Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. 2019, 53, 10092−10101

pubs.acs.org/est

Urban Trees Are Sinks for Soot: Elemental Carbon Accumulation by Two Widespread Oak Species

Jenna E. Rindy,[†] Alexandra G. Ponette-González,[*,†,$] Tate E. Barrett,[†] Rebecca J. Sheesley,[‡] and Kathleen C. Weathers[§]

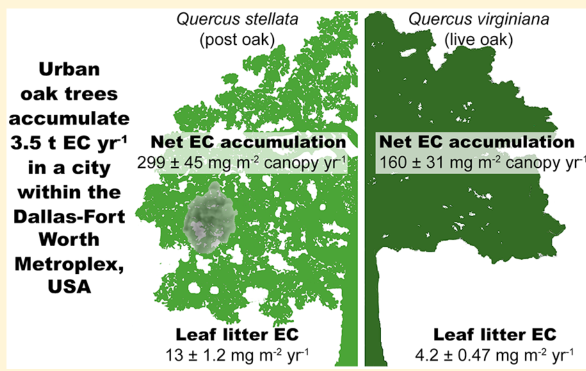
[†]Department of Geography and the Environment, University of North Texas, 1155 Union Circle #305279, Denton, Texas 76203, United States

[‡]Department of Environmental Science, Baylor University, 1 Bear Place #97266, Waco, Texas 76798, United States

[§]Cary Institute of Ecosystem Studies, Box AB, Millbrook, New York 12545, United States

Supporting Information

ABSTRACT: Urban trees could represent important short- and long-term landscape sinks for elemental carbon (EC). Therefore, we quantified foliar EC accumulation by two widespread oak tree species—*Quercus stellata* (post oak) and *Quercus virginiana* (live oak)—as well as leaf litterfall EC flux to soil from April 2017 to March 2018 in the City of Denton, Texas, within the Dallas-Fort Worth metropolitan area. Post oak trees accumulated 1.9-fold more EC (299 ± 45 mg EC m^{-2} canopy yr^{-1}) compared to live oak trees (160 ± 31 mg EC m^{-2} canopy yr^{-1}). However, in the fall, these oak species converged in their EC accumulation rates, with ∼70% of annual accumulation occurring during fall and on leaf surfaces. The flux of EC to the ground via leaf litterfall mirrored leaf-fall patterns, with post oaks and live oaks delivering ∼60% of annual leaf litterfall EC in fall and early spring, respectively. We estimate that post oak and live oak trees in this urban ecosystem potentially accumulate 3.5 t EC yr^{-1}, equivalent to ∼32% of annual vehicular EC emissions from the city. Thus, city trees are significant sinks for EC and represent potential avenues for climate and air quality mitigation in urban areas.



INTRODUCTION

Urban areas cover <1% of the Earth's land surface,[1,2] yet they represent globally significant sources of two major climate-forcing agents: carbon dioxide (CO_2) and black carbon (hereafter elemental carbon (EC)[3−5]). A product of fossil fuel/biofuel combustion and biomass burning, EC—commonly referred to as "soot" in urban areas—is emitted directly into the atmosphere in the form of fine particulate matter (<2.5 μm in diameter, $PM_{2.5}$). In urban areas, diesel fuel exhaust is the primary source of atmospheric EC.[4] Although airborne EC comprises a small fraction of total $PM_{2.5}$ in U.S. (∼12%; reference 6) and European cities (∼<15%; reference 7), arguably, it constitutes one of the most significant components of urban $PM_{2.5}$: first, EC absorbs incoming solar radiation in a broader range of wavelengths than CO_2, and in urban areas, its warming potential can be enhanced upon interaction with other pollutants.[8] Second, as a component of $PM_{2.5}$, EC contributes to reduced visibility[9] and poor air quality. Inhalation of EC particles has been shown to cause cardiovascular and respiratory complications as well as mortality.[10−12] Because EC resides in the atmosphere for days to weeks,[13] these atmospheric and human health impacts tend to be concentrated around urban and other source regions.[14]

Urban vegetation has been purported to filter pollutants[15−18] thus improving air quality in cities. Fine particles, including EC, dry-deposit directly onto leaf surfaces or adhere to leaf epicuticular waxes[15,19] where they accumulate on leaf surfaces. In fact, maintaining urban vegetation may meet the twin goals of climate mitigation[20] and improved air quality.[21−23]

Tall tree canopies likely represent important sinks for EC on the urban landscape because of their efficiency in filtering particles from the atmosphere.[24−26] It is well established that particle inputs to tree canopies, with their high leaf area and surface roughness, are often greater than those to short-statured vegetation (e.g., references 27−30). Empirical research shows that considerable amounts of $PM_{2.5}$ can deposit to—and accumulate on—leaf surfaces with strong contrasts among tree species.[15−17,31−37] Following deposition, particles

Received: May 28, 2019
Revised: August 11, 2019
Accepted: August 12, 2019
Published: August 12, 2019

DOI: 10.1021/acs.est.9b02844
Environ. Sci. Technol. 2019, 53, 10092−10101

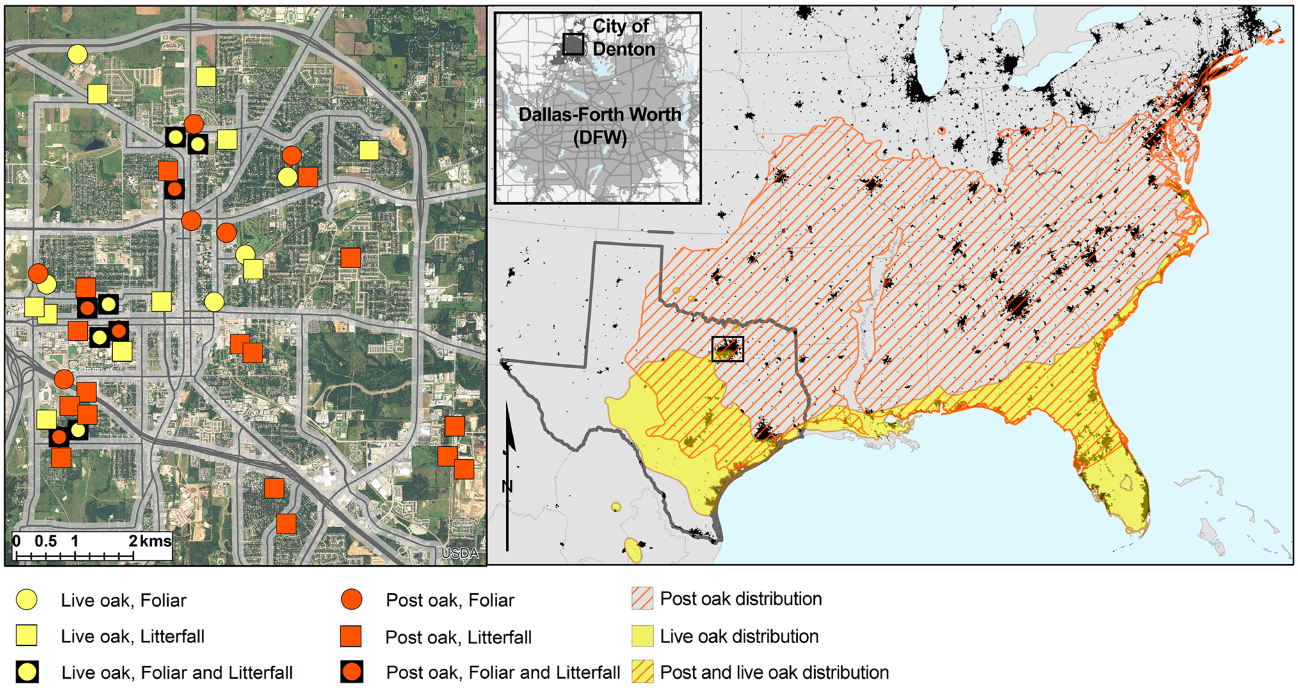


Figure 1. Sites in the City of Denton, Texas (left), where foliar elemental carbon and litterfall sampling were conducted from April 2017 to March 2018. Situation of the City of Denton downwind of the Dallas-Fort Worth metropolitan area (right inset), and the distribution of post oak and live oak in the southern U.S. and its cities (black areas).

can be resuspended back to the atmosphere, washed from surfaces into throughfall, and/or retained in the canopy until leaf fall. Though seldom measured (but see reference 38), EC transported to soil with litter may become incorporated into a slow cycling carbon pool and contribute to long-term carbon sequestration.[39,40]

In order to assess the potential for urban trees to function as EC sinks, coupled measurements of EC accumulation on leaf surfaces and EC flux to soil are critical. Here, our objectives were to (1) quantify EC accumulation on two widespread oak species at leaf- and canopy-scales; (2) quantify the magnitude of leaf litterfall EC fluxes to soil; (3) examine the influence of species and season on EC accumulation and leaf litterfall EC flux; and (4) make a back-of-the envelope calculation of the potential annual vehicular EC emissions scavenged by urban trees and redistributed to soils.

