of herbaceous seed germination and the density of seedlings were also higher on soils with added BC, offsetting some of the respiratory C release. It is unclear whether the heightened rates of respiration and productivity in the study system resulted in a net C loss or gain, but the land surrounding kiln sites that had been abandoned for more than a century were shown to have higher soil C values than the surrounding area. Furthermore, Zackrisson *et al.* (1996) found BC to effectively adsorb certain phenolic phytotoxins, and suggest that boreal charcoal deposits from forest fires act as important catalysts in forest regeneration.

Evidence of the benefits conferred to soil by BC is perhaps best observed in the soils of the Amazon rainforest, where farming was practiced sustainably for at least 2,500 years despite the naturally low soil fertility (Glaser *et al.*, 2001). The soils in this region are oxisols; the high precipitation and temperatures, combined with a low concentration of stabilising minerals produce and average SOM residence time of only four years. However, within this depleted soil are dispersed pockets, many hectares in size, of nutrient-rich, productive, dark earth called Terra Preta. This phenomenon is explained by the traditional farming and cooking practices that enriched the soil with recalcitrant bio-char, which boosts SOM levels and nutrient holding capacity. Once these enriched soils were formed, they appear to have become self-sustaining, as the higher biomass production of the land fed back into the soil as increased litter input, and the soils maintain their high fertility today, even centuries since being abandoned. In a short-term study by Rondón *et al.* (2005), BC addition to oxisols was also found to significantly decrease emissions of the greenhouse gases nitrous oxide (N₂O) and CH₄, due to its ability to adsorb to N- and C-containing molecules, thereby limiting their availability. However, these positive effects of BC probably depend on soil type and land management.

Because of its long residence time, BC in soil layers can useful evidence of natural and anthropogenic activity during the earth's history. BC can reveal information about past industrial activity, household and farming practices, and incidence of wildfire, to name a few. In fact, a study in Nanjing, China, found BC levels to vary according to historical land use (residential areas had on average ten times less BC than commercial or industrial zones), and based on cultural practices during different periods of human history. For instance, during more prosperous dynasties, soil BC levels rose as industrial activity increased (He and Zhang, 2009).

BC commonly co-occurs with another type of pollution: heavy metals, such as iron, lead and zinc can be released during combustion of fossil fuels (Huhn, 1995; Harrison and Jones, 1995). Heavy metals have various detrimental effects on soil ecosystems: they are toxic to terrestrial organisms, can reduce rates of decomposition and microbial metabolism, and thus alter biogeochemical cycles and food webs (Pavao-Zuckerman, 2008). The co-correlation of BC and heavy metal concentrations in soil is attributed to two causes: heavy metals are a residue concentrated by combustion, and can even be contained within BC molecules (Novakov and Hansen, 2004), and because of the sorption affinity of BC for heavy metals. The co-occurrence of BC and heavy metals in soils can also indicate past industrial and cultural practices; for example, high lead concentrations are a sign of coal-burning activity (He and Zhang, 2009).

BC management

Addition of BC to soil could simultaneously increase soil quality, as previously discussed, and increase the recalcitrant soil C pool, thus potentially mitigating climate change. The synthetic creation of bio-char is an alternative to biofuels for reducing atmospheric CO₂, but to date has been less popular. Creating bio-char by pyrolysis of plant biomass would capture the C in a recalcitrant form, and create a usable energy source, rather than simply offsetting emissions (Jacobson, 2002). The gaseous products of pyrolysis could be captured and used for heat, electricity, or biofuel production (Lehmann, 2007). The resultant bio-char could be used in soils as a fertiliser, or stored in a reservoir conducive to a long residence time, such as deep underground or in sea sediments. This strategy is more energy-efficient and arguably more fail-safe than the practice of pumping CO₂ into impermeable rock formations, such as is being attempted in the Sleipner Gas Field in the North Sea (Jacobson, 2002). The economic worth of this approach is that it can eliminate

costs associated with waste processing, it can create valuable byproducts such as syngas and bio-oils, and increase agricultural activity (Fowles, 2007).

Another strategy that exploits the recalcitrance of BC in order to mitigate climate change is the act of practicing slash-and-char, rather than slash-and-burn, agriculture. Instead of burning biomass from a cleared area, charring it in pits in a simple method similar to charcoal production will produce a soil conditioner that is a recalcitrant store of SOC, while releasing less CO₂ in the process (Lehmann and Rondón, 2003).

Control of BC emissions presents a promising opportunity for combating climate change, due to the short residence time of BC in the atmosphere. If all BC emissions were suddenly to cease, the vast majority of BC would settle into the soil within a matter of weeks. According to a model by Jacobson (2002), the cessation of fossil fuel derived BC production could eliminate 8-18 % of total global warming within 3 to 5 years. In comparison, a one-third reduction in CO₂ emissions would take 50-200 years to have the same effect. As BC emissions are essentially technology-dependent, and not an unavoidable product of combustion, research in this field is crucial.

BC cycling

Although BC has been detected in 13,000 year-old ice cores (Chylek *et al.*, 1992), and has a high resistance to many different chemical oxidants (Skjemstad *et al.*, 1996), a significant portion of the BC being emitted cannot be accounted for in environmental deposits, and questions exist about whether a proportion of BC is in fact being degraded. The reasoning is this: the annual BC production rate is estimated to be 50-270 Mt yr⁻¹ (Kuhlbusch, 1995). 160 Mt OC yr⁻¹ is deposited in the oceans and, as previously mentioned, BC comprises 3-10 % of sedimentary OC (Hedges and Keil, 1995). Therefore, approximately 4.8-16 Mt BC yr⁻¹ is transported to the oceans. This figure is appreciably less than the total BC

production rate, and although a portion of the difference can be accounted for by storage in soils, the discrepancy has led some scientists to question whether BC is being degraded (Masiello, 2004). Not only this, but recent work by Dickens *et al.* (2004) indicates that a significant proportion of the BC in marine sediments is not combustion-derived, but rather a product of graphitic rock erosion. An explanation for part of the missing BC is dissolved organic carbon (DOC) in fresh and marine water; Mannino and Harvey (2004) showed BC to constitute 5-12 % of DOC in coastal Atlantic waters. However, it is likely that some BC is being degraded and lost as CO₂, and the degree to which it is degraded depends on the conditions of its formation and extent of charring (Masiello, 2004).

A study by Baldock and Smernik (2002) indicated that thermal treatment of red pine wood significantly decreased the ability of microbes to mineralise C from the samples, although microbial activity was still evident to a small extent even in the most extensively charred wood. Certain species of fungi have the ability to degrade lignite, which is a low-rank coal with some characteristics of peat. These fungi do so by means of extracellular enzymes that depolymerise the coal into fulvic acids, which the fungi further decompose to obtain energy (Hofrichter *et al.*, 1999). While coal is not pyrogenic and therefore not considered BC, it is a type of highly aromatised OC, and evidence of its fungal degradation implies that certain forms of BC that were not extensively aromatised during combustion (e.g. chars) could undergo a similar degradation. Goldberg (1985) identified photochemical breakdown as a method of BC degradation, and charred materials have also been observed to decompose in acidic, anoxic lacustrine environments (Winkler, 1985). Even soot can be chemically oxidised in a matter of minutes if exposed to high concentrations of atmospheric oxidants such as ozone. Oxidation solubilises soot, thus allowing it to enter DOC pools (Seinfeld and Pandis, 1998). Therefore, Gélinas *et al.* (2001) suggest that the longevity of

BC is partially determined by its formation conditions, and how long it is exposed to oxygen; rapid burial and integration into deeper anoxic zones will favour a long residence time in soil (Forbes *et al.*, 2006). Despite the various methods for BC degradation, it has been found in many soil depth samples with ^{14}C ages of over 1000 years (Glaser *et al.*, 2001), and is thought to have a similar residence time in ocean sediments (Masiello and Druffel, 1998).

BC quantification

As yet there is no single accepted method for detecting and quantifying BC. Difficulties arise in developing a detection procedure because of the vast array of BC structures that exist, caused by varying parent material and formation conditions. There are four principal difficulties in creating a method to quantify BC: (i) creation of BC during analysis by charring of OC, (ii) loss of BC during analysis, (iii) detection of non-charred C as BC, (iv) failure to detect entire spectrum of BC structures (Masiello, 2004). Therefore a range of different methods exists, each with different advantages and disadvantages. The basic approaches to BC quantification are optical, chemical, and thermal detection, the former of which is used primarily for atmospheric samples. Chemical and thermal techniques typically utilise the highly resistant nature of BC, and involve the removal of C that is not combustion-derived, and subsequent detection of the remaining C content of the sample. Other detection options include spectroscopic identification of IR bands or NMR regions that correlate to specific combustion products, and the use of molecular markers to measure the concentration of BC-related compounds.

In a study by Schmidt *et al.* (2001) that compared six of the most frequently employed methods, the amount of BC detected in a single sample varied by up to a factor of 571. A more extensive study by Hammes *et al.* (2007) compared 12 samples (including

confounding non-BC materials, laboratory manufactured BC standards, and environmental samples) which were each analysed using 7 different methods. As expected, it was found that each method detected a different segment of the BC spectrum, and some were more susceptible to pitfalls such as false positives and loss of BC than others. The more promising methods for BC detection in soils were chemothermal oxidation (CTO), thermogravimetric analysis coupled with differential scanning calorimetry (TG-DSC), and chemical oxidation with NaClO.

The CTO-375 method involves a chemical pretreatment involving a series of acid and alkali washes to remove IC, some OC, and silicates, which reduces the amount of material that could be charred during thermal oxidation (Kuhlbusch, 1995). The thermal oxidation is performed at 375°C so as to remove the maximum amount of labile C while causing minimal charring, and retaining all BC in the sample. Subsequent to this treatment, the sample is analysed for total C content, and all remaining C is presumed to be BC. CTO-375 rarely detects interfering non-BC particles, with the exception of melanoidin, an organic polymer, which was detected by CTO-375 with a BC/OC ratio of 2.4 %. The weakness in this method is that some of the char-BC is in fact lost during the oxidation process, so this method is best for detecting the most refractory BC, such as soot produced by diesel fuel combustion. BC could also be lost during the centrifugation and decantation steps involved with the chemical pretreatment (Kuhlbusch, 1995).

TG-DSC involves the gradual heating of samples while measuring the loss of mass as a function of temperature, and inferring the type and amount of chemical released at certain temperature intervals (labile C being given off at lower temperatures while recalcitrant BC compounds are released over a higher temperature interval). This method has the disadvantage of overestimating BC by detecting such refractory non-BC materials

as coal, and also quantifying as BC the release of impurities such as structural water in clay. Chemical pretreatment to remove some of the non-organic matter could ameliorate some of these issues (Hammes *et al.*, 2007; De la Rosa *et al.*, 2008).

Alternately, the NaClO oxidation technique removes interfering non-BC compounds such as lignin and other aromatic structures, and is followed by ^{13}C NMR spectroscopy to determine the proportion of aromatic C, the results of which are applied to an elemental total C analysis to compute BC levels. However, NMR spectroscopy is expensive, which makes this procedure impractical for large quantities of samples. UV photooxidation is another method of BC quantification tested in the Hammes *et al.* (2007) ring trial, which resulted in a gentler oxidation process that appeared to oxidise a smaller proportion of BC than the previous methods, but required NMR analysis and a purpose-built photooxidation apparatus that was costly to build and use.

Further research is required to determine an accepted standard protocol that would allow intercomparison of experimental results. The different methods each have their own advantages and disadvantages depending on the type of BC analysed and the environmental matrices in which they occur, thus there is currently no widely-accepted method for BC quantification (Hammes *et al.*, 2007). Rawlins *et al.* (2008) suggest two simple, inexpensive methods as proxies for estimating BC. The first method involves HCl treatment to remove IC, and a thermal treatment at 450°C to remove labile OC and some BC, followed by elemental analysis for remaining TC. The amount of TC remaining was found to have a strong linear correlation with the amount of BC detected by CTO-375, with an r^2 of 0.97. Therefore, this technique is an efficient means of obtaining BC values similar to those produced by the CTO-375 method. The second proposed proxy involves a simple thermal treatment at 450°C, with the assumption that a consistent proportion of BC is lost

at this temperature. The linear correlation between these results and the results of CTO-375 was lower, with an r^2 of 0.81, likely reflecting the absence of a chemical pretreatment that would reduce the amount of labile OC that becomes charred during analysis. However, the efficacy of these proxies depends on whether the CTO-375 method is truly an accurate means of quantifying BC; due to their dependence on thermal techniques these proxies may be restricted to detecting only highly recalcitrant BC forms.

Research aims

The research presented in this thesis is part of a large multidisciplinary project entitled '*Measurement, mapping, modelling and management: An evidence-based methodology for understanding and shrinking the urban carbon footprint.*' This study, the 4M Project, is a collaboration between five universities, and aims to further our understanding of all aspects of the urban C footprint, including domestic, commercial, industrial and transport emissions, and biological C sequestration, using Leicester as a model city. Researchers at the University of Sheffield are currently investigating urban C storage by quantifying C in plant and soil samples taken from a variety of land use types across the city. The focus of the soil analysis has been on total OC and IC, but has not thus far considered the relative proportions of labile C and BC that constitute the OC pool. This distinction is important for understanding urban C cycling, and the management practices that increase soil C sequestration.

The aims of the work presented here are to quantify the distribution of BC in urban soils on two different scales: across different land use types and in relation to point sources of BC pollution. A study in Nanjing by He and Zhang (2007), of which only the abstract is available in English, reports findings of substantial differences in soil BC concentration based on land use type. Soil PAH concentrations, which are known to be linked to BC

levels due to the sorption affinity of BC, have also been found to differ considerably by land use type (Masih and Taneja, 2006). The effect of roads and trees on soil BC distribution was chosen for this study in order to understand small-scale variances in soil BC concentrations. Roads are a known point source of BC pollution, being a thoroughfare for diesel-burning vehicles, which produce several orders of magnitude more particulate matter than those run on petrol (Miguel *et al.*, 1998; Maricq *et al.*, 1999). The spatial heterogeneity of BC in the atmosphere would indicate that soil BC may also be found to have higher concentrations near BC sources such as roadways. The effect of trees was selected for this study because of the known ability of tree foliage to provide a barrier against dispersal of particulate pollutants (Maher *et al.*, 2008). An effect of roadside trees on soil BC concentrations may indicate whether vegetation can provide a barrier for the dispersal of this pollutant, thus shortening its residence time in the atmosphere and reducing its detrimental effect on the environment and human health.

The work presented in this thesis will act as a means of refining estimates of city-wide BC levels, and understanding the variation in soil BC distribution, thereby improving our understanding of urban C pools and ecosystems. Urban soils are often omitted from consideration in large-scale analyses of C cycling and soil properties (Jobágyi and Jackson, 2000; Janssens *et al.*, 2003; Ostle *et al.*, 2009). However, recent research by the 4M Project indicates that previous approximations of urban SOC stores have vastly underestimated their capacity to act as a C stock (Bradley *et al.*, 2005). Data from an extensive, city-wide study of soil BC stocks could help to change preconceptions of the value and function of urban soils.

The first step in this process will be to select a BC quantification technique. Testing of the CTO-375 method and the more consistent of the two proxy methods suggested by

Rawlins *et al.* (2008) will be performed using known amounts of BC standards. If necessary, procedural amendments will be made to improve BC quantification of the more accurate technique. The TG-DSC method will also be used for a small number of samples to corroborate the results obtained by the chosen technique. Next, a sub-set of soil samples from the Leicester soil C survey will be selected in order to investigate BC stocks in urban soil, and its distribution by land use type. Soil samples will also be taken at increasing distance from main roads and large trees in order to determine whether the presence of a point source or a vegetative barrier has an effect on small-scale BC distribution in soils.

The ability to confidently detect BC in soils using a method with known BC recovery will allow more accurate estimations of soil BC stocks in this and future studies. Estimation of soil BC stocks is important for understanding urban biogeochemical cycling and, moreover, the magnitude of this anthropogenic C sink. These results will ultimately enrich our knowledge of the urban C budget and may be used to refine the C footprint estimations of the 4M Project.

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Chapter 2: The development of a procedure for quantifying BC in soils

Introduction

There are many proposed methods for quantifying BC within the various environmental matrices in which it occurs. The three basic approaches to BC detection are optical, chemical, and thermal. Optical detection utilises the degree of blackness of BC, for example by determining the reflectance or transmittance of a sample (e.g. Chow *et al.* 1993, Huang *et al.*, 2006), an approach which is most effective for detecting aerosol BC.

Chemical detection can involve treatment to remove SOC (here defined as OC that has not undergone combustion) prior to elemental analysis (Lim and Cachier, 1996; Simpson and Hatcher, 2004 a & b), or to identify chemical markers that indicate the presence of BC (Glaser, 1998). Thermal methods are used to remove SOC (Kuhlbusch, 1995; Gustaffson, 1997), or as a means of releasing and quantifying C of varying stabilities (de la Rosa *et al.*, 2008). The latter two approaches are most often applied to the quantification of BC in soils and sediments, sometimes in conjunction with one another.

Quantification of BC is difficult because it does not have a single structure, rather it constitutes a range of organic, C-containing molecules that have been partially combusted. Materials that can be pyrolysed to produce BC include biomass and fossil fuels. The origin of the parent material, in addition to the conditions prevalent at the time of formation (e.g. oxygen availability, combustion temperature and whether the OC undergoes a gaseous intermediate phase), result in a range of BC compounds with various physical and chemical properties (Mackay and Roberts, 1982; Chughtai *et al.*, 2002). As a consequence of the diversity of these BC compounds, reliable quantification is difficult.

Within soils, it is necessary to distinguish between BC and SOC that has not been combustion-derived. One common approach to achieving this is differentiating between C of low and high resistance to chemical or thermal oxidation, under the assumption that highly resistant OC is BC. Two such quantification methods have been developed by Kuhlbusch (1995) and Gustaffson *et al.* (1997). These methods both involve a chemical oxidation pre-treatment to remove some SOC and IC (Kuhlbusch, 1995), or solely IC (Gustaffson *et al.*, 1997), followed by thermal treatment to remove any remaining SOC. These methods are therefore termed chemothermal oxidation (CTO). However, the structural heterogeneity of BC leads to different levels of resistance to oxidation, and it is therefore difficult to isolate based on its recalcitrance alone.

Soot forms at high temperatures and therefore undergoes a gaseous condensation phase during which it forms very stable aromatic C rings (Ogren and Charlson, 1983). These particles form aggregates in hundreds (Kölyü *et al.*, 1995), thereby creating an additional physical barrier, reducing oxygen availability to the particles in the interior of the aggregation. For these reasons soot is stable at temperatures exceeding 400 °C (Nguyen *et al.*, 2004), and laboratory-produced n-hexane soot has been found to totally oxidise only when temperatures exceed 630 °C (Leifeld, 2007). However, BC that has been formed without undergoing a gaseous phase, i.e. thermally altered residues that remained in solid form during pyrolysis, oxidise at considerably lower temperatures (Leifeld, 2007). These residues are known as chars which, unlike soot, retain certain characteristics of their previous uncombusted form; thus, the thermal stability of chars is in part determined by their parent material (Elmqvist *et al.*, 2006; Leifeld, 2007).

To an extent, the thermal stabilities of combusted and non-combusted material are distinct from one another. A recent laboratory trial by Leifeld (2007) revealed that the temperature at which 50% weight loss was achieved during thermal oxidation (T_{50}) varied significantly between different types of vegetation and char. Fresh grass reaches T_{50} at temperature of 366 °C, whereas rice straw char attained T_{50} at 398 °C. Chestnut wood attains T_{50} at 435°C, while chestnut wood char did not undergo 50% weight loss until 469 °C. However, certain aromatic, yet not combustion-derived, materials such as bituminous coal can be very stable, with a T_{50} of 512 °C. Therefore, there is no clear threshold temperature at which all OM is lost while all BC remains, and this complicates attempts to quantify BC using a thermal treatment. The issue of thermal oxidation as a means of BC quantification is further confounded by the fact that SOC may become charred during a thermal step, leading to a misrepresentation of the amount of BC originally in the sample (Kuhlbusch, 1995).

The difficulties of false positives and true negatives are equally problematic to the development of other techniques. There is, as yet, no generally accepted method known to detect the entire spectrum of BC without also mistakenly quantifying certain types of non-black C. In a recent study by Hammes *et al.* (2007), seven methods of BC quantification were tested for their (i) percent recovery of pure, laboratory-produced BC samples (soot, wood char and grass char), (ii) percent recovery of unknown amounts of BC in soil, sediment, and atmospheric samples, and (iii) their detection of non-BC materials as BC. The CTO method described by Kuhlbusch (1995) was analysed alongside various other optical, chemical, and thermal techniques. The advantages were that CTO detected virtually none of the four potentially interfering materials (PIMs: melanoidin, shale, lignite

coal and bituminous coal). It also had a relatively high level of reproducibility, and the chemical pre-treatment step removes much of the IC and SOC contained in the sample. If elemental analysis facilities are available, the procedure is quite simple and cost-effective. CTO has also been commonly used in previous BC studies (e.g. Gustafsson *et al.*, 1997; Reddy *et al.*, 2002; Elmquist *et al.*, 2004; Lorenz *et al.*, 2006; Hammes *et al.*, 2007; Rawlins *et al.*, 2008), thereby producing comparable results. However, Hammes *et al.* (2007) found that CTO detected only approximately 50% of the available soot, and almost none of the wood char or grass char. Therefore these data suggest that this method may significantly underestimate BC in real-world situations, and CTO was concluded to be a useful method for detecting only the most thermally-stable BC.

