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Realizing the opportunities of black carbon in urban soils: implications for water quality management with green infrastructure

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Abstract

Soils and associated microbial processes regulate the carbon cycle and provide a sink for atmospheric black carbon (BC). Particularly in urban areas, present and accumulated soil BC may act as an effective sorbent of anthropogenic contaminants in green spaces. We characterized carbon pools that have accumulated in urban soils (organic carbon, BC, and inorganic C) and determined soil physical attributes (soil texture, hydraulic conductivity) from urban soil assessments (surface and sub-surface horizons) carried out in eleven cities in the United States. We used both ordinary least squares and non-parametric classification and regression tree (CART) methods to discern trends in soil BC concentrations with regard to soil, landscape, and emission characteristics. We found that for all cities, regional traffic density and vegetation were good predictors of soil BC concentration. Additionally, the thickness of the top soil horizon explained additional variation in sub-surface BC concentration. Sites with coincident BC stocks and favorable infiltration rate were discussed as per their potential for improving water quality in multifunctional green infrastructure installations. In the broader sense, the high sorption capacity of existing, accumulated soil BC can contribute to regulation of contaminant cycling in urban areas and may enhance the overall value of urban soils in terms of ecosystem services.

Keywords

stormwater runoff; contaminant sink; ecosystem services; stormwater management; urban hydrology; passive green infrastructure

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1. Introduction

Urbanization is characterized by ongoing cycles of development and demolition, followed by fallowing or redevelopment. Throughout this process, the underlying soils act as a record of the local historical (e.g., residential) or regional (e.g., industrial) land use. One way in which this record is made is through airborne deposition of anthropogenic black carbon (BC) particles, which are defined as soot and chars derived from incomplete combustion of fossil fuels from industry, automobiles, home heating or biomass burning (Masiello, 2004; Morel et al., 2015; Schifman and Boving, 2015). Dry and wet deposition of these particles occurs in the proximity of an emission source, where it can accumulate in soils (Edmondson et al., 2015; Masiello, 2004; Shores et al., 2013; Van Metre et al., 2000). BC particles are highly recalcitrant forms of carbon that also act as strong environmental sorbents for other contaminants due to their hydrophobicity (Masiello, 2004; Morel et al., 2015; Cornelissen et al., 2005; Lohmann, 2003; Lohmann et al., 2005; Semple et al., 2013).

As a result of these different mechanisms of source, transport, and deposition of carbonaceous materials, soil carbon pools in urban areas differ from those in agricultural and forested land uses (Pouyat et al., 2002). Starting in the atmosphere, BC makes up ~0.5% of the rural aerosol mass compared to 10% for OC. This shifts dramatically, in urban areas with BC making up ~10% and OC 30% of aerosol masses (see Lohmann 2003 and references therein). In soils and sediments, the distinction between BC and OC in rural and urban landscapes is similar. In rural environments remote from urban centers, BC makes up <0.01% to 0.1% of dry soil weight, whereas in urban environments, mass proportion of the same ranges between 0.1 and 1% (Lohmann 2003, Bucheli et al. 2004). Overall, BC in soils is generally multiples less concentrated than OC (Lohmann 2003). Nevertheless, BC and SOC combine to comprise the largest global terrestrial carbon stocks (Jobbágy and Jackson, 2000). Among carbonaceous materials, BC is among the more recalcitrant forms and typically resistant to chemical, thermal, and microbial degradation, especially at ambient temperatures. This is in contrast to more labile sources of carbon (e.g., soil organic carbon (OC)), which are introduced to soils through deposition of plant biomass and its subsequent decomposition.

Differences in soil BC concentrations along urban to rural land use gradients have been extensively documented (Edmondson et al., 2015; Hamilton and Hartnett, 2013; Liu et al., 2011), where authors relate BC concentrations to emission sources and anthropogenic factors (Hamilton and Hartnett, 2013; Liu et al., 2011; Yang et al., 2010), and study the fate of BC as a function of soil texture and depth (Edmondson et al., 2015).

The presence of BC in the environment presents a set of tradeoffs among detrimental and nominally beneficial outcomes. Unlike SOC, BC and particulate matter in the air and work environment are considered a potential public health concern due to their carcinogenic properties (Chalbot et al., 2017; Eklund et al., 2014; Grahame et al., 2014; Singh et al., 2017). Due to their toxicological effects, BC particulates have also been documented as a threat to faunal biodiversity and habitat degradation in fragmented, urbanized ecosystems (Leonard and Hochuli, 2017). Yet, in urban settings that rely on green spaces to retain stormwater runoff, the physicochemical characteristics of BC in soil may contribute to

stormwater quality management through enhanced filtration (e.g., contaminant binding) in soils (Cornelissen et al., 2005; Koelmans et al., 2006; Lohmann, 2003). Since BC regulates the transport of contaminants, there is potential to improve the quality of or otherwise protect both surface and urban groundwater resources (Gabor et al., 2017). Examples of contaminants that strongly sorb to BC are ones commonly found in urban areas related to nonpoint source combustion processes (Cornelissen et al., 2005; Lohmann, 2003; Lohmann et al., 2005; Semple et al., 2013) and stormwater runoff (Mahler et al., 2005; Van Metre et al., 2000; Yang et al., 2010; Schifman et al. 2016), including heavy metals, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls, among other compounds.