■ MATERIALS AND METHODS

Study Area. This study was conducted in the City of Denton (33.2148°N, 97.1331°W), Texas, located in the Dallas-Fort Worth (DFW) metropolitan area (Figure 1). Climate in the area is humid subtropical, with hot summers, cool winters, and high inter- and intra-annual rainfall variability. Daily temperature is highest during summer, ranging from 27 to 38 °C, and lowest in winter, ranging from 0.6 to 13 °C.[41] Mean annual rainfall (1981−2010) measured at Denton Enterprise Airport (KDTO) is 983 ± 233 mm (±1 SD; reference 41). During this study, from April 2017 to March 2018, rainfall measured at an urban weather station (KTXDENTO30) totaled 946 mm (Figure 2). Periods of heavy and intense rainfall occur during spring and fall and are followed by dry spells of varying duration during summer and winter.[41]

The City of Denton is part of one of the fastest growing counties in the U.S. (i.e., Denton County: 17% rate of increase from April 2010 to July 2017; reference 42). Although the City of Denton has a smaller population (∼136000) than the cities of Fort Worth (∼874000) and Dallas (∼1341000), it experiences poor air quality due to its location along two major interstate highways and downwind of the metropolitan core area (Figure 1). The Texas Commission on Environmental Quality (TCEQ) monitors nitrogen oxides (NO_x), ozone (O_3), and $PM_{2.5}$ at Denton Airport South Continuous Ambient Monitoring Station (CAMS 56). From 2016 to 2018, the City of Denton's mean annual $PM_{2.5}$ concentration was 7.7 $\mu g\ m^{-3}$.[43] The primary National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$ is an annual average of 12 $\mu g\ m^{-3}$ averaged over three years. The city's fourth highest daily maximum 8 h average O_3 concentration during this 3-year period was among the highest in the State of Texas, 75 ppb,[43] exceeding the NAAQS of 70 ppb.[44]

According to an urban forest resource assessment conducted in 2016, the City of Denton has ∼3.5 million trees, which cover 30% of the city's area.[45] The City of Denton is thus similar to other U.S. cities, where urban tree cover is, on average, ∼ 39%.[46]

Tree Selection and Foliar Elemental Carbon Sampling. Two tree species with broad geographic distribution throughout the urban U.S. south (Figure 1) and that are widespread in the greater DFW area were selected to examine the role of tree canopies as sinks for elemental carbon (EC). The focal species were post oak (*Quercus stellata* Wang.) and live oak (*Quercus virginiana* Mill.)

We quantified EC accumulation on the leaf surface (hereafter on-surface EC) and in the leaf wax (hereafter in-wax EC) of 20 urban oak trees distributed across the City of Denton. Elemental carbon accumulation is an underestimate of dry EC deposition (i.e., total accumulation) because there is some resuspension of dry-deposited particles from leaf

DOI: 10.1021/acs.est.9b02844
Environ. Sci. Technol. 2019, 53, 10092−10101

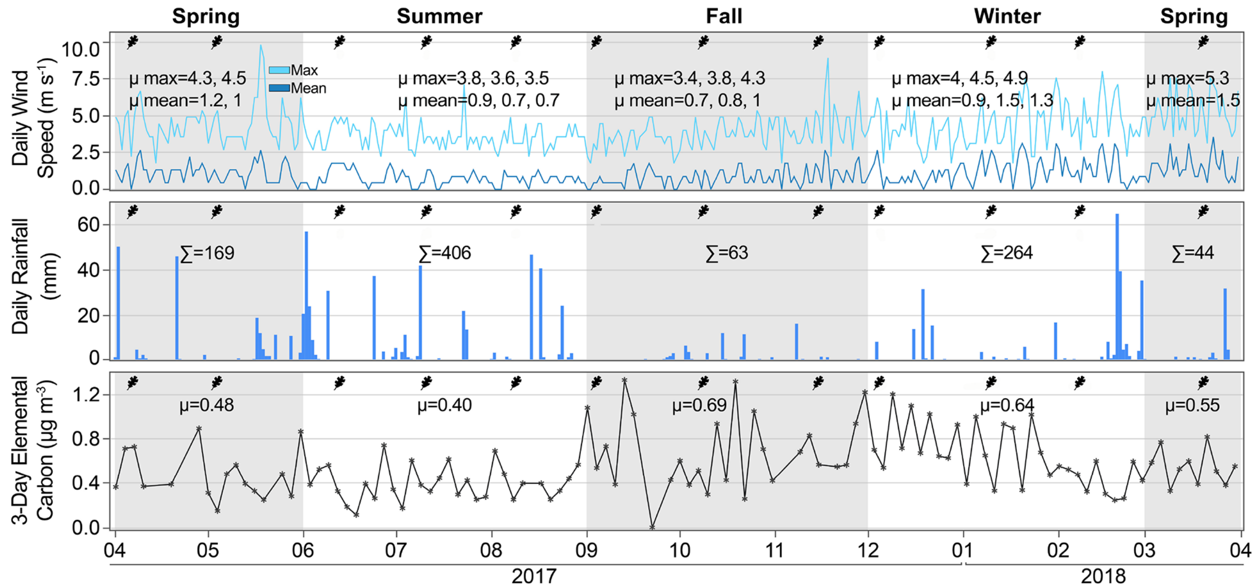


Figure 2. Daily maximum (light blue) and mean (dark blue) wind speed (m s^{-1}) and daily rainfall (mm) measured at an urban weather station (KTXDENTO30) in the City of Denton, Texas, and 3-day atmospheric elemental carbon concentrations (μg m^{-3}) measured at the Chemical Speciation Network Dallas Hinton site from April 2017 to March 2018. Black leaves indicate sampling dates. Monthly mean (μ) wind speeds, total (Σ) rainfall, and mean (μ) elemental carbon concentrations per season are reported.

surfaces. Therefore, hereafter, we use the term *net EC accumulation* to describe what we measured.

Ten post oak and ten live oak trees were selected for foliar sampling (Figure 1; Table S1) based on accessibility as well as proximity to roads (≤100 m, > 100 m). To the extent possible, post oak and live oak trees in close proximity were chosen to ensure that species differences were not confounded by local emissions sources. Six pairs of trees were located ≤200 m apart, while four pairs were sampled in similar settings (i.e., near or far from road but were not colocated). Trees were generally large, with tree diameter at breast height (dbh) ranging from 32 to 88 cm and tree height ranging from 9 to 16 m. Leaf area index (LAI) ranged from 2 to 4.75 m^2 m^{-2}. On average, the dbh, height, and LAI of post oak and live oak trees were similar, and at the time of sampling, all trees appeared healthy and vigorous.

Foliar sampling was conducted once a month during the growing season. Samples were collected from April 2017 to November 2017 for post oak and from April 2017 to March 2018 for live oak for a total of 8 and 12 sampling periods per species, respectively (Figure 2). During each sampling period, a Notch Equipment Big Shot line-launcher was used to remove small clusters of leaves from three locations on the outer surface of the crown. Leaves were sampled from the south-facing side of each tree between 135 and 225 degrees. We sampled consistently the south-facing side of trees[47] because during most of the year, prevailing winds are from the south, where the dominant EC emissions sources (i.e., DFW, highways) in our region are located. More details on foliar sampling are provided in the Supporting Information.