Thermogravimetry and differential scanning calorimetry analysis (TG-DSC) was another method tested by Hammes *et al.* (2007), and this procedure revealed more accurate recovery of BC, but with the disadvantage of also detecting high amounts of PIMs as BC. TG-DSC measures the weight loss of a substance over a gradually-increasing temperature gradient. Peaks of weight loss at different temperature intervals indicate the release of various components of the sample, with the most easily oxidised molecules lost at lowest temperatures, and BC assumed to be oxidised within the temperature interval of 490-650 °C. This method had very high recovery (>90%) for soot and wood char, and 60% recovery for grass char (Hammes *et al.*, 2007). However, it also identified a large proportion of shale, lignite coal and bituminous coal as BC, and the method itself is highly time-consuming and requires specialised equipment.

For the purposes of this study, CTO was selected as a potential method for accurate and efficient BC detection in a large number of urban soil samples. CTO was chosen, despite its drawbacks, because of (i) its use in many previous studies of BC (ii) its

suitability for detecting soot, which is likely to be a prevalent form of BC in urban British soils; (iii) its tendency towards more conservative estimates of BC when compared to other quantification methods; (iv) the potential to modify the procedure to optimise BC recovery; and (v) the availability of the necessary equipment and the low cost of the procedure. Due to the complications involved in thermal apportionment of OC, a new variation of this method which omitted the thermal oxidation step was also tested. This new method shall be referred to as chemooxidation (CO).

A recent study by Rawlins *et al.* (2008) suggested an alternate, proxy method to BC quantification. This study proposed that the C remaining after this simplified treatment may represent a consistent proportion of the total BC in the soil. This is based on findings that the amount of BC quantified by the proxy method is very strongly correlated with the quantity of BC detected by CTO. If proven accurate, this method would be an extremely time- and cost-efficient means of quantifying BC. Therefore, the proxy method was also tested for its accuracy and reproducibility in order to determine if it is a viable substitute for some of the more complex and costly methods.

The primary goal of this study was therefore to test the accuracy of the proxy, CO, and CTO methods in detecting known concentrations of pure BC added to urban soils with high and low OC contents. This was accomplished by adding known amounts of laboratory-produced charcoal to two different soil samples, and by testing the CO method on various forms of pure BC and PIM.

Methods

Soil sampling

Soil samples were taken using an auger (Eijkelkamp, ring kit C) from under two contrasted vegetation types and at two different depths in a large greenspace area in the city of Leicester, in the East Midlands, UK. Sample D20 was taken from 70-90 cm depth, under herbaceous vegetation in a golf course. Sample D21 was taken from surface soil (0-20 cm) in a wooded area of the same golf course. These sampling locations were chosen to give the greatest disparity in soil characteristics, particularly in SOC concentrations, to determine whether soil type affects the accuracy of the method, and because they were relatively far from point sources of BC (e.g. roads and industrial premises).

Soil samples were dried in an oven ($105\text{ }^{\circ}\text{C} \pm 5$) for 24 hours, then ground and homogenised using a ball mill and sieved to remove any particles larger than 1 mm (typically pebbles and anthropogenic debris). After homogenising, soil samples were again dried at $105\text{ }^{\circ}\text{C} \pm 5$ for 24 hours and placed in an air-tight container for storage.

Proxy Method

Reagent-grade charcoal (Fisher Scientific, formerly Fisons Plc., Loughborough, UK) was chosen for this method test because it has intermediate thermal stability, being more stable than vegetative chars, but less so than soot (Leifeld, 2007). Charcoal was added to soils D20 and D21 at three different concentrations: 0.40 %, 2.0 %, and 16 % of soil dry mass. CN analysis (Vario EL Cube, Elementar, Hanau, Germany) found charcoal to contain $70.01\% \pm 0.13\text{ C}$ by mass; thus the BC concentration in these soil samples was 0.28%, 1.4%, and 11%, respectively. For each soil type and charcoal concentration, four replicate samples were created.

The soils were subsampled for CN analysis before treatment, and then incubated with 7.5 ml 5.7 M HCl for one hour. To remove the supernatant the soil samples were centrifuged at 3000 rpm for 15 minutes. Subsequently, samples were dried at 105 ± 5 °C for 24 hours, then pulverised and homogenised in a ball mill, and subsampled for CN analysis. The soil samples were next placed in ceramic crucibles in a muffle furnace for 5 hours at 340 °C, and once again ground, homogenised and subsampled for CN analysis.

CTO and CO Methods

Four types of laboratory-produced BC were used for this trial: n-hexane soot, chestnut wood char, risotto rice char, and charcoal (the latter being the same as used in the proxy method). Details of soot and char production conditions and source can be found in Hammes *et al.* (2007). The four BC standards were each added to dried, homogenised D20 and D21 soils at concentrations of 0.5%, 1%, 2% and 5% of the total mass. Replicate blanks (soil without BC added) were also CT oxidised.

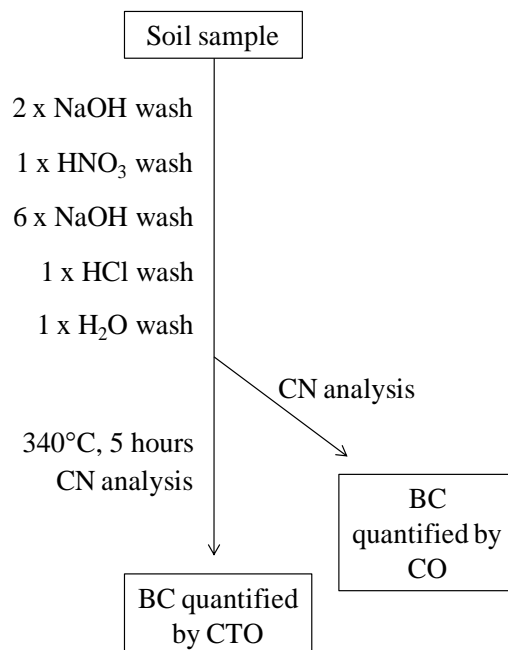


Figure 2.1. A depiction of soil sample analysis by the CO and CTO methods.

The CTO procedure (Kuhlbusch, 1995) involves a series of chemical washes, followed by thermal oxidation at 340 °C. The chemical washes are as follows: 2 x 1M NaOH, 1 x 70 mass % HNO₃, 6 x 1M NaOH, 1 x 1 mass % HCl, 1 x 18 MΩ H₂O. Each step involves the addition of 12.5 ml of solvent per 1 g of sample, then sonication in a heated ultrasonic bath (Ultrawave Q Series, Ultrawave Ltd., Cardiff, UK) for 15 minutes at 40 °C, followed by centrifugation for 15 minutes at 3000 rpm, and finally discarding of the supernatant. The premise behind these washes is that the NaOH removes the large portion of SOC that is alkali-soluble, thereby reducing the possibility of charring SOC during the subsequent thermal step. The concentrated HNO₃ removes all IC (carbonates) which are released in the form of CO₂. The 1 % HCl wash ensures that the sample is acidic at the end of the treatment, so no new carbonates can form. The second acid wash is also included so that the pH of the sample changes a second time, avoiding the isoelectric points of organic compounds such as amino acids, proteins, and nucleic acids, which results in maximum dissolution of OC (Kuhlbusch, 1995). After this series of washes, the soil sample will only contain OC that is alkali-insoluble and BC.

Although Kuhlbusch (1995) and Rawlins et al (2008) suggest two ultra-high purity water washes at the end of the procedure, it was observed in preliminary trials of this study that the supernatant of the second water wash typically turned grey or black. Kuhlbusch gives no explanation as to why these water washes were included, and it is to be assumed that their purpose was to dilute any remaining HCl before the samples were put in an oven under pure oxygen flow. However, in this study the muffle furnace (containing atmospheric air rather than oxygen, as implemented by Rawlins) was not in danger of suffering damage from HCl vapour. Therefore, to avoid the loss of any suspended or H₂O-

soluble BC, which has been shown to degrade into a water-soluble state in anoxic, acidic conditions (Winkler, 1985), the second water wash was eliminated.

After the washing sequence was complete, ~200mg subsamples were taken from each soil sample and placed in aluminium trays for oven-drying overnight (105 ± 5 °C). Subsamples were then ground using a pestle and mortar, homogenised, and analysed for TC. These subsamples represent the soil / BC mixture that had been treated with the CO procedure, and the C values produced by the CN analyser represent the quantity of BC detected by CO.

The thermal oxidation step as described by Kuhlbusch involves placing the samples in an oven at 340 °C for two hours, under a flow of pure oxygen. However, a revision of this procedure by Rawlins *et al.* (2008) suggested that the thermal treatment be conducted at 340 °C and in air, as oxygen is still in excess under these conditions. After thermal oxidation, the samples were ground and homogenised, then two replicate subsamples taken from each for elemental analysis. The TC concentration of these treated subsamples is operationally defined by CTO as the BC content of the soil.

Potentially Interfering Materials and Pure BC Standards

It is necessary to determine whether a BC quantification method distinguishes BC from similar substances that have not undergone combustion. These substances are termed potentially interfering materials (PIMs) (Hammes *et al.*, 2007), and for the sake of intercomparison, the PIMs used here were sourced from the same providers as detailed in Hammes *et al.* (2007); melanoidin which is OM (similar to humified SOC) resistant to chemical degradation, having undergone heating but no combustion (Benzing-Purdie and Ripmeester, 1983; obtained from the Geography Department at the University of Zurich);

green river shale: containing kerogen, which is recalcitrant OC with a low degree of aromatisation (U.S. Geological Survey, Denver, CO, USA); and two types of coal. Lignite coal is a soft, immature coal, and bituminous coal is a mature coal that has been transformed by heat and pressure (Argonne National Laboratories, Argonne, IL, USA).

Each of the four PIMs were subsampled and CN analysed, then three 0.5 g replicates were analysed using the CO method (due to the amount of each PIM available, a reduced sample mass was necessary). The volume of solvent added during each wash was reduced to 6.25 ml, in proportion to the reduction in substrate. The weight of each sample was recorded prior to, and after, CO. The chemooxidised subsamples were prepared for elemental analysis (dried at 105 ± 5 °C overnight, ground using a pestle and mortar, and homogenised). Each chemooxidised sample was subsampled in duplicate for elemental analysis, to determine if any C remained. The remainder of the chemooxidised sample was thermally treated per the CTO method, and elementally analysed in duplicate to determine which method was most effective in rejecting PIMs as BC.

Five pure BC standards were also tested for detection by CO. Laboratory-produced wood and grass char and n-hexane soot were selected for the purpose of comparison to other methods tested by Hammes *et al.* (2007), and obtained from the same sources detailed therein. To include a larger range of BC materials, laboratory-produced charcoal (see Proxy Method section of methods) and vehicular diesel soot were also analysed. Diesel soot was obtained from vehicular diesel particulate filters (Emission Control Ltd., London, UK), and therefore its purity and homogeneity could not be established. However, this substance was included in the trial nonetheless because diesel soot is the most prevalent type of BC currently emitted in the UK (Novakov and Hansen, 2004), and therefore highly relevant to this study. These samples were analysed according to the same procedure that

was applied to the PIMs. Percent recovery of pure BC and PIMs accounted for both the relative C concentration before and after CO, and the initial and final mass of each sample.

Six soil samples which were analysed using the CO method were also subsampled for analysis using the TG-DSC method (according to the procedure detailed by Lopez-Capel *et al.*, 2005), in order to compare the relative recovery of both. This was done because of the high recovery of BC by the TG-DSC method (Hammes, *et al.*, 2007), in order to determine whether the CO method is a viable alternative to this relatively accurate method of BC detection.

Results

Proxy Method

The proxy method, though found to remove IC effectively, was not found to remove consistent proportions of OC, nor to leave a consistent proportion of BC unoxidised (Fig. 2.2). The mean percent recovery of BC using the proxy method was $129.3 \% \pm 60.3$. Individual BC concentrations ranged from 37.1 to 418.1% recovery. BC detection varied depending on how much BC the soil sample contained; on average, BC quantification was overestimated at 0.4 % charcoal (281.5 % recovery), relatively accurate at 2.0 % charcoal (73.2 % recovery), and underestimated at 16.0 % charcoal (33.1% recovery).

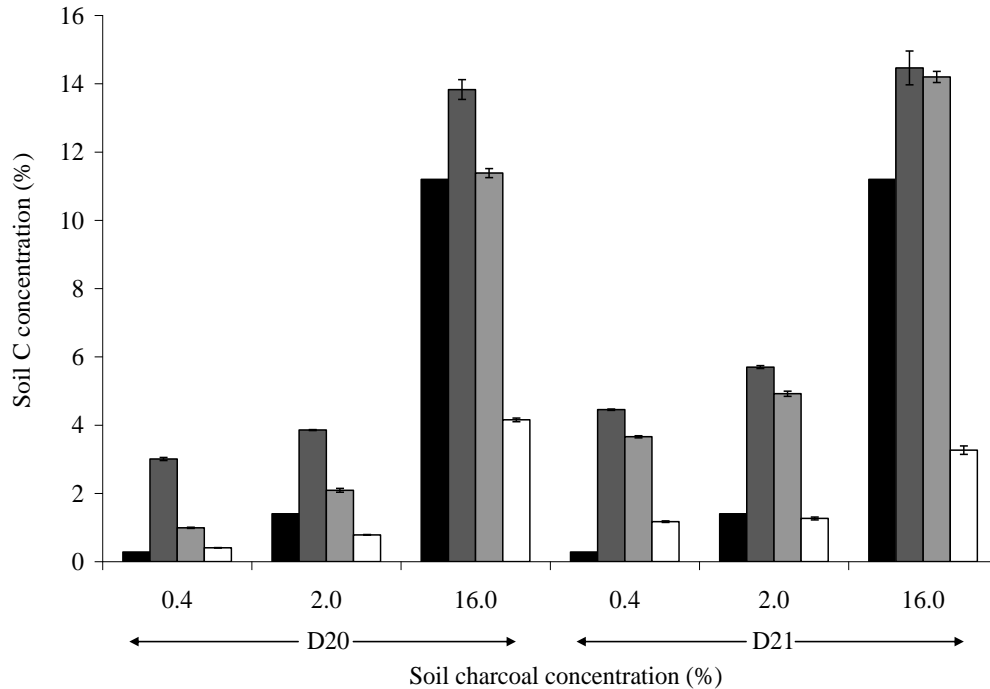


Figure 2.2. The C content of soils D20 (soil taken from 1m depth under herbaceous vegetation) and D21 (a surface soil sampled from underneath woody vegetation) at each stage of the proxy method trial. Black bars, the actual amount of BC contained in the charcoal added to the soil; dark grey bars, TC of each soil sample (including SOC and added BC); light grey bars, the amount of C remaining after the HCl wash; white bars, the amount of C remaining after HCl wash and thermal treatment at 320 °C (error bars represent 1 standard error).

CTO and CO Methods

The efficacy of CO and CTO to accurately quantify BC in soils can be seen in Fig. 2.3 (a-d). The CTO method was found consistently to underestimate the amount of BC actually present. This was particularly true for the grass and wood chars, for which CTO detected $22.1\% \pm 6.4$ and $21.6\% \pm 4.4$ of the BC originally added, respectively. Mean recovery was slightly higher for charcoal, at $33.2\% \pm 5.4$ of the actual BC detected, and highest for soot at $59.9\% \pm 4.1$. The mean BC recovery of the CTO method was $34.2\% \pm 2.9$.

The CO method had much higher recovery, and seemed to overestimate the amount of BC in the sample, with a mean observed to expected BC concentration ratio of $140.8 \% \pm 7.2$. Grass and wood char exhibited lowest recovery, and charcoal the highest. Much of the overestimation of the CO method occurred in soils to which 0.5 % BC had been added. When the recovery values of these samples were disregarded, the mean per cent recovery of soils to which 1 – 5 % BC had been added was $115.3 \% \pm 4.2$. In contrast, CTO recovery increased to $40.6 \% \pm 7.6$ when the lowest BC samples were omitted. The CO method was found to have high reproducibility. The coefficients of variation of two soil samples, one taken from woodland and one from grassland, each subsampled and chemooxidised 5 times, were 0.0682 and 0.0700, respectively.

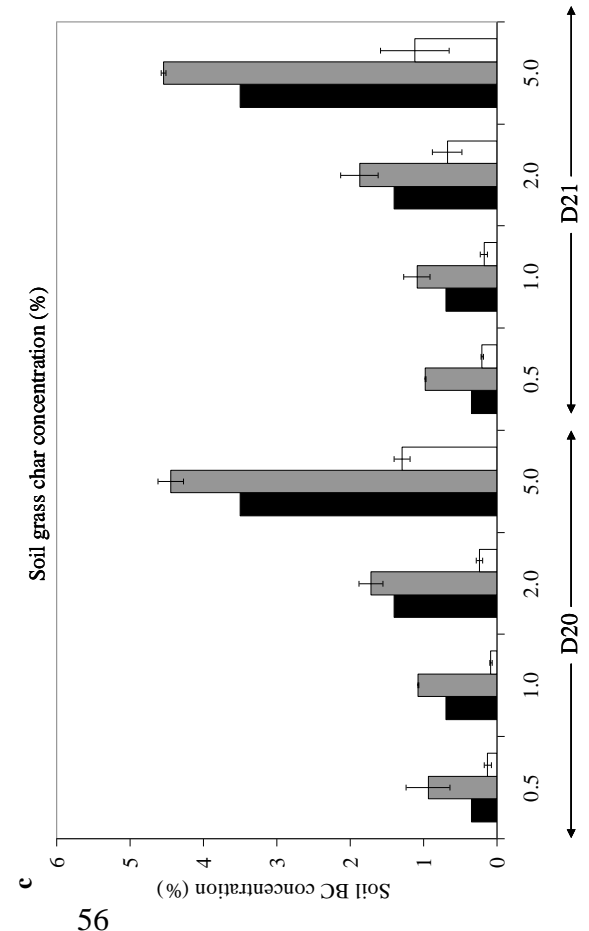
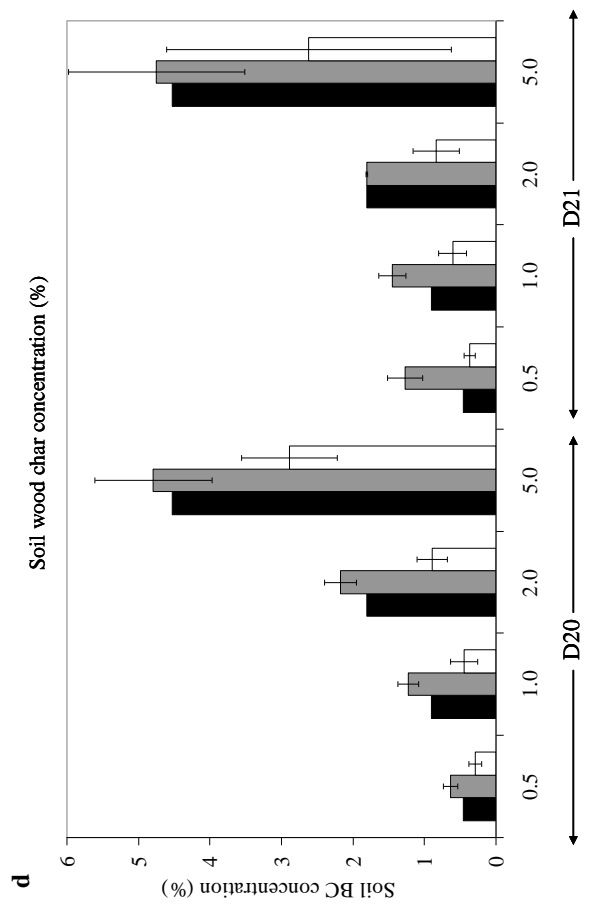
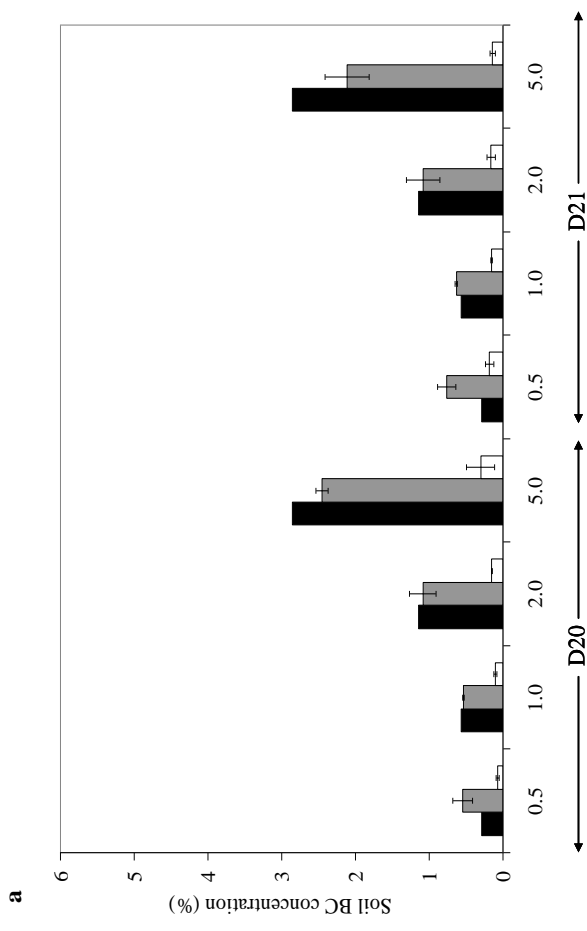
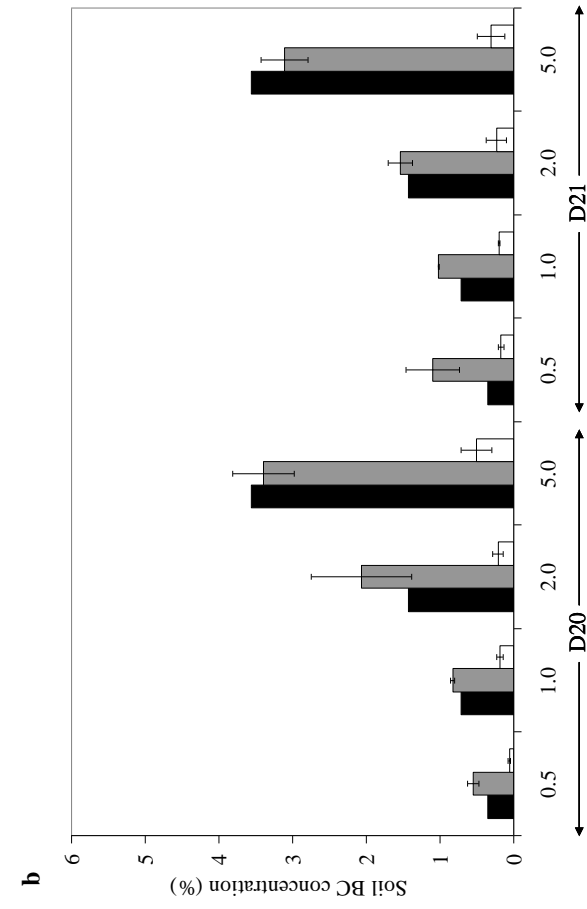


