Environmental Science & Technology

Article

pubs.acs.org/est

Black Carbon Contribution to Organic Carbon Stocks in Urban Soil

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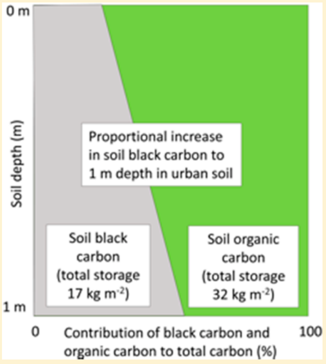
Supporting Information

ABSTRACT: Soil holds 75% of the total organic carbon (TOC) stock in terrestrial ecosystems. This comprises ecosystem-derived organic carbon (OC) and black carbon (BC), a recalcitrant product of the incomplete combustion of fossil fuels and biomass. Urban topsoils are often enriched in BC from historical emissions of soot and have high TOC concentrations, but the contribution of BC to TOC throughout the urban soil profile, at a regional scale is unknown. We sampled 55 urban soil profiles across the North East of England, a region with a history of coal burning and heavy industry. Through combined elemental and thermogravimetic analyses, we found very large total soil OC stocks (31–65 kg m^{-2} to 1 m), exceeding typical values reported for UK woodland soils. BC contributed 28–39% of the TOC stocks, up to 23 kg C m^{-2} to 1 m, and was affected by soil texture. The proportional contribution of the BC-rich fraction to TOC increased with soil depth, and was enriched in topsoil under trees when compared to grassland. Our findings establish the importance of urban ecosystems in storing large amounts of OC in soils and that these soils also capture a large proportion of BC particulates emitted within urban areas.



INTRODUCTION

Terrestrial ecosystems store nearly three times more carbon than is present in the atmosphere as CO_2, and soils hold approximately 75% (2344 Pg) of this total organic carbon (TOC) stock.[1−3] However, globally, soils have lost between 40 and 90 Pg of TOC as a result of land-use change increasing rates of organic matter (OM) oxidation, particularly from cultivation of agricultural land.[4] By comparison, anthropogenic emissions of CO_2 to the atmosphere are approximately 8.7 Pg yr^{-1},[2] with the atmospheric concentration of CO_2 rising by 3.2–3.8 Pg yr^{-1}, the remainder being sequestered by the oceans and terrestrial ecosystems.[5] In order to monitor changes in organic carbon (OC) stocks and their potential release to the atmosphere, signatories to the Kyoto Protocol are required to produce accurate inventories of OC held in terrestrial ecosystems. To date, such national carbon inventories do not include any measured urban carbon stocks. Instead, these areas have either been excluded from such assessments (e.g., in France)[6] or have been estimated using the very conservative assumptions that urban centers hold no soil OC and suburban areas have half the storage capacity of agricultural grasslands (in Northern Ireland;[7] in the UK;[8] and in the Republic of Ireland[9]).

Recent research measuring OC stocks in urban soils to 1 m depth,[10−13] including under roads and pavements,[11] has overturned these assumptions, for example showing that in a midsized UK city soil OC stocks in gardens are at least three times larger than the assumption-based estimates.[8] In the urban center, previously assumed to hold no OC, even under the roads and pavements the remaining soil holds more OC per unit area[11] than previously assumed to be found in gardens.[8] One component that may lead to increased concentrations of carbon in urban soils is the deposition of black carbon (BC). This comprises soots and chars arising from incomplete combustion of fossil fuels and biomass,[14−17] as well as geological sources such as coalified carbon[18] and graphite. BC is operationally defined as the group of compounds that are resistant to thermal or chemical degradation, dependent on the method of quantification.[19] As it is a relatively stable form of TOC some of which can be resistant to decomposition over geological time scales,[20−22] it is ubiquitous in soils and sediments globally.[15,18,20]

Knowledge of the soil BC pool, its interactions with, and contribution to TOC, is vital to better understanding the biogeochemical carbon cycle in soils.[22−24] This may help to provide improved predictions of the impact of global warming on CO_2 emissions from soil respiration since BC and OC differ markedly in recalcitrance.[22] This is reflected in the recent interest in adding biochar BC to agricultural soils to improve crop production and soil quality, to enhance OM content and increase sequestration of OC into soils potentially locking this up rather than it being returned to the atmosphere by respiration.[25]

Received: January 19, 2015
Revised: May 29, 2015
Accepted: June 11, 2015
Published: June 26, 2015

DOI: 10.1021/acs.est.5b00313
Environ. Sci. Technol. 2015, 49, 8339−8346

Due to variations in source materials, conditions of partial combustion, and condensation of residues, BC is physically and chemically highly heterogeneous occurring in a continuum of states from slightly charred biomass to highly refractory soots.[20−22] BC is characterized by greater thermal stability than most OM derived from decomposition of plant litter, and is often quantified as the portion of TOC that remains after heating to a specified temperature in an unrestricted air supply.[18] However, there are no standardized procedures that fully discriminate between BC and nonpyrolyzed OC,[26] and some methods do not distinguish between BC and coal, asphalt, and coal tar, which also occur in urban soils.[26,27] A widely used chemo-thermal oxidation method that uses a threshold of 375 °C gives only 25−86% recovery of standard BC reference materials,[18] and at this thermal threshold some recalcitrant OM produced by decay processes rather than pyrolysis may be included in the BC-rich fraction. In UK urban soil samples, it was found that the total carbon remaining after loss on ignition at 450 °C accounted for 64% of the BC detected by chemo-thermal oxidation following heating to 340 °C, with very strong linear correlations between these pairwise measurements.[26] These data suggest that for the kinds of BC found in urban soils, weight loss from samples on heating above 450 °C provides a robust means of quantifying BC abundance.

In urban areas in postindustrial countries, diesel powered vehicles are the dominant source of BC at present.[28] However, historically, emissions from the onset of the industrial revolution and associated urbanization came mainly from coal combustion by heavy industry and domestic fires and stoves.[17,28] Despite improvements in combustion technology, global emissions of BC have risen steadily from 5.3 to 9.1 Tg year^{-1} between 1960 and 2007 driven by population growth in developing countries increasing emissions from domestic heating and cooking and increasing numbers of motor vehicles.[28] Urban trees, as a result of their large foliar surface areas compared to grass or unvegetated surfaces, have been implicated in increasing the trapping and immobilization of fine particulate air pollution.[29] Pollution pathway modeling suggests that planting of additional trees in urban greenspaces of the West Midlands, UK, could increase the annual deposition and entrapment of airborne particulates by 10s−100s of tonnes per year, among which BC would be a major constituent.[30] This could lead to enrichment of urban soils with BC, in proximity to trees due to autumn leaf senescence or leaf surface runoff following precipitation.