Green infrastructure (GI) is traditionally aimed at management of stormwater quantity in response to the Clean Water Act (1972), such that runoff from impervious or saturated pervious surfaces is routed to a rain garden or other retention-detention strategy, instead of being routed directly to the wastewater collection system. The throughput of stormwater in these control measures can be considerable (Shuster et al., 2017), with the potential to receive and accumulate extremely high concentrations of contaminants dissolved or carried along by stormwater runoff (Schifman et al., 2016). In most cases, GI installations are comprised of engineered soils that aim to improve soil infiltration rates that allow quick drainage. As the capacity for contaminant capture generally correlates with standing stocks of sorptive organic carbon compounds (Lohmann, 2003; Weinstein et al., 2010), stormwater filtration can be also be improved by adding biochar or other sources of organic matter to these engineered soils (Mohanty et al. 2018, Lorenz and Lal, 2012; Reddy et al., 2014). The increasingly common use of blended, engineered soils to achieve water quantity and quality management objectives has resulted in stormwater control measures with improved contaminant filtration and removal (Reddy et al., 2014; Ulrich et al., 2015). However, atmospherically-deposited BC could also passively and additionally impart these same contaminant-regulating services to stormwater control measures that are otherwise provided by biochar amendments. These prospects raise the question as to whether urban soils have coincidentally sufficient hydraulic conductivity and standing stocks of BC to be beneficial in creating an effective sink for both stormwater runoff volume and the contaminants carried with it (Chen et al., 2014; Koelmans et al., 2006).

In order to determine urban land uses in which sufficient hydraulic conductivity and standing stocks of BC are coincident, we require novel urban soils data that includes information on soil hydrology and BC. Current soils databases do not have enough information on the physical and chemical characteristics of urban soils (Schifman et al. 2018) and do not typically document BC concentrations. To improve our understanding of urban ecosystems, urban soils need to be properly characterized (Shuster et al. 2014, Shuster et al. 2015 Herrmann et al. 2016) and the related field data needs to be included in geospatial databases. Availability of more complete urban soils databases lead to an improved understanding of how these characteristics relate to, for example, the number of nearby BC sources, such as particulate matter emitting facilities, annual average daily traffic counts, or landscape features that may influence the extent to which BC may be accumulated (e.g., depression area or canopy coverage) at the landscape level. This information can also be used for city planning and environmental health studies.

While preliminary relationships between BC concentrations in soil can be obtained using ordinary least squares, linear statistical model assumptions can be difficult to satisfy in these same models, especially where spatial environmental data is involved (Reimann and Filzmoser, 2000). Therefore, non-parametric approaches may hold promise to reveal relationships otherwise obscured by non-linearities in data. Classification and regression tree (CART) methods have been applied to discern trends in lead concentrations as a function of soil, landscape, and emission metrics (Schwarz et al., 2013). These statistical methods would also be effective in identifying areas where BC stocks and favorable soil permeability (i.e., infiltration rate) are coincident.

The objectives of this work are to study the environmental processes that shape our urban environments and expand the use of existing urban soil resources as passive regulation of stormwater runoff quantity and quality. With this work we present how atmospherically deposited BC from anthropogenic sources turns from a public health risk in the atmosphere to a contaminant sink in urban soils as it gets trapped, acts as a sorption site, and offers ecosystem services through downstream water quality protection. Here, we determined soil carbon pools (OC, BC, and inorganic carbon; IC) and soil physical attributes from urban soil assessments conducted in the core areas of eleven United States cities. We applied geospatial analysis and CART techniques to identify relationships between non-point BC sources and measured soil BC concentration and other landscape-level environmental factors.

2. Methods

2.1 Soil Sampling and Subsampling for BC analysis.

Samples were collected as part of an urban soils assessment between 2010 and 2016. Midsized cities in the United States were selected to represent the 10 of the 12 dominant soil orders as defined by the United States Department of Agriculture (USDA; excepting cryosols and gelisols). The cities assessed were: Atlanta, GA; Camden, NJ; Cincinnati, OH; Cleveland, OH; Detroit, MI; New Orleans, LA; Omaha, NE; Phoenix, AZ; Portland, ME; San Juan, PR; and Tacoma, WA. Site selection was opportunistic and acquired with right of entry permission granted by either municipalities or individual land owners. Within a given city, and for the sites available for assessment and sampling, different land use types were captured, which included vacant lots, parks, sports fields, school yards, parking lot medians, public right of ways, and GI installations. We measured hydraulic conductivity at near-saturated conditions with tension infiltrometers set to -2 cm hydraulic head (DecagonDevices, 2016). This method reduces variability associated with flow into macropores (Beven and Germann, 2013; Chen et al., 2014; Shuster et al., 2014), and results in a conservative measurement of hydraulic conductivity emphasizing the hydraulics of the surficial soil matrix.

Soil was sampled from cores measuring 7.6 cm in diameter taken up to a depth of 3.7 m with a tracked or truck-mounted Geoprobe unit; one core at each site. The soil cores were separated by horizon, and the top two horizons analyzed for different forms of carbon. Not all soil cores were analyzed for BC analysis. To select a subset of cores for analysis we first determined OC in the top horizons for each sampling site by loss on ignition (Ball, 1964) at 400°C for 16 hours and categorized the data into three groups (low, medium, high). Within

each of these categories, two to three topsoil samples were selected at random to capture variability within and across cities. This amounted to 9 sites per city, for 10 cities, except for New Orleans, where this analysis was limited to 5 sites due to limited amounts of archived soil. The average depth of the top and second soil horizons of the analyzed soils was 21.8 cm and 67.2 cm, respectively. Additional details on city-wide horizon depths are in Table S1.