Figure 2.3. The recovery of a) grass char, b) wood char, c) charcoal and d) soot, using the CTO and CO methods. Black bars, the concentration of BC added to the soil; grey bars, the BC concentration detected by CO; white bars, the BC concentration detected by CTO; error bars indicate $1 \pm S.E.$

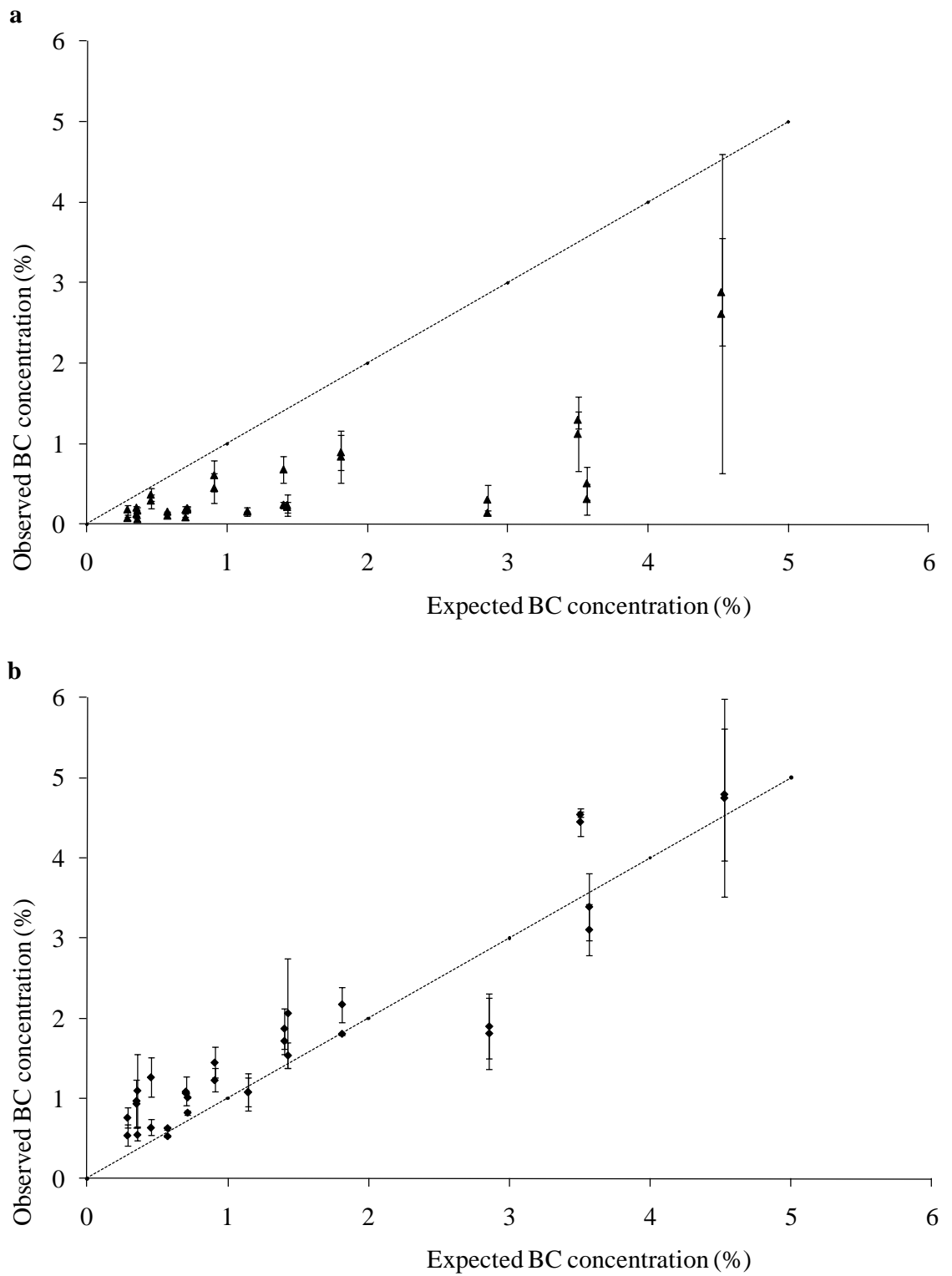


Figure 2.4. Observed and expected soil BC concentrations for (a) the CTO method and (b) the CO method (error bars represent ± 1 standard error), displayed with a 1:1 line.

Pure BC and PIM study

Charcoal, diesel soot, and n-hexane soot had the highest percent recovery of the pure BC samples tested, at 96.6, 84.6, and 92.4 %, respectively (Fig. 2.5a). Only 49.7 % of the grass char was detected, and 67.8 % of the wood char remained after CO. The only PIM to be completely undetected was melanoidin, which dissolved completely in the NaOH by the end of the series of alkali washes (Fig. 2.5b). Very little lignite coal was detected, as most lignite coal was lost during the NaOH washes, rendering only 7.7% recovery. Bituminous coal and shale, however, were recovered in proportions similar to those of true BC, indicating that these substances are largely detected as BC by the CO method.

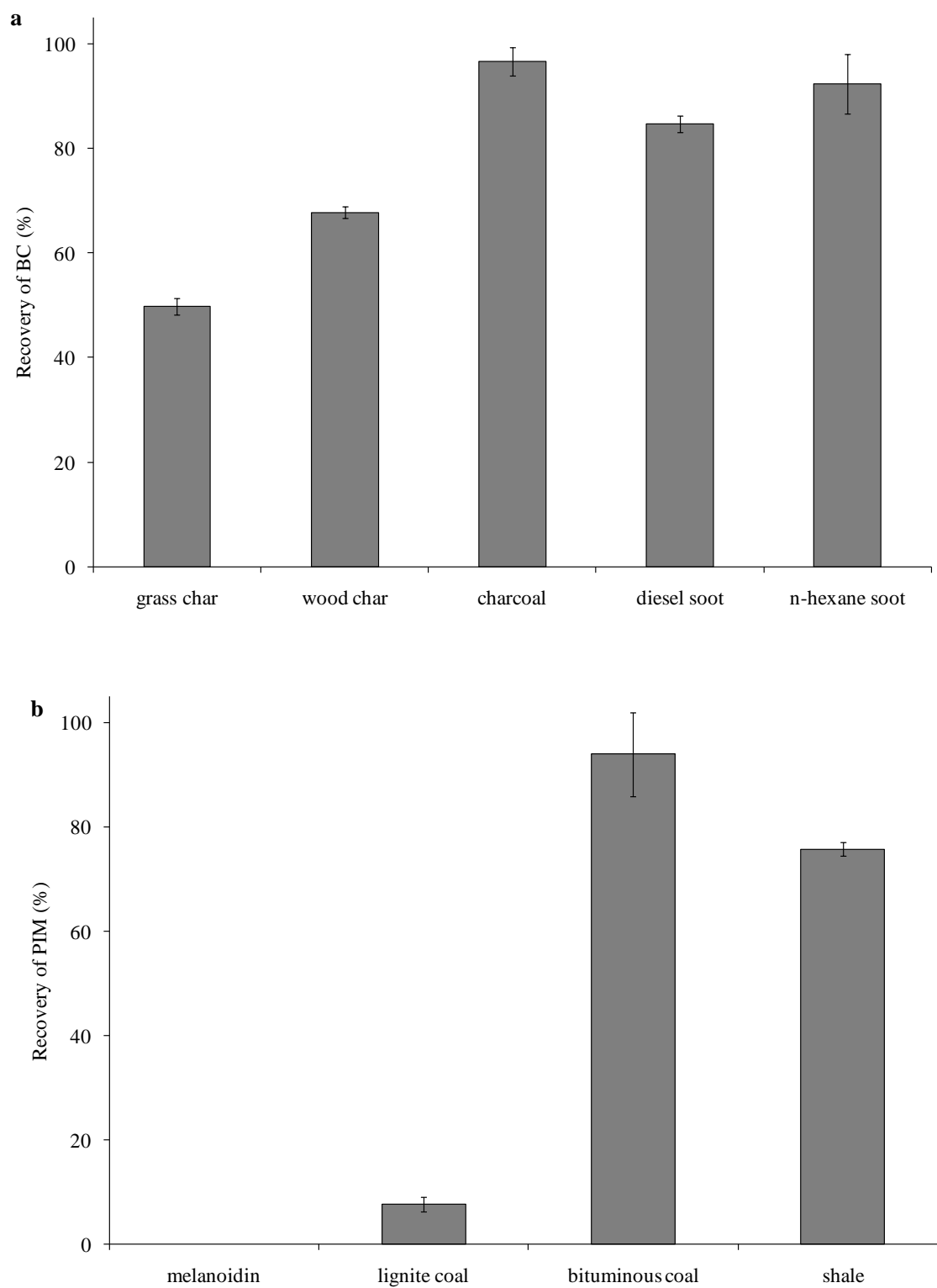


Figure 2.5. The percent recovery of (a) pure BC and (b) PIMs after treatment with the CO method (error bars represent 1 standard error).

TGA results

CO and TGA revealed similar BC concentrations for the six soil samples upon which they were tested, and a strong positive relationship was observed. There did not appear to be any systematic bias to under- or overestimate BC by either method in comparison to the other. However, a larger sample size would be more indicative of the relative sensitivities of both methods. TGA was found by Hammes *et al.* (2007) to detect a range of BC forms in concordance with the amount detected by most other quantification methods tested. These results indicate relatively high agreement between the established TGA method for BC detection and the newly-developed CO technique.

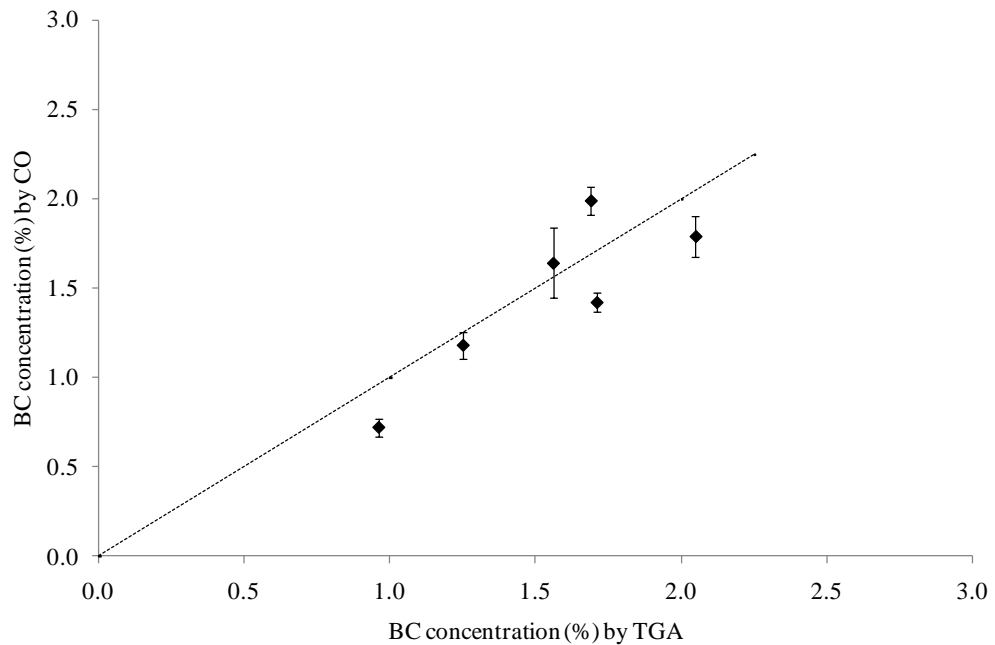


Figure 2.6. Percent recovery of BC in six soil samples using the CO and TGA methods, and a 1:1 line (error bars represent ± 1 standard error).

Discussion

Proxy Method

The results of the proxy method test provided evidence of the unreliability of a thermal step in BC detection methods. The HCl step removed a consistent amount of C (D20, 2.06 % \pm 0.07; D21, 0.62 % \pm 0.07), regardless of the amount of BC added. However, after the thermal treatment, BC detection was highly inconsistent between different charcoal concentrations, with underestimation at high BC concentrations and overestimation at low BC concentrations. Charcoal is more thermally stable than charred wood, and less thermally stable than soot (Leifeld, 2007), meaning that the proxy method is also likely to be inconsistent for different forms of BC. Elmquist *et al.* (2006) found that standard n-hexane soot does not lose any mass during TG analysis until temperatures exceed 320 °C, and therefore this form of BC could be detected more accurately by the proxy method than grass and wood chars, which begin to lose mass at temperatures below 100 and 200°C, respectively. However, standard diesel soot was found to begin mass loss at 270 °C (Elmquist *et al.*, 2006), suggesting that even for soot the thermal treatment is likely to remove a large and inconsistent proportion of BC. Overall, the findings from the proxy method study support the hypothesis that thermal treatment is not conducive to detecting the entire spectrum of BC (Hedges *et al.*, 2000, Masiello, 2004; Hammes *et al.*, 2007).

CTO and CO Methods

The results of the CTO accuracy trial revealed findings similar to those of Hammes *et al.* (2007); only about half of the total soot remained at the end of the CTO process, and far less grass char, wood char, and charcoal was detected (Fig. 2.3). These results are corroborated by Elmquist *et al.* (2006), who, upon monitoring the weight loss of four types of BC over gradually increasing temperature, found that a portion of BC can be oxidised at

temperatures much lower than the temperatures used for thermal apportionment of OC in CTO. In particular, a fraction of grass char was found to oxidise at temperatures lower than 100 °C, and all four BC types exhibited some weight loss at a lower temperature than the thermal oxidation temperature of 340 °C, used by Rawlins *et al.* (2008). It has also been determined that certain PIMs (river natural organic matter, melanoidin and shale) are more or equally resistant to thermal oxidation than particular types of BC, particularly the chars (Elmqvist *et al.*, 2006).

The CO accuracy trial, however, proved more successful. This method seems to overestimate the amount of BC in soil, with an average BC recovery of 140.8 %, over the range of BC additions, potentially due to residual SOC that has resisted removal by NaOH. This is indicated by the trend the data exhibit for much higher overestimations in samples with 0.5 % BC added. With these samples disregarded, the BC recovery of CO is reduced to 115 %, signifying that the method may be more accurate in soils where BC concentration exceeds 1 %.

However, it is entirely possible that much of this overestimation arises from the presence of BC in the soil before the known amounts of BC were added. BC has been detected in significant amounts in rural agricultural soils (Chapter 3 of this work), in large proportions in urban soils at depths ranging from 0 - 190 cm (Lorenz and Kandeler, 2005; Rawlins *et al.*, 2008), and in aerosol samples from the Arctic (Heintzenberg, 1982) so it is unfeasible to obtain soil samples that can be assumed completely devoid of BC. The existence of BC in D20 and D21 before the addition of pure BC samples could not only be responsible for the overestimation by CO, but also indicate that the recovery of the CTO method (on average, 34.2%) was lower than reported here.

Using the CO method, soils D20 and D21 were found to contain 0.72 and 1.11 % BC before any standard BC was added. When these initial BC concentrations were added to the concentration of standard BC in each sample to provide an amended “expected” value for BC recovery, the mean recovery of CO was reduced to 70.1 % (CTO, as expected, detected far lower blank BC concentrations, at 0.17 % for D20 and 0.45% for D21, which further reduced the calculated CTO recovery to 24.5 %). However, if CO does overestimate BC by incompletely removing SOC before CN analysis, then the blank values detected by CO are too high and the amended recovery value of 70.1 % is an underestimation of the true recovery of CO.

Grass and wood char were underestimated by CO when added at high concentrations (5 % of soil mass), which may indicate that a portion of char is being lost, and when added at lower concentrations is compensated for by the small proportion of remaining non-BC. The lower degree of aromatisation in chars in comparison to soots (Fernandes *et al.*, 2003) could account for this fractional loss. Despite this, CO seems to have a far more accurate percent recovery across all BC types, as indicated by Fig. 2.4. CO represents between a 30% underestimation and a 40% overestimation of BC concentration, as compared to the systematic three-fold underestimation of BC by CTO. The analysis of blank D20 and D21 soil samples by a reliable third method, such as TG-DSC, would provide helpful information for determining accurate “expected” BC concentrations, and thus elucidate the true accuracy of the CO method. This study offers new insight into the capability of chemical oxidation methods for quantifying BC, refuting the statement by Masiello (2004) that chemical oxidation can only be effectively used to detect the highly stable portion of the BC structure spectrum (i.e. soot and charcoal), and not the less-refractory chars.

Pure BC and PIM study

Pure BC samples were all recovered in high proportions of their initial mass, except grass char, of which only half the original amount was detected. This is likely due to the composition of grass char; being low in lignin precursors, it is not as chemically recalcitrant as wood char (Shafizadek, 1984; Li *et al.*, 2002; Sharma *et al.*, 2004), which was recovered at 67.8% of its original C content (Sharma *et al.*, 2004). The low recovery of grass char in comparison to the other BC standards is not necessarily as much of an issue in a British city as it may be in other environments: the BC produced from diesel combustion, coal burning, and even wood burning are likely to vastly outweigh the amount of BC produced by grass burning. However, this systematic error could be very significant in grassland ecosystems that are susceptible to wildfires, or that undergo periodic managed burning. Hammes *et al.* (2007) found highest recovery of grass char BC by the optical (thermal/optical transmittance and reflectance) and photooxidation methods, so these may be more advisable for use in detecting grass-derived BC.

The highest BC recovery was found in the charcoal and soots, which are the most stable forms of BC (Masiello, 2004; Leifeld, 2007). The recovery of diesel soot was lower than that of n-hexane soot (84.6 % compared to 92.4 %), despite their similar stabilities (Leifeld, 2007), and this may be due to impurities in the diesel soot, such as C that has not undergone partial combustion. Such impurities may exist because the diesel soot was obtained from vehicular diesel particulate filters, and is not laboratory-produced under controlled conditions as a standard.

It should be noted that BC contained in soils is likely to experience higher recovery than pure BC, for three reasons: (i) BC contained in soils may sorb to other organic molecules, increasing the weight of BC particles and thus reducing the amount of BC that

is lost during washes while discarding supernatant (ii) BC in the environment may acquire a surface layer of sorbed organic molecules that protect it from chemical oxidation (iii) BC lost due to suspension in the supernatant in the case of incomplete centrifugation (sometimes pellets are slightly eroded during decanting of supernatant) may be lost in a similar proportion to the loss of soil particles occurring for the same reason, thereby retaining the original proportion of BC to soil.