To date, quantification of BC in urban soils is limited, focusing on topsoils sampled in the UK to 15 cm depth,[26] the U.S. to 10 cm,[31] and China to 20 cm.[32] The three UK cities studied previously, Glasgow, Stoke-upon-Trent, and Coventry, differ in their historical extent of heavy industry. Their soil BC concentrations ranged from <1−52.5 mg g^{-1}, in 10 samples randomly selected from each decile of between 740 and 1400 grassland topsoil samples per city ranked by their loss-on-ignition at 450 °C.[26] The highest urban topsoil BC concentrations in this case far exceed the average OC concentration (30.7 mg g^{-1}) of topsoil in British arable fields.[33] In Stuttgart, Germany, highly variable soil BC concentrations ranging from 0 to 294 mg g^{-1} were found in 10 urban soil profiles 0.4−1.6 m deep, most of which were contaminated with coal, ash, charcoal, plastics, and rubble.[23,34] As the sampling strategy used in this case targeted soils that had been affected by anthropogenic inputs it is unclear how representative these values are at a city-wide scale.

Here, we quantify the proportional contribution of BC to total organic carbon (TOC) to 1 m depth in soil in urban parks at a regional scale, using the North East of England as a case study area. This extends our previous measurements of TOC to 1 m depth in urban soils in the city of Leicester,[11] to encompass a much larger area within the UK. Urban parks provide one of the largest areas of greenspace within cities and towns and previous research has demonstrated that TOC concentrations within urban parks were representative of other greenspace land-uses.[12,13] Furthermore, we investigate the relationship between soil OC and BC with depth, and the effects of greenspace land-cover (tree or grassland) and soil texture on this relationship. We tested four hypotheses:

1. The BC-rich fraction makes an important contribution to urban soil TOC stocks in our study region where there is a long history of heavy industry and coal burning.
2. As with OC, soil BC-rich concentration declines with depth, but as a result of its inputs occurring mainly via aerial deposition it shows stronger proportional enrichment in the topsoil.
3. The BC-rich fraction in soil under trees is enriched relative to that in adjacent grassland as a result of pollutant trapping by the trees enhancing deposition into the soil.
4. TOC concentrations vary in relation to soil texture, with the BC-rich fraction forming a higher proportion of these stocks in coarser textured (low clay content) soils in which nonpyrogenic OC is more readily oxidized.

■ MATERIALS AND METHODS

Study Area. Our study focused on the North East of England (Figure 1), a region of 8600 km^2,[35] with a population of 2.6 million, over 80% of whom reside in urban areas.[36] Population density in the region is lowest in Northumberland at 62 people km^{-2}, and increases toward the south into the conurbation of Tyneside (Newcastle, Gateshead, North and South Tyneside) and through Middlesbrough with 2643 people km^{-2}.[35] The region experiences a temperate climate, receiving 803 mm of precipitation annually and average annual daily minimum and maximum temperatures of 5.1 and 13.1 °C respectively.[37] The characteristics of the dominant soils in the

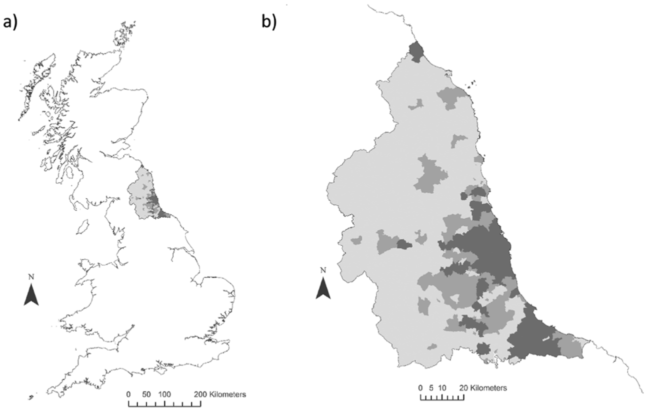


Figure 1. (a) Map of Great Britain with the study region of the North East of England shaded gray and (b) detailed map of the North East of England. Urban areas shaded dark gray, rural and urban fringe areas shaded pale gray. Data source: Office for National Statistics, 2011 rural/urban classification for small area geographies.

region are deep clays and loams. Vegetation within the urban areas is dominated by mown grassland, interspersed with patches of urban woodland and individual trees, the majority of which are deciduous.

Soil Sampling. A sampling strategy was designed to encompass the major urban areas across the North East of England. In each urban area publicly managed parks were identified, as these comprise some of the largest areas of greenspace, and permission was sought from the relevant authority to sample in two or more locations in each city or town. Parks were selected for soil sampling to 1 m depth as there is a much smaller risk of intercepting any of the buried infrastructure, such as pipes or cables, than soil sampling along roadside verges or within residential gardens.[11] Within each park soil samples were taken from at least one representative patch of managed grassland and beneath an individual park tree or area of woodland. Samples were taken, where possible, to approximately 1 m depth using a bulk density corer (Eijkelkamp, Holland). The soil cores were taken in 7 cm sections, assisted in the deeper samples by widening the access hole using an auger designed specifically to aid soil sampling.[11] In total, soil profiles were sampled at 55 sites, 25 beneath park grassland and 30 beneath trees.

Ten distinct soil types were sampled according to the National Soil Map for England and Wales, produced by Cranfield University: Brickfield 3, Wharfe, Dunkeswick, Nercwys, Wick 1, Alun, Crewe, Foggathorpe 1, Newport 1, Salop. These 10 soil types were then aggregated into seven groups determined by their detailed characteristics: deep sandy; deep loam; seasonally wet deep loam; seasonally wet deep red loam to clay; seasonally wet deep loam to clay; seasonally wet deep red clay; and seasonally wet deep clay.