Foliar Extraction and Elemental Carbon Analysis. Leaf samples were transported in brown paper bags to the Ecosystem Geography Laboratory at the University of North Texas, where on-surface and in-wax net EC accumulation were determined using a two-step foliar extraction technique.[15,38] First, leaves were rinsed in 250 mL of double-deionized (DDI) water for 60 s to remove on-surface EC particles. To increase EC recovery, 1.5 g of ammonium dihydrogen phosphate ($(NH_4)H_2PO_4$) per 100 mL of water were added to each rinsewater sample.[48] Samples were then sonicated in a HealthSonics Ultrasonic Cleaner T3.3C (HealthSonics, Algonquin, IL) for 15 min, poured into a glass amber bottle, and refrigerated overnight. The following day, rinsewater samples were filtered through an Advantec 13 mm filter funnel into a Buchner flask over a 13 mm^2 punch of Pall quartz-fiber filter (Pall Corp., Washington, NY). Leaves were then rinsed with 150 mL of chloroform to dissolve the epicuticular wax layer and extract in-wax EC. Chloroform extracts were filtered using the same process as the rinsewater samples.

Two lab blank samples (i.e., one rinsewater blank, one chloroform blank) per sampling period (n = 24 blanks total) were extracted following the procedures described above. Filters were placed in individual clean Petri dishes, desiccated overnight, and stored in a freezer until analysis could be performed. A total of 200 water samples and 200 chloroform samples were analyzed, with 24 total sample blanks.

Samples were analyzed on a Sunset Laboratory Organic Carbon/Elemental Carbon (OC/EC) Aerosol Analyzer (Sunset Laboratories, Inc., Tigard, OR). Briefly, the OC/EC instrument determines the split of OC and EC through a thermal optical process. Samples are heated first in a 100% helium (He) atmosphere for determination of organic carbon and then a 10% oxygen/He mixture is introduced into the system for the determination of EC. The transmission of a 678 nm laser through the filter is continuously monitored throughout the analysis to determine the split between OC and EC. For quality assurance, one oven blank was analyzed each time the instrument was turned on, and two sucrose spike samples [5 μL (17.58 μg C) and 10 μL (35.16 μg C)] were analyzed to ensure calibration after every 10 samples. The minimum limit of detection for the instrument was 0.21 μg of EC per cm^2 of filter. See Supporting Information for details on foliar extraction and EC determination.

Litterfall Site Selection and Sampling. To quantify leaf litterfall EC flux to below-canopy soils, 20 post oak and 15 live oak trees were selected for litterfall sampling across the City of

DOI: 10.1021/acs.est.9b02844
Environ. Sci. Technol. 2019, 53, 10092−10101

Table 1. Seasonal and Annual On-Surface and In-Wax Net Elemental Carbon (EC) Accumulation at Leaf- and Canopy-Scales for 10 Post Oak and 10 Live Oak Trees Sampled in the City of Denton, Texas, from April 2017 to March 2018[a]

	On surface ($mg\ m^{-2}$ leaf)		In wax ($mg\ m^{-2}$ leaf)	
	Post oak	Live oak	Post oak	Live oak
Spring 2017	5.4 ± 0.99	1.06 ± 0.17	5.0 ± 2.01	0.75 ± 0.53
Summer 2017	29 ± 6.7	2.3 ± 0.54	0.56 ± 0.11	0.13 ± 0.018
Fall 2017	83 ± 12	34 ± 10	1.4 ± 0.43	0.15 ± 0.029
Winter 2017	0	9.9 ± 1.8	0	0.13 ± 0.020
Spring 2018	n.s.	3.04 ± 0.64	n.s.	1.3 ± 0.30
Annual	118 ± 17	51 ± 13	6.9 ± 2.1	2.4 ± 0.59
	On surface ($mg\ m^{-2}$ canopy)		In wax ($mg\ m^{-2}$ canopy)	
	Post oak	Live oak	Post oak	Live oak
Spring 2017	12 ± 1.7	3.4 ± 0.45	12 ± 4.9	2.0 ± 1.2
Summer 2017	69 ± 15	7.2 ± 1.2	1.3 ± 0.19	0.43 ± 0.055
Fall 2017	201 ± 36	103 ± 23	3.2 ± 1.2	0.51 ± 0.11
Winter 2017	0	31 ± 6.4	0	0.40 ± 0.50
Spring 2018	n.s.	8.7 ± 1.9	n.s.	3.5 ± 6.9
Annual	282 ± 45	153 ± 30	16.5 ± 5.6	6.8 ± 1.5

[a]Numbers do not always sum due to rounding; "n.s." indicates "not sampled".

Denton (Figure 1). Litterfall sampling sites were located in residential and other surveilled areas where traps were less likely to be disturbed or stolen. Eleven trees selected for foliar sampling did not have associated leaf litterfall measurements because these trees were located in public spaces where litterfall trap installation was restricted. Litterfall traps were constructed following the National Atmospheric Deposition Program (NADP) Litterfall Mercury Monitoring Initiative protocol.[49] Each litterfall trap consisted of a 33.02 cm^2 plastic crate with 27.94 cm walls on each side. Fiberglass 2 mm thick screenware mesh lined the bottom and sides of the box to allow water drainage. Samplers were placed midway between the base of the tree and the outer canopy, on the south side of the between 135 and 225 degrees. Samples were collected every 2 weeks from 2 April 2017 to 1 April 2018 for a total of 26 sample weeks. Samples were placed in brown paper bags, transported to the laboratory, and sorted into leafy and nonleafy (e.g., twigs, seeds) categories. Samples were oven-dried (Thermo Fisher Scientific, Waltham, MA) at 65 °C for 2 days and then weighed to the nearest hundredth, and sample weight (g) was recorded.

Statistical Analyses. Net EC accumulation and leaf litterfall EC fluxes were calculated per tree for each season and year. At leaf- and canopy-scales, we estimated total net EC accumulation as the sum of on-surface and in-wax net EC accumulation. We estimated total potential EC flux to the ground via leaf litterfall as the sum of on-surface and in-wax leaf litterfall EC flux. Detailed calculations and equations are provided in the Supporting Information and Figure S1.

All variables were first tested for normality using the Shapiro-Wilk W goodness of fit test. Where variables did not fit a normal distribution, they were log-transformed. To examine differences in on-surface, in-wax, and total net EC accumulation, a two-way ANOVA was conducted to test for the effects of species, season, and species by season interactions.[50] Similarly, we used a two-way ANOVA to examine the effects of species, season, and species by season interactions on leaf litterfall EC fluxes. When interactions were significant, simple effects were analyzed using one-way ANOVA followed by Tukey's posthoc test for seasonal comparisons.[50] Significance was set at $p < 0.1$. All calculations and statistical analyses were performed using JMP v14.[51]

3. RESULTS AND DISCUSSION

Our findings demonstrate that two oak tree species widespread across the southern U.S. represent significant short-term sinks for urban EC and, via litterfall, important EC inputs to the soil. Annually, post oak trees accumulated 125 ± 17 mg EC m^{-2} leaf (299 ± 45 mg EC m^{-2} canopy) while live oak trees accumulated 53 ± 13 mg EC m^{-2} leaf (160 ± 31 mg EC m^{-2} canopy) during dry periods (Table 1). We know of only one other empirical study conducted in Tokyo, Japan—the largest metropolitan area in the world—of net EC accumulation by urban tree canopies. In that study, net EC accumulation by konara oak (*Quercus serrata*) leaves quantified using a foliar rinse method similar to ours was ~43−50 mg EC m^{-2} leaf yr^{-1},[38] similar to estimates for live oak but ~3-fold lower than for post oak.

A recent synthesis by Barrett et al.[52] found that, on average, rainfall delivers 0.16 mg EC m^{-2} d^{-1} (58 mg EC m^{-2} yr^{-1}) to urban sites in the Northern Hemisphere. Assuming a similar wet EC deposition rate in the DFW metropolitan area and assuming that net EC accumulation is a good proxy for dry deposition, dry EC deposition to urban oak tree *canopies* represents 73−84% of total (wet + dry) EC deposition. In a tropical deciduous forest in Thailand, dry deposition (212 mg EC m^{-2} yr^{-1}) comprised 92% of total EC deposition.[53] Though few in number, these studies confirm that tree canopies scrub significant amounts of atmospheric EC by enhancing dry deposition.