2.2 Sample Preparation and Analysis.

Soil samples were air-dried, ground, and homogenized. Any anthropogenic materials, including glass, plastic, brick, wood chips, and rocks were removed before grinding. The samples were sieved using a standard size 60 mesh sieve (0.25 mm, $\phi = 2$) and dried at 60 °C for 24 h to constant weight. An average of 52.5 ± 9.4 mg of oven-dried sample ($n = 203$) was weighed out into 100 μ L platinum pans for analysis in a thermogravimetric analyzer (TGA Q500, TA Instruments, New Castle, DE). The sequence of isothermal or gradient conditions was: 80 °C for 20 minutes, 80 °C to 800 °C at 30 °C min⁻¹, under air flow at 30 mL min⁻¹. To determine SOC, BC, and inorganic carbon (IC) content, we calculated percent weight loss between 200–470 °C, 470–600 °C, and 700–800 °C, respectively (Edmondson et al., 2015). Even though we report IC concentrations in this manuscript, we recognize that the applied method is not ideal and may underrepresent IC concentrations. However, for BC and OC concentrations this method has been applied in other studies (e.g., Edmonson et al. 2015) and is valid.

2.3 Quality Assurance.

A temperature calibration using three Curie Temperature reference materials (Alumel®, nickel, and Ni 83% Co 17%) was carried out, and the material decomposition occurred within 3.7%, 0.2%, and 1.1%, respectively of the reference material's Curie Point. Chernozem 2013 standard reference material (SRM) for BC in soils (Schmidt and Noack, 2000) was used for quality control along with a lab standard. The lab standard was a homogenized loam soil sample (Sand: 37.6%, Silt: 48.4%, Clay: 14%) taken from the topmost horizon (0 – 40 cm) of a core acquired in Cleveland, OH. This sample was selected for its OC content (42.6 mg g^{-1}), which is close to the mean OC content of the top horizon for the analyzed samples (40.7 mg g^{-1}). Both standards were run prior to each of the 11 city-sets of samples. For most cities, a set would consist of 18 samples; New Orleans was the only exception with 10 samples. The average proportion of SOC, BC, and IC content in the 11 SRM samples was $31.5 \pm 1.1 \text{ mg g}^{-1}$, $12.5 \pm 0.3 \text{ mg g}^{-1}$, and $1.7 \pm 2.4 \text{ mg g}^{-1}$, respectively. The average BC fraction, BC content with respect to SOC content, was $0.4 \pm 0.01 \text{ mg g}^{-1}$ for the SRM. This falls well within the range of reported BC proportions of Chernozem reference materials in a comparison study using a similar method (Hammes et al. 2007). The average mass proportion of SOC, BC, and IC content in the 11 lab standard samples was $27.6 \pm 2.5 \text{ mg g}^{-1}$, $12.3 \pm 1.4 \text{ mg g}^{-1}$, and $2.2 \pm 0.2 \text{ mg g}^{-1}$, respectively; the BC fraction here was $0.5 \pm 0.02 \text{ mg g}^{-1}$.

2.4 Geospatial and Statistical Analysis.

A between city comparison of BC concentration in each horizon was carried out using an ANOVA to test whether statistically significant differences were evident. Georeferenced BC concentration data were tested for spatial autocorrelation and visualized as kriged plots

based on both covariance and semivariogram relationships, and inverse distance weighting (IDW) tools (ArcMap 10.5; ESRI Redlands, WA). For models that showed weak or no spatial structure in data (Krivoruchko, 2011), an Ordinary Least Squares (OLS) model was determined based on the ArcMap Exploratory Regression (ER) results. Landscape-level environmental data were generated for each sample point (Table 1) from commonly-available spatial databases. We used the ER tool to build models between BC and environmental data for each horizon and tested the strongest of the resulting models with the Global Moran's I tool as a final check whether the final OLS models were not biased due to spatial variability in the constituent data. We built classification and regression trees (CART) to predict BC concentrations in each of the upper (first) and lower (second) soil horizons with the R package rpart (R Core Team, 2016; Therneau et al., 2015). For each horizon we built a regression tree based on all available data, and then pruned it such that the complexity parameter of each model was equal to 0.015. The complexity parameter selected in both models showed relative errors of 0.64, such that the model for the top horizon had 5 splits, and that of the second horizon had three splits. Due to the small dataset, the observations were not separated into training and subsequent model validation datasets. Finally, we estimated the maximum sorption capacity of passive GI for selected contaminants of concern as a function of urban soil BC concentrations.

We calculated the average mass of BC in the metropolitan area of four cities (Atlanta, GA; Camden, NJ as the Philadelphia metropolitan area; Portland, ME; and San Juan, PR) from parameters obtained through our urban soils assessment and the area occupied by parks, golf courses, and cemeteries present in metropolitan areas using the ESRI World StreetMap. Using these measured soil characteristics and a modeled maximum sorption capacity parameter $\log(q_{\max, \text{phenanthrene : traffic soot}}) = 5.02 \text{ nmol/(g of sorbent)}$ obtained from Van Noort et al. (2004) we calculated the maximum BC sorption capacity in top horizons of urban green spaces. We selected to use the maximum sorption capacity of phenanthrene for traffic soot (Van Noort et al., 2004) because traffic soot is a common urban pollutant that is a combustion-by product and likely one of the main anthropogenic inputs of BC to urban soil. We base our calculations on the assumption that BC is evenly distributed (Table S1) throughout the top horizon at a particular site and that neither top horizon depth nor bulk density vary greatly within each of these selected cities.