Sample Preparation and Analysis. Individual soil core samples were dried at 105 °C for 24 h and then weighed. All soil samples were subsequently homogenized into a fine powder in an agate ball-mill prior to analysis (Pulverisette, Fritsch, Idar-Oberstein Germany), this left intact any stones or anthropogenic debris, such as plastics present within the sample. The milled samples were each passed through a 1 mm sieve and redried at 105 °C for 24 h.[11−13] Any material greater than 1 mm in diameter was retained, weighed, and subtracted from the initial dried sample weight to calculate fine earth soil bulk density (g cm^{-3}).[38] All carbon concentration values (mg g^{-1}) were converted to carbon density (mg cm^{-3}) using sample specific soil bulk density. To remove any inorganic carbon (IC) within the sample, 10 mL HCl (5.7 M) was added to 2.5 g of each soil sample,[26] which was then centrifuged at 1800*g* for 10 min, with the supernatant removed and the soil pellets dried at 105 °C for 24 h. These samples were subsequently analyzed in duplicate for TOC concentration in a CN analyzer (Vario EL Cube, Elementar, Hanau, Germany).[11] The TOC remaining after removal of IC comprises nonpyrogenic ecosystem-derived OC, referred to henceforth as OC, and also BC.

Thermogravimetric analysis (TGA), a method for measuring soil OC fractions in relation to their thermal stability,[39,40] was used to determine the relative proportions of the ecosystem-derived OC and the BC-rich fraction according to the method established by Lopez-Capel et al. (2005).[40] Soils were analyzed at three depths (approximately 10 cm, 50 and 100 cm) from each sample site. Approximately 40 mg of sample was heated in a thermogravimetric analyzer (PerkinElmer, TGA 4000) at a rate of 30 °C min^{-1}, from 20 to 1000 °C in an air flow of 30 mL min^{-1}, following initial trials that established weight loss at this temperature rate was not different from loss at 10 °C min^{-1}, and sample weight was recorded 200 times per minute. Previous research using TGA differential scanning calorimetry (TGA-DSC) has established the temperature ranges associated with the exothermic peaks for ecosystem-derived OC (200−470 °C) and the BC-rich fraction (470−600 °C) present in soils and these established temperature ranges were used herein.[41−43] The weight loss measured by TGA between 200 and 470 °C and 470−600 °C was used to determine the proportional contribution of ecosystem-derived OC and the BC-rich fraction respectively to the TOC measured using elemental analysis. For example, a soil with a TOC concentration of 5 mg g^{-1} with 80% of total weight loss measured between 200 and 470 °C, and 20% measured between 470 and 600 °C would contain 4 mg g^{-1} and 1 mg g^{-1} ecosystem-derived OC and BC-rich fraction, respectively. Weight loss associated with IC is unlikely to affect our estimates of the proportional contribution of OC and the BC-rich fraction to total soil OC, as thermal decomposition of IC tends to occur at a temperature range above that for the TOC fraction in soil (for example calcite, the dominant form of IC in soils, starts to decompose at approximately 620 °C reacting mostly in the range 700−800 °C).[44] We analyzed a subset of 18 soil samples, taken from six sample sites within the dominant soil type in the region, seasonally wet deep loam to clay, at the three sample depths used for TGA analysis using TGA-DSC coupled with quadrupole mass spectrometry (TGA-DSC-QMS), to validate the temperature ranges used herein (see Figure S1b for an example of the DSC curve and Supporting Information for details of the subset of soils and TGA-DSC-QMS methodology).

Although TGA has been used to assess the proportional contribution of OC and BC to TOC the loss of structural water from clay minerals present in the soil may affect this estimation.[19,40] We characterized the clay minerals present in the subset of using X-ray powder diffraction (XRD) (see Supporting Information for XRD methodology). This revealed that the dominant form of clay mineral present was chlorite (see Supporting Information Figure S2 for XRD analyses), which releases structural water in two clearly defined dehydration reactions between 550 and 600 °C and at 850 °C (see Supporting Information for details). However, we also analyzed CO_2 evolution by coupling a thermogravimetric analyzer with differential scanning calorimetry and quadrupole mass spectrometry (TGA-DSC-QMS; see Supporting Information for methodology). There was a highly significant correlation for both ecosystem derived OC and the BC-rich fraction in the subset of soil samples between estimation using TGA and CO_2 evolution from TGA-DSC-QMS (Supporting Information Figure S3) with a slope of approximately 1:1. This reveals that any weight loss associated with water released from the clays in our samples did not make a significant difference to estimation of soil BC concentration. In addition, calcite (or any other carbonate mineral) was not detected by XRD analysis.

Most methods for estimation of BC in soil, including TGA, do not distinguish BC from coal carbon in soils.[19] Coal seams are present in the bedrock geology of the North East, however, if coal were present in the soil samples there would be traces of sulfur species (m/z 32 and 64) detected by TGA-DSC-QMS at the temperature at which coal carbon fully oxidizes (~500 °C). In the subset of soils analyzed using TGA-DSC-QMS only one sample had traces of the sulfur species typically associated with the thermal decomposition of coal. These analyses suggests that