The negative controls melanoidin and lignite coal were detected at 0 % and 7.7 % recovery, respectively, indicating that these materials do not interfere with BC quantification in the CO method. This is largely due to their apparent dissolution in NaOH over the course of the six alkali wash treatments. The presence of lignite coal was observed to diminish gradually with each NaOH wash, therefore the addition of a seventh NaOH wash may have been sufficient to eliminate its detection completely. However, in true soil samples that are only partially comprised of lignite coal, this is not likely to be necessary. Bituminous coal was not removed by the series of acid and alkali washes. This could be remedied by amending the method to include a heating step during the HNO₃ wash, as Kinney and Ockert (1956) found that up to 78.8 % of the C contained in bituminous coal can be rendered alkali-soluble when heated to 120 °C in HNO₃, although this could have the undesired effect of degrading BC components as well. Protocols are available for the oxidation of shale (Kinney and Schwartz, 1957; Leonard, 1959; Kinney and Leonard, 1961), which was also detected as BC by CO, and the incorporation of one of these procedures into the CO wash treatment may reduce the false-positive effect of this PIM. However, further research is necessary to determine modification how this would affect the true BC recovery of CO.

TG-DSC study

Analysis of soil samples by TG-DSC did not indicate any systematic bias of CO in relation to this method. Each method rendered BC concentrations similar to the other, signifying that CO is similar in accuracy to the TG-DSC method. Both methods report similar results for PIMs (for TG-DSC results, see Hammes *et al.*, 2007), with high detection of bituminous coal and shale, and little or no detection of melanoidin and lignite coal, although TG-DSC detection of lignite coal is approximately 20 %, whereas that of CO is 7.7 %. TG-DSC and CO both have similar recovery of pure BC; above 90 % for diesel soot, and less than 60% for grass char. However, TG-DSC had very high recovery of wood char, whereas CO rendered only 67.7 % detection. The CO method has the advantage of being less time-consuming; TG-DSC analysis of one sample takes 2 – 3 hours, whereas 40-50 samples can be chemooxidised in one series of washes, including elemental analysis, over the span of 3 days. TG-DSC has the added disadvantage of detecting the loss of structural water (contained within mineral impurities such as clays) within the temperature range of BC loss, and thus could overestimate BC in this manner (Hammes *et al.*, 2007). Furthermore, because BC recovery by CO depends on the weight of sample retained at the end of the washes, the recovery of CO is likely to be higher for BC contained in environmental matrices than in the pure samples studied here, for the three reasons provided in the previous section.

Conclusion

This study has demonstrated the ability of CO to quantify BC in a quick and cost-effective manner. The detection of BC in soil samples is estimated to be between 70.1 and 140.8 % of the actual amount of BC, an interval which can be made more precise by determining the amount of background BC contained in the soils used here. CO has the disadvantage of

detecting shale and bituminous coal as BC, although future amendments to the chemical wash procedure may reduce the extent to which these false positives are detected. The CTO method and proxy method are determined to be inaccurate and imprecise, due to the lack of a clear distinction between the oxidation temperatures of BC and SOC, and are not recommended for use in BC quantification.

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Chapter 3: The relationship between urban land use type, soil C and N content, and soil black carbon concentrations

Introduction

Soil is the largest terrestrial repository of OC worldwide, containing two to three times as much C as stored in living vegetation (Schlesinger, 1990), and efforts to understand and quantify the cycling of these stocks are paramount to mitigating climate change. Recent findings by Bellamy *et al.* (2005) indicate that during the last quarter of the twentieth century, soils in England and Wales lost OC at a mean rate of 0.6% per year. Globally, C losses from the soil are estimated to be ten times higher than C emissions from fossil fuel burning (Raich and Potter, 1995). These losses are attributed to anthropogenic activity such as land use change, agricultural intensification, loss of vegetative cover, and climate change (Robinson and Sutherland, 2002; Bellamy *et al.*, 2005). Land use is an important driver of the soil C stocks and fluxes at a regional scale (Bellamy *et al.*, 2005; Smith, 2008; Ostle *et al.*, 2009), as it influences not only the productivity and biogeochemical cycling in that area but also the anthropogenic perturbations such as pollution and physical disturbance.

BC exists in considerable amounts in every natural reservoir, and its production is estimated at 50 – 270 Tg yr⁻¹, 80 – 90 % of which remains in the terrestrial environment (Kuhlbusch and Crutzen, 1995). BC has been detected in significant quantities in the soils of many semi-natural ecosystems, including those of North American prairies (Glaser and Amelung, 2003), tropical forests (Glaser *et al.*, 2000), European temperate forests (Uvarov, 2000), and a range of surface soils from Australian ecosystems (Schmidt *et al.*, 2001). Soil BC concentrations vary greatly in magnitude, and initial observations indicate that some of

this disparity may be attributed to land use (Glaser *et al.*, 2001; Czimczik and Masiello, 2007); for example, a study in Nanjing reported significant differences between the soil BC content of residential and industrial areas (He and Zhang, 2009). Urban soils hold particular pertinence for BC, as concentrations are likely to be high due to the intensity of human activity in these areas, yet very little is known about the BC that is generated and stored in cities. Soils in Stuttgart, sampled from a range of disturbance levels, were often found to contain extremely high levels of BC, up to 85% of the total organic carbon (TOC, here referring to BC and SOC together; SOC refers to non-black OC). Initial studies in Glasgow, Stoke-on-Trent, and Coventry indicate the presence of heterogeneous stocks of BC in urban soils; median soil BC concentrations in Glasgow were found to be three times higher than those in the other two cities (Rawlins *et al.*, 2008).

When contained in soils, BC has been reported to have wide-ranging and sometimes contradictory effects, with little consensus on the net impact of BC inputs on soil biogeochemistry. BC has been found to increase soil respiration (Wardle *et al.*, 2008), and decrease soil greenhouse gas emissions (Rondón *et al.*, 2005), to increase nutrient availability (Rondón *et al.*, 2007), and cause nutrient immobilisation in the soil (Lehmann and Rondón 2006), and to affect the soil hydrology (Glaser *et al.*, 2002; Gaskin *et al.*, 2007). It is likely that the effects of BC on soil are dependent upon many factors, including soil biogeochemistry (particularly, pH and nutrient availability), climate, soil invertebrate species composition, and vegetation characteristics.

Urban soils are now being recognised as an important yet characteristically distinct stock of sequestered C. Urban areas are growing in global significance; more than 50 % of the world's population live in cities, with 95 % of future population growth predicted to occur in these areas (Grimm *et al.*, 2008). The high population density of urban areas leads

to intense land management, and anthropic amendments to the soil such as sealing, compaction, physical disruption and pollution create a unique biogeochemistry of urban soils (Pavao-Zuckerman, 2008). Seventy-eight percent of C emissions are produced in cities, and 76 % of industrial wood use occurs in these environments (Brown, 2001). Although urban soils are by their nature highly altered, they still provide many vital ecosystem services, such as modulating hydrological processes, providing a substrate for vegetation, agriculture, recreation, and edifices, and acting as a store of OC (Rawlins *et al.*, 2008). Despite this, urban soils are poorly understood (Churkina *et al.*, 2010), and much research is necessary in order to enact management strategies that will preserve their structure and function.

The aim of this chapter is to improve understanding of BC in urban soils, and the long-term storage of SOC this provides. Firstly, this study examines the distribution of BC pools at a city-wide scale and investigates how they vary by land use type across the city of Leicester, as a case study. Soil BC concentrations in agricultural land surrounding the city were measured in order to provide a regional context for these results. It was hypothesised that soils within the city would have higher BC concentrations than agricultural soils, due to the high density of pollution sources that occurs in cities. It was also anticipated that soils under woody vegetation would have a higher BC concentration than those under herbaceous vegetation, due to the collection of airborne BC particles on the surfaces of leaves, and subsequent accumulation in the underlying soil. Secondly, we investigate the correlation between BC concentration and other soil biogeochemical properties; namely, SOC and N content, and the CN ratio of soils. This research will improve understanding of the relative contribution of BC to urban soil C pools, permit more refined estimations of city-wide BC stocks, and provide a preliminary indication of the potential links between

BC and SOC and N concentrations within urban soils. A positive relationship between concentrations of BC and SOC, and BC and N was hypothesised to occur, due to the sorption ability of BC for nutrients and OM, and previous findings of its fertilising effect on soils (Glaser *et al.*, 2002; Lehmann *et al.*, 2003).

Methods

Study site

The study site for this research was the city of Leicester in the East Midlands, UK (52°38'N, 1°08'W). The unitary authority boundary of Leicester covers an area of approximately 73km², with an estimated population of 300,000 (Leicester City Council, 2009). As such, Leicester is considered representative of a mid-sized UK city. Leicester has a temperate climate, with 606 mm mean annual precipitation and mean minimum and maximum temperatures of 5.8°C and 13.5°C, respectively (Met Office, 2009). The underlying bedrock of Leicester is composed of three groups: Lias Group (Jurassic), Mercia Mudstone Group (Triassic), and Penarth Group (Triassic). The bedrock is covered in large part by superficial deposits of alluvium, colluvium, glaciolacustrine deposits, and glacial till (Rice, 1968). Bedrock and superficial deposit data for Leicester are available from British Geological Survey DiGMapGB-10 digital data (1:10000 scale; http://www.bgs.ac.uk/products/digitalmaps/digmapgb_10.html).

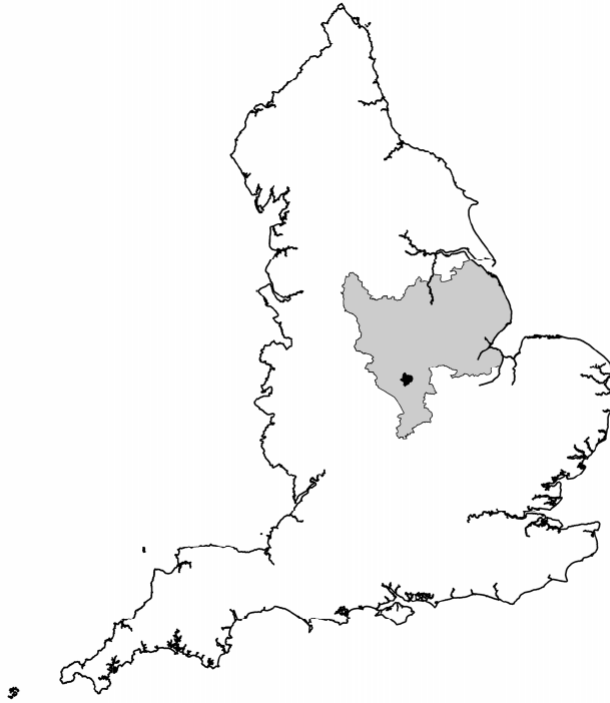


Figure 3.1. The position of Leicester (black) within the East Midlands (grey) and England (white).

Sampling strategy

Land cover characteristics were identified using a GIS, using the land cover polygons of Infoterra and Ordnance Survey within their LandBase and Master Map (Murray & Shiel, 2003) digital cartographic datasets. This allowed tree cover and vegetation patches to be mapped to within 0.25 m². Urban greenspace was split into non-domestic land and domestic gardens, and within these was stratified by vegetation cover (herbaceous and woody), thus creating four land use types within the city: non-domestic herbaceous, non-domestic woody, domestic herbaceous, and domestic woody. The woody categories included any land that was vegetated with shrubs or trees, whereas herbaceous land contained grasses or non-woody vegetation. In contrast to the previous four land use types, which were sampled solely within the unitary authority boundary of Leicester, agricultural land samples were taken from a 7.5 km buffer area surrounding the city. This was done in

order to provide a regional context for the urban data, constituting land that is not proximal to urban sources of pollution.

Forty-five random GPS points were generated for each land use type, and approximately twenty of each were soil sampled. When it was impossible to sample at a particular point (for example, due to safety concerns or access not being granted), the next GPS point in the randomly-generated list was visited instead. Sampling in gardens was conducted by visiting the street at which a GIS point was located, and samples were taken from one house per selected street, once sampling permission was granted. Where there was a variety of vegetative cover in a garden, soil samples were taken from both herbaceous and woody land uses.

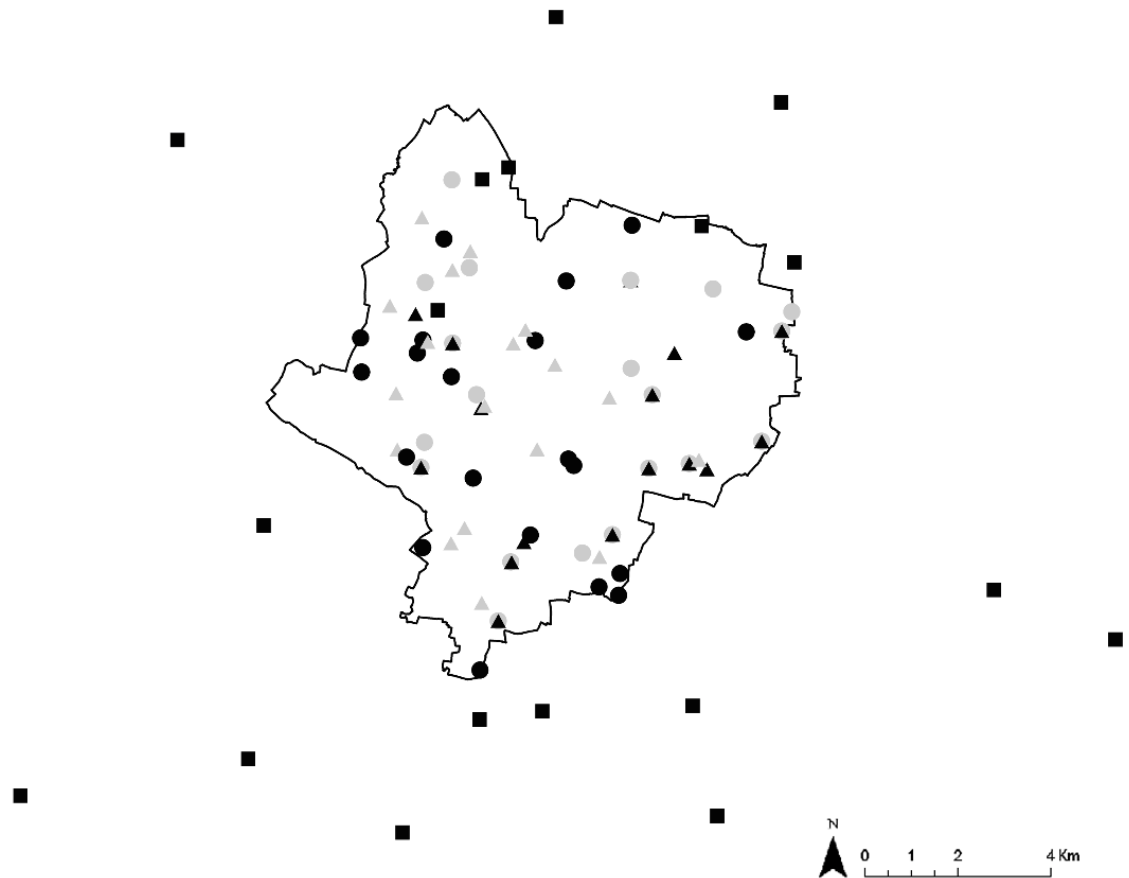


Figure 3.2. The location of sampling points within the unitary authority boundary of Leicester (including the position of agricultural sampling points within a 7.5 km radius around the city); black circle, herbaceous; grey triangle, woody; grey circle, garden herbaceous, black triangle, garden woody; black square, agricultural.

Soil analysis

Soil samples were taken using a sample ring corer (Soil sample ring kit C, Eijkelkamp), which allowed a known volume of soil to be taken. Four replicate surface soil samples (0-7cm depth) were taken within a 1 m² quadrat at each sampling point. Soils were dried in an oven (105 ± 5°C) for 24 hours and weighed. Soils were then ground and homogenised using a ball mill and sieved to remove any particles larger than one mm. These particles, typically stones and non-biodegradable anthropogenic debris (e.g., rubble, metals, plastics), were also weighed. After homogenising, soils were again dried at 105°C and placed in an

air-tight container for storage. Soil density was calculated using the total soil dry weight, not including the mass of any particles larger than 1 mm, as these did not contain soil C.

Soil pH was measured, and this was used to guide whether samples contained IC in the form of calcium or other alkali metal carbonates. This was achieved by taking a 5 g subsample from one of the four dried, ground replicate soil samples taken at a site. To the subsample was added 10 ml of 18 MΩ H₂O, and this was shaken on a rotary shaker for 10 minutes, then left to settle for 30 minutes. The suspension was next shaken vigorously by hand for ten seconds, and a pH reading was taken with a Jenway 3030 pH meter (Bibby Scientific, Staffordshire, UK).

For each sampling point, the four replicates were subsampled and mixed in proportion to their relative bulk densities to give a total of 4 g of mixed soil. Each sample was subsequently analysed for total C and N using a CN analyser (Vario EL Cube, Elementar, Hanau, Germany). One-gram subsamples of each mix were then analysed for BC using the chemooxidation (CO) method (Chapter two), and CN analysed again to provide the BC concentration of the soil.

The CO method does not isolate combustion-derived N, as it does for C, so it was impossible to distinguish between BC-associated N (BN) and non-combustion-altered N using CO. This is because the CO process involves treatment with HNO₃, and nitrate anions may bind to the BC as hydrogen cations are released from HNO₃ in the removal of carbonates from the soil. For this reason, N is represented in this study as total N, measured before CO, rather than BN.

Statistics

Statistical analysis of results was performed using SPSS (version 16.0, SPSS Inc.). The dataset could not be transformed to meet the requirements of normality for parametric analysis and due to the unequal variances across land use types, multiple Wilcoxon rank sum tests were used. This approach was applied to determine significant land use type effects on the concentration of BC per cm³ of soil (BC density), BC percent concentration of total soil mass (BC concentration), and SOC density. A Bonferroni correction was used to account for the multiple comparisons, and differences with a significance of $p < 0.005$ were reported. As the correlation data did not conform to parametric test assumptions, a Spearman's Rank correlation was used.

Results

BC stocks in Leicester

The mean concentration of BC in the surface soil across all land use types in Leicester was 1.91 % (S.E. \pm 0.15) of soil dry weight, which was more than twice the mean agricultural soil BC concentration of 0.94 % (S.E. \pm 0.08). This represented a mean 28.1 % of the TOC in Leicester soils at 0 – 7 cm depth. The pH analysis indicated that soil pH was exclusively lower than 7 in all samples, thus all soil C was assumed to be OC.

BC by land use type

There was a significant effect of land use type on soil BC concentration (Fig. 3.3). The highest individual BC concentration was found in a garden woody soil where BC concentration was 6.98% of soil dry weight, constituting 76% of TOC. BC was ubiquitous in the soil, although it ranged from 0.42 % in agricultural soils up to 6.98 % in soils under woody vegetation within gardens. The highest variation in BC concentrations was observed in garden woody soils. The soil BC densities of each land use type were consistent with the relative magnitude of the soil BC concentrations (Fig. 3.4). Although the mean herbaceous soil BC density exceeded that of woody soil, this difference was not significant.

Accounting for the relative area of each land use type, the weighted mean BC concentration dropped slightly to 1.69 %, representing 26.9 % of soil TOC (Table 3.4). Using mean BC density and land use type area, it was roughly approximated that there are ~44,500 tonnes of BC in the surface soils of Leicester. However, due to the heterogeneous nature of soil composition, the sampling strategy in this study was not extensive enough for this figure to be more than a rough estimate. BC was found to comprise between 20 and 37% of TOC in

Leicester soils, depending on land use type. BC comprised the smallest proportion of TOC in woody soils, and the largest proportion in garden woody soils. The mean proportion of BC to TC was significantly higher in garden soils than non-domestic or agricultural soils, at 34.3 % (S.E. = ± 2.2), compared to 22.1 % (S.E. = ± 1.0) and 21.9 % (S.E. = ± 1.3), respectively.