3. Results and Discussion

3.1 Carbon pools.

Concentrations of soil organic carbon (SOC) had the broadest range from 4.3 mg g^{-1} to 228.6 mg g^{-1} in all samples, whereas black carbon (BC), and inorganic (IC) concentrations fell in narrower ranges from 3.0 mg g^{-1} to 103.5 mg g^{-1} , and 0.4 mg g^{-1} to 99.2 mg g^{-1} , respectively. (Table 2). On average, the SOC, BC, and IC concentrations in the first horizon were 1.73, 1.15, and 0.91 times higher, respectively, than those in the second horizon (Table 2). We attribute SOC being concentrated in the surface horizon to deposition of senescent plant and other carbonaceous materials and their subsequent weathering from at the soil-atmosphere interface (Decina et al., 2016). For BC accumulation we attribute similar mechanisms, i.e. deposition and weathering, however, we relate the source of BC to

particulate matter emitted from anthropogenic activities (Edmondson et al., 2015). Finally, the process of SOC mineralization produces IC (Edmondson et al., 2015), which is eluviated (i.e., washed in), and accumulates in the second, deeper horizon; with the co-product of this process, CO₂, lost to the atmosphere (Decina et al., 2016).

We next examined BC as a proportion of OC, and found that when averaged across all cities, the BC/OC ratio for the first and second soil layers were 0.29 ± 0.07 , and 0.73 ± 0.06 , respectively (Table 2). This ratio indicates that anthropogenic carbon sources either accumulate to a greater extent in the lower than upper horizon, or that BC remains steady across horizons and OC is more prevalent in upper horizons (Brodowski et al., 2007; He and Zhang, 2009; Zong et al., 2016). If BC does accumulate to a greater extent in the deeper soils layers compared to surficial soil, the mechanisms can be attributed to either translocation and washing in of BC particles from the surface, legacy accumulation (e.g., hearth ash, cinders), placement as human-transported backfill material, or dumping of petroleum distillates. However, the exact sources of BC were not determined. Alternatively, this accumulation may result from the preferential degradation or uptake of OC as a carbon source compared to the more recalcitrant BC (He and Zhang, 2009; Zong et al., 2016).

A between-city comparison for BC concentrations in each soil layer revealed that in both horizons, the BC concentrations differ significantly between cities ($F_{10,84}=3.2$, $p<0.01$ for 1st horizon, $F_{10,84}=7.1$, $p<0.001$ for 2nd horizon). Based on post-hoc analyses (Tukey HSD), we found that in the first horizon BC was always significantly higher in San Juan, compared to all other cities. In the second horizon, BC concentrations in Atlanta, San Juan, and New Orleans were significantly higher than in any other cities. Atlanta, San Juan, and New Orleans are located in subtropical climates and San Juan and New Orleans are also underlain by soils rich in organic matter. We hypothesize that beyond the anthropogenic influences that homogenize BC concentrations across all other cities, there are also natural processes that may further influence BC concentrations in subtropical cities like Atlanta, San Juan, and New Orleans.

A re-analysis of the data in the top horizon with San Juan removed from the dataset reveals that BC concentrations are not different between cities ($F_{9,76}=1.6$, $p=0.14$). Similarly, removing the cities in subtropical climates from the analysis of the second horizon also reveals no significant differences in BC concentrations in the second horizon ($F_{7,64}=2.1$, $p=0.51$). Based on these analyses and the BC/OC ratios, we can postulate that the processes that lead to homogenization exert a strong control on the distribution of BC in the top horizon, but less so in the deeper horizons. We hypothesize that the processes that control transport of BC to deeper depths, such as soil characteristics and microbial processes, exert stronger control on the redistribution of BC at depth than the anthropogenic activities that influence the surface horizon, which exhibits BC concentrations that are similar across cities. This finding is similar to others related to nutrient pools in surface soils (Groffman et al. 2014).

3.2 Regression relationships.

For the first horizon, BC concentration was best predicted by:

$$BC_{hz1} = 19.27 + (1.3 \times 10^{-4} \times AADT_{10\text{ km}}) - (21.74 \times NDVI)$$

with an adjusted $r^2 = 0.13$ (Table S2).

BC concentrations in the second horizon were best predicted by:

$$BC_{hz2} = 17.14 + (1.7 \times 10^{-4} \times AADT_{10\text{ km}}) - (0.13 \times hz_1) - (21.22 \times NDVI)$$

with an adjusted r^2 of 0.31 (Table S3). Additional information on model selection can be found in the supplemental information.

Each predictive model shows that BC concentration for both horizons is dependent on regional traffic density, which is estimated within a 10 km radius of the site as the annual average daily traffic ($AADT_{10\text{ km}}$), and local density of vegetation (as NDVI). The thickness of the surface horizon (hz_1) inversely correlates with BC concentration for the second horizon. Numerous studies have documented the contribution of regional traffic pollution to BC concentrations in the atmosphere, where it is then available for deposition (Bläsing et al., 2015; de Miranda et al., 2017; Pérez et al., 2010; Shores et al., 2013; Weichenthal et al., 2014; Zong et al., 2016). Even though AADT was evaluated within different buffer radii of the selected site, it was the 10 km radius that showed the strongest correlation with BC concentrations. Our observations are consistent with those of Shores et al. (2013), who evaluated atmospheric BC concentrations and modeled airborne transport direction and residence time from the point of emission. The authors found that BC emissions were highest in the urban centers of their study sites within a distance ranging from 4 to 12 km from their emission source, with some dependence on predominant wind direction (Shores et al., 2013).