Net EC Accumulation Differs between Urban Oak Tree Species. Leaf surfaces were the dominant site of EC accumulation for post oak and live oak (Figure 3), yet these species exhibited pronounced differences in the magnitude of net EC accumulation (Figure 3; Table 1). On-surface, in-wax, and total (on-surface + in-wax) net EC accumulation by post oak leaves was consistently higher than that by live oak leaves (all p-values < 0.0001), with post oaks accumulating 2.5−12-fold more EC on leaf surfaces and in leaf waxes depending on the season. At the canopy-scale, species differences were also significant for both sites of deposition (on-surface and in-wax,

DOI: 10.1021/acs.est.9b02844
Environ. Sci. Technol. 2019, 53, 10092−10101

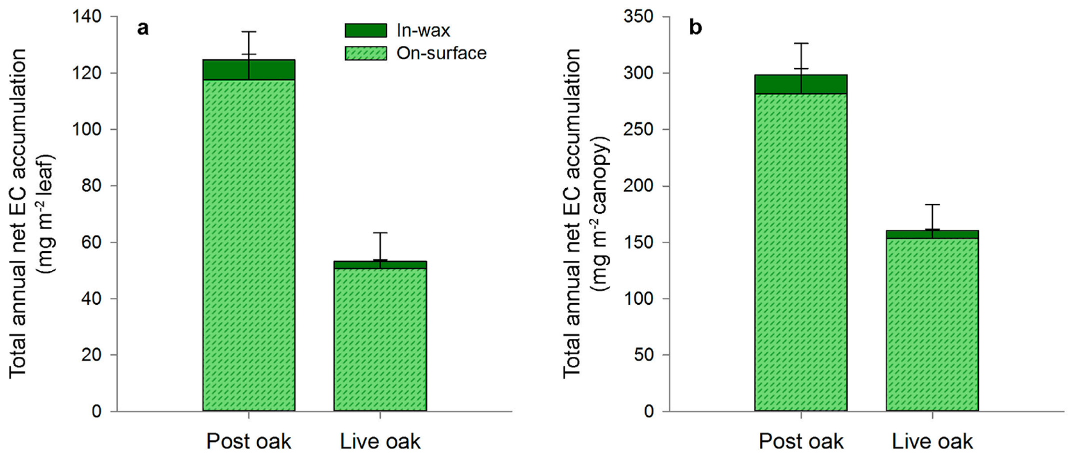


Figure 3. Total (on-surface + in-wax) annual net elemental carbon (EC) accumulation at (a) leaf- and (b) canopy-scales for 10 post oak and 10 live oak trees sampled in the City of Denton, Texas, from April 2017 to March 2018.

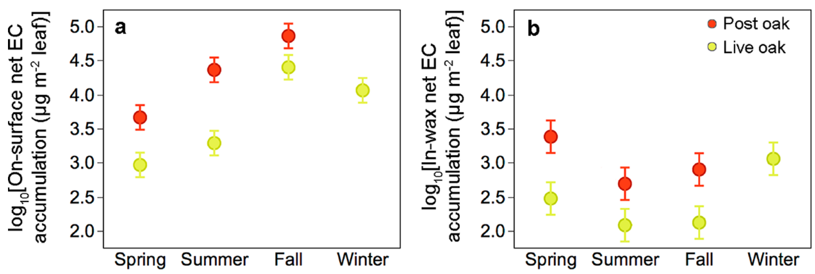


Figure 4. Seasonal patterns of leaf-scale (a) on-surface and (b) in-wax net elemental carbon (EC) accumulation for 10 post oak and 10 live oak trees sampled in the City of Denton, Texas, from April 2017 to March 2018.

$p < 0.0001$) but were slightly smaller because of the lower LAI of post oak compared to live oak (2.4 and 3.4, respectively). Annually, post oak leaves accumulated 2.3 times more total net EC than live oak leaves (Figure 3a), while post oak canopies accumulated 1.9-fold more total EC than live oak canopies (Figure 3b).

Numerous studies show wide variation in PM accumulation by trees in urban areas owing to some combination of leaf (e.g., size, complexity, surface properties) and/or canopy (e.g., habit, leaf density) characteristics.[15−17,31,32,34,35,54−57] In general, PM accumulation has been shown to increase with trichome presence and/or density.[17,31,58,59]

Our preliminary observations of immature post oak and live oak leaves revealed only sparse trichomes on the upper leaf surface of both species. With the exception of post oaks, most oaks, including live oaks, lose these adaxial trichomes with leaf age.[60] However, on the lower surface, live oak leaves had trichomes that were more densely packed and layered compared to those of post oak leaves (Supporting Information, Figure S2). These qualitative observations suggest that neither trichome presence nor greater trichome density is likely to contribute to higher net EC accumulation by post oak leaves. Leaf dimension also cannot explain the species difference we observed. The surface area of post oak leaves was ∼3-fold greater than that of live oak leaves, but larger leaves have thicker boundary layers and thus a lower collection efficiency of ultrafine particles than smaller leaves.[61] Because the magnitude of the species difference was similar for both sites of EC accumulation (on-surface and in-wax), canopy structure (e.g., tree architecture) may have played a more important role than leaf traits in controlling net EC accumulation.

Seasonal Changes in Net EC Accumulation. Post oak and live oak trees differed in the magnitude of net EC accumulation but followed similar seasonal accumulation patterns (Figure 4; Table 1). The amount of on-surface EC accumulation was lowest in spring, intermediate in summer, and highest in fall at leaf- and canopy-scales (all p-values <0.1; Figure 4a). Seasonal differences were due to variations in daily net EC accumulation rather than total number of dry days per season, which was similar among individual trees and seasons (Figure S3). In-wax EC showed the opposite pattern with higher accumulation in spring compared to summer ($p < 0.001$) and fall ($p < 0.01$; Figure 4b).

Although our data are not extensive enough to provide definitive answers, these seasonal changes in particulate accumulation may be due to differences in atmospheric EC concentrations, meteorological conditions, and/or interactions between EC particles and leaf surfaces.[62] Our measurements revealed that the vast majority (∼70% of on-surface, ∼ 67% of total) of EC accumulation occurred during fall (Table 1), when atmospheric EC concentrations in Dallas are elevated[63] (Figure 2). The fall/winter maximum in atmospheric EC that characterizes Dallas likely reflects the combined influence of increased residential wood burning and/or vehicle exhaust and a shift from prevailing southerly winds in spring/summer to northerly winds in fall/winter.[64] Together with changes in local emissions and source region, it is possible that drier than average fall conditions (Figure 2) exacerbated the spike in fall net EC accumulation.

Meteorological factors also directly influence particle accumulation on vegetation surfaces through effects on dry deposition and resuspension. Particle deposition generally

DOI: 10.1021/acs.est.9b02844
Environ. Sci. Technol. 2019, 53, 10092−10101

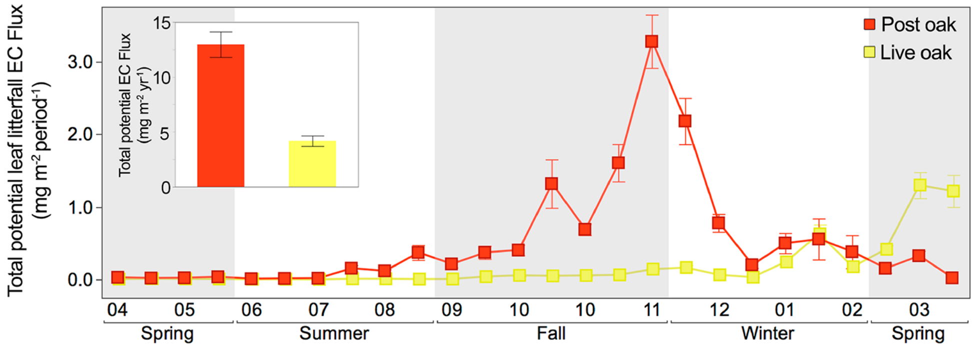


Figure 5. Total potential leaf litterfall elemental carbon (EC) flux under 20 post oak and 15 live oak trees sampled in the City of Denton, Texas, from April 2017 to March 2018. Inset: total potential leaf litterfall EC flux per year (19 post oak, 13 live oak).