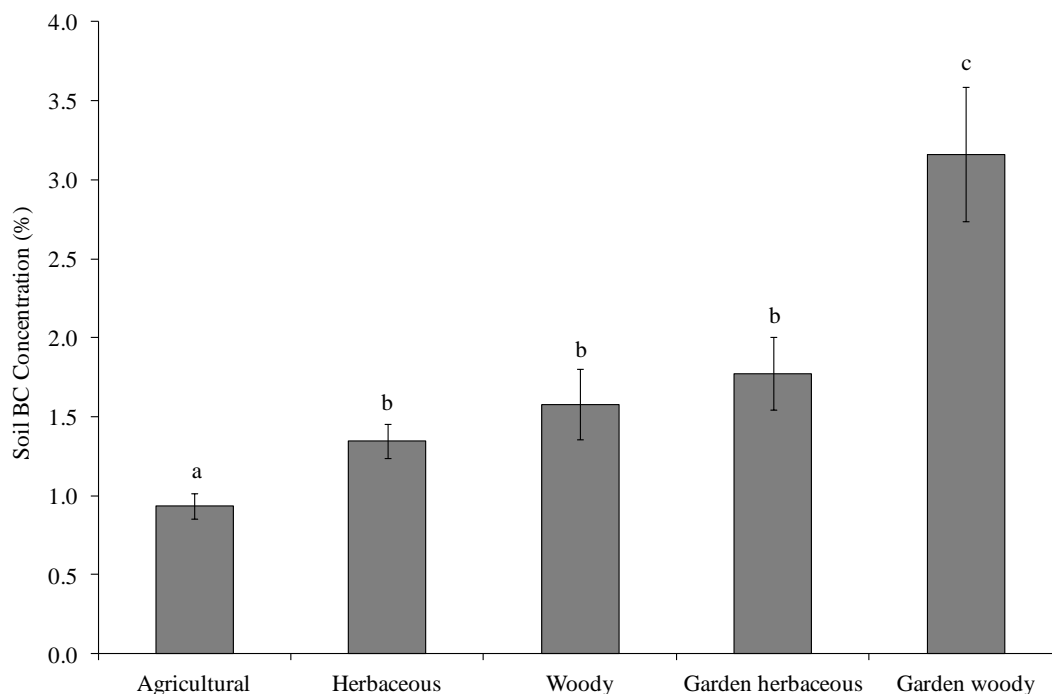


Figure 3.3. BC concentrations (percentage of soil dry weight) in surface soils across Leicester by land use type. Error bars indicate ± 1 S.E. Different letters indicate statistical significance of land use type ($p < 0.005$, $n = 96$), as shown in Table 3.1.

Table 3.1. Test statistic and significance of individual Wilcoxon rank sum analyses of soil BC concentration data by land use type. Significant differences after Bonferroni correction are shown in bold.

Land use type	Herbaceous	Woody	Garden Herbaceous	Garden Woody
Agricultural	W = 305 $p = 0.003885$	W = 281 $p = 0.002571$	W = 359 $p < 0.001$	W = 314 $p < 0.001$
Herbaceous		W = 162 $p = 0.6129$	W = 164 $p = 0.2382$	W = 33 $p < 0.001$
Woody			W = 154 $p = 0.3351$	W = 41 $p < 0.001$
Garden Herbaceous				W = 61 $p < 0.001$

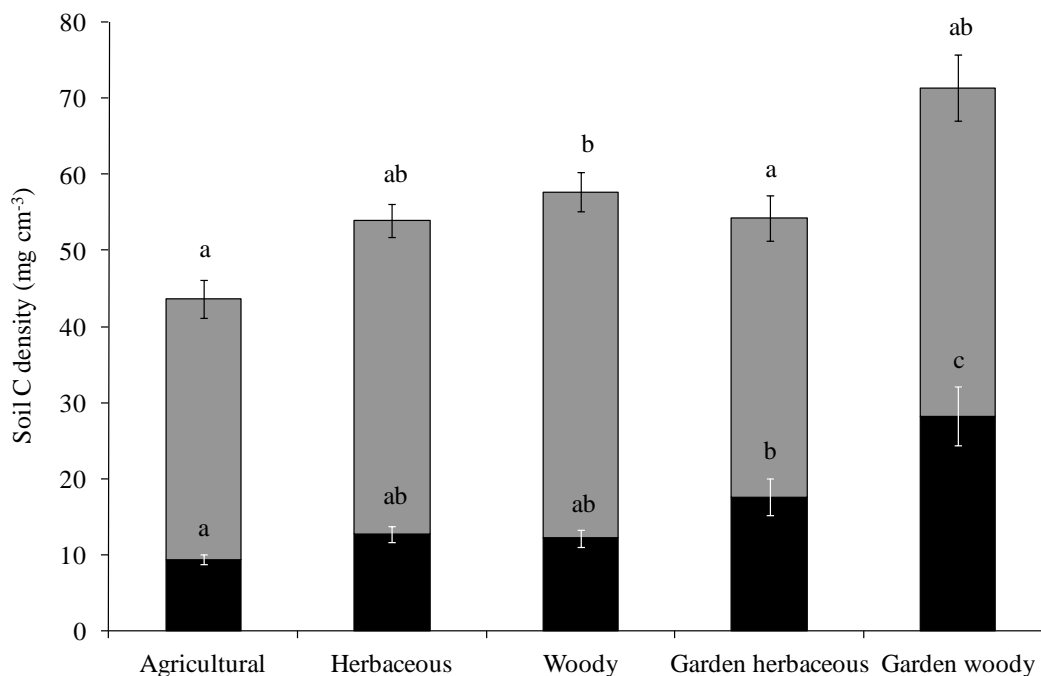


Figure 3.4. Proportion of BC and SOC density by land use type. BC, black bars; SOC, grey bars. Error bars indicate ± 1 S.E. Different letters indicate statistical significance of land use type ($p < 0.005$, $n = 96$), as shown in Tables 3.2 and 3.3.

Table 3.2: Test statistic and significance of individual Wilcoxon rank sum analyses of soil BC density data by land use type. Significant differences after Bonferroni correction are shown in bold.

	Herbaceous	Woody	Garden Herbaceous	Garden Woody
Agricultural	W = 301 $p = 0.005618$	W = 245 $p = 0.05874$	W = 354 $p < 0.001$	W = 314 $p < 0.001$
Herbaceous		W = 187 $p = 0.8511$	W = 150 $p = 0.1215$	W = 34 $p < 0.001$
Woody			W = 100 $p = 0.1147$	W = 25 $p < 0.001$
Garden Herbaceous				W = 66 $p = 0.001301$

Table 3.3: Test statistic and significance of individual Wilcoxon rank sum analyses of soil organic carbon density data by land use type. Significant differences after Bonferroni correction are shown in bold.

	Herbaceous	Woody	Garden Herbaceous	Garden Woody
Agricultural	W = 296 <i>p</i> = 0.008712	W = 289 <i>p</i> = 0.001043	W = 251 <i>p</i> = 0.2943	W = 230 <i>p</i> = 0.0256
Herbaceous		W = 119 <i>p</i> = 0.07678	W = 281 <i>p</i> = 0.06555	W = 158 <i>p</i> = 0.9624
Woody			W = 291 <i>p</i> = 0.003436	W = 182 <i>p</i> = 0.1985
Garden Herbaceous				W = 117 <i>p</i> = 0.1226

BC and soil composition

The data revealed a positive correlation between SOC and BC concentrations in non-domestic and agricultural land uses (Fig. 3.5). There was no correlation between SOC and BC concentrations in gardens, so these data are excluded from the figure. Soil N values also showed a positive correlation to soil BC concentration (Fig. 3.6). Again, there was no correlation observed between N and BC in garden soils, therefore garden data have been omitted from Figure 3.6 and the correlation. Soil N values tended to be lower in agricultural soils than in non-domestic soils. Additionally, a positive correlation was observed between BC and the C to N ratio of Leicester soils across all land use types (Fig. 3.7). Soil BC concentrations and CN ratios were lowest in agricultural soils and the highest range and variability in values was seen in the garden soils.

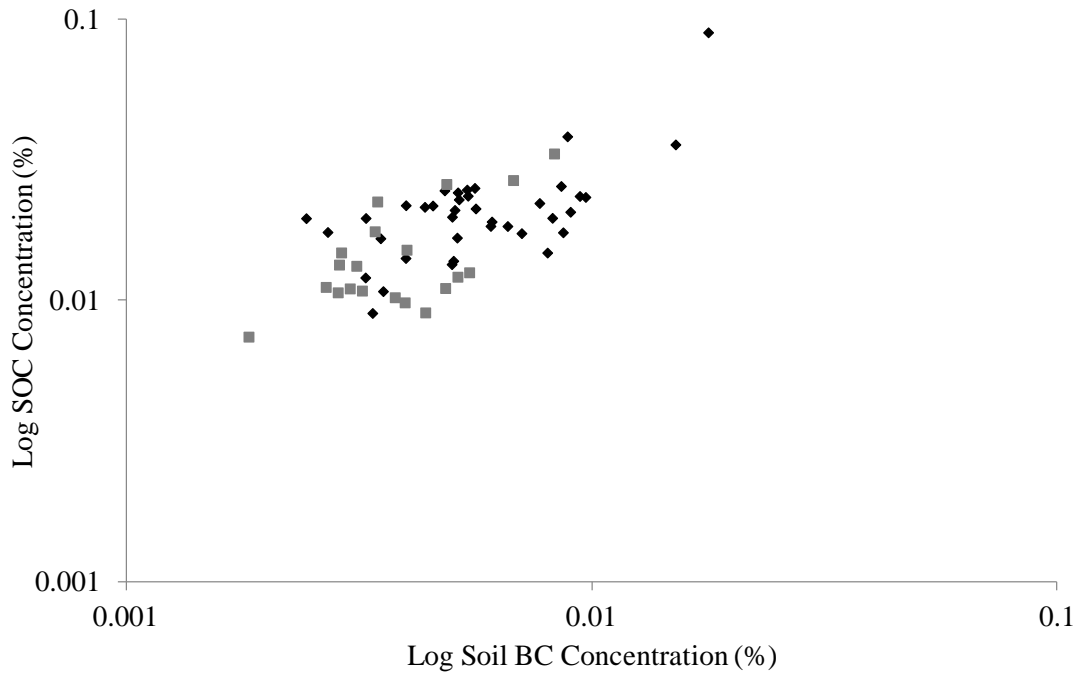


Figure 3.5. The correlation between SOC concentration and BC concentration (percentage soil dry weight) in Leicester soils; black diamond, non-domestic land use; grey square, agricultural land use; $p < 0.001$, $R_S = 0.627$.

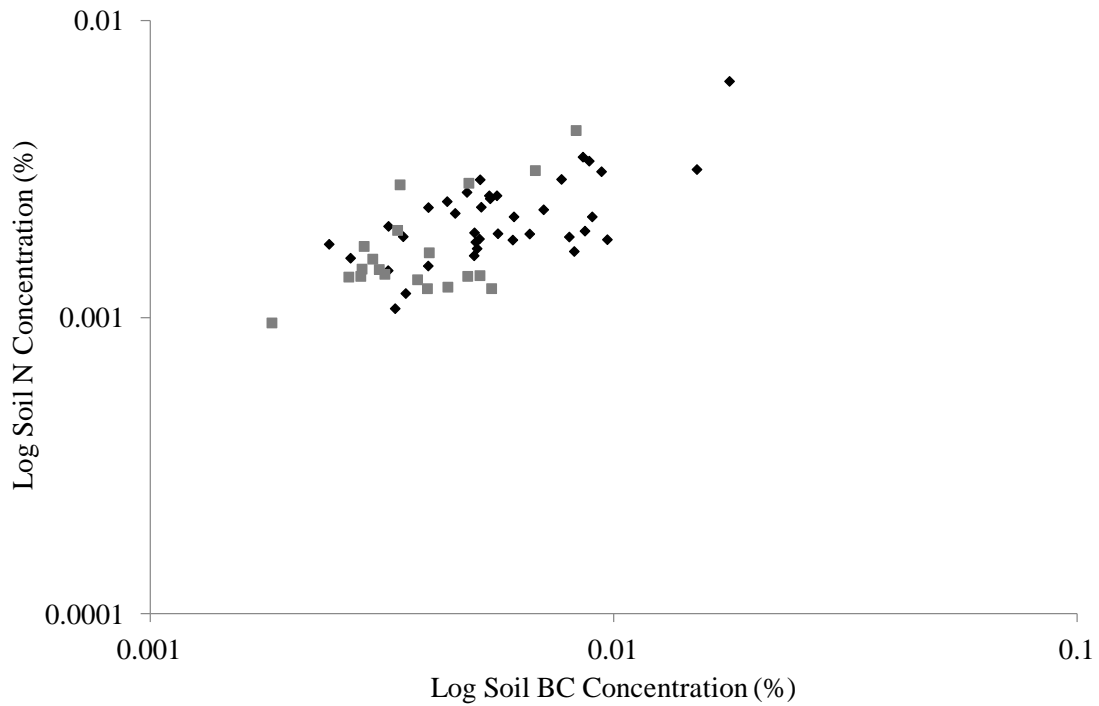


Figure 3.6. The correlation between N concentration and BC concentration (percentage soil dry weight) in Leicester soils; black diamond, non-domestic soils; grey square, agricultural soils; $p < 0.001$, $R_S = 0.620$.

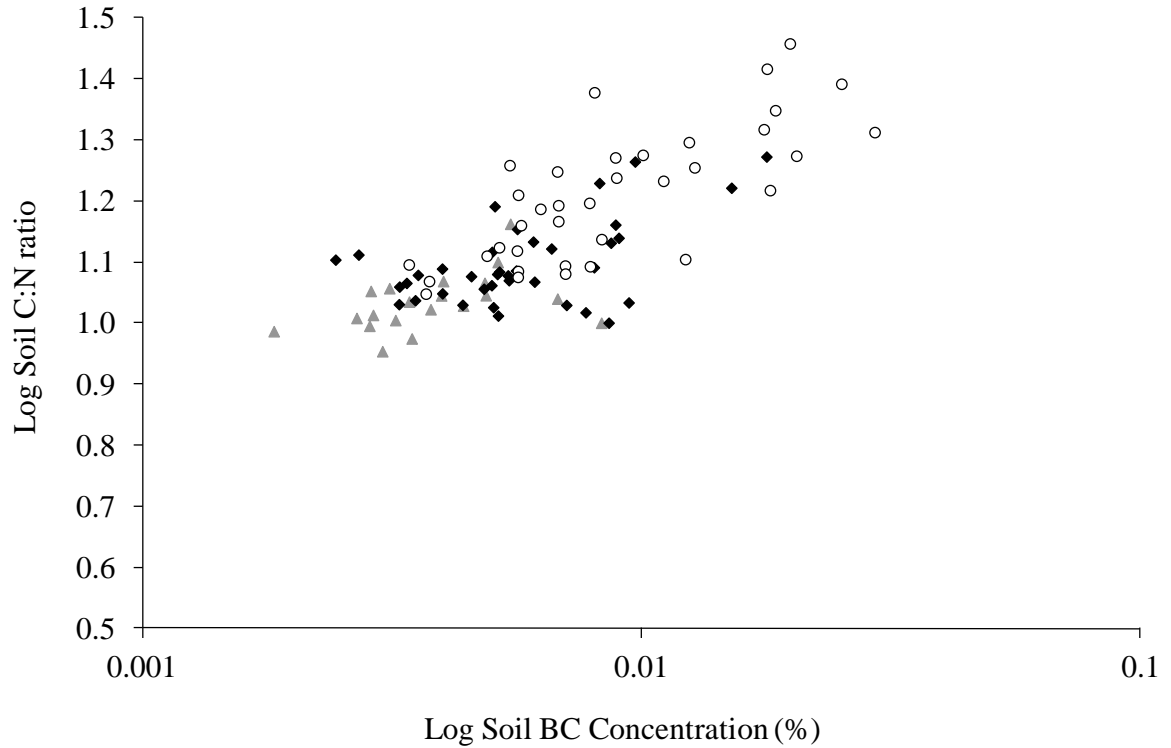


Figure 3.7. Correlation between soil CN ratio and soil BC concentration (percentage soil dry weight) across all land uses; black diamond, non-domestic land use; grey triangle, agricultural soils land use; grey; white circle, garden land use; $p < 0.001$, $R_s = 0.681$.

Discussion

BC variation by land use type

Agricultural samples contained the lowest BC levels, and at 0.94 % BC on average, were significantly lower in BC concentration than all other land use types. These values are similar to those obtained by Glaser and Amelung (2003) for BC values in rural North American prairie soils, and this may be attributed to the scarcity of main roads and centres of industry in rural areas. However, BC concentrations in agricultural soil are by no means negligible, comprising over one-fifth of total SOC. This may be caused by agricultural pollution point sources, such as the charring of crop stubble, or fuel combustion by farm machinery. Other sources of BC to agricultural soils in Leicestershire could include power

stations, neighboring conurbations such as Birmingham and Nottingham, and the M1 motorway, which runs north to south through Leicestershire, to the west of the city. However, non-point sources must also be considered; rural atmospheric BC levels in the UK are approximated at 10^3 ng m^{-3} , a value indicative of moderate to heavy levels of pollution for the middle latitudes of the Northern Hemisphere (Novakov and Hansen, 2004). The residence time of BC in the atmosphere varies based on particle size and climatic factors, ranging from 40 hours to 1 month (Ogren and Charlson, 1983). This latter value provides time enough for BC to be transported to even such distant locations as the remote arctic (Heintzenberg, 1982). Therefore, a large proportion of the BC observed in the hinterland of Leicester could be the result of deposition of background, non-point-source BC.

The amount of BC in agricultural surface soil is not necessarily directly comparable to the other land use types, due to the common practice of tilling in arable land. Tilling homogenises the top layer of the soil to depths often exceeding 30cm (Balesdent *et al.*, 2000), therefore it is likely that the concentration of BC in tilled soils declines less rapidly with depth than in undisturbed soils, and perhaps BC stocks in deeper agricultural soils exceed those in untilled land. This idea is supported by the finding of Major *et al.* (2010) that only 1% of surface-applied BC was vertically transported through a South American oxisol during a two-year observation period. Thus, vertical mobilisation of BC can be relatively uncommon, and tilling could potentially increase BC storage at depth. Further studies are necessary to determine how BC concentrations change with soil depth, and how this variation affects the apportionment of BC by land use type.

The highest BC concentration was observed in garden soil with woody vegetative cover. A likely cause of this is the practice of discarding charred materials in an

inconspicuous location within the garden. Ashes and char generated by such activities as barbeques, bonfires, or domestic wood-burning are far more likely to be disposed of within leaf litter or dense vegetation rather than on a managed lawn. Furthermore, any burning that occurs within the garden (for example, as a means of green waste disposal) is likely to be conducted in a similarly inconspicuous location. Garden land with woody vegetative cover had the largest range of BC concentrations, from a minimum of 1.31% to a maximum of 6.98% BC, and the largest range of BC densities: 14.15 to 65.59 g cm⁻³. This is probably due to the large range of management practices inherent within gardens that could affect BC inputs and accumulation, including the previously mentioned burning practices, removal or disturbance of soil, and disposal of household waste.

Historical land management is also likely to be a determinant of soil BC content, due to the long residence time of BC in soils. BC inputs to residential soil were probably more intense when solid fuel such as coal, coke and wood were commonly burnt for the purposes of heating and cooking, and various organic and domestic wastes were burned on garden bonfires. Ash comprised the vast majority of English household waste in the 19th and early 20th centuries (Ravetz, 1995). Furthermore, wood char and ash were traditionally used as residential soil amendments, as these materials can have a liming effect and act as a potash fertiliser (Meyers and Kopecky, 1998). Garden soils can thus represent a repository of historic BC accumulation, but this will depend on the age of the garden and the level of soil disturbance the land has encountered.

The practices of grass clipping and leaf litter removal, which are most often observed in herbaceous land and particularly in gardens (Osmond and Hardy, 2004), could reduce the amount of BC reaching the soil. Deposition of BC particulates settling out of the atmosphere are likely to alight first on vegetation such as tree foliage or herbaceous

land cover, later becoming washed into the soil by rain. The collection and translocation of grass clippings and fallen leaves is likely to reduce the amount of BC that enters the soil in the managed area. If this litter is deposited elsewhere within the garden, rather than removed as waste, it is likely to be placed in the less-conspicuous shrubby or wooded areas of the garden or park, rather than the intensively-managed herbaceous areas, potentially enhancing BC stores. The high surface area of tree foliage in relation to the amount of ground it covers is known to cause a proportionally higher amount of particulate deposition on tree leaves (Tam *et al.*, 1987; Gautam *et al.*, 2005). The roughness of tree foliage is known to increase air turbulence in the immediate vicinity of the leaves, increasing particulate deposition onto leaf surfaces (Fritschen and Edmonds, 1976; Manning and Feder, 1980). It may also be that the high proportion of hard surface found in gardens (23 % of garden soils in Leicester are capped with an impervious surface) acts to concentrate BC in the soils that are not capped, as BC that has settled onto impervious surfaces is washed into the soil by rain.

When the total area of each land-use type was taken into account, the total mass of BC contained within each varied starkly from the relative magnitude of BC concentrations (Table 3.4). This is largely due to the urban land-use type with the lowest BC concentration (non-domestic herbaceous) comprising the largest area of urban greenspace, and the land with the highest BC concentration (garden woody) comprising the smallest area. Taking land use area into consideration, each land use type stored a similar mass of BC within the top 7cm of soil, with the exception of herbaceous land, which stored approximately twice as much as all the others. It is interesting to note that despite garden woody land covering only half as much area as garden herbaceous or non-domestic woody land, it stored a similar amount of BC. However, it must be remembered that these city-

wide BC estimations are based on a sample size of 20 per land use type, and a more extensive study is necessary for an accurate scaled-up estimate of city-wide BC.