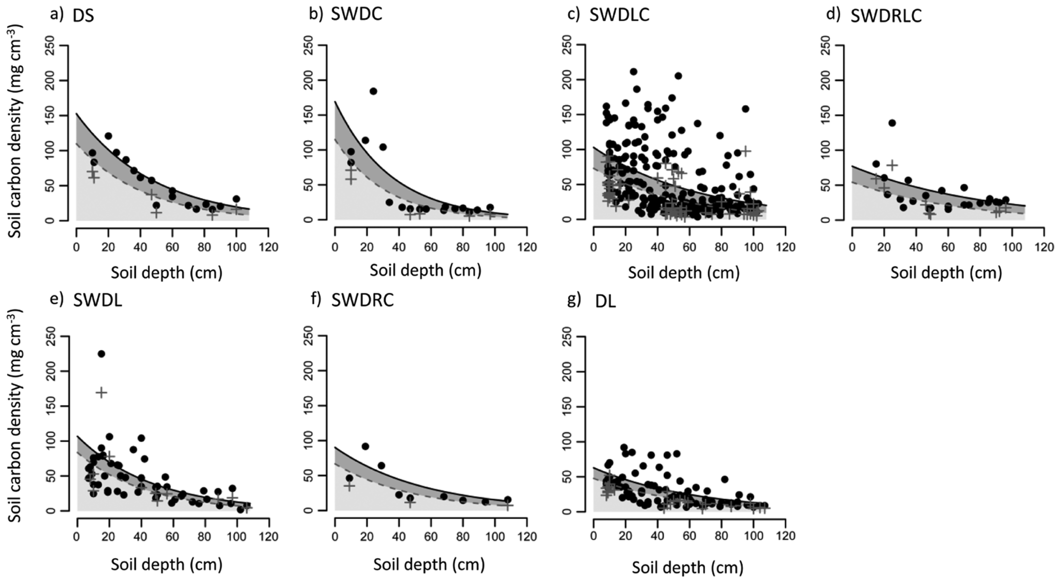


Figure 2. Modeled relationship between soil TOC (solid fitted line), OC (pale gray shaded area under dotted fitted line) and BC (dark gray shading between the fitted lines) by depth in urban areas for (a) deep sandy soils, (b) seasonally wet deep clay soils, (c) seasonally wet deep loam to clay soils, (d) seasonally wet deep red loam to clay, (e) seasonally wet deep loam soils, (f) seasonally wet deep red clay, and (g) deep loam soils. Data points for OC are shown (+), and for TOC are represented by black circles (●).

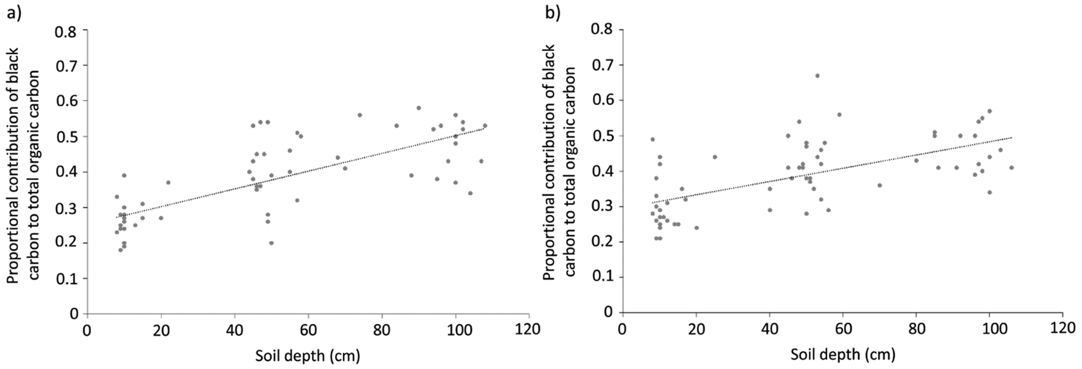


Figure 3. Proportional contribution of black carbon to soil total organic carbon beneath a) urban grassland (linear regression line y = 0.0025 (± 0.0003 SE) x + 0.252 (± 0.0024 SE)) and b) urban trees and woodland (linear regression line y = 0.0019 (± 0.0003 SE) x + 0.296 (± 0.0173 SE)).

while there may be some contamination of our urban soils with coal, it is likely that this will only occur at a small number of sites, and only at trace levels relative to the other sources of carbon detected as BC.

Statistical Analysis. We used Markov Chain Monte Carlo (MCMC) sampling methods to fit generalized linear mixed models (glmms) to the data in a Bayesian framework (see Supporting Information), and describe below the specific structures of those models in terms of the response variable, fixed explanatory variables and their interactions, and random effects. All models were run for 500 000 iterations, with a burnin of 50 000 iterations and a thinning interval of 250. All models mixed and converged well, with consistent outputs from multiple chains and low autocorrelation within chains.[45]

The first set of analyses fitted negative exponential curves of TOC by depth and its interaction with soil type and land-cover. The full model included two fixed effect interactions: depth and soil type, and depth and land-cover, with exponentially distributed residual error structure and a negative log link function. The second set of models fitted linear relationships between OC and depth and its interaction between soil type and land-cover. OC density and proportion of TOC as OC were arcsin transformed prior to analysis to ensure normality of residuals. For both sets of models, the full model and all nested fixed effects combinations were fitted twice: first with a random intercept by sampling site, and second with a random intercept and slope by sampling site. These two random effects structures were compared using the Deviance Information Criterion (DIC), where a smaller DIC indicates a better model fit. For all fixed effects combinations, DIC was much smaller for models with just a random intercept by site, indicating that slopes of depth curves are not consistently different between sites. Significance of fixed effects interactions was determined by evaluating the overlap of 95% credible intervals (CIs) for slope parameters with one another (e.g., if CIs for slope of the depth curve under trees do not overlap the mean slope of the depth curve under grass, there is a significant interaction between land-cover and depth). If fixed effects interactions were not found to be significant, then significance of categorical fixed effects was determined by evaluating the overlap of CIs for intercept parameters with one another (e.g., if CIs for intercept of the depth curve under trees do not overlap the mean intercept for the depth curve under grass, there is a significant influence of land-cover on TOC). All statistical analyses were conducted using the MCMCglmm package[45] in R (see Supporting Information for R coding).[46]

TOC stocks in kg m^{-3} were estimated by calculating the area under a depth curve (TOC in mg cm^{-3}) between 0 and 100 cm depth. To find depth curves for OC density, we scaled TOC density depth curves by fitted linear relationships between OC and depth. Stocks of OC, estimated using the TGA method, were found using the same method as for TOC using these scaled depth curves. As BC nominally constitutes the remainder of TOC in the soil, then estimated stocks of BC equal TOC-OC.