Table 2. Seasonal and Annual Leaf Litterfall and Total, On-Surface, and In-Wax Net Elemental Carbon (EC) Delivered to the Ground via Leaf Litterfall for 20 Post Oak and 15 Live Oak Trees Sampled in the City of Denton, Texas, from April 2017 to March 2018[a]

	Leaf litterfall ($g\ m^{-2}$)		Total leaf litterfall EC ($mg\ m^{-2}$)	
	Post oak	Live oak	Post oak	Live oak
Spring 2017	19 ± 4.02	38 ± 5.1	0.096 ± 0.017	0.038 ± 0.0049
Summer 2017	21 ± 4.4	17 ± 3.2	0.52 ± 0.11	0.032 ± 0.0062
Fall 2017	198 ± 26	70 ± 18	7.2 ± 0.87	0.36 ± 0.078
Winter 2017	107 ± 14	83 ± 15	4.0 ± 0.46	1.2 ± 0.23
Spring 2018	7.1 ± 2.0	164 ± 20	0.39 ± 0.086	2.7 ± 0.33
Annual	375 ± 38	366 ± 34	13 ± 1.2	4.2 ± 0.47
	On-surface leaf litterfall EC ($mg\ m^{-2}$)		In-wax leaf litterfall EC ($mg\ m^{-2}$)	
	Post oak	Live oak	Post oak	Live oak
Spring 2017	0.033 ± 0.0055	0.015 ± 0.0019	0.064 ± 0.012	0.023 ± 0.0030
Summer 2017	0.43 ± 0.097	0.014 ± 0.0027	0.093 ± 0.018	0.018 ± 0.0036
Fall 2017	6.3 ± 0.76	0.25 ± 0.056	0.92 ± 0.11	0.11 ± 0.023
Winter 2017	3.5 ± 0.39	0.92 ± 0.19	0.57 ± 0.065	0.27 ± 0.048
Spring 2018	0.34 ± 0.074	1.9 ± 0.23	0.057 ± 0.013	0.85 ± 0.10
Annual	11 ± 1.01	2.9 ± 0.34	1.8 ± 0.16	1.2 ± 0.13

[a]Seasonal values may not sum to annual values (19 post oak, 13 live oak) due to varying number of litterfall traps.

increases with wind speed (e.g., 2-fold with a 5-fold increase in wind speed for *Quercus robur*; reference 65) up to a point after which deposition reaches a plateau.[24,32] In our urban ecosystem, daily mean and daily maximum wind speeds are higher in spring and lower in summer and fall (Figure 2), opposite seasonal patterns of on-surface and total net EC accumulation. Very high wind speeds (e.g., $\geq$ 10 m s^{-1}; reference 66) can also drive resuspension, but infrequent occurrence of such high wind speeds coupled with the small size of EC particles—which are thought to undergo little resuspension[67,68]—suggest that this process was not a major factor driving low spring EC accumulation.

Species Convergence in Net EC Accumulation Over Time. We detected a significant species by season interaction effect, whereby leaf- and canopy-scale differences in on-surface and total net EC accumulation between post oak and live oak were highest in summer and lowest in fall (all *p*-values <0.05). Seasonal changes in atmospheric EC concentrations coupled with alterations in leaf morphology and wettability[69,70] likely contributed to the convergence in on-surface net EC accumulation rates between species during the fall season (Figure 4a). During leaf expansion, leaves synthesize epicuticular waxes that coat the leaf cuticle. This waxy layer has several functions, including protection against water and nutrient loss, pathogen attack, and toxins.[71] With respect to particle deposition, some research has shown a positive correlation between species leaf wax content and in-wax particle accumulation.[15,17,35,72] The microroughness caused by wax structures has also been found to enhance fine particle deposition by reducing the leaf boundary layer and increasing the surface area available for capture.[37,73] However, because leaf waxes are hydrophobic, particles that deposit to waxy leaf surfaces (as opposed to adsorbing to the wax itself) can be readily washed off with rain, a phenomenon referred to as the "Lotus effect".[74] In other words, epicuticular waxes enhance in-wax and on-surface particle deposition while reducing on-surface particle *retention*. Thus, in-wax particle accumulation tends to be relatively more important in seasons (e.g., spring) when wax content is high[75] and/or leaves are more water repellent due to undamaged wax structures.[69,70]

Indeed, we found that rates of in-wax EC accumulation peaked in spring but then decreased sharply from April to June (Figure 4b). Though the effects are species-dependent, it is well established that leaf epicuticular waxes undergo chemical and structural changes over time as a result of diverse environmental factors,[76] including rain,[77] wind,[78] gaseous (e.g., O_3; nitric acid; reference 79; Figure 2) and particulate[80,81] deposition, and biological processes.[82] For example, Neinhuis and Barthlott[69] showed that *Quercus robur* leaves were water repellent for about 2 weeks following leaf expansion in spring,

DOI: 10.1021/acs.est.9b02844
Environ. Sci. Technol. 2019, 53, 10092−10101

after which they observed a rapid decline in hydrophobicity (i.e., an increase in wettability). Wang et al.[70] also found that the leaves of urban tree species became less water repellent with leaf age. In all of these studies, this apparent "wax degradation" was accompanied by a consistent increase in on-surface particle accumulation from spring to fall, indicating greater particle retention on leaf surfaces with time.

EC Fluxes to the Ground via Leaf Litterfall. Post oak and live oak trees produced similar quantities of leaf litter, yet EC flux to the soil varied 3-fold between species ($p < 0.0001$; Figure 5; Table 2). Although not all trees sampled for foliar EC had associated litterfall measurements, leaf litterfall EC fluxes did not differ among trees with and without matched sampling. This suggests that our sampling design did not significantly affect our estimates of leaf litterfall EC fluxes. In fact, our estimate for post oak (13 mg m^{-2} yr^{-1}) was comparable to that for konara oak (~11 mg m^{-2} yr^{-1}) in Tokyo, Japan.[38] It is important to note, however, that both studies underestimate total potential EC flux to the soil with litter because EC falls to the soil not only on leaves but also on twigs, branches, and leaf and wood fragments. We did not quantify EC accumulation on these canopy surfaces but nonleaf litterfall was ~50% of the total litterfall mass, suggesting its potential importance in EC transfer from canopy to ground.

Seasonally, leaf litterfall EC fluxes mirrored leaf fall patterns (Table 2). Like konara oak, post oak is deciduous, therefore there was a large pulse of EC to the ground during the fall season that was higher compared to that during other seasons ($p < 0.0001$; Figure 5; Table 2). For live oak, the highest EC fluxes occurred in spring 2018 ($p < 0.0001$; Figure 5; Table 2). In fact, 55% of the total annual potential leaf litterfall EC flux under post oak occurred during fall whereas for live oak 64% of the annual flux occurred during spring 2018. Species differences in total potential EC flux to the ground were exacerbated during fall (~20-fold higher for post oak than live oak) due to the combined effect of post oak leaf abscission and elevated on-surface net EC accumulation (Figure 4a).

These asynchronous peaks in leaf litterfall EC could have implications for the release of EC from litter. In situ rates of leaf litter decomposition vary widely among urban tree species[83] but increase with warmer and wetter conditions. Thus, we might expect faster rates of EC release from litter during spring compared to fall as a result of higher decomposition rates. In addition, we showed that for both species, most of the EC transported to the ground with leaf litter likely resides on leaf surfaces (~85% for post oak, ~ 70% for live oak) rather than in leaf waxes, with potential effects on the mobility of EC and subsequent incorporation into soil. Where trees overhang paved areas, leaf litterfall EC may be transported with runoff into storm drains and eventually into streams and lakes or reservoirs,[83,84] thereby affecting long-term, terrestrial EC retention. Clearly, the cycling and fate of EC under urban trees following litterfall warrants further attention.[85]

Urban Oak Trees Have High EC Scavenging Potentials. In 2016, there were an estimated 301937 post oak trees with a total leaf area of 26 km^2 and 23665 live oak trees with a total leaf area of 3.1 km^2 in the City of Denton.[45] Using these leaf area data, we estimate that post oak and live oak trees in our study area together potentially accumulate around 3.5 t EC yr^{-1}, a fraction of which is delivered to the ground via leaf litterfall. We find that this is equivalent to ~32% of annual vehicular EC emissions (10.9 t EC yr^{-1}) from the City of Denton (see Supporting Information for calculations).