Leicester in relation to other European cities

Previous studies have examined the soil BC concentrations of Glasgow, Stoke-on-Trent, and Coventry in the UK (Rawlins *et al.*, 2008) and Stuttgart, Germany (Lorenz and Kandeler, 2005). The average soil BC concentrations for the British cities were reported at 2.31, 1.17, and 0.72 %, respectively, and an average soil BC concentration of 2.48 % was found in Stuttgart. Neither of these studies were designed to provide a comprehensive account of the soil BC content of these cities, due to the low number of sampling sites (10 for each UK city, and 7 in Stuttgart). Furthermore, the CTO method of BC quantification used by Rawlins *et al.* (2008) and Lorenz and Kandeler (2005) is thought to underestimate BC concentrations. Therefore, these results are not directly comparable to the present study. However, it is interesting to note that despite CTO being a more conservative method of BC quantification than the CO method used in this study, Glasgow mean BC concentrations were still found to be much higher than those in Leicester, potentially due to Glasgow's high dispersal of coal ash. The mean Stuttgart BC concentration is higher still than that found in Glasgow, and could be due to the presence of lumps of charcoal in the city's soil, as observed in a previous study (Holland, 1996).

That such a considerable proportion of SOC is BC suggests that BC deposition onto urban soils could be exerting an impact on urban biogeochemical cycling. For instance, if existing soil BC stocks are principally the result of historic wood and coal burning, this may mean that recent losses of SOC from British soils (Bellamy *et al.*, 2005) could be partially attributed to a decline in BC inputs to the soil in relation to the amount of BC lost from the soil (i.e. by leaching or erosion). This hypothesis is supported by the finding of

Novakov and Hansen (2004) that since 1980, ambient BC levels in the atmosphere have leveled out, remaining approximately threefold lower than their concentration in the 1960s. Conversely, if BC is not lost from the soil at significant rates, and has actually been accumulating in recent years, then this could indicate greater losses of SOC than previously thought. More research is needed to determine the fate of BC in British soils, particularly how concentrations change in response to changing emissions rates, in order to determine the significance of these substantial soil BC levels.

Correlation between BC and soil properties

The positive correlation between SOC and BC (Fig 3.5) has many possible causes and implications. The high surface area of BC, with surface to mass ratios reaching $10^3 \text{ m}^2 \text{ g}^{-1}$ (Donnet and Voet, 1976), is known to create microhabitats for soil microorganisms, so the increase in SOC could be in part due to increased soil microbial biomass and microbial exudates (Pietikäinen *et al.*, 2000). An increase in soil microbes (which could amplify nutrient availability within the soil) could have the positive feedback of increasing plant rhizodeposition and root biomass (Bardgett, 2005). However, increased microbial biomass can signify an increase in soil respiration (Jones and Donnelly, 2004; Rogovska *et al.*, 2008), thus enhancing losses of C to the atmosphere, and the net effect of BC on soil C stocks remains unclear.

Another possible cause of this correlation is the tendency of BC surface molecules to adsorb to other organic molecules, immobilising them in the soil (Lehmann *et al.*, 2003). This increases retention of OM in the soil by decreasing the amount of OM that is lost by leaching or erosion (Cornelissen *et al.*, 2005). BC production is often associated with the production of polyaromatic hydrocarbons (PAH; a type of POP that is also produced by the combustion of organic materials), so co-deposition of these molecules, either independently

or while adsorbed to BC, could be another reason for the positive relationship between BC and SOC (Glaser *et al.*, 2005; Masih and Taneja, 2006). Conversely, it may be that soil that is more organic (e.g. garden soil) has a higher retention of BC, due to its affinity for organic molecules, and hence high BC levels are not actually the cause but the result of high SOC. Further research is necessary to distinguish the cause and effect of this correlation.

One striking implication of this positive correlation is the suggestion that BC is potentially increasing soil SOC concentrations. If this, and not the converse, is the case, it supports the argument that the production and application of BC in the form of bio-char is a viable strategy for reducing the CO₂ content of the atmosphere (Lehmann, 2007). Furthermore, it indicates that soil BC may be reducing the net C footprint of the urban area in which it occurs. Opponents of this theory contend that BC may increase soil microbial respiration or prime passive SOC for decomposition (Rogovska *et al.*, 2008; Wardle *et al.*, 2008). Regardless of differentiating cause and effect, these results give no indication that BC is causing the loss of SOC from Leicester soils. Recent findings by Liang *et al.* (2010) indicate that BC-containing soils mineralised 25 % less added OM than adjacent non-BC soils, which may have been due to the lower metabolic quotient that was reported in BC-rich soils. Liang *et al.* (2010) also found that transfer of added OM to the stable organo-mineral fraction of soil was achieved at a higher rate in BC-containing soils. Although this research was conducted in tropical soils containing biochar, it is possible that a similar effect occurs in temperate urban soils containing soot BC. Further research is necessary to elucidate the effects of BC in urban soils, namely by measuring SOC content and microbial activity before and after the addition of BC.

Agricultural and non-domestic land revealed similar correlations between SOC and

BC, and N and BC. However, no correlation was observed in garden soils for either SOC or N. This is probably largely due to the generally higher variety and intensity of land management in gardens: soil addition, removal, disturbance, and fertilisation, as well as compost addition, grass cutting and wood or scrub burning could all affect the relative amounts of BC, SOC and N contained within the soil. Therefore, the ratios of SOC and N to BC are less likely to equilibrate as they are in the less-disturbed systems of non-domestic and agricultural land. While non-domestic and agricultural lands do undergo some of these processes, the lower intensity is likely to allow a more uniform reaction of SOC to BC inputs, and illustrate the effects of BC in the soil with less interference.

As previously mentioned, it is impossible using this method to distinguish between organic N and black N. BC is typically only 60-90% C, with other elements characteristic of organic molecules (N, O, H, P, S) comprising the remainder of its structure (Goldberg, 1985). However, the CN ratio of laboratory-produced BC ranges from 49.0 (grass char) to 529 (wood char) (pers. obs.), and so could be considered on average to be about an order of magnitude larger than that of a typical Leicester soil (the average C:N of soil samples in this study was 14.03 [S.E. = \pm 0.45]). Therefore, the N content of the soil is not likely to be raised in proportion to C by the N contained within the structure of BC. The cause of the heightened N levels could be the ability of BC to retain organic molecules in the soil (or again, perhaps the propensity of organic soil to retain BC). The large surface area of BC, enabling higher microbial colonization of the soil, could also be a contributing factor, as soil microbes play a crucial role in N cycling. Another possibility is that N-containing particulates or oxides are being produced alongside BC during combustion, and thus exhibiting a similar pattern of soil deposition. In future work, it may be useful to determine the proportion of N that is bioavailable, and whether this is affected by BC. This would

give an indication to the source of the N, and what effects the heightened N values could be having on the soil. Lorenz and Kandeler (2005), in a previous study of Stuttgart soils, reported a slight positive correlation between BC levels and soil biotic properties, which may be further corroboration of the effects seen here.

Although soil N content increased with BC content, the positive correlation between SOC and BC outstripped that of N and BC, and this was reflected in the positive correlation between the CN ratio and the BC concentration of soils. Again, it is difficult to determine to what extent this positive correlation is due to the molecular composition of BC, and to what extent it is the result of alterations of BC to soil processes and chemistry. This trend could be due simply to the higher CN ratio of BC than soil, or it could be that BC preferentially sorbs to molecules with a high CN ratio. Perhaps the compounds that sorb to BC are further along the decomposition process (and thus have a higher CN ratio), or these older molecules are more mobile in the soil and therefore more likely to encounter a BC particle for adhesion. Alternatively, it could be that molecules bonded to the surface of BC encounter higher rates of decomposition due to microbial colonization of pore space, and thus a higher CN ratio of OM results from association with BC. However, if molecules that are attached to the surface of BC are subject to a higher rate of decomposition, this may refute the idea that BC is causing the retention of SOC in the soil. More research is needed into the fate of BC-bound organic molecules in order to elucidate the effects of BC in the soil, particularly pertaining to soil C sequestration.

Conclusion

BC comprises a significant proportion of urban SOC, and stocks vary significantly by land-use type. In particular, garden woody land exhibits highly concentrated soil BC. Further research is needed to determine the precise cause of these phenomena, although proposed causes include the high surface area and surface roughness of woody foliage, differential land management in urban wooded areas, and burning practices inherent to homes and gardens, particularly in a historical context. Rural agricultural land has significantly lower BC than urban land, which is likely caused by its distance from industrial, residential, and transport emissions, as well as tillage of BC to greater depths, and increased rates of erosion due to tillage (Gregorich *et al.*, 1998). However, BC was still found to constitute over one-fifth of agricultural SOC, and more than one quarter of urban SOC in surface soils.

High soil BC values co-occur with elevated soil N and SOC, a trend that is more clearly observed in non-residential land. This implies favourable effects of BC on soil fertility and soil OC sequestration, although the underlying mechanisms that have caused these correlations are not clear from this study. Furthermore, the ecological consequences of these alterations to soil biogeochemistry are little understood, and require clarification in order to determine the most favourable land management strategies for ecosystem function and soil C storage.

Leicester's soil BC represents a large C stock that has been transformed by human activity into a geological reservoir. These inputs of BC could have many different effects on the soil, from priming SOC and increasing soil respiration, to concealing losses of labile SOC due to anthropic activity, or causing the retention of SOC that would otherwise be lost to leaching or decomposition. Understanding BC stocks is essential to understanding changes

in SOC. Many management practices now aim to increase the amount of C stored in the soil in order to mitigate the effects of global warming (Prentice, 2001; Smith, 2008; Ostle *et al.*, 2009). BC and SOC must be distinguished from one another in order to understand whether these changes are actually a result of such efforts as increased plant biomass and lower soil disturbance, or simply driven by historical and present-day pollution. This research highlights the need for an improved understanding of the fluxes of BC within soils, in order to determine the role of BC in the C balance of the UK.

Table 3.4: Leicester land use type area and BC density, and estimation of total BC in surface soil (0-7 cm) by land use type. BC density is provided with one S.E. of the mean.

Land cover	Area (km²)	Proportion of greenspace (%)	BC mg cm⁻³	Tonnes BC in surface soil
Herbaceous	19.1	46.0	12.7 ± 1.03	17,000
Woody	9.3	22.4	12.2 ± 1.13	7,920
Garden herbaceous	8.4	20.2	17.5 ± 2.43	10,300
Garden woody	4.7	11.3	28.2 ± 3.84	9,280
Total	41.5			44,500

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Chapter 4: Small-scale heterogeneity in soil BC concentrations in relation to the presence of tree foliage and proximity to a main road.

Introduction

At present, the principal source of BC in the UK is diesel fuel combustion (Novakov and Hansen, 2004), global production of which is estimated at 7.96 Tg per year (Cooke and Wilson, 1996). Diesel fuel burning and industrial and residential coal use produce 90 % of British BC emissions (<http://www.aeat.co.uk/netcen/airqual/statbase/emissions/bs-99.html>). Once produced, BC particles can remain in the atmosphere for days or months before settling into a terrestrial or aquatic reservoir (Ogren and Charlson, 1983). BC that is contained within the atmosphere has numerous repercussions for humans and the environment. In particular, atmospheric BC is known to have a variety of adverse effects on human respiratory health, principally due to the occurrence of organic pollutants and heavy metals in diesel emissions, which can be adsorbed by the surface of particulate BC (Bucheli and Gustafsson, 2000; Wang *et al.*, 2003; Cornelissen *et al.*, 2004; Masih and Taneja, 2006). The permeation of small BC particles into the alveolar region of human lungs has been linked to elevated incidence rates of bronchitis and asthma in cities (Künzli *et al.*, 2000), and heightened levels of particulate matter in the air have been linked with increased death rates in humans (Hoek *et al.*, 2002; Kreyling *et al.*, 2003). The health risks created by particulate matter are widespread: between 1997 and 2002, an estimated 25-55 % of the EU population was subject to concentrations of particulate matter that exceeded levels deemed safe for 24-hour exposure.

Aerosol BC is known to have a strong radiative forcing of 0.9 W m^{-2} , due to its ability to absorb solar energy, thus heating the atmosphere, and is a major contributor to global warming (Andreae, 2001; Ramanathan and Carmichael, 2008). Furthermore, the deposition

of BC onto snow and ice has created a detrimental climate change feedback loop, in which melting is caused by the light-absorbing properties of BC, then causing a shift in ground cover from highly light-reflective snow to the darker, more light-absorptive ground underneath (Jacobson, 2002). For this reason, BC is thought to be the cause of one-half of arctic warming (Shindell and Faluvegi, 2009). Due to these, and other consequences of aerosol BC (Chapter one), understanding the dispersal of pollutant BC is crucial to reducing its deleterious effects on human health and the environment.

Diesel exhaust particles, including BC, are known to have high spatial heterogeneity in the atmosphere, which is strongly influenced by proximity to and levels of diesel fuel-burning traffic (Patel *et al.*, 2009). For example, although BC represents only a small proportion of aerosols worldwide (Fig. 4.1, the soot and biomass burning portions), it was found to constitute 97% of aerosols in New York City (Novakov, 1982).

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Figure 4.1. Global aerosol proportions by major categories (adapted from Andreae, 1995)

There are many other reports of high variation in BC concentration over a small spatial scale, and of the reduction in concentrations of aerosol particulate matter with increasing distance from roads (Shi *et al.*, 1999; Zhu *et al.*, 2002). In a study of urban American high schools in New York City, BC aerosol concentrations were found to be significantly higher at schools located near main highways (Patel *et al.*, 2009). In two cities in Norway, atmospheric black smoke concentrations (used as a proxy for BC concentration) were 2.6 times higher near a main road than at urban locations set > 200 m away from the nearest road (Janssen *et al.*, 1997). A study by Glaser *et al.* (2005) found that BC concentrations in a roadside soil near Bayreuth, Germany were twice as high as those in an agricultural soil 50 m away from the road. He and Zhang (2009) found that mean soil BC concentrations in Nanjing varied from

0.91 g kg⁻¹ in a historically residential area of the city to 8.62 g kg⁻¹ in a traditionally industrial sector.

The extent to which local atmospheric BC variation is mirrored in small-scale soil BC concentration depends on particulate deposition; how long BC remains airborne, and thus subject to aeolian transport, before it settles onto the soil. There are five main types of aerosol deposition: sedimentation, which is settling due to gravity; diffusion, random motion of particles resulting in a general movement down their concentration gradient; turbulence, deposition via air movement; occult deposition, the absorption by particles of ambient moisture from mist or clouds, and subsequent descent towards the earth; and washout, the encapsulation of particles in falling rain or snow droplets (Beckett *et al.*, 1998). The prevalence of these modes of deposition, as well as the climatic conditions which cause them (e.g. humidity, precipitation, wind), influence the length of time that BC remains in the atmosphere, how far it travels while contained there, and where it is eventually deposited. For example, high levels of humidity and precipitation will decrease the mean residence time of an aerosol (Cao *et al.*, 2009), and thus the mean distance between its source and site of deposition. Wet deposition is particularly relevant to urban areas, as the urban heat island effect has been known to increase average rainfall in cities (NASA, 2002). High winds can also contribute to turbulent deposition (Beckett *et al.*, 2000), but are also linked with particulate transport. Particularly pertinent to aeolian deposition in cities is the effect of roadways on air movement; traffic speed and vehicle size are known to influence, and typically increase, atmospheric turbulence (Cooper, 1984; Baker, 1996), and thus the transport and deposition of aerosols. Furthermore, the type of surface upon which an aerosol is deposited will determine whether it remains adhered, or becomes resuspended by air movement. Rough, wet, and electrically charged surfaces are more conducive to aerosol settling (Pye, 1987).

Various models have been produced to account for the distribution of stocks of aerosol BC (Cooke and Wilson, 1996; Liousse *et al.*, 1996; Park *et al.*, 2005), and estimates of global BC storage in the soil and sediments are also available (Kuhlbusch and Crutzen, 1995; Masiello and Druffel, 1998; Masiello, 2004). However, as yet the spatial heterogeneity of BC on a small scale has not been accounted for. Moreover, much of the work published thus far has focussed on the BC created by wildfires, with little emphasis on the BC produced in urban environments. Thus, the final objective of this project was to detect small-scale patterns in the BC concentration of urban soils, in order to obtain a more detailed understanding of BC distribution across the city.

It was hypothesised that soil BC concentrations would be higher in soil beneath tree foliage. Various observations support this postulate: firstly, the relatively high concentration of BC observed in woodland soils across Leicester – as reported in Chapter three – indicate that woody vegetative cover may increase the amount of BC that accumulates in the underlying soil. Secondly, the “rough” structure of tree foliage creates a microclimate of turbulent air and higher wind speeds which cause trees to have the highest incidence of particulate deposition of any vegetation type (Fritschen and Edmonds, 1976; Manning and Feder, 1980). Thirdly, heavy metal pollution from the atmosphere has been found to settle in elevated quantities on woody vegetation due to the high ratio of its foliage surface area to the area of the ground it covers (Tam *et al.*, 1987; Gautam *et al.*, 2005). Maher *et al.* (2008) detected elevated deposition of heavy metals on the leaves of roadside trees, particularly on the roadside-proximal side of the tree, indicating that the trees effectively created a barrier to the dispersal of vehicle-derived pollutants. Due to the ability of woody foliage to act as a “scavenger” of particulate matter, soils beneath woody vegetation can also be expected to contain elevated levels of pollutants. For instance, forest soils in the UK have been found to

contain 3-20 times more lead than grassland soils (Gallagher *et al.*, 2002; Fowler *et al.*, 2004).

If detected, the preferential deposition of particulate BC upon woody vegetation and the underlying soil would have certain consequences for woody plants, for example altered soil biogeochemistry (Lehmann and Rondón, 2003) and decreased light transmission to leaves (Bergin *et al.*, 2001). Furthermore, it would indicate that trees are effective barriers to the spread of point-source aerosol BC pollution, perhaps reducing the residence time of BC in the atmosphere. An understanding of micro-scale BC distribution in an urban environment will also allow more refined estimates of BC stocks across the city and provide insight into how to reduce human exposure to high levels of atmospheric BC. Moreover, an understanding of the effects of trees on soil BC could enable strategic greenspace management to prevent the spread and shorten the atmospheric residence time of this pollutant, with the consequent benefit of improving human health and reducing the C footprint of urban areas. Bealey *et al.* (2007) concluded that the planting of large numbers of trees could reduce particulate matter concentrations by 7-20 % in Glasgow and Wolverhampton, and McDonald *et al.* (2007) similarly found that increasing the total tree cover in the West Midlands of the UK from 3.7 to 16.5 % would reduce mean particulate matter concentrations by 10 %. While the increase in tree cover suggested by these authors may not be entirely feasible, the strategic implementation of smaller planting regimes may still have a considerable benefit. Due to the “edge effect” of tree foliage on the deposition of aerosols, rows of trees can have a greater impact on particulate matter concentrations than will a forest (McDonald *et al.*, 2007).

Proximity to main roads was also hypothesised to influence the concentration of BC in the soil, due to the high level of diesel emissions generated by vehicular transport. Examining the concentration of soil BC at increasing distance from a main road could

indicate the extent of point source, traffic-related BC dispersal. This information may be interpreted from a human health perspective, as it could suggest the need for a 'buffer zone' between main roads and pedestrian or residential areas. A roadside study may also elucidate one cause of the heterogeneity of BC concentrations in the soils, facilitating future attempts to model urban soil BC stocks and refine urban C budgeting. Furthermore, the results of a roadside study are applicable to the relationship between BC concentration and tree foliage, as vegetative borders are a common management practice for reducing the spread of airborne pollutants near roadways (Adrizal *et al.*, 2008; Fuller *et al.*, 2009).

This study aimed to determine whether (i) tree canopies and (ii) proximity to a main road affected BC concentrations in the soil. This was achieved by quantifying BC in the soil of the central reservation of a main Leicester road at varying distances from large trees, and at various points along the roadside verge at increasing distance from the road. The study site, Narborough Road, was chosen because of its high traffic volume, the presence of wide grassed verges along its margins, and its use in previous studies of the relationship between vehicular transport and atmospheric pollutants (Agus *et al.*, 2007; Gulliver and Briggs, 2007; Chen *et al.*, 2008). It was hypothesised that soil next to tree trunks would have the highest mean BC concentration, and soil that did not lie under the canopy of the trees would have the lowest mean BC concentration, due to the collecting effect of tree foliage on airborne pollution. It was also hypothesised that soil nearest the road would have the highest BC concentration, as it lies closest to the source of pollution, and that soil BC concentration would have a negative relationship with distance from road.