RESULTS

Total organic carbon density (mg cm^{-3}) declined exponentially with depth, and soil type significantly affected the intercept and slope of the relationship between TOC and depth (Figure 2; see Supporting Information Table S1 for model outputs). The concentration of the BC-rich fraction also declined with depth as hypothesized (Figure 2), however its proportional contribution to TOC increased with depth (Figure 3), contrary to the second hypothesis that there would be stronger proportional enrichment of the BC-rich fraction in the topsoil. In the surface soils (0−20 cm) median soil OC concentration was 42.0 mg g^{-1}, declining to 5.5 mg g^{-1} in the subsoil to 1 m. The BC-rich fraction declined from a median value of 16.8 mg g^{-1} in the topsoil to 5.7 mg g^{-1} at approximately 1 m depth. The relationship between soil depth and proportion of TOC that was the BC-rich fraction was not affected by soil type, contrary to the hypothesis that BC would form a higher proportion of TOC stocks in lighter textured soils, but it was affected by land-cover. The soils beneath trees had a greater intercept and shallower slope in their proportional contribution of the BC-rich fraction to TOC with increasing soil depth (Figure 3b) than those beneath park grassland (Figure 3a; see Supporting Information Table S1 for model outputs). Consequently, the upper layers of topsoil under tree-covered land contained proportionally more of the BC-rich fraction to TOC than the grasslands, consistent with our third hypothesis that BC concentration would be enriched beneath trees when compared to grassland. However, averaged over the full 1 m depth profile the proportions were not significantly different under the two land-cover types, with soil BC-rich fraction in grassland ranging from 18.2−58.4% of TOC (mean 37.4 ± 1.4 SE) whereas beneath trees it ranged from 21.1−66.9% (mean 38.5 ± 1.2 SE). There was a strong positive correlation between BC and OC ($r^2 = 0.79$; $F = 497.16$; $p < 0.001$) (Figure 4), the slope of the line (β) being 0.74, with nearly a fifth of samples lying above the 1:1 line and therefore containing more of the BC-rich fraction than OC.

TOC storage to 1 m depth was smallest in the deep loam soils at 31.7 kg m^{-2} and more than doubled to 64.9 kg m^{-2} in deep sandy soil (Figure 5). BC storage to 1 m depth was greatest at 22.9 kg m^{-2} (35% of TOC storage) in deep sandy soil, declining to 10.0 kg m^{-2} (32% of TOC storage) in deep loam soil (Figure 5). In the seasonally wet deep red clay soils the BC-rich fraction was the least important in terms of proportional contribution to TOC storage (28% of total), whereas in all other soil types it ranged from 32 to 39% of TOC (Figure 5). Contrary to the expectations of our fourth hypothesis, the coarser textured soils did not show higher proportional contributions of BC to TOC.

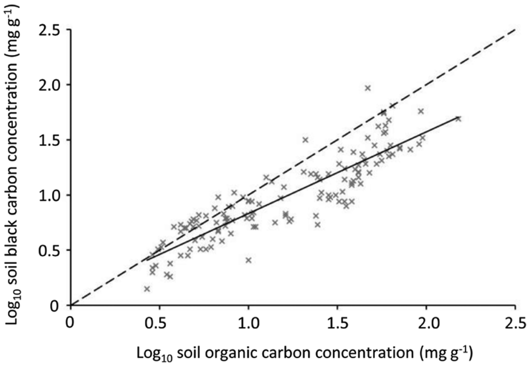


Figure 4. Relationship between soil organic carbon concentration (mg g^{-1}) and soil black carbon (mg g^{-1}). Continuous line is line of best fit ($y = 0.742$ (± 0.033 SE) $x + 0.089$ (± 0.043 SE)) Dashed line is a 1:1 line.

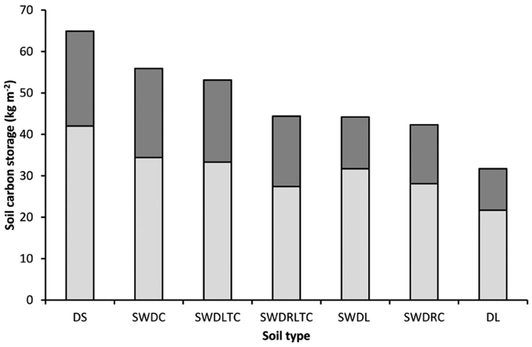


Figure 5. Proportional contribution of organic carbon and black carbon to soil total organic carbon storage to 1 m depth beneath deep loam (DL), seasonally wet deep clay (SWDC), seasonally wet deep loam to clay (SWDLC), seasonally wet deep red loam to clay (SWDRLC), seasonally wet deep loam (SWDL), seasonally wet deep red clay (SWDRC) and deep loam (DL). Pale gray shading represents organic carbon storage and dark gray shading represents black carbon storage.

DISCUSSION

We report large, previously unmeasured, soil TOC stocks in urban soils of the North East of England that range from 32 to 65 kg m^{-2}, and comprise a mixture of ecosystem-derived OC and a BC-rich fraction. To contextualize these findings, soil under seminatural vegetation in the UK national inventory stores 32 kg OC m^{-2},[8] and OC storage in peat, to 1 m depth, is estimated at 52 kg m^{-2}.[47] Our previous research found 14.4 kg m^2 TOC in soil across the entire urban area of Leicester, UK,[11] which exceeded the concentrations in agricultural pasture and arable soils in England and was only 3 kg m^{-2} lower than the average for soils under English woodlands.[8] Our new results corroborate, strengthen and extend the evidence[11,26] that UK urban soils are highly enriched in TOC and will make a much larger contribution to national soil OC stocks than estimated in the current inventory.[8]

Our research reveals, for the first time, the contribution made by the BC-rich fraction to urban TOC storage to a depth of 1 m (the required depth for the national carbon inventory), with values ranging from 10.0 to 22.9 kg BC m^{-2} comprising between 28 and 39% of TOC storage (Figure 5). The 10.0 kg BC m^{-2} storage value was similar to TOC in arable soils in the UK (12 kg m^{-2}).[8] However, to contextualise our findings, the upper storage estimate (22.9 kg BC m^{-2}) in deep sandy soil was in excess of estimated OC storage in UK pasture soils and only 3 kg m^{-2} less than UK woodland soils across all soil types.[8]

Rawlins et al.[26] measured concentrations of BC and OC in the top 15 cm of urban grassland soils in three UK cities. They reported that BC comprised a mean of 23.4% (±2.6 SE) of the topsoil TOC concentrations, with values ranging from 2.3 to 60.8%. The upper part of this range was consistent with the values recorded in the North East (18.2−66.9%) and was recorded in Glasgow, a UK city with a similar industrial legacy. However, the lower proportion was considerably greater in the North East when compared to the less heavily industrialized city of Coventry included in Rawlins analysis.[26] Topsoil median BC in Glasgow was 19.5 mg g^{-1},[26] similar to the median topsoil concentration of the BC-rich fraction in the North East urban soils (16.8 mg g^{-1}).