Our findings are especially relevant for cities across the southern U.S. where post oak and live oak are broadly distributed (Figure 1) and where, under future climate change scenarios, models project an expansion in their potential distributions.[86] Moreover, compared to the western U.S., atmospheric EC concentrations in the eastern U.S. are elevated.[87] Although rainfall increases east of the DFW area, even in these wetter climates dry deposition can comprise an important fraction of total (wet + dry) atmospheric deposition.[88] Thus, these urban oak trees are significant sinks for EC, with implications for climate and air quality mitigation in U.S. cities.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b02844.

> Additional details provided on focal tree species, foliar sampling, foliar extraction and elemental carbon analysis, calculations, and scanning electron microscope observations (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +1 940 565 4012. E-mail: alexandra@unt.edu.

ORCID

Alexandra G. Ponette-González: 0000-0003-2908-2938

Author Contributions

$J.E. Rindy and A.G. Ponette-González contributed equally to this work and should be considered as joint first authors.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.G.P.G., J.E.R., and K.C.W. conceived the study, J.E.R. collected the data, J.E.R., T.E.B., R.J.S., and A.G.P.G. analyzed the data, A.G.P.G. created the figures, J.E.R. and A.G.P.G. cowrote the paper, and all authors edited the paper. We owe our gratitude to City of Denton residents, City of Denton Parks and Recreation, UNT Facilities, Texas Woman's University, Eco-W.E.R.C.S., and Denton Public Library North Branch for allowing us to conduct sampling in Denton's urban yards and greenspaces. We thank Brett W. Luce for assistance with field sampling, Kajetan Dzierźanowski and Bethel Steele for assistance with protocol development, Subin Yoon for assistance with the Sunset OC/EC, and David Hoeinghaus for providing additional laboratory resources. We are grateful to Matt Fry for creating Figure 1, Rebecca Dickstein and Steve Wolverton for comments on the M.S. thesis from which this paper was developed, and two anonymous reviewers for thoughtful feedback on the manuscript. Scanning Electron Microscope work was performed at the University of North Texas's Materials Research Facility: a shared research facility for multidimensional fabrication and characterization. Ponette-González received funding for this research from the National Science Foundation CAREER grant #1552410.

DOI: 10.1021/acs.est.9b02844
Environ. Sci. Technol. 2019, 53, 10092−10101

REFERENCES

(1) Schneider, A.; Friedl, M. A.; Potere, D. A new map of global urban extent from MODIS satellite data. *Environ. Res. Lett.* **2009**, *4* (4), 044003.
(2) Zhou, Y.; Smith, S. J.; Zhao, K.; Imhoff, M.; Thomson, A.; Bond-Lamberty, B.; Asrar, G. H.; Zhang, X.; He, C.; Elvidge, C. D. A global map of urban extent from nightlights. *Environ. Res. Lett.* **2015**, *10* (5), 054011.
(3) Acuto, M.; Parnell, S.; Seto, K. C. Building a global urban science. *Nat. Sustain.* **2018**, *1* (1), 2−4.
(4) Bond, T. C.; Doherty, S. J.; Fahey, D. W.; Forster, P. M.; Berntsen, T.; DeAngelo, B. J.; Flanner, M. G.; Ghan, S.; Karcher, B.; Koch, D.; Kinne, S.; Kondo, Y.; Quinn, P. K.; Sarofim, M. C.; Schultz, M. G.; Schulz, M.; Venkataraman, C.; Zhang, H.; Zhang, S.; Bellouin, N.; Guttikunda, S. K.; Hopke, P. K.; Jacobson, M. Z.; Kaiser, J. W.; Klimont, Z.; Lohmann, U.; Schwarz, J. P.; Shindell, D.; Storelvmo, T.; Warren, S. G.; Zender, C. S. Bounding the role of black carbon in the climate system: A scientific assessment. *J. Geophys. Res.- Atmos.* **2013**, *118* (11), 5380−5552.
(5) Seto, K. C.; Dhakal, S.; Bigio, A.; Blanco, H.; Delgado, G. C.; Dewar, D.; Huang, L.; Inaba, A.; Kandal, A.; Lwasa, S.; McMahon, J.; Müller, D. B.; Murakami, J.; Nagendra, H.; Ramaswami, A. Chapter 12 - Human settlements, infrastructure and spatial planning. In *Climate Change 2014: Mitigation of Climate Change; IPCC Working Group III Contribution to AR5*; Cambridge University Press: New York, 2014.
(6) *Report to Congress on Black Carbon*; U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards: Washington, DC, 2010; https://www3.epa.gov/airquality/blackcarbon/2012report/fullreport.pdf.
(7) Fuzzi, S.; Baltensperger, U.; Carslaw, K.; Decesari, S.; Denier van der Gon, H.; Facchini, M. C.; Fowler, D.; Koren, I.; Langford, B.; Lohmann, U.; Nemitz, E.; Pandis, S.; Riipinen, I.; Rudich, Y.; Schaap, M.; Slowik, J. G.; Spracklen, D. V.; Vignati, E.; Wild, M.; Williams, M.; Gilardoni, S. Particulate matter, air quality and climate: lessons learned and future needs. *Atmos. Chem. Phys.* **2015**, *15* (14), 8217−8299.
(8) Peng, J.; Hu, M.; Guo, S.; Du, Z.; Zheng, J.; Shang, D.; Levy Zamora, M.; Zeng, L.; Shao, M.; Wu, Y.; Zheng, J.; Wang, Y.; Glen, C. R.; Collins, D. R.; Molina, M. J.; Zhang, R. Markedly enhanced absorption and direct radiative forcing of black carbon under polluted urban environments. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113* (16), 4266−4271.
(9) Han, S.; Bian, H.; Zhang, Y.; Wu, J.; Wang, Y.; Tie, X.; Li, Y.; Li, X.; Yao, Q. Effect of aerosols on visibility and radiation in spring 2009 in Tianjin, China. *Aerosol Air Qual. Res.* **2012**, *12*, 211−217.