Methods

The site chosen for this study was Narborough Road (NR), a typical urban arterial thoroughfare connecting the M1 and M69 motorways to Leicester city centre. The speed

limit on this road ranges between 30 and 50 mph, but was 30 mph near all transects in this study, and there are a number of junctions regulated by traffic lights along the extent of the road. Agus *et al.* (2007) estimate the average bi-directional traffic flow of Narborough Road to be 1100 vehicles per hour, a figure which varies considerably by time of day. Using data collected by Harris *et al.* (2003), Agus *et al.* (2007) estimate that the daytime traffic is comprised of 88.3 % cars, 7.6 % LGVs, 1.7 % HGVs, 1.7 % buses and 0.7 % motorcycles. The road is lined with shops, small businesses, and houses, and in places these buildings are separated from the road by a grassed verge. The land that comprises the central reservation and verge is council-owned and managed, and contains trees and herbaceous vegetation that is mown every two to four weeks during the growing season, with clippings left on the ground rather than collected. In total, the sampling strategy constituted 11 transects: five on the verge and six within the central reservation of NR.

Central reservation tree study

The central reservation transects were taken in relation to one of two trees (A or B), both being of the species *Prunus avium*. For each tree, three transects were taken: one > 5 m outside the expanse of the canopy (abbreviated NT, no tree), one under the canopy (UC), and one directly next to the trunk (TT). Tree A has a trunk circumference of 153 cm at breast height, and a canopy diameter of approximately 12m. Tree B has a trunk circumference at breast height of 147 cm, and a canopy diameter of approximately 13 m.

The central reservation was approximately 5 m wide throughout its entire length. Each central reservation transect was comprised of five sampling points: N0m signifies soil samples taken 0 m away from the northbound carriageway; N1m, 1 m away from the northbound carriageway; M, centre of reservation; S1m, 1 m away from the southbound

carriageway; S0m, 0 m away from the southbound carriageway.

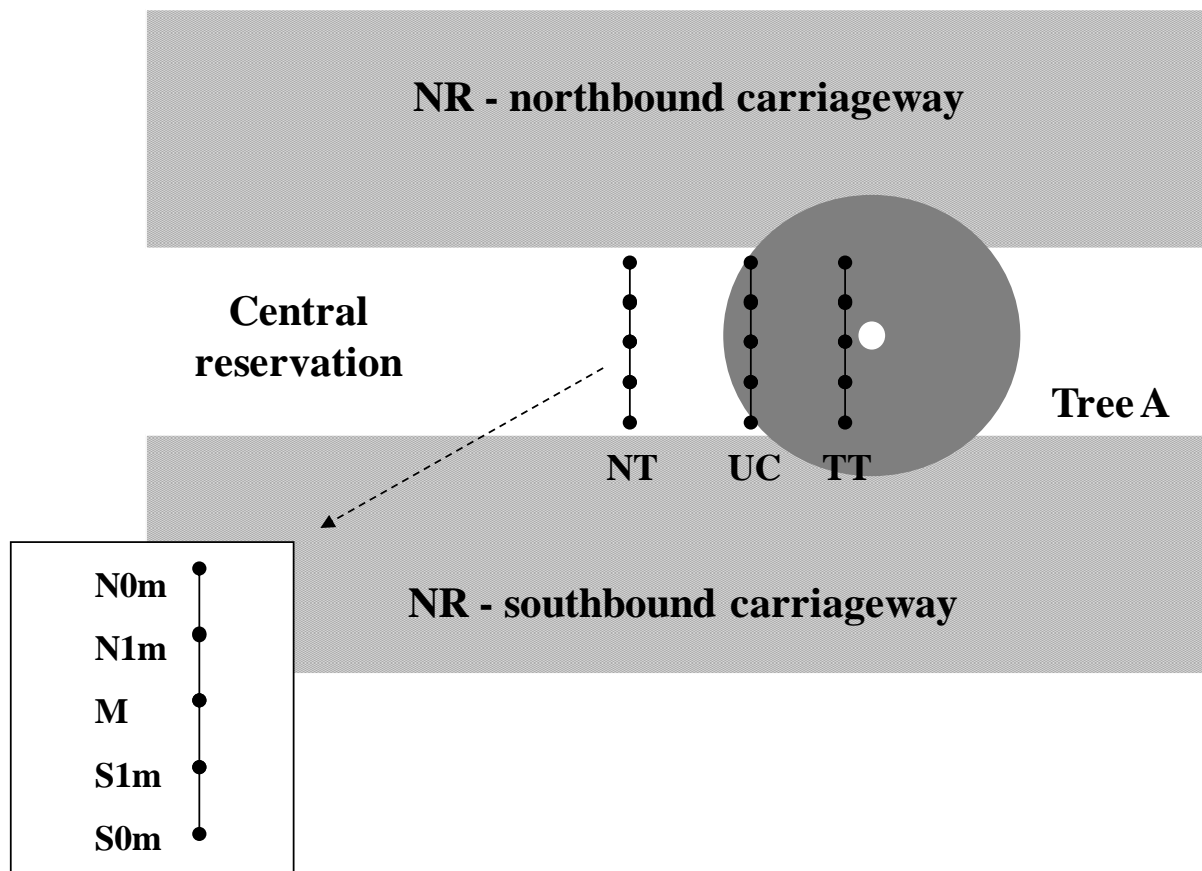


Figure 4.2. Diagram of sampling strategy for NR central reservation: solid grey area represents the extent of the tree canopy, solid white circle represents the tree trunk. A solid black line signifies a transect, and each ● indicates the placement of a soil sampling point, at which four replicate soil samples were taken. NT = no tree transect, UC= under canopy transect, TT = tree trunk transect. The sampling design for tree B was identical, apart from minor differences in tree size. The expanded transect diagram details the naming of each sampling point.

Table 4.1: Description of NR tree transects, denoting GPS location using British National Grid coordinates (± 4 m), sampling position in relation to the tree, and distance to the tree.

Transect Name	Coordinates	Transect Position	Distance to tree
T1 – tree A	SK 56962 02601	NT	11.4 m (6.2 m from tree canopy)
T2 – tree A	SK 56963 02605	UC	3.4 m
T3 – tree A	SK 56964 02607	TT	0 m
T4 – tree B	SK 56843 02422	NT	11.5 m (5.2 m from tree canopy)
T5 – tree B	SK 56843 02422	UC	3.5 m
T6 – tree B	SK 56843 02419	TT	0 m

Verge study

The roadside verge was used to study (i) how BC concentrations changed as distance from NR increased, and (ii) whether the presence of trees in the roadside verge affected BC concentrations in the soil. Transect sampling sites were chosen at a range of points along NR, contingent on the presence of a wide roadside verge for the verge transect study. Verge transects involved as many sampling points as reasonably possible (typically 4-6 points were selected at increasing distance from the road for each transect), depending on the presence of obstacles such as pavements and buildings. Every sampling point included four replicate surface soil samples (0-7 cm depth) taken at the same distance from the road, and all within 1m of each other. For both the tree and verge study, soil sampling and analysis was conducted according to the same procedure as reported in Chapter three.

Table 4.2: Description of NR verge transects, including British National Grid coordinates (\pm 4 m) of each transect's start and end point.

Name	Coordinates	Tree present
V1	SK 57793 04057 to SK 57777 04058	No
V2	SK 57803, 04084 to SK 57796 04093	Yes
V3	SK 56968 02631 to SK 56958 02639	Yes
V4	SK 56938 02586 to SK 56925 02597	No
V5	SK 56880 02494 to SK 56869 02503	Yes

Statistics

Statistical analysis of results was performed using SPSS (version 16.0, SPSS Inc.). Datasets were tested for normality using a one-sample Kolmogorov-Smirnov test (soil BC concentration data in decimal form were arcsin transformed for this analysis), and for homogeneity using Levene's Test of Equality of Error Variances (Levene, 1960). Verge data conformed to parametric test assumptions and were analysed with a Pearson's Correlation, where the linear correlation was considered significant if $p < 0.05$. A one-way ANOVA was used to analyse untransformed soil BC density data, and the Tukey *post hoc* test was performed to compare differences. Differences with a significance of $p < 0.05$ were reported.

Results

As expected, a negative correlation was observed across all verge transects between soil BC concentration and distance from NR (Fig. 4.3). Variability was highest closer to the road; roadside (0 – 8 m away from NR) BC values ranged from 0.78 to 4.42 %, whereas land

8.1 – 25 m away from the road contained 0.52 – 1.54 % BC. The highest BC concentrations were found in transect V4, which also exhibited the most variation in BC concentration, while transect V5 exhibited lowest BC concentrations and variability.

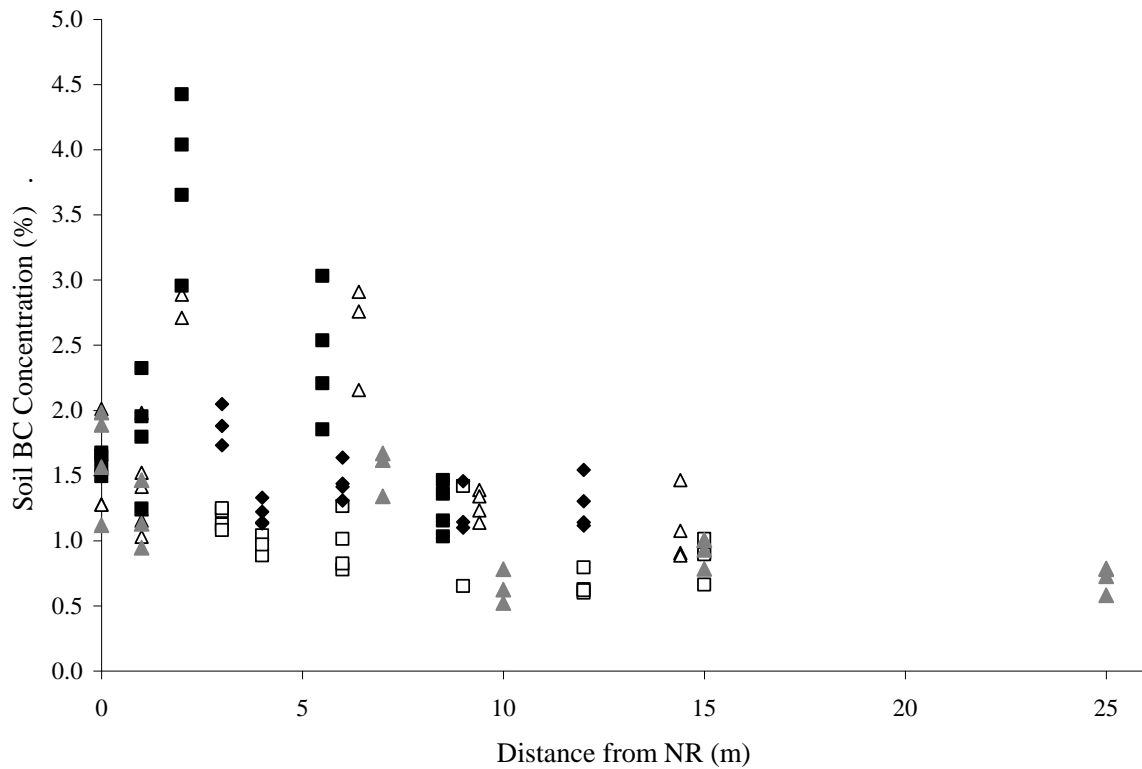


Figure 4.3. Relationship between BC concentration and distance from road; white square, V1; black diamond, V2; white triangle, V3; black square, V4; grey triangle, V5. Inverse-square correlation: $R = 0.5812$, $p < 0.001$, $N = 104$.

When soil bulk density was used to calculate BC density in the soil, and the four replicate BC values from each site averaged, a similar negative correlation was detected (Fig. 4.4).

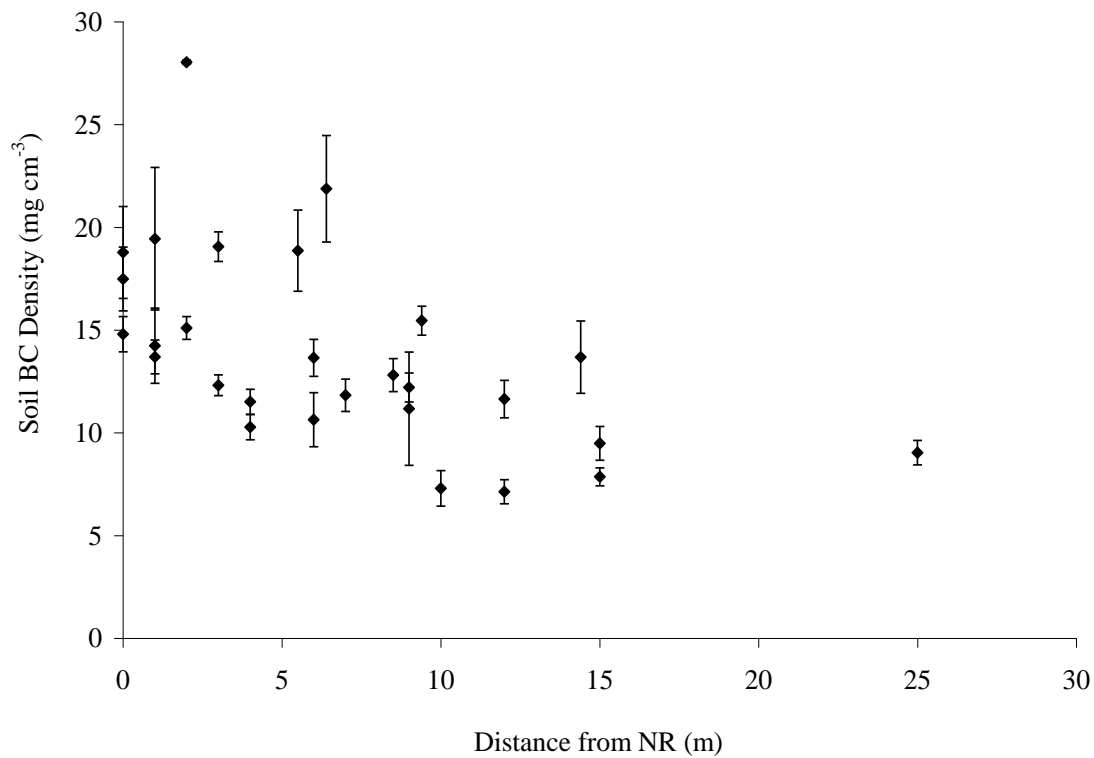


Figure 4.4. Mean density of BC in the soil at increasing distance across the roadside verge of NR (± 1 S.E.). Inverse-square correlation: $R = 0.5689$, $p < 0.001$, $N = 101$.

The central reservation transects did not reveal any significant impact of position within the central reservation (whether N0m, N1m, M, S1m, or S0m) on soil BC (Fig. 4.5). However, soils taken from under the tree canopy (UC samples) were found to have a significantly lower BC concentration than soil from NT or TT transects ($F = 5.452$, $p = 0.006$, d.f. = 2, 112). Furthermore, soil sampled near tree A (in NT, UC, and TT transects) had a significantly higher mean BC concentration than soil sampled near tree B: $2.40\% \pm 0.07$ compared to $2.00\% \pm 0.07$.

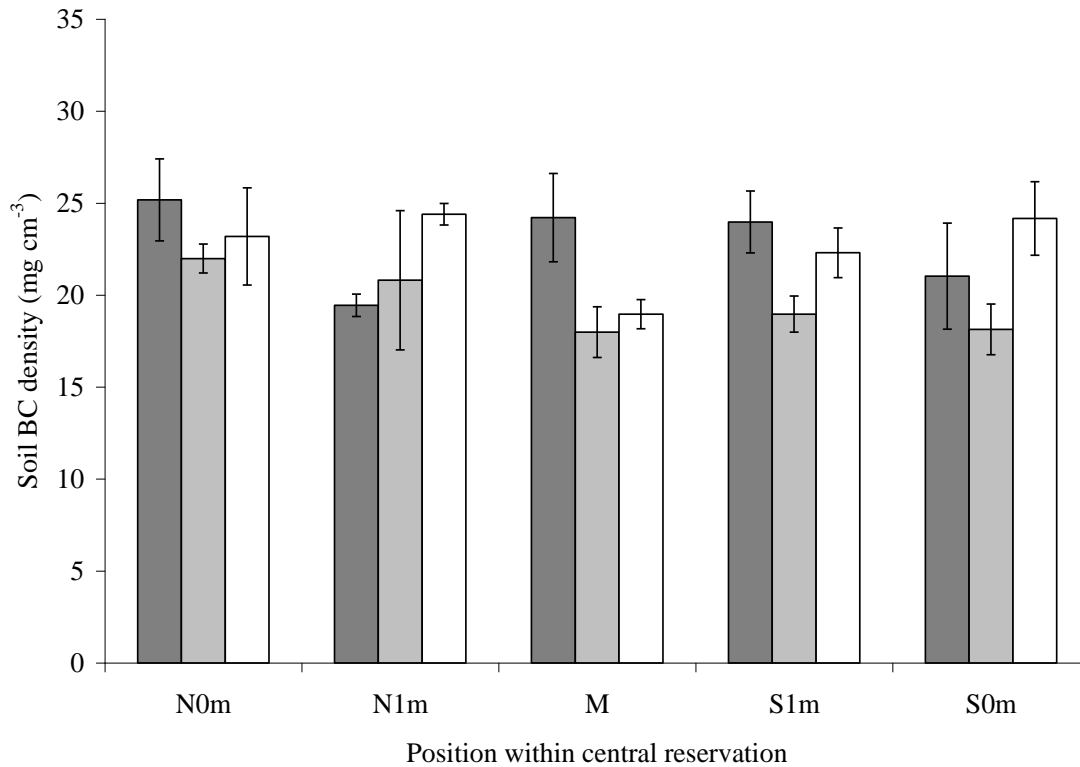


Figure 4.5. The mean BC density of soils taken from transects across the central reservation (± 1 S.E.). Dark grey bars, NT soils; light grey bars, UC soils; white bars, TT soils.

Three of the five verge transects contained a tree, and the location of the tree's trunk, along with soil BC concentration, is depicted in Fig. 4.6. Transects V5 and V3 both indicate a peak in BC concentrations on the road-proximal side of the tree, then a sharp drop in soil BC concentration on the road-distal side of the tree. Transect V2 does not exhibit this trend, although soil samples were not taken from the road-distal side of the tree so it is not possible to know whether soil BC concentrations decreased in the lee of the tree's canopy. Figure 4.7 displays the same data for the two transects that did not contain trees, V4 and V1. While V1 has relatively similar BC concentrations throughout the transect, indicating no peaks or troughs in BC concentration, transect V4 contains a very sizeable peak in soil BC concentration that cannot be explained by the presence of a vegetative buffer.