The role of vegetation and canopy cover is commonly represented by NDVI, where “greener” pixels in the landscape represent more densely vegetated areas. These high-value NDVI sites have been identified as an environmental sink because BC and particulate matter concentrations in surrounding soils and air are negatively-correlated with vegetation density (Ahmed et al., 2017; Janhäll, 2015; Nowak et al., 2013; Wu et al., 2015). In locations where canopy cover is high and vegetation is dense, particulate matter is intercepted and held on the surface of vegetation. Therefore, the extent of urban vegetation has been used to estimate the role that canopy cover plays in the removal and capture of particulate matter that is suspended in the atmosphere (Nowak et al., 2013), and how urban vegetation can influence environmental health outcomes (Eklund et al. 2014). In the case of the second soil horizon, its depth also influences BC concentration. Our model predicts that thicker surface horizons result in lower concentrations of BC in the second horizon. The trend of decreasing BC concentration with depth (Table 2) is in agreement with other findings from northeast England (Edmondson et al., 2015), Germany (Brodowski et al., 2007), and China (Zong et al., 2016).

3.3 Classification and Regression Trees.

For each the top and the second horizon, we used classification and regression tree (CART) modeling that was based on the same parameters that were used in the ER model input. The models sequentially categorized BC concentrations in soil in the top horizon based on the following 5 variables: Zn concentrations in the top horizon, AADT_{10 km}, clay content of the soil, K_{unsat} (near-saturated infiltration rate) measured at the surface, and average NDVI for a 5-year period leading up to the point of sample collection (Figure 2). Based on these variables, the model categorized the BC concentrations into 6 leaves (terminal nodes) that had an average of 16.8 sites included (min=7, max=34) with predicted BC concentrations ranging from a mean of 10.3 to 38.3 mg g⁻¹. Overall, the density of automobile traffic and its associated BC emissions (de Miranda et al., 2017; Pérez et al., 2010; Weichenthal et al., 2014), vegetation density (Janhäll, 2015), and soil characteristics that influence immobilization and mineralization of BC, as K_{unsat} , and clay percentage, respectively, influence BC concentrations in soil (Ahmed et al., 2017; Czimczik and Masiello, 2007; Glaser and Amelung, 2003; Nguyen and Lehmann, 2009). The presence of Zn is the greatest influence in splitting BC concentrations into nodes of high or low concentration (Figure 2). Zn is often found in urban stormwater runoff and is dispersed in the environment through automobile wear (e.g., brake linings; Brown and Peake, 2006; Göbel et al., 2007) and has also been found to sorb to biochar and BC (Bogusz et al., 2015; Davis et al., 2003; Houben et al., 2013). Following this, with BC emissions strongly tied to automobile emissions, AADT_{10 km} contributes as the next split. As we found with regression relationships, automobile emissions are deposited within a predictable distance proximate to its source (Schifman and Boving, 2015; Shores et al., 2013). Even though Zn and AADT share a correlation coefficient of 0.3, we decided to keep both in the analysis as Zn represents a more local source compared to AADT acting as a more regional source (Brown and Peake, 2006, Shores et al. 2013). The next most influential characteristics describing the model are soil clay content and infiltration rate. Clay acts as a strong sorbent for many hydrophobic particles (Edmondson et al., 2015; Oyanedel-Craver et al., 2007; Zhu et al., 2015), but also can physically protect BC trapped between soil particles and aggregates (Czimczik and Masiello, 2007).

With the infiltration rate influencing the vertical transport of soil material, a hydrologically-restrictive soil can prevent deeper transport or eluviation of BC. In addition, movement between saturated and unsaturated conditions can also contribute to mineralization of BC over time (Nguyen and Lehmann, 2009). Thus, sites with lower K_{unsat} result in longer periods of saturation between precipitation events and result in higher mineralization rates of soil organic matter and BC that also can regulate the vertical translocation of BC. Both infiltration and mineralization rate can reduce the amount of particulate BC found in a composite sample of the first horizon, especially if the first horizon is deep. Although uncharacterized in the present study, the water-soluble fraction of BC (dissolved BC) may still be present and subject to transport through successive soil layers (Fu et al., 2017).

Finally, NDVI is an important variable for both regression tree and OLS models. The influence of vegetation on BC concentrations here is suspected to be similar in that vegetation acts as a BC trap, preventing its accumulation in surface soils because BC instead

is trapped on the vegetation (Janhäll, 2015). This is in contrast with a study in Boston, where the urban tree canopy contributed to higher growing season inputs of nitrogen, phosphorous, and organic carbon inputs to soil (Decina et al. 2018). Also, areas with greater amounts of vegetation might also be found where there is reduced road density, traffic, or development, resulting in overall lower BC concentrations, which is usually observed in studies along rural-urban gradients (Wong et al., 2004). Yet, soils in regions with overall low NDVI are likely to be the sole sink for BC, resulting in an enhancement of BC accumulation in soils. For the second horizon, the regression tree is in agreement with the OLS model, such that AADT_{10 km}, NDVI, and surface horizon thickness all contributed to the prediction of sub-surface BC concentration. Here, the four leaves result in describing an average of 25.3 sites (min=11, max=57) and average predicted BC concentrations ranging from 10.5 mg g⁻¹ to 28.3 mg g⁻¹ (Figure 3).