(10) Lin, W.; Huang, W.; Zhu, T.; Hu, M.; Brunekreef, B.; Zhang, Y.; Liu, X.; Cheng, H.; Gehring, U.; Li, C.; Tang, X. Acute respiratory inflammation in children and black carbon in ambient air before and during the 2008 Beijing Olympics. *Environ. Health Perspect.* **2011**, *119* (10), 1507−1512.
(11) Magalhaes, S.; Baumgartner, J.; Weichenthal, S. Impacts of exposure to black carbon, elemental carbon, and ultrafine particles from indoor and outdoor sources on blood pressure in adults: A review of epidemiological evidence. *Environ. Res.* **2018**, *161*, 345−353.
(12) Mar, T. F.; Norris, G. A.; Koenig, J. Q.; Larson, T. V. Associations between air pollution and mortality in Phoenix, 1995−1997. *Environ. Health Perspect.* **2000**, *108* (4), 347−353.
(13) Ogren, J. A.; Charlson, R. J. Elemental carbon in the atmosphere: Cycle and lifetime. *Tellus, Ser. B* **1983**, *35* (4), 241−254.
(14) Bond, T. C.; Sun, H. Can reducing black carbon emissions counteract global warming? *Environ. Sci. Technol.* **2005**, *39* (16), 5921−5926.
(15) Dzierżanowski, K.; Popek, R.; Gawrońska, H.; Sæbø, A.; Gawroński, S. W. Deposition of particulate matter of different size fractions on leaf surfaces and in waxes of urban forest species. *Int. J. Phytorem.* **2011**, *13* (10), 1037−1046.
(16) Mo, L.; Ma, Z.; Xu, Y.; Sun, F.; Lun, X.; Liu, X.; Chen, J.; Yu, X. Assessing the capacity of plant species to accumulate particulate matter in Beijing, China. *PLoS One* **2015**, *10* (10), No. e0140664.
(17) Saebø, A.; Popek, R.; Nawrot, B.; Hanslin, H. M.; Gawronska, H.; Gawronski, S. W. Plant species differences in particulate matter accumulation on leaf surfaces. *Sci. Total Environ.* **2012**, *427*, 347−354.
(18) Sgrigna, G.; Sæbø, A.; Gawronski, S.; Popek, R.; Calfapietra, C. Particulate matter deposition on *Quercus ilex* leaves in an industrial city of central Italy. *Environ. Pollut.* **2015**, *197*, 187−194.
(19) Wang, L.; Gong, H.; Peng, N.; Zhang, J. Z. Molecular adsorption mechanism of elemental carbon particles on leaf surface. *Environ. Sci. Technol.* **2018**, *52* (9), 5182−5190.
(20) Grieshop, A. P.; Reynolds, C. C.; Kandlikar, M.; Dowlatabadi, H. A black-carbon mitigation wedge. *Nat. Geosci.* **2009**, *2* (8), 533.
(21) Grote, R.; Samson, R.; Alonso, R.; Amorim, J. H.; Carinanos, P.; Churkina, G.; Fares, S.; Thiec, D. L.; Niinemets, U.; Mikkelsen, T. N.; Paoletti, E.; Tiwary, A.; Calfapietra, C. Functional traits of urban trees: Air pollution mitigation potential. *Front. Ecol. Environ.* **2016**, *14* (10), 543−550.
(22) Nowak, D. J.; Hirabayashi, S.; Bodine, A.; Greenfield, E. Tree and forest effects on air quality and human health in the United States. *Environ. Pollut.* **2014**, *193*, 119−129.
(23) Willis, K. J.; Petrokofsky, G. The natural capital of city trees. *Science* **2017**, *356* (6336), 374−376.
(24) 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* (8), 995−1003.
(25) Nowak, D. J.; Crane, D. E.; Stevens, J. C. Air pollution removal by urban trees and shrubs in the United States. *Urban Forest. Urban Gree.* **2006**, *4* (3−4), 115−123.
(26) Terzaghi, E.; Wild, E.; Zacchello, G.; Cerabolini, B. E.; Jones, K. C.; Di Guardo, A. Forest filter effect: role of leaves in capturing/releasing air particulate matter and its associated PAHs. *Atmos. Environ.* **2013**, *74*, 378−384.
(27) Fowler, D.; Cape, J. N.; Coyle, M.; Flechard, C.; Kuylenstierna, J.; Hicks, K.; Derwent, D.; Johnson, C.; Stevenson, D. The global exposure of forests to air pollutants. *Water, Air, Soil Pollut.* **1999**, *116* (1−2), 5−32.
(28) Ponette-González, A. G.; Weathers, K. C.; Curran, L. M. Tropical land-cover change alters biogeochemical inputs to ecosystems in a Mexican montane landscape. *Ecol. Appl.* **2010**, *20* (7), 1820−1837.
(29) Ponette-González, A. G.; Curran, L. M.; Pittman, A. M.; Carlson, K. M.; Steele, B. G.; Ratnasari, D.; Weathers, K. C. Biomass burning drives atmospheric nutrient redistribution within forested peatlands in Borneo. *Environ. Res. Lett.* **2016**, *11*, 085003.
(30) Slinn, W. G. N. Predictions for particle deposition to vegetative canopies. *Atmos. Environ.* **1982**, *16* (7), 1785−1794.
(31) Chen, L.; Liu, C.; Zhang, L.; Zou, R.; Zhang, Z. Variation in tree species ability to capture and retain airborne fine particulate matter ($PM_{2.5}$). *Sci. Rep.* **2017**, *7* (1), 3206.
(32) Freer-Smith, P. H.; El-Khatib, A. A.; Taylor, G. Capture of particulate pollution by trees: A comparison of species typical of semi-arid areas (*Ficus nitida* and *Eucalyptus globulus*) with European and North American species. *Water, Air, Soil Pollut.* **2004**, *155* (1−4), 173−187.
(33) Mori, J.; Hanslin, H. M.; Burchi, G.; Sæbø, A. Particulate matter and element accumulation on coniferous trees at different distances from a highway. *Urban Forest. Urban Gree.* **2015**, *14* (1), 170−177.
(34) Muhammad, S.; Wuyts, K.; Samson, R. Atmospheric net particle accumulation on 96 plant species with contrasting morphological and anatomical leaf characteristics in a common garden experiment. *Atmos. Environ.* **2019**, *202* (1), 328−344.
(35) Popek, R.; Gawrońska, H.; Wrochna, M.; Gawroński, S. W.; Sæbø, A. Particulate matter on foliage of 13 woody species: deposition on surfaces and phytostabilisation in waxes−a 3-year study. *Int. J. Phytorem.* **2013**, *15* (3), 245−256.