By comparison, 0−20 cm depth soils in Beijing (population >20 000 000) were found to have BC concentrations of 7 mg g^{-1} in the inner city, falling to 3.4 mg g^{-1} approximately 7 km from the center,[32] lower than the median BC concentration measured in the topsoils of the North East of England (16.8 mg g^{-1}). Across this urban gradient the proportion of TOC as BC fell from 39% in the center of Beijing to 33% outside the fifth ring road and to 31% in the rural plain.[32] However, there was a larger discrepancy between the concentration of the BC-rich fraction measured in the North East and the arid urban ecosystems of Phoenix, Arizona (a rapidly growing young city with low soil TOC concentrations), where topsoil (0−10 cm) BC concentration was only 2.5 mg g^{-1}.[31]

A regional scale study of rural, predominantly agricultural, topsoils in central France also found much lower BC concentrations (0.1−4.7 mg g^{-1}; average 0.8 mg g^{-1}) than in the present study, with the proportional contribution of BC to TOC ranging from 1 to 32%, averaging 5% of TOC.[24] In this case, crop residue burning was one of the major sources of soil BC, and there were no significant effects of proximity to the modest-sized urban areas (e.g., Orleans and Tours, with populations of 113 000−135 000) on agricultural topsoil BC concentration.[24]

To date, with the exception of the analysis of highly anthropogenically altered soils in Stuttgart,[23] nothing is known of the depth profile distribution of BC in urban soils.

As the relative importance, in terms of contribution to TOC, of BC increases with depth, previous studies focusing on BC concentrations in topsoils[26,31,32] are likely to have underestimated its contribution to urban carbon stocks. We establish that although the concentration of the BC-rich fraction in urban soil declines with depth, its proportional contribution to TOC increases under grass and trees, respectively, from surface values of 25% and 30%, to 50% and 49% at 1 m depth. A similar trend was observed in arable soils in Germany in which BC ranged from 3 to 10% of TOC in the 0−30 cm ploughed layer of the profile, but below this increased with depth to about 30% at 1 m.[48] The proportionally larger contribution of the BC-rich fraction to TOC in topsoil beneath trees when compared to grassland partially supported our fourth hypothesis that trees enhance particulate pollution interception,[49,50] increasing incorporation into the underlying soil with autumn leaf senescence and leaf surface runoff. However, the convergence of the contribution of the BC-rich fraction to TOC with soil depth and the lack of effect of trees versus grassland on BC stocks and proportions of TOC over the 1 m depth profile do not support our fourth hypothesis. The increasing proportional contribution of the BC-rich fraction with depth is likely due to two factors; first the greater stability of BC than OC in soil leads to relative accumulation at depth, and second some OC components at depth are so inert and heavily bound to clays that they may be operationally indistinguishable from BC using the TGA method.

Experimental studies investigating the fate of biochar BC applied to soil have revealed significant down-profile migration of particulate and dissolved components of BC.[51] This research suggests that extremely fine soot particles produced in the urban areas we have studied are likely to be washed and transported down urban soil profiles, into the less biologically active layers in which OC is mineralized very slowly, where they may help stabilize OC. Such processes may explain the greater storage of the BC-rich fraction in the coarsest textured soil (deep sand) and the associated greatest overall TOC storage as water transport would be greatest in these coarse textured soils. Further work is required to resolve the effect of soil type and the form of BC on the relative importance of rates of BC oxidation at different depths, and its transportation into the subsoil by leaching and bioturbation, controlling its profile distribution, accumulation, and effects on OC stability.

The strong positive relationship we have found between soil OC and the BC-rich fraction in urban soils in the North East suggests that these forms of pyrolyzed carbon may substantially increase the stability of OC. This is supported by research in the U.S. where soils sampled from former charcoal blast furnace sites were found to contain high concentrations of BC and also held significantly more OC than adjacent uncontaminated soils.[52] However, we need to interpret these results with some caution as a significant amount of OC may be generated during the pyrolysis that generated BC, with 50% being suggested as the proportion of BC:TOC for products of fossil fuel burning as detected by thermal oxidation,[32] so the relationship may reflect parallel inputs of BC and OC from fossil fuels. Furthermore, decomposition of BC is likely to release products that lack the thermal stability of their parent molecules and thus are functionally indistinguishable from OC in thermal analysis. Currently the absence of routine methods that reliably discriminate between fossil-fuel (geological) derived BC and ecosystem-derived OC (as biochar or of nonpyrogenic origins) hampers the detailed characterisations required to resolve some of these issues.

Our findings emphasize the importance of considering the contribution of BC to TOC especially in urban soil profiles, and corroborates recent evidence that urban-specific factors are needed to estimate carbon stocks and their variability in urbanized regions.[53] As a highly recalcitrant, although not completely inert, suite of compounds the residence time of fossil-fuel derived BC pools are likely to be 100s−1000s of years.[20−22] Our findings suggest this may enhance the storage of OC in urban soils, but this requires additional research to provide unequivocal evidence. BC is likely to continue to accumulate in urban soils due to ongoing emissions of this persistent pollutant from industry, vehicle emissions and biomass burning. Detailed characterization of the historical sources of BC in urban soils, their transformations, fate, and interactions with OC pools are now needed to gain better understanding of its impact on C cycling. This is also required to resolve the benefits of trapping particulate pollution in urban ecosystems and the role of trees in intercepting such particles and their subsequent fate in soils. Future research should focus on improving understanding of BC accumulation in soil, to 1 m depth, in urban areas with different industrial legacies and within the surrounding landscape at a national−global scale. Our studies raise the question as to the potential contribution of fossil-fuel derived BC in assisting sequestration of atmospheric CO_2 in soils via enhanced stabilization of ecosystem carbon inputs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supporting Information contains additional information relating to XRD, TGA-DSC-QMS, and statistical methodology including R coding for the GLMMS. Table S1 contains detailed model outputs. Figure S1 provides an example of TGA-DSC output from our soil analysis, Figure S2 contains an example of XRD output, and Figures S3 and S4 compare OC and BC quantified using weight loss from TGA and CO_2 evolved using QMS. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00313.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by EPSRC Sustainable Urban Environments Thematic grant EP/I002154/1. We gratefully acknowledge Northumberland County Council, Durham County Council, Newcastle City Council, North Tyneside Council, South Tyneside Council, Gateshead Council, Middlesbrough Council, Darlington Borough Council, and Sunderland City Council for access to their land. The soil type data were provided by Soils Data Cranfield University (NSRI) and the Controller of HMSO 2012. We thank Keith Penny for technical assistance.