3.4 Influences of scale, built and natural environment features, and climate.

BC concentrations in urban soils are location-dependent and can apparently vary at the sub-parcel scale. Factors that influence BC concentrations include ordinary features of the built environment including traffic density and urban vegetation, or the local soil physical characteristics including clay content, infiltration rates, or surface horizon depth. Since our analysis focused on a variety of cities located in different climate regions, we believe our relationships describe general, higher-level processes that can control BC concentrations in the urban environment. Similar phenomena have been studied with regard to flora (Kühn and Klotz 2006; Schwartz et al. 2006), fauna (Kühn and Klotz 2006), microclimate (Hall et al. 2016), soil layering (Herrmann et al. 2018), and biochemical cycles and nutrient pools (Groffman et al. 2014; Polsky et al. 2014). Evidence for homogenization of BC concentrations in soils due to a generalized urbanization process is highlighted by two cities; Detroit, MI and Phoenix, AZ have a very similar distribution of BC in their soils even though they are situated in contrasting ecoregions (Table 2, Figure 1). While many other studies have found that slope, curvature, precipitation, and temperature are variables that influence BC concentrations in soil along climate gradients in rural areas (Ahmed et al., 2017; Cheng et al., 2008), these factors are likely too subtle in comparison to specific extent and intensity of local and regional anthropogenic impacts in urban systems that can lead to the homogenization of soil BC stocks in urban areas. The urban homogenization phenomenon related to traffic emissions and their connection with elevated BC concentrations in urban soils have furthermore been established in various studies around the globe (de Miranda et al., 2017; Edmondson et al., 2015; Eklund et al., 2014; Hamilton and Hartnett, 2013; Hu et al., 2009; Liu et al., 2011; Shores et al., 2013; Weichenthal et al., 2014; Zong et al., 2016).

3.5 Implications for passive green infrastructure.

While BC in the atmosphere is linked to various public health concerns (Eklund et al., 2014; Grahame et al., 2014), the soil functions as a sink for this material. In the soil, BC can absorb hydrophobic contaminants that are commonly found in urban soils and stormwater (Agarwal and Bucheli, 2011; Cornelissen et al., 2005; Lohmann et al., 2005; Semple et al., 2013). Even the dissolved fraction of BC can act as a strong sorbent for polar hydrophobic

contaminants like polycyclic aromatic hydrocarbons and chlorobenzenes, outperforming other sources of dissolved carbon (e.g., soil humic acids; Fu et al., 2017).

A common transport process for many urban contaminants of concern is through atmospheric deposition or infiltration of runoff. In both cases, green spaces in cities, e.g. vacant lots or interstitial areas, even if not designed as green infrastructure, can act as passive regulators of biochemical and hydrological cycles (Herrmann et al., 2016; Shuster et al., 2015) that control runoff, contribute to aquifer recharge, and regulate contaminant cycling. Due to the present, accumulated BC in these soils there is likely a passive and underappreciated function of water quality improvement that takes place, which can generate additional ecosystem services. Cities that are located in more arid environments can benefit from such passive infiltrative GI as it slowly recharges aquifers. For example, Phoenix, AZ, which is located in an arid climate and has measured infiltration rates ranging from 4 to 17 mm hr⁻¹ at the sites investigated, could be a good candidate for taking advantage of BC in its urban soils for aquifer recharge.

3.6 Potential as a contaminant sink.

Atmospheric deposition of polycyclic aromatic hydrocarbons (PAH), a contaminant group that is a by-product of combustion processes, has been measured to be 3.26 t yr⁻¹ in Providence, RI and 9.6 t yr⁻¹ in Galveston Bay, TX (Park et al., 2001; Schifman and Boving, 2015). To evaluate how much PAH deposition could be retained in soil due to BC alone, we investigated four cities, Atlanta, Camden, Portland, and San Juan in more detail. Depending on the amount of pervious area and BC concentration we calculated a sorption capacity of 2.26*10³ t for phenanthrene, a PAH, for Portland, ME and a sorption capacity of 8.05*10⁴ t for Camden, NJ (Table 3). These estimates give an approximation the atmospheric deposition of BC to date, but also the subsequent contaminant retention capacity of urban soils. The calculated estimates may constitute upper bounds for several reasons: 1) The maximum sorption capacity used in this calculation was based on sorption parameters derived from pure traffic soot. This form of BC likely exhibits more uniform sorption characteristics, and may have undergone less oxidation than the BC analyzed in this study which is of varying age, and only constitutes one source of BC to soil (Cornelissen et al., 2005; Van Noort et al., 2004; Van Noort et al., 2003); 2) maximum sorption characteristics are determined under laboratory conditions that require sorbents to be exposed to contaminants until equilibrium is reached (Schwarzenbach et al., 2002), therefore, these values may present the upper bound sorption capacities resulting from idealized processes that may be otherwise incomplete (non-equilibrium) in the environment; and finally, 3) sorption capacities are calculated for single species of contaminants, and since urban areas are known to harbor a wide variety of pollutants, it is likely other elements or compounds (some of which may be contaminants) take up sorption sites on BC particles, thereby reducing the apparent, overall sorption capacity for phenanthrene that is calculated here.

The urban soil sorption capacity estimates presented here do not consider residential soils in yards and other private property, all of which can also be important contributors to nutrient cycles. Furthermore, since residential parcels were not included in our calculation, the urban soils studied here may provide even higher sorption capacities for contaminants.

Nevertheless, the estimates presented here can put into perspective how urban soils can play a large role in regulating contaminant cycling in the soil ecosystem.

Even though we make the case for relying on native soils as passive green infrastructure, we do not argue against the installation of more highly-engineered green infrastructure that is specifically designed to capture runoff or generate additional ecosystem services. In some cases, an urbanized soil cannot offer adequate ecosystem services due to compaction or native soil composition, and engineered soils can offer functions that are similar to more natural or undisturbed soils (Morel et al., 2015). In contrast, some urban soils exhibit suitable infiltration rates – which should be confirmed by actual measurement – and soil hydrology may be further improved over the long term through maintenance of a vegetative cover and active rooting zones. Such vegetative features may enhance soil structure and thereby infiltration (Chen et al., 2014; Herrmann et al., 2016; Shuster et al., 2015; Schifman et al. 2018).