DOI: 10.1021/acs.est.9b02844
Environ. Sci. Technol. 2019, 53, 10092−10101

(36) Przybysz, A.; Sæbø, A.; Hanslin, H. M.; Gawroński, S. W. Accumulation of particulate matter and trace elements on vegetation as affected by pollution level, rainfall and the passage of time. *Sci. Total Environ.* **2014**, *481*, 360−369.
(37) Wang, L.; Gong, H.; Liao, W.; Wang, Z. Accumulation of particles on the surface of leaves during leaf expansion. *Sci. Total Environ.* **2015**, *532*, 420−434.
(38) Hara, H.; Kashiwakura, T.; Kitayama, K.; Bellingrath-Kimura, S. D.; Yoshida, T.; Takayanagi, M.; Yamagata, S.; Murao, N.; Okouchi, H.; Ogata, H. Foliar rinse study of atmospheric black carbon deposition to leaves of konara oak (*Quercus serrata*) stands. *Atmos. Environ.* **2014**, *97*, 511−518.
(39) Cusack, D. F.; Chadwick, O. A.; Hockaday, W. C.; Vitousek, P. M. Mineralogical controls on soil black carbon preservation. *Global Biogeochem. Cy.* **2012**, *26* (2), 4109 DOI: 10.1029/2011GB004109.
(40) Forbes, M. S.; Raison, R. J.; Skjemstad, J. O. Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. *Sci. Total Environ.* **2006**, *370* (1), 190−206.
(41) Denton Enterprise Airport; https://forecast.weather.gov/MapClick.php?lat=33.20505&lon=-97.20061#.XI6AbShKi71.
(42) Denton, TX, https://www.census.gov/quickfacts/dentoncountytexas.
(43) Denton Airport South C56/A163/X157; https://www.tceq.texas.gov/cgi-bin/compliance/monops/daily_summary.pl?cams=56.
(44) 2015 National Ambient Air Quality Standards (NAAQS) for Ozone; https://www.epa.gov/ground-level-ozone-pollution/2015-national-ambient-air-quality-standards-naaqs-ozone.
(45) State of the Denton Urban Forest; https://www.itreetools.org/resources/reports/2016_State_of_the_Denton_Urban_Forest_Preservation_Tree.pdf.
(46) Nowak, D. J.; Greenfield, E. J. Declining urban and community tree cover in the United States. *Urban For. Urban Gree.* **2018**, *32*, 32−55.
(47) Rautio, P.; Fürst, A. Tree foliage: sampling and chemical analyses. In *Developments in Environmental Science*; Elsevier: Oxford, 2004; pp 223−236.
(48) Torres, A.; Bond, T. C.; Lehmann, C. M.; Subramanian, R.; Hadley, O. L. Measuring organic carbon and black carbon in rainwater: evaluation of methods. *Aerosol Sci. Technol.* **2014**, *48* (3), 239−250.
(49) National Atmospheric Deposition Program (NADP). *Litterfall Mercury Monitoring Initiative Protocol*; Madison, WI, 2012. http://nadp.slh.wisc.edu/newissues/litterfall/LitterfallProtocolsV1.1.pdf.
(50) McDonald, J. H. *Handbook of Biological Statistics*, 3rd ed; Sparky House Publishing: Baltimore, MD, 2014.
(51) *JMP, Version 14*. SAS Institute Inc.: Cary, NC, 1989-2019.
(52) Barrett, T. E.; Ponette-González, A. G.; Rindy, J. E.; Weathers, K. C. The importance of wet deposition of black carbon: a synthesis of removal rates by rain. *Atmos. Environ.* **2019**, *213*, 558−567.
(53) Matsuda, K.; Sase, H.; Murao, N.; Fukazawa, T.; Khoomsub, K.; Chanonmuang, P.; Visaratana, T.; Khummongkol, P. Dry and wet deposition of elemental carbon on a tropical forest in Thailand. *Atmos. Environ.* **2012**, *54*, 282−287.
(54) Cai, M.; Xin, Z.; Yu, X. Spatio-temporal variations in PM leaf deposition: A meta-analysis. *Environ. Pollut.* **2017**, *231* (1), 207−218.
(55) Hwang, H. J.; Yook, S. J.; Ahn, K. H. Experimental investigation of submicron and ultrafine soot particle removal by tree leaves. *Atmos. Environ.* **2011**, *45* (38), 6987−6994.
(56) Liu, J.; Zhang, R.; Liu, H.; Duan, J.; Kang, J.; Guo, Z.; Xi, B.; Cao, Z. Assessing the particulate matter removal abilities of tree leaves. *J. Visualized Exp.* **2018**, *7* (140), No. e58026.
(57) Yang, J.; Wang, H. X.; Xie, B. Z.; Shi, H.; Wang, Y. H. Accumulation of particulate matter on leaves of nine urban greening plant species with different micromorphological structures in Beijing. *Res. J. Environ. Sci.* **2015**, *28* (3), 384−392.
(58) Jamil, S.; Abhilash, P. C.; Singh, A.; Singh, N.; Behl, H. M. Fly ash trapping and metal accumulating capacity of plants: Implication for green belt around thermal power plants. *Landsc. Urban Plan.* **2009**, *92* (2), 136−147.
(59) Weber, F.; Kowarik, I.; Säumel, I. Herbaceous plants as filters: Immobilization of particulates along urban street corridors. *Environ. Pollut.* **2014**, *186*, 234−240.
(60) Hardin, J. W. Patterns of variation in foliar trichomes of eastern North American *Quercus*. *Am. J. Bot.* **1979**, *66* (5), 576−585.
(61) Huang, C. W.; Lin, M. Y.; Khlystov, A.; Katul, G. G. The effects of leaf size and microroughness on the branch-scale collection efficiency of ultrafine particles. *J. Geophys. Res.-Atmos.* **2015**, *120* (8), 3370−3385.
(62) Ponette-González, A. G.; Ewing, H. A.; Weathers, K. C. Interactions between precipitation and vegetation canopies. In *A Biogeoscience Approach to Ecosystems*; Johnson, E., Martin, Y., Eds.; Cambridge University Press: New York, 2016; pp 215−253.
(63) Chemical Speciation Network (CSN); http://www.epa.gov/ttnamti1/speciepg.html.
(64) Barrett, T. E.; Sheesley, R. J. Urban impacts on regional carbonaceous aerosols: Case study in central Texas. *J. Air Waste Manage. Assoc.* **2014**, *64* (8), 917−926.
(65) Reinap, A.; Wiman, B. L.; Svenningsson, B.; Gunnarsson, S. Oak leaves as aerosol collectors: Relationships with wind velocity and particle size distribution. Experimental results and their implications. *Trees* **2009**, *23* (6), 1263−1274.
(66) Pullman, M. *Conifer $PM_{2.5}$ deposition and resuspension in wind and rain events*. Master's Thesis. Cornell University, Ithaca, NY, 2008.
(67) Gillette, D. A.; Lawson, R. E., Jr; Thompson, R. S. A "test of concept" comparison of aerodynamic and mechanical resuspension mechanisms for particles deposited on field rye grass (*Secale cercele*). Part 1. Relative particle flux rates. *Atmos. Environ.* **2004**, *38* (28), 4789−4797.
(68) Pryor, S. C.; Larsen, S. E.; Sørensen, L. L.; Barthelmie, R. J. Particle fluxes above forests: Observations, methodological considerations and method comparisons. *Environ. Pollut.* **2008**, *152* (3), 667−678.
(69) Neinhuis, C.; Barthlott, W. Seasonal changes of leaf surface contamination in beech, oak, and ginkgo in relation to leaf micromorphology and wettability. *New Phytol.* **1998**, *138* (1), 91−98.
(70) Wang, H.; Shi, H.; Li, Y.; Yu, Y.; Zhang, J. Seasonal variations in leaf capturing of particulate matter, surface wettability and micromorphology in urban tree species. *Front. Environ. Sci. Eng.* **2013**, *7* (4), 579−588.
(71) Koch, K.; Bhushan, B.; Barthlott, W. Multifunctional surface structures of plants: An inspiration for biomimetics. *Prog. Mater. Sci.* **2009**, *54* (2), 137−178.
(72) Saebø, A.; Hanslin, H. M.; Torp, T.; Lierhagen, S.; Gawronska, H.; Dzierzanowski, K.; Gawronski, S. Chemical composition of vegetation along urbanisation gradients in two European cities. *Environ. Pollut.* **2015**, *198*, 116−125.
(73) Burkhardt, J.; Peters, K.; Crossley, A. The presence of structural surface waxes on coniferous needles affects the pattern of dry deposition of fine particles. *J. Exp. Bot.* **1995**, *46* (7), 823−831.
(74) Barthlott, W.; Neinhuis, C. Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* **1997**, *202* (1), 1−8.
(75) Jenks, M. A.; Gaston, C. H.; Goodwin, M. S.; Keith, J. A.; Teusink, R. S.; Wood, K. V. Seasonal variation in cuticular waxes on *Hosta* genotypes differing in leaf surface glaucousness. *HortScience* **2002**, *37* (4), 673−677.
(76) Shepherd, T.; Griffiths, D. W. The effects of stress on plant cuticular waxes. *New Phytol.* **2006**, *171* (3), 469−499.
(77) Baker, E. A.; Hunt, G. M. Erosion of waxes from leaf surfaces by simulated rain. *New Phytol.* **1986**, *102* (1), 161−173.
(78) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants. *Environ. Sci. Technol.* **1993**, *27* (13), 2700−2711.
(79) Padgett, P. E.; Cook, H.; Bytnerowicz, A.; Heath, R. L. Foliar loading and metabolic assimilation of dry deposited nitric acid air pollutants by trees. *J. Environ. Monit.* **2009**, *11* (1), 75−84.

(80) Burkhardt, J.; Pariyar, S. Particulate pollutants are capable to 'degrade' epicuticular waxes and to decrease the drought tolerance of Scots pine (*Pinus sylvestris* L.). *Environ. Pollut.* **2014**, *184*, 659−667.
(81) Burkhardt, J.; Zinsmeister, D.; Grantz, D. A.; Vidic, S.; Sutton, M. A.; Hunsche, M.; Pariyar, S. Camouflaged as degraded wax: hygroscopic aerosols contribute to leaf desiccation, tree mortality, and forest decline. *Environ. Res. Lett.* **2018**, *13* (8), 085001.
(82) Fonte, S. J.; Schowalter, T. D. Decomposition in forest canopies. In *Forest Canopies*; Lowman, M. D., Rinker, B. H. (Eds.); Elsevier: Oxford, 2004; pp 413−422.
(83) Hobbie, S. E.; Baker, L. A.; Buyarski, C.; Nidzgorski, D.; Finlay, J. C. Decomposition of tree leaf litter on pavement: implications for urban water quality. *Urban Ecosyst* **2014**, *17* (2), 369−385.
(84) Decina, S. M.; Templer, P. H.; Hutyra, L. R. Atmospheric inputs of nitrogen, carbon, and phosphorus across an urban area: unaccounted fluxes and canopy influences. *Earth's Future* **2018**, *6* (2), 134−148.
(85) Hutyra, L. R.; Duren, R.; Gurney, K. R.; Grimm, N.; Kort, E. A.; Larson, E.; Shrestha, G. Urbanization and the carbon cycle: Current capabilities and research outlook from the natural sciences perspective. *Earth's Future* **2014**, *2*, 473−495.
(86) Iverson, L. R.; Prasad, A. M.; Matthews, S. N.; Peters, M. Estimating potential habitat for 134 eastern U.S. tree species under six climate scenarios. *For. Ecol. Manage.* **2008**, *254*, 390−406.
(87) Bergen, S.; Sheppard, L.; Sampson, P. D.; Kim, S.-Y.; Richards, M.; Vedal, S.; Kaufman, J. D.; Szpiro, A. A. A national prediction model for $PM_{2.5}$ component exposures and measurement error−corrected health effect inference. *Environ. Health Perspect.* **2013**, *121* (9), 1017−1025.
(88) Weathers, K. C.; Ponette-González, A. G. Atmospheric Deposition. In *Forest Hydrology and Biogeochemistry*; Springer: Dordrecht, 2011; pp 357−370.

DOI: 10.1021/acs.est.9b02844
Environ. Sci. Technol. 2019, 53, 10092−10101