■ REFERENCES

(1) Batjes, N. H. Total carbon and nitrogen in soils of the world. *Eur. J. Soil Sci.* **1996**, *47*, 151−163.

(2) Lal, R. Carbon sequestration. *Philos. Trans. R. Soc., B* **2008**, *363*, 815−830.

(3) Stockmann, U.; et al. The knowns, known unknowns and unknowns of sequestration of soil organic carbon. *Agric. Ecosyst. Environ.* **2013**, *164*, 80−99.

(4) Smith, P. Land use change and soil carbon dynamics. *Nutr. Cycling Agroecosyst.* **2008**, *81*, 169−178.

(5) Denman, K. L., et al. Couplings between changes in the climate system and biogeochemistry. In *Climate Change 2007: The Physical Science Basis*, ontribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.; Soloman, S., Qin, D., Manning, M., Chen, Z., Marqui, M., Averyt, K. B., Tignor, M., Miller, H. L., Eds.; Cambridge University Press: Cambridge, United Kingdom, 2007.

(6) Arrouays, D.; Deslais, W.; Badeau, V. The carbon content of topsoil and its geographical distribution in France. *Soil Use Manage.* **2001**, *17*, 7−11.

(7) Cruikshank, M. M.; Tomlinson, R. W.; Devine, P. M.; Milne, R. Carbon in the vegetation and soils of Northern Ireland. *Proc. R. Ir. Acad. B* **1998**, *98B*, 9−21.

(8) Bradley, R. I.; Milne, R.; Bell, J.; Lilly, A.; Jordan, C.; Higgins, A. A soil carbon and land use database for the United Kingdom. *Soil Use Manage.* **2005**, *21*, 363−369.

(9) Xu, X.; Liu, W.; Zhang, C.; Kiely, G. Estimation of SOC stock and its spatial distribution in the Republic of Ireland. *Soil Use Manag.* **2011**, *27*, 156−162.

(10) Pouyat, R. V.; Yesilonis, I. D.; Golubiewski, N. E. A comparison of soil organic carbon stocks between residential turf grass and native soil. *Urban Ecosyst.* **2009**, *12*, 45−62.

(11) Edmondson, J. L.; Davies, Z. G.; McHugh, N.; Gaston, K. J.; Leake, J. R. Organic carbon hidden in urban ecosystems. *Sci. Rep.* **2012**, *2*, 963.

(12) Edmondson, J. L.; Davies, Z. G.; McCormack, S. A.; Gaston, K. J.; Leake, J. R. Land-cover effects on soil organic carbon stocks in a European city. *Sci. Total Environ.* **2014**, *472*, 444−453.

(13) Edmondson, J. L.; Davies, Z. G.; Gaston, K. J.; Leake, J. R. Urban cultivation in allotments maintains soil qualities adversely affected by conventional agriculture. *J. Appl. Ecol.* **2014**, *51*, 880−889.

(14) Goldberg, E. D. *Black Carbon in the Environment: Properties and Distribution*; Wiley: London, UK, 1985.

(15) Kuhlbusch, T. A. J. Black carbon and the carbon cycle. *Science* **1998**, *280*, 1903−1904.

(16) Jacobson, M. Z. Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature* **2001**, *409*, 695−697.

(17) Novakov, T.; Hansen, J. E. Black carbon emissions in the United Kingdom during the past four decades an empirical analysis. *Atmos. Environ.* **2004**, *38*, 4155−4163.

(18) Agarwal, T.; Bucheli, T. D. Adaptation, validation and application of the chemo-thermal oxidation method to quantify black carbon in soils. *Environ. Pollut.* **2010**, *159*, 532−538.

(19) Hammes, K.; et al. Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. *Global Biogeochem. Cycles* **2007**, *21*, GB3016.

(20) Schmidt, M. W. I.; Noack, A. G. Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges. *Global Biogeochem. Cycles* **2000**, *14*, 777−793.

(21) Masiello, C. A. New directions in black carbon organic geochemistry. *Mar. Chem.* **2004**, *92*, 201−213.

(22) Lehmann, J.; Skjemstad, J.; Sohi, S.; Carter, J.; Barson, M.; Falloon, P.; Coleman, K.; Woodbury, P.; Krull, E. Australian climate-carbon cycle feedback reduced by black carbon. *Nat. Geosci.* **2008**, *1*, 832−835.

(23) Lorenz, K.; Kandeler, E. Biochemical characterization of urban soil properties from Stuttgart, Germany. *Soil Biol. Biochem.* **2005**, *37*, 1373−1385.

(24) Paroissien, J.-B.; Orto, T. G.; Saby, N. P. A.; Martin, M. P.; Jolivet, C. C.; Ratie, C.; Caria, G.; Arrouays, D. Mapping black carbon content in topsoils of central France. *Soil Use Manage.* **2012**, *28*, 488−496.

(25) Lehmann, A.; Stahr, K. Nature and significance of anthropogenic urban soil. *J. Soils Sed.* **2007**, *7*, 247−260.

(26) Rawlins, B. G.; Vane, C. H.; Kim, A. W.; Tye, A. M.; Kemp, S. J.; Bellamy, P. H. Methods for estimating types of soil organic carbon and their application to surveys of UK urban areas. *Soil Use Manage.* **2008**, *24*, 47−59.

(27) Yang, Y.; Mahler, B. J.; Van Metre, P. C.; Ligouis, B.; Werth, C. J. Potential contributions of asphalt and coal tar to black carbon quantification in urban dust, soils, and sediments. *Geochim. Cosmochim. Acta* **2010**, *74*, 6830−6840.

(28) Wang, R.; et al. Trend in black carbon emissions from 1960 to 2007. *Environ. Sci. Technol.* **2014**, *48*, 6780−6787.