Cities exhibit a diversity of land uses, and even if variable in size, urban green spaces are highly interspersed within conurbations (Pouyat et al., 2002; Ramos-González, 2014; Van Dillen et al., 2012; Wolch et al., 2014). While the long-term fate and role of BC in plant and animal uptake remains an unanswered question, the role of sequestered BC contributing as a contaminant sink in water and soil has been established. Realizing this potential of urban green spaces and their capacities for not only regulating runoff or providing recreational space, but also leveraging this stored carbon form toward capturing other pollutants associated with urban emissions is an example of the advancements in thinking related to urban science. This type of information, properly translated to governance, can inform a more holistic view of green space and how its characteristics may be leveraged in the pursuit of overall environmental quality.

3.7 The role of soils in urban science.

With cities are moving towards a new urban science, not only social scientists but also natural scientists work to understand the processes and functions of the complex urban ecosystem (Anft 2017, Acuto et al. 2018, Groffman et al. 2017, Solecki et al. 2013). We have arrived at a new era, where interdisciplinary and transdisciplinary research objectives in urban systems are meant to inform policy decisions and impact human well-being. Urban soils, just like their rural counterparts, regulate nutrient and water cycles and with that influence how land can be re-developed. In this capacity, soil BC has the potential to, for example, regulate contaminant cycles by sequestering an airborne pollutant or improve soil filtration of runoff that infiltrates and percolates and may end up as groundwater. This is important for cities that rely on locally drawn groundwater resources. This body of work adds an understanding of how significant of a contaminant sink urban soils can be and posits that urban soils should be valued beyond their role as a geotechnical substrate to support buildings. Taking on this view of urban soils can move cities to more sustainable solutions as decision makers realize the potential of urban soil characteristics and processes that until now, are mimicked by engineered soil blends. With this realization, the use of existing soils in urban greening projects can also result in a simultaneous cost-savings and reduction in emissions due to a reduced demand for trucked-in engineered soil.

Conclusion

Here we argue that the historically deposited BC in soils can act as a contemporary contaminant sink, while we also recognize its presence in the atmosphere remains a public health risk. Urban soils in part regulate contaminant sequestration and stormwater volume. The physicochemical properties of accumulated soil BC impart unique filtration characteristics to a geographically-diverse representation of urban soils. We focus on the present, extant accumulation of soil BC and how it may enhance filtration services passively provided by urban soils. In this paper we assess BC concentrations of soils in 11 cities in the United States and relate the findings to urban emission sources and soil characteristics. We report that although the cities spanned various climate regions, some predictor variables that explain BC concentrations in surficial urban soils were consistent throughout the United States, and differ from those determined on rural or agricultural soils. Specifically, we find that AADT within 10 km of a sampling site (transportation corridors as a source) and NDVI (vegetation as a sink) are drivers for BC concentration in both the top and second horizons. The depth of the top horizons can contribute in explaining some variation of BC concentrations in the second, deeper sub-surface soil horizon. Further, the high sorption capacity of extant, sequestered soil BC can contribute to regulating contaminant cycling in urban areas and overall contributes to the value that urban soils offer in terms of ecosystem services.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- We assessed surface and subsurface soil BC concentrations in 11 US cities
- Soil BC is influenced by surface horizon thickness, traffic, and vegetation density
- Native urban soil can regulate contaminant cycling in passive green infrastructure

Figure 1.

Overview of BC concentrations in the first and second horizons of the 11 cities assessed, alphabetically ordered by city. The dashed lines in each plot represent the mean BC concentration across all cities and the shaded boxes encompass points that fall within one standard deviation of the mean. Individual points highlight all sampled sites in addition to boxplots.

Figure 2.

Flowchart of the CART model for determining BC concentrations in the top horizon.

Following a path to the left indicates “yes”, whereas following a path to the right indicates a “no” to the statement.

Figure 3.

Flowchart of the CART model for determining BC concentrations in the second horizon.

Following a path to the left indicates “yes”, whereas following a path to the right indicates a “no” to the statement.

Table 1.

Black Carbon Explanatory Variables

Pathway	Variable
Anthropogenic Sources	Fuel Dealers – Count of number of fuel dealers.
	New Car Dealers – Count of number of new car dealers.
	Used Car Dealers – Count of number of used car dealers.
	All Car Dealers – Count of all car dealers.
	Average Annual Daily Traffic (AADT) – annual volume of vehicle traffic on a road divided by 365 days within 1-, 5-, 10-, and 15 km buffers of sample points.
	Facility Registry Service Locations – Count of number of permitted facilities within 1-, 5-, 10-, and 15 km buffers of sample points.
	Zinc – Concentration (ppm).
Soil Conditions	Cooper – Concentration (ppm).
	Soils – Percent sand, silt, and clay.
	Vegetation (NDVI) – Five-year average from sample date Normalized Difference Vegetation Index (NDVI).
	Cation Exchange Capacity (CEC) – Centimol positive charge per kg of soil.
	Sample Depth – Depth from surface (cm); lower samples only.
	pH – Sample pH.
	Unsaturated Conductivity - Surface unsaturated hydraulic conductivity (mm hr^{-1}).
Landscape Factors: <i>Pedogenesis</i>	Elevation – Elevation (10 m DEM).
	Slope Percent – Slope (10 m DEM).
	Aspect – Aspect (10 m DEM).
	Curvature – Curvature (10 m DEM).
	Age of Disturbance – City Age.

Table 2.
City-level summary statistics of soil OC, BC, inorganic carbon, and average BC/OC ratio with standard error.