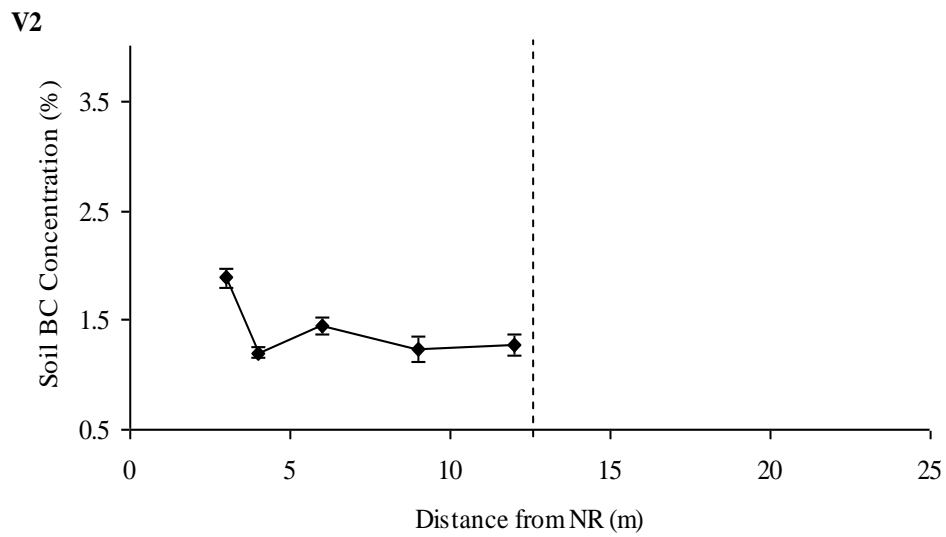
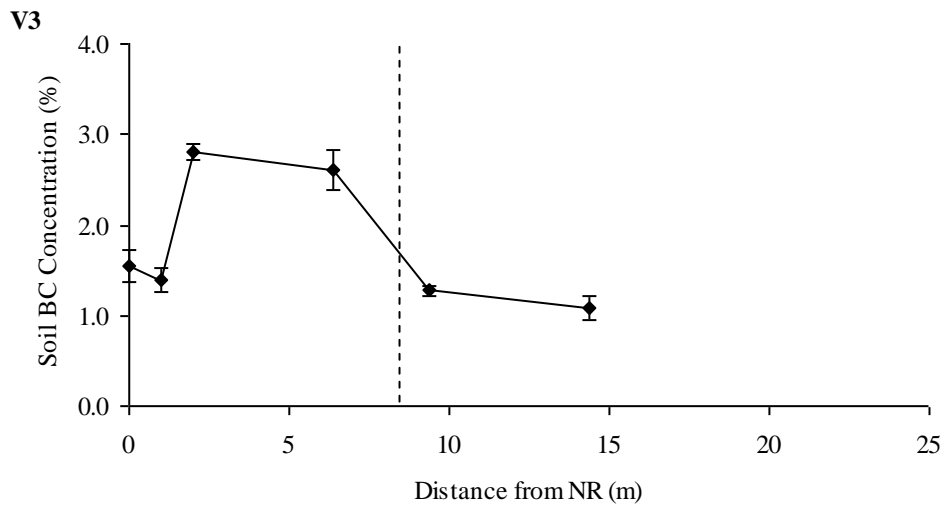
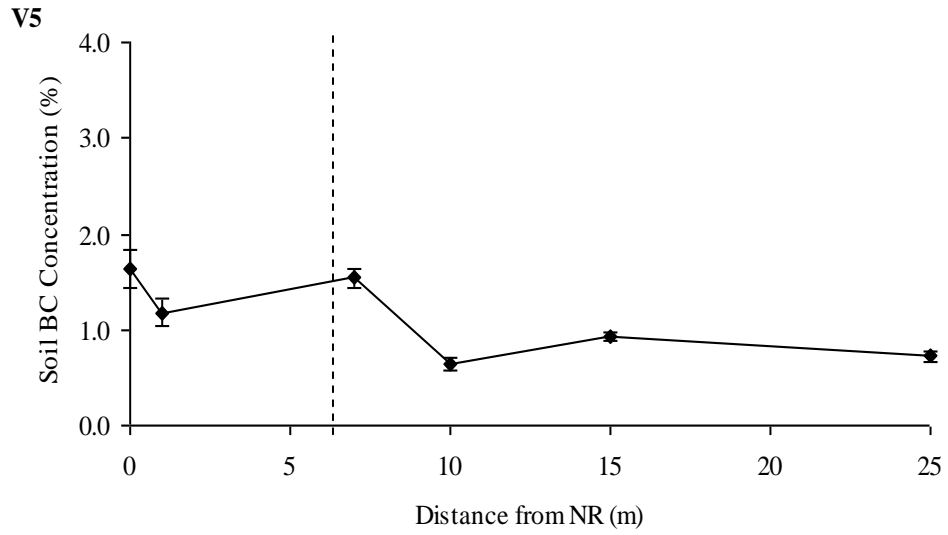


Figure 4.6. The relationship between BC concentrations in the soil across the verge (± 1 S.E.), and presence of trees. - - - - indicates position of tree.

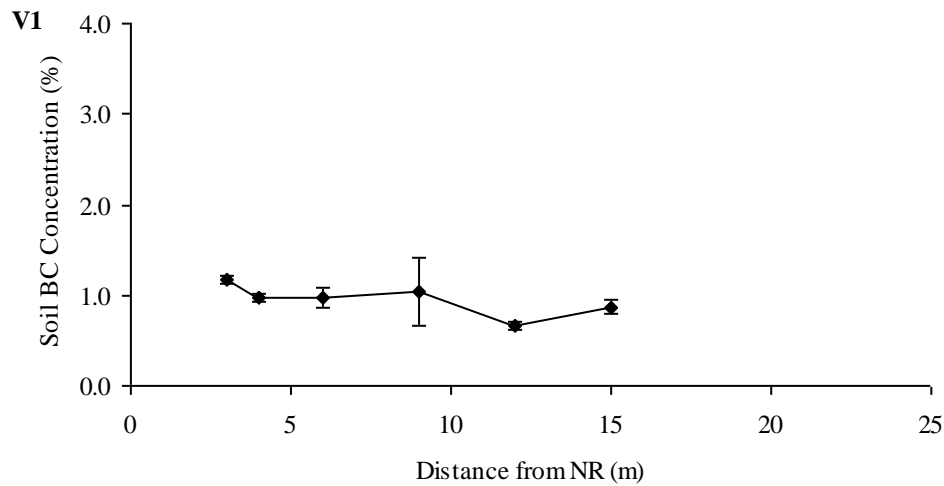
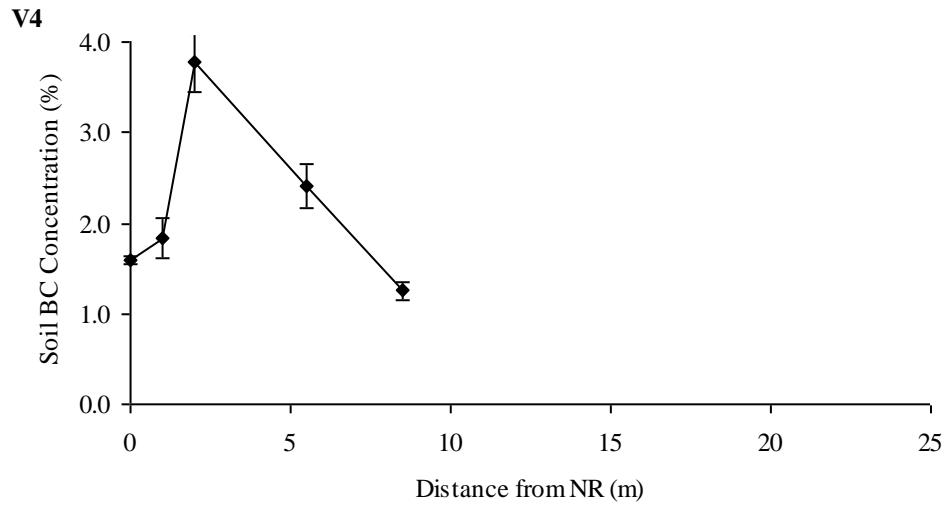


Figure 4.7. The relationship between BC concentrations in the soil across the verge (± 1 S.E.), in the absence of trees.

Discussion

BC and distance to road

The negative correlation between soil BC and distance from road conforms to the hypothesis that higher BC concentrations are found nearer the road. This trend may be due in part to the deposition of BC soot particles produced by motor vehicles. Soil within two meters of the road had an average BC density of 18.1 mg cm^{-3} , which is almost 50 % higher than the mean BC density found in Leicester non-domestic herbaceous land of 12.7 mg cm^{-3} , and higher than the BC density of all Leicester land use types except garden woody land (Chapter three).

However, these data indicate that the maximum deposition of BC is not closest to the road, but often peaks a few meters away from the kerb, which may be due to air turbulence created by the movement of vehicles.

The cause of the high amount of variation in soil BC concentration nearer the road is uncertain; one possible explanation, however, is the abrasion of tyres and brake lining. Both of these substances are made of C-rich organic polymers, and can often char as they are eroded during braking. Hildemann *et al.* (1991) found laboratory-produced tyre dust to contain 15.3 % BC, and brake lining dust to contain 2.61 % BC. Moreover, the majority of tyre and brake dust particles are coarse in size (these particles can be up to 100 μm in diameter, whereas aggregates of soot particles rarely exceed 1 μm [Ogren and Charlson, 1983; Boulter, 2005]), and this could account for the lack of homogeneity in BC content between replicates taken < 8 m away from the road. This hypothesis is substantiated by the location of V4, the transect with greatest variation in BC concentration. Transect V4 is a grassed verge next to the northbound carriageway, just 80m south of a large junction, where heavy braking is likely to occur. However, the many mechanisms of deposition, and environmental factors that influence these processes, are also likely to have contributed to the heterogeneity in soil BC concentrations. It was difficult to measure the full effect of vehicular emissions on soil BC levels, due to the presence of houses along the span of NR preventing sampling at greater distance from the road, and an urban environment is likely to contain a high level of non-point source aerosol BC, the deposition of which will interfere with a point-source (traffic) pattern being detected in the soil. Furthermore, the high incidence of physical disturbance to the soil that occurs in urban areas (Lorenz and Kandeler, 2005) will confound the detection of particulate deposition patterns in the soil.

It can be seen from this study that pavements, which are typically located 0 – 3 m away from NR, are located in areas of especially high soil BC concentration. These

heightened soil concentrations imply that atmospheric BC is similarly elevated in these areas, causing pedestrian exposure to high levels of airborne pollution. The results of Maher *et al.* (2008) point to a similar conclusion: concentrations of lead and iron, measured from the surface of foliage taken from roadside vegetation, were highest at ~0.3 and 1.5 – 2.0m above the ground, indicating that roadside particulate pollution is highest at human head height. Further work is needed to determine what proportion of near-road soil BC is due to coarse particles such as tyre and brake lining particles, and what proportion is aerosol BC of a much smaller particle size, in order to elucidate the relationship between aerosol and soil BC concentrations. An understanding of the distribution of BC detected in urban soils would also indicate areas of heightened risk to human health. Identifying areas of elevated exposure to aerosol BC will facilitate urban planning that reduces respiratory health risks to cyclists and pedestrians.

Verge tree study

Of the three roadside verge transects that contained a tree, two of these (V5 and V3) showed a marked increase in BC in soil sampled within 1 m of the tree trunk. The tree in the third transect (V2) was approximately twice as far away from the road as the tree in the first two (12 m as opposed to 5 m and 7 m), and only a slight increase in soil BC was observed under the canopy of this tree. It is interesting to note that soil samples taken next to the trees in V5 and V3 had 69% and 107% more BC than soil in the surrounding area, respectively. The increase in soil BC under trees along the verge may signify that the hypothesised BC-concentrating effect of tree foliage is occurring in these areas, which are more removed from the homogenising effects of air turbulence caused by vehicular traffic than are the trees in the central reservation. A substantial drop in soil BC concentration can also be seen on the road-distal side of the tree in transects V5 and V3, which may indicate that trees are reducing the dispersal and atmospheric residence time of particulates. However, of the two transects that

did not contain trees, one also exhibited a sharp peak in BC concentrations (V4). Thus it is difficult to conclude from this pilot study whether trees were having a significant effect on soil BC concentration. In future studies, higher replication of the transect design may help to produce more conclusive results.

Maher *et al.* (2008) found that the concentration of heavy metals on roadside foliage was higher on the road-proximal side of trees, indicating that the vegetation served to prevent the transport of aerosols and, by providing a surface for their deposition, shorten their residence time in the atmosphere. Due to the simultaneous production of heavy metals and BC in diesel fuel burning, and the affinity of heavy metals for the surface of BC particles, the metal concentration of foliage may be indicative of the amount of BC coating foliar surfaces. However, direct quantification of BC on the surface of leaves taken from roadside plants may be the best means of understanding the effect of vegetation on BC transport and deposition. In particular, the quantification of BC on leaves of plants at increasing distance from the main road could be examined in conjunction with soil BC concentrations to determine how plant presence affects soil BC distribution. As in the Maher *et al.* (2008) study, the concentration of BC on leaves growing at different heights from the ground may help to understand the settling of aerosol BC from the atmosphere, and to explain why BC concentrations seem to peak a few meters from the kerb. The sorption of BC particles to foliage is likely to vary by plant species, due to factors such as leaf surface area, the physical properties of the leaf surface (e.g. roughness or waxiness) and stomata, and the height distribution of leaves (Hewitt, 2003; Freer-Smith *et al.*, 2004). Research into these areas may help to determine the most effective means of using vegetation as a barrier to the transport of vehicle-derived pollutants.

Central reservation tree study

The hypothesised effect of trees on soil BC was not observed in the central reservation study. Although soil BC was found to be significantly lower in UC soil than NT or TT soil, TT soil did not contain significantly more BC than UC soil. It is possible that the lower BC concentrations found in UC soils are due to tree foliage preventing some atmospheric BC from settling on the ground below, and that the BC caught on leaves is being washed down the tree's branches and into the soil directly surrounding the trunk. However, as the soil from outside the canopy had the same BC concentration as the soil next to the trunk, it is difficult to say whether these results can be attributed to the effect of tree leaves.

There are many possible confounding factors that could prevent a relationship between BC and tree foliage being detected, particularly in a central reservation. Perhaps one of the most difficult influences to account for is the amount of air turbulence caused by passing traffic. Constant air movement may have a homogenising effect on particulate concentrations in the atmosphere (Coppalle, *et al.*, 2001), thereby making it more difficult to detect differences in the pattern of BC concentration in the soil. Turbulent air can also disturb the deposition of leaf litter, spreading the leaves which will settle, decompose, and release any adhered BC particles. Coarse BC-containing particulates, such as abraded tyre and brake lining particles, are another confounding factor within the central reservation. These are unlikely to be subject to extensive atmospheric transport due to their large size, and it is more probable that they are deposited near the site of their production, regardless of tree canopy cover.

The higher soil BC concentrations near Tree A relative to Tree B could be due to tree position along NR. Tree B is positioned 300 m away from the nearest junction, whereas Tree A is located only 60 m away from a junction. One effect of Tree A's proximity to the junction is that there will likely be more braking by vehicles in this stretch of the road, which leads to the abrasion of tyres and brake lining. Furthermore, the stoplight at the junction

causes frequent queues of cars idling, then accelerating in the stretch of NR preceding the junction. These actions will increase the mean length of time spent by a car next to Tree A. Furthermore, acceleration requires more energy than the maintenance of a steady speed, so this will also cause increased BC emissions near Tree A, much in the same way that increased emissions are detected near uphill stretches of road when compared to downhill or flat (Kean *et al.*, 2003). These results indicate that soil BC values may vary due to the type of traffic flow along a road, and whether it is punctuated by stoplights, or free-flowing. Further replicates of this study design are needed to determine whether traffic flow is indeed the cause of this variation in soil BC concentrations. An effect of traffic flow on soil BC concentrations would be more effectively detected using traffic flow monitoring data than relative proximity to junctions. If such an effect were detected, it could help to refine estimations of soil BC stocks and to elucidate how soil chemistry is altered by road traffic.

Conclusion

Higher and more highly variable soil BC concentrations were found as distance to a main road decreased. This effect is attributed to BC produced by vehicular traffic, particularly diesel soot BC created by the combustion of diesel fuel, and BC produced by the abrasion of brake lining and tyre particles. The latter may be the cause of higher variability near the roadside, as abraded tyre and break particles are typically much larger than soot particles, and are thus likely to have a much shorter atmospheric residence time before settling into the soil, and to create higher spatial heterogeneity in soil BC distribution.

The results of this study indicate that there may be a BC-collecting effect of tree foliage, but that further research is needed to determine this. Such findings would support the already strong argument that the planting of woody vegetative buffers along roadsides will benefit urban ecosystems and human inhabitants. Heightened BC concentrations near the

road indicate that roadside verges are ideal areas for strategic use to prevent dispersal of traffic-related pollution. Direct measurement of BC concentration on tree foliage would effectively further understanding of the role woody vegetation plays in reducing aerosol particulate matter concentrations. Future work should include a higher number of replicates, and an ideal study site would be a main road with alternating stretches of herbaceous and woody vegetation along its verge. Vegetative buffers, as well as sequestering C within their biomass, contributing to soil C inputs, and improving the health and enjoyment of pedestrians and cyclists, could reduce the length of time that BC remains in the atmosphere before it assumes a more innocuous role in the soil.

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Chapter 5: Conclusion

This thesis has evaluated, tested and applied CO, a modified approach to BC detection, which demonstrates distinctly improved BC quantification in comparison to the previously-established CTO method. The advantages and disadvantages of CO have been revealed, including > 90 % detection of n-hexane soot and charcoal, with 68 % wood char and 50 % grass char recovery, but also false-positive detection of shale and bituminous coal. These results represent a great improvement on the CTO method, which detects only half the available amounts of n-hexane soot, and negligible amounts of wood and grass char (Hammes *et al.*, 2007). The research presented in this thesis facilitates informed implementation of the new method in future studies. The high recovery of soot and charcoal by CO make it an ideal method for the detection of BC in urban soils, where diesel fuel and coal burning are likely to be the dominant soil BC inputs. However, CO is not as suited for use in ecosystems such as grasslands managed by firing where the charring of herbaceous biomass is the dominant BC input, nor for detecting BC in shale-rich sediments, or soils high in mature coal content. Detection of vegetative chars may be accomplished more accurately by an optical method such as thermal/optical transmittance and reflectance (Chow *et al.*, 1993; Schauer *et al.*, 2003), or photooxidation (Skjemstad *et al.*, 1996; Skjemstad *et al.*, 1999), however these methods both have moderate interference from certain PIMs (Hammes *et al.*, 2007). Thus, as a catch-all method, the CO technique is probably one of the most successful options currently available for detecting the entire spectrum of BC in soils, with minimal interference from non-BC materials.

The CO method was used to estimate the contribution of BC to total C in surface soils in Leicester, and revealed that over one-quarter of the soil C was BC, a finding which indicates that BC comprises a substantial, chemically distinct urban C pool. These results

demonstrate the need for an improved understanding of the production, distribution, and fluxes of BC in urban ecosystems, in order to better comprehend C storage and cycling in cities. BC seems to provide an exception to the rule of a threshold soil C capacity that is dictated by environmental and biotic conditions (Gupta and Rao, 1994; Freibauer *et al.*, 2004; Lal, 2004), as its accumulation in soils is not limited by primary productivity or decomposition rates. As such, urban soils may represent a large sink of anthropogenic C, biogeochemically dissimilar to the surrounding area. However, little is yet known about how stocks of BC change over time, and the relative magnitude of inputs and losses of soil BC. More work in this area is necessary in order to understand the role of urban soils as a C sink, and the effects that BC has on soil function and ecosystem services. For instance, the ability of BC to adsorb and immobilise inorganic and organic pollutants could increase the quality of water and food production in urban areas (Koelmans *et al.*, 2006; Leake *et al.*, 2009). The fertilising effects BC has on soil (caused by nutrient retention and increased porosity) could augment plant productivity, microbial and faunal densities, and help to counteract the soil degradation caused in areas of concentrated human activity (Pavao-Zuckerman, 2008). However, anthropogenic BC is a pollutant and as such could have detrimental effects on belowground ecosystems (Wardle *et al.*, 2008). A thorough understanding of its effects in soils is still lacking.

BC was shown to be heterogeneously distributed within Leicester, with significant differences in soil BC stocks between land use types. It is likely that there are several drivers of BC deposition onto and accumulation within urban soils; these include vegetation type, green space management, features of the built and green urban landscape, and location relative to pollutant sources. The results presented in Chapter 4 provide an indication that roadways and trees could be two such drivers, although further research is needed to clarify their role in BC dispersal. The observed increase in BC concentrations near roadways

corresponds with previous findings of source-specific BC dispersal patterns (Janssen *et al.*, 1997; Glaser *et al.*, 2005; Patel *et al.*, 2009), and implies that effective measures might be taken near roadsides to reduce the dispersal and atmospheric residence time of this pollutant, with a potential role for urban vegetation in this process. Preliminary results show that trees may be one such barrier to longer-range aeolean transport of BC, and connotes that woody vegetative buffers could help to reduce the detrimental effects of BC on humans and the environment. Further research incorporating a larger sample size and a variety of vegetation types is necessary to draw decisive conclusions about the existence and magnitude of this proposed effect.

In Leicester soils, SOC and N concentration, and soil CN ratio exhibited a positive correlation with soil BC content. There are many possible reasons for these observations, but the cause of these associations remains unclear. The diverse range of BC compounds with differing structures and properties not only complicates quantification, but also results in difficulties understanding its effects on soils and biogeochemical cycling. The porosity, stability, and molecular composition of BC vary based on feedstock type and combustion conditions (Sohi *et al.*, 2009). These characteristics of a BC particle may determine the extent to which it is colonised by soil bacteria and fungi (Thies and Rillig, 2009), thereby influencing its incorporation into soil aggregates and sorption to other soil molecules. Thus soil residence time and effects of BC in both urban and semi-natural environments can be highly variable, and more research is needed in order to determine the specific effects and cycling of BC in a range of soils. Nonetheless, these findings reinforce the suggestion that the BC content of urban soils creates unique soil characteristics, whether due to the preferential accumulation of BC in certain soil types, or BC-induced changes in soil biogeochemistry.

Despite the small proportion of land covered by urban land use (3% globally), these areas undergo extremely high levels of anthropogenic amendment, and are the source of 78% of global C emissions (Brown, 2001). Urban soils are heavily relied upon by over half of the world's population for a range of ecosystem services, from filtration of contaminants to support of flora and fauna, sequestration of C and providing a substrate for human activities and structures. The impact of urban areas extends greatly outside the urban area itself and thus the provision of ecosystem services in urban areas is highly relevant from both an ecological and social perspective. The effect of BC on ecosystem service provision within built-up areas is poorly understood and these results demonstrate the clear need for further research. Despite the ecological challenges they face, urban soils are the more vital for the high human population density they support. An understanding of anthropogenic amendments to urban soils, and the resultant changes in soil chemistry and ecology, is essential to preserving and enhancing these services for the future. Storage of BC in soils represents not only the sequestration of C and containment of pollution, but also a new challenge to understanding urban ecology.

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