(29) Beckett, K. P.; Freer-Smith, P. H.; Taylor, G. Particulate pollution capture by urban trees: Effect of species and windspeed. *Global Change Biol.* **2000**, *6*, 995−1003.

(30) McDonald, A. G.; Bealey, W. J.; Fowler, D.; Dragosits, U.; Skiba, U.; Smith, R. I.; Donovan, R. G.; Brett, H. E.; Hewitt, C. N.; Nemitz, E. Quantifying the effect of urban tree planting on concentrations and depositions of PM_{10} in two UK conurbations. *Atmos. Environ.* **2007**, *41*, 8455−8467.

(31) Hamilton, G. A.; Hartnett, H. E. Soot black carbon concentration and isotopic composition in soils from an arid urban ecosystem. *Org. Geochem.* **2013**, *59*, 87−94.

(32) Liu, S.; Xia, X.; Zhai, Y.; Wang, R.; Liu, T.; Zhang, S. Black carbon (BC) in urban and surrounding rural soils of Beijing, China: Spatial distribution and relationship with polycyclic aromatic hydrocarbons (PAHs). *Chemosphere* **2011**, *82*, 223−228.

(33) Emmett, B. A.; Reynolds, B.; Chamberlain, P. M.; Rowe, E.; Spurgeon, D.; Brittain, S. A.; Frogbrook, Z.; Hughes, S.; Lawlor, A. J.; Poskitt, J.; Potter, E.; Robinson, D. A.; Scott, A.; Wood, C.; Woods, C. *Countryside Survey: Soils Report from 2007*, Technical Report No. 9/07; NERC/Centre for Ecology & Hydrology (CEH Project Number: C03259), 2010.

(34) Lorenz, K.; Preston, C. M.; Kandeler, E. Soil organic matter in urban soils: Estimation of elemental carbon by thermal oxidation and characterization of organic matter by solid-state C-13 nuclear magnetic resonance (NMR) spectroscopy. *Geoderma* **2006**, *130*, 312−323.

(35) ONS. *Regional Profiles: Key Statistics—North East, August 2011*; Office for National Statistics: London, UK, 2012.

(36) ONS. *2011 Census Analysis—Comparing rural and urban areas of England and Wales*; Office for National Statistics: London, UK, 2013.

(37) Met Office. http://www.metoffice.gov.uk/climate/uk/datasets/# (accessed January 2014).

(38) Edmondson, J. L.; Davies, Z. G.; McCormack, S. A.; Gaston, K. J.; Leake, J. R. Are soils in urban ecosystems compacted? A citywide analysis. *Biol. Lett.* **2011**, *7*, 771−774.

(39) Siewert, C. Rapid screening of soil properties using thermogravimetry. *Soil Sci. Soc. Am. J.* **2004**, *68*, 1656−1661.

(40) Lopez-Capel, E.; Sohi, S.; Gaunt, J. L.; Manning, D. A. C. Use of thermogravimetry-differential scanning calorimetry to characterize modelable soil organic matter fractions. *Soil Sci. Soc. Am. J.* **2005**, *69*, 136−140.

(41) Fernandez, J. M.; Peltre, C.; Craine, J. M.; Plante, A. F. Improved characteristics of soil organic matter by thermal analysis using CO_2/H_2O evolved gas analysis. *Environ. Sci. Technol.* **2012**, *46*, 8921−8927.

(42) Lopez-Capel, E.; Abbott, G. D.; Thomas, K. M.; Manning, D. A. C. Coupling of thermal analysis with quadrupole mass spectrometry and isotope ratio mass spectrometry for simultaneous determination of evolved gases and their carbon isotopic composition. *J. Anal. Appl. Pyrol.* **2006**, *75*, 82.

(43) De la Rosa, J. M.; Lopez Capel, E.; Gonzalez-Vila, F. J.; Gonzalez-Perez, J. A.; Manning, D. A. C. Direct detection of black carbon in soils by Py-GC/MS, 13C NMR spectroscopy and thermogravimetric techniques. *Soil Sci. Soc. Am. J.* **2008**, *72*, 258−267.

(44) Washbourne, C.-L.; Renforth, P.; Manning, D. A. C. Investigation carbonate formation in urban soils as a method for capture and storage of atmospheric carbon. *Sci. Total Environ.* **2012**, *431*, 166−175.

(45) Hadfield, J. D. MCMC Methods for Multi-Response Generalized Linear Mixed Models: The MCMCglmm R Package. *J. Stat. Software* **2010**, *33*, 1−22.

(46) R Core Team. *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing, Vienna, Austria, 2012; ISBN 3-900051-07-0, http://www.R-project.org/.

(47) Milne, R.; Brown, T. A. Carbon in the vegetation and soils of Great Britain. *J. Environ. Manage.* **1997**, *49*, 413−433.

(48) Brodowski, S.; Amelung, W.; Haumaier, L.; Zech, W. Black carbon contribution to stable humus in German arable soils. *Geoderma* **2007**, *139*, 220−228.

(49) Tiwary, A.; Sinnett, D.; Peachey, C.; Chalabi, Z.; Vardoulakis, S.; Fletcher, T.; Leonardi, G.; Azapagic, A.; Hutching, T. R. An integrated tool to assess the role of new planting in PM_{10} capture and the human health benefits: A case study in London. *Environ. Pollut.* **2009**, *157*, 2645−2653.

(50) Tallis, M.; Taylor, G.; Sinnett, D.; Freer-Smith, P. Estimating the removal of atmospheric particulate pollution by the urban tree canopy of London, under current and future environments. *Landscape Urban Plann.* **2011**, *103*, 129−138.

(51) Major, J.; Lehmann, J.; Rondon, M.; Goodale, C. Fate of soil-applied black carbon: Downward migration, leaching and soil respiration. *Global Change Biol.* **2010**, *16*, 1366−1379.

(52) Cheng, C.-H.; Lehmann, J.; Thies, J. E.; Burton, S. D. Stability of black carbon in soils across a climatic gradient. *J. Geophys. Res.* **2008**, *113*, G02027.

(53) Vasenev, V. I.; Stoorvigel, J. J.; Vasenev, I. I.; Valentini, R. How to map soil organic carbon stocks in highly urbanized regions? *Geoderma* **2014**, *226−227*, 103−115.