City	Horizon	N	OC [mg g ⁻¹]				BC [mg g ⁻¹]				Inorganic Carbon [mg g ⁻¹]				BC/OC				
			Median	Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Mean	SE
Atlanta GA	1	9	48.4	44.7	± 12.4	28.4	59.8	24.3		± 6.9	12.5	36.3	1.8	2.2	± 1.3	0.9	5.0	0.55	± 0.05
	2	9	31.6	33.0	± 8.6	22.9	44.1	29.4		± 8.9	14.0	46.6	3.5	6.7	± 10.5	1.5	34.3	0.99	± 0.18
Camden NJ	1	9	54.1	73.0	± 62.6	20.2	212.9	15.9	25.4	± 30.2	5.7	103.5	3.1	10.7	± 22.4	1.1	70.0	0.32	± 0.04
	2	9	27.1	29.9	± 15.7	13.3	65.7	12.5	17.5	± 13.7	3.3	47.8	3.8	11.8	± 18.5	0.4	58.0	0.50	± 0.06
Cincinnati OH	1	9	46.8	42.6	± 20.5	13.2	82.7	16.6	22.2	± 16.0	4.7	50.2	12.6	28.3	± 29.9	1.2	71.5	0.41	± 0.05
	2	9	19.9	22.2	± 10.0	13.6	46.9	14.4	17.7	± 9.2	10.5	40.1	36.8	35.7	± 27.1	1.2	67.9	0.94	± 0.33
Cleveland OH	1	9	34.3	31.2	± 15.2	5.4	58.3	18.7	15.8	± 10.0	3.1	32.4	5.8	7.5	± 9.4	0.4	31.4	0.45	± 0.06
	2	9	15.1	16.6	± 7.9	4.3	28.0	7.0	10.4	± 7.0	3.0	22.6	3.1	6.1	± 9.5	0.3	30.6	0.62	± 0.12
Detroit MI	1	9	32.7	31.3	± 10.6	12.0	48.8	13.4	13.3	± 4.5	4.4	20.7	12.6	17.3	± 17.2	0.8	51.8	0.37	± 0.05
	2	9	16.4	20.2	± 9.8	8.2	37.3	8.8	8.9	± 4.7	3.0	18.9	1.4	6.3	± 12.0	0.5	36.3	0.39	± 0.05
New Orleans LA	1	5	20.9	26.8	± 19.4	10.8	59.0	9.3	13.5	± 8.7	7.6	28.4	2.9	3.9	± 1.9	2.4	7.1	0.32	± 0.04
	2	5	36.5	34.8	± 12.2	22.6	52.2	24.2	26.7	± 17.6	12.1	55.4	5.9	11.9	± 10.7	3.5	29.2	0.44	± 0.06
Omaha NE	1	9	48.5	42.9	± 12.8	14.0	56.8	16.0	16.5	± 2.8	13.3	21.3	3.6	4.9	± 4.1	1.1	13.1	0.34	± 0.03
	2	9	18.5	17.9	± 6.8	10.5	27.0	10.2	11.0	± 2.5	8.0	15.4	1.5	3.9	± 4.1	1.1	12.2	0.48	± 0.04
Phoenix AZ	1	9	27.8	25.5	± 12.8	8.1	46.2	13.9	14.5	± 4.6	8.0	22.5	15.7	17.9	± 14.5	1.6	39.0	0.61	± 0.12
	2	9	8.0	9.2	± 3.4	6.5	16.7	8.3	9.0	± 2.0	6.1	12.1	33.5	36.7	± 34.5	2.6	99.2	1.18	± 0.15
Portland ME	1	9	49.5	48.0	± 13.9	30.6	69.4	12.5	10.6	± 2.8	5.8	13.4	1.8	2.5	± 2.0	1.3	7.6	0.22	± 0.02
	2	9	28.0	30.1	± 14.7	9.7	48.9	9.4	8.8	± 3.2	4.5	13.0	1.9	3.0	± 3.1	1.3	11.0	0.40	± 0.05
San Juan PR	1	9	47.6	66.2	± 62.6	25.7	228.6	32.2	36.9	± 16.2	18.3	74.1	4.0	13.1	± 17.5	1.5	47.7	1.49	± 0.69
	2	9	25.2	27.0	± 12.8	13.6	57.0	28.9	30.4	± 15.4	15.5	60.1	12.1	29.3	± 34.7	1.3	79.6	1.57	± 0.25
Tacoma WA	1	9	60.2	68.3	± 40.4	35.0	168.7	11.8	14.5	± 8.1	7.8	31.7	1.0	1.1	± 0.3	0.8	1.9	0.20	± 0.02
	2	9	23.5	32.2	± 22.9	11.9	86.0	7.6	10.9	± 9.8	5.1	36.4	1.1	1.1	± 0.2	0.8	1.5	0.38	± 0.05

Table 3.

Maximum sorption capacity of urban soil BC for phenanthrene in four cities in green space (parks, cemeteries, golf courses) based on modeled maximum sorption capacity parameter $\log(q_{\max, \text{phenanthrene}} : \text{traffic soot}) = 5.02$ nmol/(g of sorbent) (Van Noort et al., 2004).

Metropolitan Area	Total greenspace [km ²]	Average depth of top horizon [m]	Average Bulk Density [kg m ⁻³]	Average BC [g kg ⁻¹]	Maximum sorption capacity [t]
Atlanta-Sandy Springs-Roswell, GA	3.92*10 ²	0.13	1180	24.3	2.68*10 ⁴
Philadelphia-Camden-Wilmington, PA-NJ-DE-MD	8.66*10 ²	0.19	1090	25.4	1.73*10 ⁵
Portland-South Portland, ME	3.86*10 ¹	0.26	1140	10.6	1.61*10 ⁴
San Juan-Carolina-Caguas, PR	1.17*10 ²	0.16	1240	36.9	3.94*10 ⁴